ИНСТИТУТ ЗА ФИЗИКУ
ПРИМЉЕНО: 09. 12. 2019

Рад.јед.	број	Арх.шифра	Прилог
0801	1927/1		

Научном већу Института за физику у Београду

Београд, 09. 12. 2019. године

<u>Предмет</u>: ***Молба за покретање поступка за избор у звање виши научни сарадник***

Молим Научно веће Института за физику у Београду да, у складу с Правилником о поступку и начину вредновања и квантитативном исказивању научно-истраживачких резултата истраживача, покрене поступак за мој избор у звање виши научни сарадник.

У прилогу достављам:

1. Мишљење руководиоца пројекта са предлогом чланова комисије за избор у звање
2. Образложење за превремено покретање избора у звање
3. Стручну биографију
4. Преглед научне активности
5. Елементе за квалитативну оцену научног доприноса
6. Елементе за квантитативну оцену научног доприноса
7. Списак објављених радова и њихове копије
8. Податке о цитираности радова
9. Фотокопију решења о избору у претходно звање
10. Доказе о испуњености наведених квалитативних услова

С поштовањем,

др Андреја Стојић

научни сарадник

Институт за физику у Београду

Научном већу Института за физику у Београду

ИНСТИТУТ ЗА ФИЗИКУ
ПРИМЉЕНО: 09. 12. 2019

Рад.јед.	број	Арх.шифра	Прилог
0801	1927/2		

Београд, 09. децембар 2019. године

Предмет: Мишљење руководиоца пројекта о избору др Андреје Стојића у звање виши научни сарадник

Др Андреја Стојић је запослен у Лабораторији за физику животне средине Института за физику у Београду. Ангажован је на два пројекта интердисциплинарних истраживања Министарства просвете, науке и технолошког развоја Републике Србије ИИИ 43007 под називом *Истраживање климатских промена и њиховог утицаја на животну средину – праћење утицаја, адаптација и ублажавање* и ИИИ 41011 под називом *Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама*. На пројектима ради на темама из области опште и интердисциплинарне физике с посебним фокусом на истраживање утицаја атмосферског загађења (атмосферски аеросоли, неоргански гасни оксиди и испарљива органска једињења) на животну средину, здравље људи и климатске промене. С обзиром на то да постигнути резултати колеге др Андреје Стојића далеко премашују предвиђене услове прописане Правилником о поступку, начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача МПНТР, сагласан сам са покретањем поступка за избор др Андреје Стојића у звање виши научни сарадник по убрзаном поступку.

За чланове комисије за избор др Андреје Стојића у звање виши научни сарадник предлажем:

1. др Зоран Мијић, виши научни сарадник, Институт за физику у Београду
2. др Димитрије Малетић, виши научни сарадник, Институт за физику у Београду
3. проф. др Лазар Лазић, редовни професор, Физички факултет, Универзитет у Београду
4. проф. др Драгољуб Белић, редовни професор, Физички факултет, Универзитет у Београду

Руководилац потпројекта ПП3 ИИИ 43007

др Зоран Мијић
виши научни сарадник
Институт за физику у Београду

ИНСТИТУТ ЗА ФИЗИКУ
ПРИМЉЕНО: 09. 12. 2019

Рад.јед.	број	Арх.шифра	Прилог
0801	1927/3		

Научном већу Института за физику у Београду

Предмет: Образложење за убрзано покретање поступка за избор др Андреје Стојића у звање виши научни сарадник

Др Андреја Стојић је запослен у Лабораторији за физику животне средине, Института за физику у Београду и ангажован је на два пројекта интердисциплинарних истраживања Министарства просвете, науке и технолошког развоја Републике Србије ИИИ 43007, под називом *Истраживање климатских промена и њиховог утицаја на животну средину – праћење утицаја, адаптација и ублажавање* и ИИИ 41011 под називом *Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама*. На пројектима ради на темама из области опште и интердисциплинарне физике, као и науке о подацима с посебним фокусом на истраживање утицаја атмосферског загађења (атмосферски аеросоли, неоргански гасни оксиди и испарљива органска једињења) на животну средину, здравље људи и климатске промене.

Др Стојић је претходно изабран у звање научни сарадник 30. марта 2016. године, односно пре 3 године и 9 месеци (у тренутку подношења извештаја). Од тада је остварио изузетне научне резултате, што се може видети по томе да је објавио чак 12 радова у часописима категорије М20. Од тога је 1 рад објављен у часописима категорије М21а (међународни часописи изузетних вредности), док је 8 објављено у часописима категорије М21 (врхунски међународни часописи). Такође, др Стојић је у том периоду одржао 3 предавања на међународним скуповима, од којих је једно било предавања по позиву. Према бази *ISI Web of Science*, радови др Стојића укупно су цитирани 174 пута, док је број цитата без аутоцитата 128. Према бази *Scopus*, укупан број цитата је 220, док је број цитата без аутоцитата 154. Према подацима из обе базе, Хиршов индекс радова др Стојића је 7. Укупан импакт-фактор радова др Андреје Стојића износи 55,714, а у периоду након одлуке Научног већа Института за физику у Београду о предлогу за стицање претходног научног звања радова укупан импакт фактор је 37,003. Часописи у којима објављује др Стојић су цењени по свом угледу и вођени у његовим областима рада. Међу поменутим часописима посебно се истичу *Science of the Total Environment, Environmental Health, Ecotoxicology and Environmental Safety, Atmospheric Environment* и *Chemosphere*.

Др Стојић је учесник 8 националних, 7 међународних и 1 ненаучног пројеката који се тичу области опште и интердисциплинарне физике, као и науке о подацима. Учествовао је у израдама 2 докторске дисертације, 2 мастер рада, 3 дипломска рада, био је ментор израде 1 матурског рада и водио 1 пројекат студентске праксе. Током 2019. године учествовао је у акредитацији, а потом је ангажован и као предавач на студијском програму *Животна средина и одрживи развој* Универзитета Сингидунум у Београду, на основним, мастер и докторским студијама.

У Институту за физику у Београду др Стојић је увео нове методе у проучавање порекла, еволуције и утицаја загађујућих супстанци у атмосфери базиране на мерењима у реалном времену и примени напредних статистичких метода и алгоритама вештачке интелигенције имплементираних кроз методе машинског учења (*machine learning* – ML) и *explainable artificial intelligence* – XAI за обраду података. Знања и искуства које је стекао у теоријском моделирању и аналитичким методама у области опште и интердисциплинарне физике успешно преноси млађим сарадницима у Лабораторији за моделирању и аналитичким методама у области опште и интердисциплинарне физике успешно преноси млађим сарадницима у Лабораторији за физику животне средине и студентима кроз четири предмета студијског програма *Животна средина и одрживи развој* Универзитета Сингидунум, Београд.

С обзиром на то да далеко превазилази све предвиђене квантитативне и квалитативне услове, као и да је у тренутно научно звање научни сарадник изабран пре више од три године, у складу са Законом о научноистраживачкој делатности и Правилником о поступку, начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача МПНТР предлажемо да се за др Андреју Стојића покрене убрзани поступак за избор у звање виши научни сарадник.

У Београду, 9. децембра 2019. године

Предложени чланови комисије:

др Зоран Мијић
виши научни сарадник
Институт за физику у Београду

др Димитрије Малетић
виши научни сарадник
Институт за физику у Београду

проф. др Лазар Лазић
редовни професор
Физички факултет, Универзитет у Београду

проф. др Драгољуб Белић
редовни професор
Физички факултет, Универзитет у Београду

3. БИОГРАФСКИ ПОДАЦИ О КАНДИДАТУ

Др Андреја Стојић је рођен 3. јануара 1976. године у Јагодини где је похађао основну школу и гимназију. Дипломирао је 2007. године на Физичком факултету Универзитета у Београду на смеру Примењена физика и информатика са просечном оценом 9,32 током студија одбранивши дипломски рад *Испитивање електричних и спектроскопских карактеристика коаксијалног диелектричног баријерног пражњења* под руководством проф. др Братислава Обрадовића и проф. др Милорада Кураице.

Од јула 2007. године је запослен у Институту за физику у Београду као истраживач-приправник. Докторке студије на смеру Физика атома и молекула Физичког факултета Универзитета у Београду је завршио са просечном оценом 10. Докторат *Анализа расподела и динамике испарљивих органских једињења и аеросола у тропосфери: Лидар и масена спектрометрија (Spatio-temporal Distribution of Volatile Organic Compounds and Aerosols in Troposphere: Lidar and Mass Spectrometry)*, чијом израдом је руководио др Зоран Мијић, виши научни сарадник Института за физику у Београду, одбранио је 2015. године на Физичком факултету Универзитета у Београду. Током докторских студија кандидат се бавио проучавањем утицаја атмосферског загађења на животну средину, здравље људи и климатске промене. Бавио се увођењем методе масене спектрометрије са трансфером протона (*proton transfer reaction mass spectrometry* – PTR-MS) и мерењем концентрација великог броја испарљивих органских једињења (ИОЈ) у амбијенталном ваздуху и контролисаним, лабораторијским условима. Примарни фокус истраживања је био одређивање порекла атмосферских аеросола и ИОЈ, њихове динамике и структуре просторне расподеле, као и феномена и међусобних спрега које их дефинишу.

Кандидат је учествовао или учествује на следећим пројектима:

Међународни пројекти

1. 2019. – present NI4OS-Europe: *National Initiatives for Open Science in Europe*; European Commission, Horizon 2020, Implementing the European Open Science Cloud
2. 2018. – present *Persistent organochlorine compounds in breast milk and their effect on the level of primary DNA damage in human cells*, bilateral cooperation between the Republic of Serbia and Croatia
3. 2017–2021. *International network to encourage the use of monitoring and forecasting dust products*, COST Action CA16202, European Cooperation in Science and Technology
4. 2016–2018. GEO-CRADLE – *Coordinating and integRating state-of-the-art Earth Observation Activities in the regions of North Africa, Middle East, and Balkans and Developing Links with GEO related initiatives towards GEOSS*, Horizon 2020 (H2020) research and innovation programme under grant agreement No 690133
5. 2015-2019. No 654109: ACTRIS-2 (Aerosols, Clouds, and Trace gases Research Infrastructure) Project supported by the European Commission Horizon 2020 Research and Innovation Framework Programme
6. 2014–2017. *Atmospheric pressure plasma jet for neutralisation of CBW (chemical biological weapons)* – financed by NATO (SfP 984555)
7. 2006–2009. *Reinforcing Experimental Centre for Non-equilibrium Studies with Application in Nano-technologies, Etching of Integrated Circuits and Environmental Research* (IPB-CNP-026328), FP6

Национални пројекти

1. 2018. *Мапирање извора токсичних, мутагених и канцерогених испарљивих органских једињења на територији Града Београда*, Зелени фонд, Министарство заштите животне средине Републике Србије – руководилац пројекта
2. 2018. *Студија изводљивости имплементације националне мреже за континуално и аутоматизовано праћење значајних параметара из домена заштите животне средине*, Зелени фонд, Министарство заштите животне средине Републике Србије
3. 2018. *Временске варијације и просторне карактеристике присуства испарљивих органских једињења и атмосферских честица у широј зони Београда – Реализација кампање фиксног и мобилног прикупљања података током грејне сезоне са аналитичким инструментима минутне резолуције*, Зелени фонд, Министарство заштите животне средине Републике Србије
4. 2011–2019. *Истраживање климатских промена и њиховог утицаја на животну средину – праћење утицаја, адаптација и ублажавање* – III 43007, Министарство просвете, науке и технолошког развоја Републике Србије
5. 2011–2019. *Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама* – III 41011, Министарство просвете, науке и технолошког развоја Републике Србије
6. 2006–2010. *Емисија и трансмисија полутаната у атмосфери урбане средине* – OI 141012, Министарство просвете, науке и технолошког развоја Републике Србије
7. 2008–2010. *Примена плазма игле у медицинским и биолошким истраживањима и брза и поуздана детекција волатилних супстанци хуманог и биљног порекла* – TR 23106, Министарство просвете, науке и технолошког развоја Републике Србије
8. 2008–2009. *Развој и примена савремених археометријских-недеструктивних метода у анализи артефаката културног наслеђа* – TR 19046, Министарство просвете, науке и технолошког развоја Републике Србије

Ненаучни пројекти

1. 2016. *План квалитета ваздуха у агломерацији Београд*, Секретаријат за заштиту животне средине Града Београда

Такође, кандидат је током 2016/2017. године руководио фазама и активностима Националног центра изузетних вредности за примену плазме у нанотехнологијама, биомедицини и екологији, Института за физику у Београду.

Истраживачки рад кандидата обухвата области опште и интердисциплинарне физике, као и науке о подацима. Активности се могу поделити у три дела: (1) прикупљање података кроз експеримент (мерење концентрација великог броја загађујућих супстанци у амбијенталном ваздуху; мерење концентрација ИОЈ у реалним и симулираним мултифазним системима животне средине) и јавно доступне базе података (загађујуће супстанце – *European Environmental Agency* и US EPA; метеоролошки параметри – NOAA; морталитет – надлежне институције у Републици Србији), (2) анализа података применом великог броја статистичких метода, метода машинског учења (*machine learning* – ML) и *explainable artificial intelligence* – XAI и (3) моделирање, које обухвата и развој статистичких метода (мултифазни системи животне средине; транспорт загађења ваздуха; утицај фактора животне средине на здравље људи). Теме истраживања припадају областима интердисциплинарне физике, хемије животне средине и науке о подацима, с посебним фокусом на анализу: (1) утицаја фактора животне средине који одређују концентрације загађујућих супстанци у атмосфери и њихову еволуцију у времену и простору, (2) мултифазних система животне средине, (3) транспорта загађења ваздуха и (4) утицаја фактора животне средине на здравље људи и морталитет.

Његов досадашњи рад укључује 20 радова категорија М20, као и 10 поглавља у међународним монографијама категорија М10. Од 20 радова, 2 су објављена у часописима изузетних вредности категорије М21а, 11 у врхунским међународним часописима категорије М21. Има развијену међународну научну сарадњу са истраживачком групом у Републици Хрватској (Институт за медицинска истраживања и медицину рада).

Кандидат је учествовао у израдама 2 докторске дисертације, 2 мастер рада и 3 дипломска рада, током школске 2016/2017. године водио је пројекат студентске праксе за студенте Физичког факултета Универзитета у Београду, а током 2019. године био ментор матурског рада ученика Математичке гимназије у Београду.

Током 2019. године кандидат је учествовао у акредитацији, а потом је ангажован и као предавач на студијском програму *Животна средина и одрживи развој* Универзитета Сингидунум у Београду, на основним, мастер и докторским студијама.

4. ПРЕГЛЕД НАУЧНЕ АКТИВНОСТИ

Др Андреја Стојић се бави изучавањем утицаја фактора и процеса животне средине (природни и антропогени извори емисије, метеоролошки и биотички фактори, топографске карактеристике и др.) који одређују концентрације загађујућих супстанци у атмосфери и њихову еволуцију у времену и простору. Пораст броја становника урбаних средина, економски развој, потребе за енергијом, урбанизација и транспорт, питање загађења стављају у фокус савременог друштва, првенствено због штетних ефеката на јавно здравље, животну средину и климатски систем. Идентификација и карактеризација појединачних извора загађења, локалне и макроскопске динамике (регионалне и глобалне), просторних расподела, доприноса укупном загађењу и механизама трансформације, су од суштинског значаја за разумевање утицаја на процесе унутар природних и антропогених екосистема и њихове отпорности. Резултати ових истраживања представљају основу за формирање научно утемељених стратегија усмерених ка побољшању квалитета животне средине, унапређењу здравља људи и ублажавању ефеката климатских промена.

У свом раду кандидат користи експерименталне и теоријске методе из различитих области опште и интердисциплинарне физике и атмосферске хемије, као и концепте и методе науке о подацима. У досадашњем раду бавио се увођењем напредних, унапређењем постојећих и развојем нових метода анализе загађења ваздуха у отвореном и затвореном простору, мултифазних система животне средине, транспорта загађења ваздуха и утицаја фактора животне средине на здравље људи и морталитет. У последње време примарни фокус истраживања кандидата је усмерен на анализу глобалне еволуције загађења ваздуха засноване на јавно доступним подацима и примени најнапреднијих метода ML и XAI.

Рад кандидата се може поделити на следеће теме:

- Физика и хемија животне средине
- Мултифазни системи животне средине
- Транспорт загађења ваздуха
- Утицај фактора животне средине на здравље људи и морталитет

Напомена: радови објављени након претходног избора у звање су означени звездицом (*).

4.1 Физика и хемија животне средине

Циљ истраживања у оквиру ове теме, коју је кандидат покренуо током докторских студија, састоји се у испитивању просторно-временских расподела загађења ваздуха насталих појединачним и комбинованим утицајима фактора животне средине, попут извора емисије, дисперзије, транспорта загађења, сезоналности, механизама трансформације, топографије, итд. Истраживања су заснована на анализи ИОЈ,[1] аеросола и њиховог хемијског састава (елементни/органски угљеник, тешки метали, јони), неорганских гасних оксида (угљен моноксид, тропосферски озон, оксиди азота и сумпор диоксид) и чађи. Примена великог броја статистичких метода (методе анализе

[1] Прве научне активности кандидата су биле везане за увођење методе масене спектрометрије са трансфером протона (*proton transfer reaction mass spectrometry* – PTR-MS) и мерење концентрација ИОЈ у реалном времену

временских серија, рецепторски модели, мултифрактал и инверзна мултифрактал анализа, хибридни рецепторски модели, различите врсте поларних зависности од компоненти ветра, итд.), метода машинског учења (случајне шуме) и њихова хибридизација, омогућила је значајно побољшање квалитета и општег нивоа закључака у вези са процесима који одређују порекло и еволуцију загађујућих супстанци у ваздуху. Коришћена методологија је обезбедила прецизнију идентификацију и квантификацију локалних, регионалних и удаљених извора загађења, као и фактора животне средине који одређују нивое, промене, флуктуације и сингуларитете [1] концентрација загађујућих супстанци у тропосфери.

У оквиру ове теме су испитане могућности прогнозе концентрација PM_{10} и доприноса извора ИОЈ базиране на примени машинског учења (TMVA, ROOT). Применом рецепторских модела (позитивна факторизација матрица – PMF и *Unmix*) на концентрације ИОЈ, суспендованих честица (PM_{10}) и неорганских гасних оксида (CO, NO_x, NO, NO_2 и SO_2), израчунати су доприноси концентрацијама ИОЈ који потичу из саобраћаја и индустрије. Резултати показују да су методе стабала одлучивања и неуронских мрежа дале најбоље перформансе. Тачност прогнозе је била висока у случају извора ИОЈ (најмања релативна грешка 6%), док је у случају PM_{10} била нешто нижа (најмања релативна грешка 24,6%).

Наведени резултати су приказани у следећим радовима:

- **Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements*
  A. Stojić, S.S. Stojić, I. Reljin, M. Čabarkapa, A. Šoštarić, M. Perišić and Z. Mijić
  Environ. Sci. Pollut. R. **23(11),** 10722-10732 (2016) (ИФ: 2,741)

- **Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area*
  M. Todorović, M. Perišić, M. Kuzmanoski, **A. Stojić**, A. Šoštarić, Z. Mijić and S. Rajšić
  J. Environ. Sci. Heal. A **50(13)**, 1351-1359 (2015) (ИФ: 1,276)

- *Forecasting hourly particulate matter concentrations based on the advanced multivariate methods*
  M. Perišić, D. Maletić., S.S. Stojić, S. Rajšić and **A. Stojić**
  Int. J. Environ. Sci. Te. **14(5)**, 1047-1054 (2017) (ИФ: 2,037)
- *Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods*
  A. Stojić, D. Maletić, S.S. Stojić, Z. Mijić and A. Šoštarić
  Sci. Total Environ. **521**, 19-26 (2015) (ИФ: 3,976)

- *Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling*
  A. Stojić, S. S. Stojić, Z. Mijić, A. Šoštarić and S. Rajšić
  Atmos. Environ. **106**, 71-79 (2015) (ИФ: 3,459)

- *Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling*
  A. Stojić, S.S. Stojić, A. Šoštarić, L. Ilić, Z. Mijić and S. Rajšić
  Environ. Sci. Pollut. R. **22(17)**, 13137-13152 (2015) (ИФ: 2,76)

[1] Појава концентрација које се значајно разликују у односу на концентрације измерене пре и после

- *Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data*
  M. Perišić, M., **A. Stojić,** S.S. Stojić, A. Šoštarić, Z. Mijić and S. Rajšić
  Air Qual. Atmos. Hlth. **8(4)**, 379-389 (2014) (ИФ: 1,804)
- *Receptor modeling studies for the characterization of PM_{10} pollution sources in Belgrade*
  Z. Mijić, **A. Stojić**, M. Perišić, S. Rajšić, M. Tasić
  Chemical Industry and Chemical Engineering Quarterly, **18(4-2)**, 623-634 (2012) (ИФ: 0,533)
- *Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade*
  Z. Mijić, **A. Stojić**, M. Perišić, S. Rajšić, M. Tasić, M. Radenković, J. Joksić
  Atmos. Environ. **44(30)**, 3630-3637 (2010) (ИФ: 3,226)

4.2 Мултифазни системи животне средине

Моноароматични угљоводоници бензен, толуен, етилбензен и изомери ксилена (*benzene, toluene, ethylbenzene, xylene* – BTEX) се сматрају носиоцима загађења пореклом из антропогених извора. Повишене концентрације ових токсичних, мутагених и канцерогених једињења у урбаним срединама представљају проблем од научне и практичне важности због њиховог утицаја на животну средину и здравље људи. Циљ истраживања спроведених у оквиру ове теме био је утврђивање механизама уклањања BTEX из атмосфере процесима мокре депозиције. Истраживања су вршена у симулираним (лабораторијским) и реалним условима.

Развој и примена експерименталне методологије за анализу мултифазних система животне средине

За потребе симулације интеракција које прате мокру депозицију ИОЈ и експерименталног одређивања коефицијента расподеле ових једињења између течне и гасне фазе, развијен је оригинални динамички аналитички систем. Укратко, систем се састоји из динамичке реакционе коморе, у којој се симулирају процеси мокре депозиције, и масеног спектрометра са трансфером протона, помоћу кога се мере промене концентрација ИОЈ у реалном времену. За обраду добијених резултата мерења развијен је низ статистичких процедура за квантитативно одређивање релевантних параметара. Оне укључују примену параметарских функција за фитовање сигнала, испитивање квалитета фита, одређивање карактеристика еквилибријума (време успостављања и концентрација), израчунавање количина аналита у течној и гасној фази, итд.

У оквиру ове теме је показано да је фактор обогаћења течне фазе једињењима BTEX, дефинисан као однос коефицијента расподеле између фаза и Хенријеве константе, знатно већи од вредности коју предвиђа Хенријев закон. Иако су ароматична једињења на макроскопском нивоу хидрофобна, бензенов прстен може имати улогу акцептора водоничне везе. Афинитет BTEX према формирању водоничне везе је одређен тенденцијом једињења да отпушта електроне, исказаном кроз јонизациони потенцијал. Изразито негативна линеарна веза између фактора обогаћења и јонизационог потенцијала указује на то да водонична веза не може бити механизам који доводи до обогаћења течне фазе. Утицај адсорпције на граници фаза на обогаћење течне фазе је испитиван анализом функционалне зависности између фактора обогаћења и неколико величина, којима се адсорпција на граници фаза може квантификовати. Позитивна линеарна веза између обогаћења и хидрофобности, дефинисане логаритмом коефицијента расподеле између октанола и воде, потврђује да је адсорпција на површини фаза доминантни механизам који га одређује. Такође, потврђено је да обогаћење површине на граници фаза расте са величином молекула, као и да је обогаћење обрнуто пропорционално запремини течне фазе и молским уделима BTEX у гасној фази, што такође иде у прилог овом механизму. На крају, добијена позитивна линеарна зависност између фактора обогаћења и ван дер Валсове површине показују одређени утицај ван дер Валсове интеракције на адсорпцију (физисорпција) и расподеле BTEX у мултифазним системима.

Испитивање капацитета кише за уклањање ИОЈ из атмосфере

Поред адсорпције на граници фаза, у истраживању у реалним условима су разматрани утицаји молских удела BTEX у амбијенталном ваздуху, метеоролошких параметара и физичко-хемијских карактеристика и састава кише (утицај матрице). Утицај промене температуре на Хенријеву константу и фактор обогаћења је размотрен анализом вертикалних профила температуре између површине тла и висине базе облака. На овај начин је добијен вертикални профил фактора обогаћења, из кога се може закључити да се услови који одређују интеракције које доводе до расподеле BTEX између течне и гасне фазе не мењају значајно са повећањем висине. Применом различитих статистичких метода и метода машинског учења идентификована су четири типа извора који одређују састав кише: извор гасовитих органских једињења, извор чврсте фракције, извор који карактерише висок удео елемената пореклом из Земљине коре и извор који представља фракцију аеросола. Показано је да молски удели BTEX у амбијенталном ваздуху и поједине физичко-хемијске карактеристике имају већи утицај на расподелу ових једињења између фаза у односу на метеоролошке параметре. Утврђено је да је фактор обогаћења узорака кише већи у односу на симулиране услове због присуства молекула BTEX адсорбованих на површини аеросола.

Напредак у машинском учењу је резултирао бројним применама сложених алгоритама за предикцију, што је последњих година довело и до развоја метода за интерпретацију добијених модела. У оквиру ове теме, везе између концентрација TEX у кишници и фактора обогаћења, с једне, и многобројних фактора животне средине, са друге стране (концентрације TEX у амбијенталном ваздуху, физичко-хемијски параметри кишнице и метеоролошки параметри), су први пут моделиране применом машинског учења – ансамбли стабала одлучивања (*eXtreme Gradient Boosting* – XGBoost). Увид у физичко-хемијске процесе који управљају депозицијом TEX је остварен интерпретацијом добијених модела применом напредног метода *explainable artificial intelligence* – XAI (*SHapley Additive exPlanations* – SHAP). На овај начин су по први пут утврђене расподеле утицаја фактора животне средине на концентрације TEX у кишници и факторе обогаћења кишнице овим једињењима. Показано је да су концентрације TEX у амбијенталном ваздуху и температуре кишнице и ваздуха доминантни фактори који обликују расподеле ових једињења у кишници. Далеко мање важни утицаји се могу приписати брзини ветра, атмосферском притиску, замућености кишнице и садржају укупног органског угљеника, NO_3^-, Cl^- и K^+, док су се утицаји осталих фактора показали занемарљивим.

Наведени резултати су приказани у следећим радовима:

- **Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition*

A. Stojić, N. Stanić, G. Vuković, S. Stanišić, M. Perišić, A. Šoštarić and L. Lazić
Sci. Total Environ. **653**, 140–147 (2019) (ИФ: 5,589)

- **Rainwater capacities for BTEX scavenging from ambient air*
A. Šoštarić, S.S. Stojić, G. Vuković, Z. Mijić, **A. Stojić** and I. Gržetić
Atmos. Environ. **168**, 46-54 (2017) (ИФ: 3,708)
- **Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system*
A. Šoštarić, **A. Stojić**, S.S. Stojić and I. Gržetić
Chemosphere, **144**, 721-727 (2016) (ИФ: 4,208)

4.3 Транспорт загађења ваздуха

Идентификација и карактеризација удаљених извора емисије загађења ваздуха и њиховог доприноса измереним концентрацијама загађујућих супстанци на месту рецептора (мерно место) се може извршити применом хибридних рецепторских модела (ХРМ). Ови модели су базирани на повезивању концентрација измерених на месту рецептора и трајекторија транспорта ваздуха из удаљених области. Постоје четири основна недостатка стандардних ХРМ. Први се огледа у недовољном укључивању фактора релевантних за транспорт загађења ваздуха посматраног са места рецептора, што доводи до прецењивања утицаја удаљених извора емисије и недовољно прецизне или чак погрешне идентификације географских области које одређују порекло загађења. Други недостатак се огледа у дводимензионалном приступу, што онемогућава моделирање вертикалних расподела загађења, веома важних за анализу образаца циркулације ваздуха и процену изложености људи и животне средине. Трећи недостатак везан је за веома ниску резолуцију крајњих тачака трајекторија које укључују стандардни модели, што онемогућава задовољавајућу идентификацију области релевантних за анализу транспорта. Овај недостатак уводи и веома важно ограничење за примену ХРМ који се не могу користити за идентификацију локалних извора загађења. На крају, стандардни ХРМ се не могу користити за карактеризацију извора загађења, односно одређивање типа извора емисије.

Најважнији резултат у оквиру истраживања у овој теми се односи на развој тродимензионалног ХРМ – гранични слој отежињен концентрацијама (*concentration weighted boundary layer* – CWBL), јединог ХРМ који обезбеђује анализу континуалних вертикалних расподела загађења ваздуха дуж путања транспорта посматраних са места рецептора. По први пут су размотрени и укључени ефекти флуктуације планетарног граничног слоја и његовог утицаја на транспорт загађења и измерене концентрације на месту рецептора. Значајни резултати се огледају у развоју тродимензионалних варијанти постојећих ХРМ, попут тродимензионалне функције потенцијалних доприноса (3D *potential source contribution function* – 3D PSCF) и тродимензионалних трајекторија отежињених концентрацијама (3D *concentration weighted trajectory* – 3D CWT), који дају дискретне вертикалне расподеле загађења.

Веома значајан резултат представља и унапређење приступу анализи транспорта применом ХРМ који обухвата прецизну формулацију релевантних података и апроксимација који улазе у саме моделе у које спадају (1) издвајање удела транспортованог загађења у измереним концентрацијама дате загађујуће супстанце и (2) идентификација крајњих тачака трајекторија кретања ваздуха репрезентативних за транспорт загађења посматраног са места рецептора. Први сегмент унапређења омогућава диференцијацију апсолутног удела позадинског нивоа загађења, локалних извора и процеса транспорта за концентрације загађујућих супстанци на месту рецептора. Овим приступом се у ХРМ укључују само удели концентрација који одговарају транспортованом загађењу, чиме се у значајној мери решава проблем прецењивања утицаја удаљених извора емисије стандардних модела. Други сегмент обезбеђује критеријуме за укључивање крајњих тачака трајекторија кретања ваздуха на основу висине планетарног граничног слоја. На овај начин се из анализе транспорта искључују крајње тачке које није могуће повезати са измереним концентрацијама на месту рецептора, чиме се у значајној мери решава проблем недовољно прецизне идентификације географских области које одређују порекло загађења.

Као резултат пројекта *Мапирање извора токсичних, мутагених и канцерогених испарљивих органских једињења на територији Града Београда*, финансираног од стране Зеленог фонда, Министарства заштите животне средине Републике Србије којим је кандидат руководио, представљен је развој иновативне методологије засноване на новим локалним рецепторски оријентисаним моделима и алгоритмима вештачке интелигенције имплементиране кроз методе машинског учења, за мапирање и карактеризацију извора и просторно-временску прогнозу загађујућих супстанци у ваздуху. Резултати пројекта обезбеђују и решења за преостала два основна недостатка стандардних ХРМ, чиме се решава проблем репрезентативности области релевантне за анализу транспорта, отклања ограничење које онемогућава анализе локалних извора загађења и решава проблем карактеризације извора емисије.

У истраживањима у оквиру ове теме је показано да наведене методе издвајања удела концетрација и репрезентативних крајњих тачака трајекторија, као и нови модели, омогућавају знатно прецизнију идентификацију, али и карактеризацију локалних и удаљених извора загађења ваздуха. Сва истраживања поред испитивања расподела појединих загађујућих супстанци, обухватају и анализу расподела извора загађења, попут саобраћаја и индустрије.

Методе развијене у оквиру ове теме имају и практичну примену, што се може видети на основу резултата пројекта *Мапирање извора токсичних, мутагених и канцерогених испарљивих органских једињења на територији Града Београда* (http://bpm.ipb.ac.rs/).

Наведени резултати су приказани у следећим радовима:

- **The innovative concept of three-dimensional hybrid receptor modeling*
  Stojić and S.S. Stojić
  Atmos. Environ. **164**, 216-223 (2017) (ИФ: 3,708)

- **Levels of PM_{10} bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation*

M. Perišić, S. Rajšić, A. Šoštarić, Z. Mijić, and **A. Stojić**
Air Qual. Atmos. Hlth. **10(1)**, 93-103 (2017) (ИФ: 2,662)

- **Comprehensive analysis of* PM_{10} *in Belgrade urban area on the basis of long-term measurements*
  Stojić, S.S. Stojić, I. Reljin, M. Čabarkapa, A. Šoštarić, M. Perišić and Z. Mijić
  Environ. Sci. Pollut. R. **23(11),** 10722-10732 (2016) (ИФ: 2.741)
- *Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling*
  Stojić, S. S. Stojić, Z. Mijić, A. Šoštarić and S. Rajšić
  Atmos. Environ. **106**, 71-79 (2015) (ИФ: 3,459)

4.4 Утицај фактора животне средине на здравље људи и морталитет

Током последњих деценија загађење ваздуха је препознато као глобална претња здрављу људи. Процењује се да се 4,2 милиона смрти услед кардио-васкуларних, малигних и хроничних респираторних обољења може повезати са загађењем ваздуха.

У оквиру ове теме су испитани канцерогени и неканцерогени утицаји честичног загађења у Београду, укључујући и његов хемијски састав (тешки метали и бензо[a]пирен). Показано је да Cr и бензо[a]пирен значајно доприносе повећавању ризика за настанак канцера, док је дејство As и Ni веома токсично, нарочито на урбаним локацијама под утицајем саобраћаја. Такође, утврђено је и да утицај транспортованог загађења у одређеним периодима може бити веома значајан (36%).

Поред канцерогених и неканцерогених здравствених ризика, испитани су и утицаји краткорочне и дугорочне изложености загађујућим супстанцама (PM_{10}, SO_2, NO_2 и чађ) на морталитет изазван кардио-васкуларним и респираторним обољењима. Нелинеарна веза између изложености загађењу, ризика од смртности и одложених ефеката услед варијација температуре је моделирана применом *distributed lag nonlinear models*. Резултати су показали да краткорочна изложеност повишеним концентрацијама испитиваних загађујућих супстанци не повећава значајно ризик од смртности. С друге стране, показана је јасна веза у случају изложености од 90 дана. Утицај хроничне изложености на смртност је израженији у случају респираторних обољења у односу на кардио-васкуларна, нарочито у случају мушке популације млађе од 65 година.

У оквиру ове теме је развијена нова метода за укључивање кумулативних средњорочних ефеката загађења ваздуха у Поасонов регресиони модел за процену ризика смртности од кардио-васкуларних и респираторних обољења због климатских фактора. Реалније процене ризика од смртности повезане са екстремним климатским условима постају све важније за планирање будућих стратегија и мера прилагођавања актуелним климатским променама. Утврђено је да су кумулативни средњорочни ефекти загађења ваздуха значајнији од одложених (*lag-specific*), који су углавном укључени у регресионе моделе. Такође, показано је да постоји оптимални распон температуре унутар кога се не очекује повећање стопе смртности повезане са њеном променом, што је различито у односу на дотадашње студије. С друге стране, утврђено је да ефекти загађења ваздуха добро објашњавају ризик од смртности током хладнијег времена, који је некада био повезиван искључиво са утицајем температуре. Показано је да је процењени релативни значај честичног загађења мањи од преостале три испитиване врсте загађујућих супстанци (сумпор-диоксид, азот-диоксид и чађ), што значи да укључивање искључиво података о концентрацији аеросола није најефикаснији начин за процену утицаја загађења ваздуха на здравље људи.

Такође, у оквиру ове теме је разматрана и акумулација перзистентних органских полутаната (*persistent organic pollutants* – POPs) у мајчином млеку и њихова веза са годинама мајке и бројем рођене деце. Применом великог броја статистичких метода и ML откривена је важност конституентних дескриптора конгенера за акумулацију органохлорних пестицида (OCPs) и полихлорованих бифенила (PCBs), попут броја и положаја атома хлора прикључуеног на фенил прстен (орто-положај). Показано је да нивои PCBs не зависе од броја рођене деце. С друге стране, утврђена је значајна међусобна веза између PCB конгенера -153, -180, -170, -118, -156, -105 и -138 због њихове хемијске структуре и метаболичких процеса у телу мајке.

Наведени резултати су приказани у следећим радовима:

- *_Introducing of modeling techniques in the research of POPs in breast milk – A pilot study_
  G. Jovanović, S. Herceg Romanić, **A. Stojić**, D. Klinčić, M. Matek Sarić, J. Grzunov Letinić and A. Popović
  Ecotox. Environ. Safe., **172**, 341-347 (2019) (ИФ: 4,527)
- *_Levels of PM_{10} bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation_
  M. Perišić, S. Rajšić, A. Šoštarić, Z. Mijić, and **A. Stojić**
  Air Qual. Atmos. Hlth. **10(1)**, 93-103 (2017) (ИФ: 2,662)
- *_Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area_
  S.S. Stojić, N. Stanišić and **A. Stojić**
  Environ. Health, **15(1)**, 73 (2016) (ИФ: 3,816)
- *_Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia_
  S.S. Stojić, N. Stanišić, **A. Stojić** and A. Šoštarić
  J. Toxicol. Env. Heal. A **79(1)**, 17-27 (2016) (ИФ: 2,731)
- *_Seasonal mortality variations of cardiovascular, respiratory and malignant diseases in the City of Belgrade_
  S.S. Stojić, N. Stanišić, **A. Stojić** and V. Džamić
  Stanovništvo, 54(1), 83-104 (2016)
- _Heavy metal accumulation in wheat and barley: The effects of soil presence and liquid manure amendment_
  S.S. Stojić, L. Ignjatović, S. Popov, S. Škrivanj, A. Đorđević. and **A. Stojić**
  Plant Biosyst. **150(1)**, 104-110 (2016) (ИФ: 1,39)
- _Essential oils of two Nepeta species inhibit growth and induce oxidative stress in ragweed (Ambrosia artemisiifolia L.) shoots in vitro_
  S. Dmitrović, M. Perišić, **A. Stojić**, S. Živković, J. Boljević, J.N. Živković and D. Mišić
  Acta Physiol. Plant. **37(3),** 1-15 (2015) (ИФ: 1,563)

5. ЕЛЕМЕНТИ ЗА КВАЛИТАТИВНУ ОЦЕНУ НАУЧНОГ ДОПРИНОСА КАНДИДАТА

5.1 Квалитет научних резултата

5.1.1 Научни ниво и значај резултата, утицај научних радова

Др Андреја Стојић је у свом досадашњем раду дао кључни допринос у истраживању на укупно 20 радова објављених у категорији М20, као и 10 поглавља у књизи категорије М10, од којих је 8 објављено у истакнутим монографијама међународног значаја. Од 20 радова, 2 су објављена у часописима категорије М21а (међународни часописи изузетних вредности), 11 у часописима категорије М21 (врхунски међународни часописи), 4 у часописима категорије М22 (истакнути међународни часописи), 2 у часописима категорије М23 (међународни часописи), док је 1 објављен у категорији М24 (национални часописи међународног значаја).

У периоду након доношења одлуке Научног већа Института за физику о предлогу за стицање претходног научног звања, др Стојић је објавио 12 радова у часописима са ISI листе. Од тога је 1 рад објављен у часопису категорије М21а (међународни часописи изузетних вредности), 8 у часописима категорије М21 (врхунски међународни часописи), 2 у часописима категорије М22 (истакнути међународни часописи), док је 1 објављен у категорији М24 (национални часописи међународног значаја). Такође, кандидат је у том периоду објавио 5 поглавља у истакнутим монографијама међународног значаја категорије М13 и одржао 1 предавање по позиву на међународном скупу.

Као пет најзначајнијих радова др Стојића издвајају се:

1. *Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition*
   A. Stojić, N. Stanić, G. Vuković, S. Stanišić, M. Perišić, A. Šoštarić and L. Lazić Sci. Total Environ. **653**, 140–147 (2019), M21 (ИФ: 5,589), цитиран 2 пута.

2. *The innovative concept of three-dimensional hybrid receptor modeling*
   A. Stojić and S. Stanišić Stojić
   Atmos. Environ. **164**, 216 223 (2017), M21 (ИФ: 3,708), цитиран 1 пут.

3. *Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area*
   S. Stanišić Stojić, N. S. Stanišić and **A. Stojić**
   J. Environ. Health, **15(1)**, 73 (2016), M21a (ИФ: 3,816), цитиран 4 пута.

4. *Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements*
   A. Stojić, S. Stanišić Stojić, I. Reljin, M. Čabarkapa, A. Šoštarić, M. Perišić and Z. Mijić
   Environ. Sci. Pollut. Res. **23(11)**, 10722-10732 (2016), M21 (ИФ: 2,741), цитиран 5 пута.

5. *Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods*

A. Stojić, D. Maletić, S. Stanišić Stojić, Z. Mijić and A. Šoštarić
Sci. Total Environ. **521**, 19-26 (2015), M21a (ИФ: 3,976), цитиран 11 пута.

У свих 5 радова је кандидат дао кључни научни допринос и може сматрати основним/најважнијим аутором. Радови изузев петог су објављени у периоду након избора у претходно звање.

У првом раду су испитани фактори животне средине који одређују уклањање толуена, етилбензена и ксилена из амбијенталног ваздуха у процесу влажне депозиције унутар биогеохемијског циклуса испарљивих органских једињења. Испитане су расподеле TEX између течне и гасне фазе, као и одговарајући фактори обогаћења кишнице. Показано је да су концентрације ових једињења у амбијенталном ваздуху и температуре кишнице и ваздуха доминантни фактори који обликују расподеле TEX у кишници. Далеко мање важни утицаји се могу приписати брзини ветра, атмосферском притиску, замућености кишнице и садржају укупног органског угљеника, NO_3^-, Cl^- и K^+, док су се утицаји осталих фактора показали занемарљивим. У раду су везе између концентрација TEX у кишници и фактора обогаћења, с једне, и многобројних фактора животне средине, са друге стране (концентрације TEX у амбијенталном ваздуху, физичко-хемијски параметри кишнице и метеоролошки параметри), први пут моделиране применом машинског учења (XGBoost). Увид у физичко-хемијске процесе који управљају депозицијом TEX остварен је интерпретацијом добијених модела применом напредног метода XAI (SHAP). На овај начин су по први пут утврђене расподеле утицаја фактора животне на концентрације TEX у кишници и факторе обогаћења кишнице овим једињењима.

У другом раду су приказани резултати унапређеног приступа анализи транспорта загађења ваздуха базираног на хибридним рецепторским моделима. Основни недостаци ХРМ су се огледали у недовољном укључивању фактора релевантних за транспорт загађења посматраног са места рецептора. Такође, дводимензионални приступ (географска ширина и географска дужина) није омогућавао анализу вертикалних расподела загађења, веома важних за анализу образаца циркулације ваздуха и процену изложености људи и животне средине. Унапређење приказано у раду обухвата увођење три сегмента који обезбеђују анализу вертикалних расподела загађења ваздуха дуж путања транспорта: (1) издвајање удела транспортованог загађења у измереним концентрацијама дате загађујуће супстанце, (2) идентификацију крајњих тачака трајекторија кретања ваздуха репрезентативних за транспорт загађења посматраног са места рецептора и (3) развој тродимензионалних ХРМ. Први сегмент омогућава диференцијацију апсолутног удела позадинског нивоа загађења, локалних извора и процеса транспорта за концентрације загађујућих супстанци на месту рецептора. Овим приступом се у ХРМ укључују само удели концентрација који одговарају транспортованом загађењу. Други сегмент обезбеђује критеријуме за укључивање крајњих тачака трајекторија кретања ваздуха на основу висине планетарног граничног слоја. На овај начин се из анализе транспорта искључују крајње тачке које није могуће повезати са измереним концентрацијама на месту рецептора. Трећи сегмент представља приказ развоја првих тродимензионалних ХРМ: (1) 3Д функција потенцијалних доприноса (3D PSCF), (2) 3Д трајекторије отежињене концентрацијама (3D CWT), (3) гранични слој отежињен концентрацијама (CWBL).

У трећем раду је приказана нова метода за укључивање кумулативних средњорочних ефеката загађења ваздуха у Поасонов регресиони модел за процену ризика од смртности од кардио-васкуларних и респираторних обољења због климатских фактора. Реалније процене ризика смртности повезане са екстремним климатским условима постају све важније за планирање будућих стратегија и мера прилагођавања актуелним климатским променама. Утврђено је да су кумулативни средњорочни ефекти загађења ваздуха значајнији од одложених, који су углавном укључени у регресионе моделе. Такође, показано је постоји оптимални распон температуре унутар кога се не очекује повећање стопе смртности повезане са њеном променом, што је различито у односу на дотадашње студије. С друге стране, утврђено је да ефекти загађења ваздуха добро објашњавају ризик од смртности током хладнијег времена, који је некада био повезиван искључиво са утицајем температуре. На тај начин је показано да однос смртности која се може приписати екстремно хладном времену и смртности услед топлотних таласа од једног реда величине не важи глобално. На крају, утврђено је да је процењени релативни значај честичног загађења мањи од преостале три испитиване врсте загађујућих супстанци (сумпор-диоксид, азот-диоксид и чађ), што значи да укључивање искључиво података о концентрацији аеросола није најефикаснији начин за процену утицаја загађења ваздуха на здравље људи.

У четвртом раду је приказана широка анализа просторно-временских расподела аеросола, њиховог хемијског састава и односа са другим загађујућим супстанцама и метеоролошким факторима у урбаној средини. Примена великог броја статистичких метода (рецепторски модели, мултифрактал и инверзна мултифрактал анализа, ХРМ, различите врсте поларних зависности од компоненти ветра, итд.), метода машинског учења (случајне шуме) и њихова хибридизација, омогућила је значајно побољшање квалитета и општости нивоа закључака у вези са процесима који одређују порекло и еволуцију аеросола. Приказана методологија је омогућила прецизнију идентификацију и квантификацију локалних, регионалних и удаљених извора загађења, као и фактора животне средине који одређују нивое, промене, флуктуације и сингуларитете концентрација загађујућих супстанци у тропосфери.

У петом раду су испитане могућности прогнозе доприноса извора ИОЈ базиране на примени машинског учења (TMVA, ROOT). Применом рецепторских модела (PMF и *Unmix*) на концентрације ИОЈ измерених у реалном времену масеним спектрометром са трансфером протона (PTR-MS) и концентрације суспендованих честица (PM_{10}) и неорганских гасних оксида (CO, NO_x, NO, NO_2 и SO_2), израчунати су доприноси концентрацијама ИОЈ која потичу из саобраћаја и индустрије. Могућност прогнозе доприноса испитана је за два случаја: када су као предиктори коришћени искључиво метеоролошки параметри и када су као предиктори коришћени метеоролошки параметри заједно са концентрацијама неорганских гасних оксида. Резултати показују да су методе стабала одлучивања и неуронских мрежа дале најбоље перформансе. Тачност прогнозе је била висока (најмања релативна грешка 6%), посебно када је прогноза била заснована на метеоролошким параметрима и концентрацијама неорганских гасних оксида.

5.1.2 Позитивна цитираност научних радова кандидата

Према бази *ISI Web of Science*, радови др Стојића укупно су цитирани 174 пута, док је број цитата без аутоцитата 128. Према бази *Scopus*, укупан број цитата је 220, док је број цитата без аутоцитата 154. Према подацима из обе базе, Хиршов индекс радова др Стојића је 7.

Прилог: подаци о цитираности радова из интернет база ISI Web of Science и Scopus на дан 23.11.2019. године

5.1.3 Параметри квалитета часописа

Као елемент за процену квалитета научних радова користи се и импакт-фактор часописа у којима су радови објављени. Др Стојић је објављивао радове у часописима категорија M21a, M21, M22, M23 и M24, при чему су подвучени импакт-фактори часописа у којима су публиковани радови након одлуке Научног већа Института за физику у Београду о предлогу за стицање претходног научног звања:

- 2 рада у Science of the Total Environment (ИФ 5,589 за 1 рад и ИФ 3,816 за 1 рад)
- 1 рад у Ecotoxicology and Environmental Safety (ИФ 4,527)
- 1 рад у Chemosphere (ИФ 4,208)
- 1 рад у Environmental Health: A Global Access Science Source (ИФ 3,816)
- 4 рада у Atmospheric Environment (ИФ 3,708 за 2 рада и ИФ 3,459 за 1 рад и ИФ 3,226 за 1 рад)
- 2 рада у Environmental Science and Pollution Research (ИФ 2,76 за 1 рад и ИФ 2,741 за 1 рад)
- 1 рад у Journal of Toxicology and Environmental Health, Part A (ИФ 2,731)
- 2 рада у Air Quality, Atmosphere and Health (ИФ 2,662 за 1 рад и ИФ 1,804 за 1 рад)
- 1 рад у International Journal of Environmental Science and Technology (ИФ 2,037)
- 1 рад у Plant Biosystems (ИФ 1,39)
- 1 рад у Acta Physiologiae Plantarum (ИФ 1,563)
- 1 рад у Journal of Environmental Science and Health, Part A (ИФ 1,276)
- 1 рад у Chemical Industry and Chemical Engineering Quarterly (ИФ 0,533)

Укупан импакт-фактор радова др Стојића износи 55,714, а у периоду након одлуке Научног већа Института за физику у Београду о предлогу за стицање претходног научног звања радова сумарни импакт фактор је 37,003. Часописи у којима објављује др Стојић су цењени по свом угледу и водећи у његовим областима рада. Међу поменутим часописима посебно се истичу *Science of the Total Environment*, *Environmental Health*, *Ecotoxicology and Environmental Safety*, *Atmospheric Environment* и *Chemosphere*.

Додатни библиометријски показатељи према Упутству о начину писања извештаја о изборима у звања које је усвојио Матични научни одбор за физику приказани су у следећој табели:

	ИФ	М	СНИП
Укупно	37,003	89	13,774
Усредњено по чланку	3,084	7,417	1,148
Усредњено по аутору	8,438	19,624	3,179

5.1.4 Степен самосталности и степен учешћа у реализацији радова у научним центрима у земљи и иностранству

Од 20 објављених радова, др Стојић је први аутор на 6 радова, други наведени аутор на 4 рада, трећи аутор на 4 рада, и последњи аутор на 3 рада. На радовима који су објављени у периоду након одлуке Научног већа Института за физику о предлогу за стицање претходног научног звања, др Стојић је први аутор на 3 рада, други наведени аутор на 1 раду, трећи наведени аутор на 3 рада и последњи аутор на 3 рада. Од 10 поглавља у монографијама од међународног значаја, др Стојић је први аутор на 2, други наведени аутор на 4 и последњи аутор на 1. На поглављима објављеним у периоду након одлуке Научног већа Института за физику о предлогу за стицање претходног научног звања, др Стојић је први аутор на 1, други наведени аутор на 3 и последњи аутор на 1.

При изради поменутих публикација, др Стојић је учествовао у осмишљавању и формулацији проблема, конструкцији релевантних прикупљању података, развоју теоријских метода за анализу добијених резултата, моделирању и обради података, као и писању.

Током докторских студија кандидат се бавио проучавањем утицаја атмосферског загађења на животну средину, здравље људи и климатске промене. Бавио се увођењем методе масене спектрометрије са трансфером протона (PTR-MS) и мерењем концентрација великог броја ИОЈ у амбијенталном ваздуху и контролисаним, лабораторијским условима. Примарни фокус истраживања је био одређивање порекла атмосферских аеросола и ИОЈ, њихове динамике, структуре просторне расподеле, као и феномена и међусобних спрега које их дефинишу. Кандидат је учествовао у развоју нове методе прогнозе динамике доприноса извора загађујућих супстанци базиране на примени напредних метода машинског учења.

Након завршеног доктората, активности кандидата су усмерене ка разумевању улоге загађења ваздуха у његовом кружењу од извора загађења, преко атмосферских феномена и процеса у којима учествује, до утицаја на људе и животну средину. Активности се могу поделити у три дела: (1) прикупљање података кроз експеримент (мерење концентрација великог броја загађујућих супстанци у амбијенталном ваздуху; мерење концентрација ИОЈ у реалним и симулираним мултифазним системима животне средине) и јавно доступне базе података (морталитет – надлежне институције у Србији; загађујуће супстанце – *European Environmental Agency* и US EPA; метеоролошки параметри – NOAA), (2) анализу података применом великог броја статистичких метода и метода машинског учења за сагледавање феномена из различитих углова и (3) моделирање, које обухвата и развој статистичких метода (мултифазни системи животне средине; транспорт загађења ваздуха; утицај на здравље људи). Кандидат је покренуо истраживања усмерена ка анализи феномена из животне средине у контексту у коме се појављују применом најнапреднијих метода ML и XAI (загађење ваздуха; мултифазни системи животне средине; хумани биомониоринг). Са колегама из Института за физику у Београду и Института за медицинска истраживања и медицину рада, Република Хрватска, покренуо је истраживања перзистентних органских једињења у рибама и мајчином млеку базирана на примени најнапреднијих метода обраде података.

5.1.5 Награде

Сертификати о завршеним тренинзима на 3rd, 4th и 7th *Hands on PTR-MS* (2009, 2011, и 2019. године, Аустрија).

Прилог: сертификат о завршеном тренинг курсу

5.2 Ангажованост у формирању научних кадрова

Др Андреја Стојић је учествовао у израдама 2 докторске дисертације (Мирјана Перишић, 2016. година, *Примена хибридних рецепторских модела у анализи квалитета ваздуха и транспорта загађујућих материја у Београду*, Физички факултет Универзитета у Београду; Андреј Шоштарић, 2017. година, *Механизми уклањања лако испарљивих моноароматичних угљоводоника (BTEX) из амбијенталног ваздуха мокром депозицијом*, Хемијски факултет Универзитета у Београду), 2 мастер рада (Ружица Шебек, 2017. година, *Сезонске варијације концентрација PM_{10} за Београд рачунате дисперзионим моделом*, Физички факултет Универзитета у Београду; Наташа Станојковић, 2019. година, *Климатске промене: могући утицај на здравље и морталитет у Новом Саду*, Животна средина и одрживи развој, Универзитет Сингидунум) и 3 дипломска рада (Никола Петровић, 2008. година, *Мониторинг испарљивих органских једињења у ваздуху*, Физички факултет Универзитета у Београду; Драгослав Ристић, 2010. година, *Мерења испарљивих органских једињења масеним спектрометром са трансфером протона*, Физички факултет Универзитета у Београду; Марија Тодоровић, 2012. година, *Мерење испарљивих органских једињења масеним спектрометром са трансфером протона – проблеми при мерењу у зависности од услова у реакционој комори*, Факултет за физичку хемију Универзитета у Београду).

У сарадњи са Регионалним центром за таленте Земун, кандидат је током 2012. године радио на изради експерименталних радова са ученицима који су учествовали на Републичком такмичењу младих талената за основне школе.

Током 2019. године кандидат је био ментор матурског рада *Примена метода машинског учења у физици животне средине* Лазара Златића, Математичка гимназија у Београду.

Кандидат је током школске 2016/2017. године водио пројекат студентске праксе *Истраживање квалитета ваздуха*, на коме су учествовала два студената треће године Физичког факултета у Београду.

Током 2019. године кандидат је учествовао у акредитацији, а потом је ангажован и као предавач на студијском програму *Животна средина и одрживи развој* Универзитета Сингидунум у Београду, на основним, мастер и докторским студијама.

Прилог:

- *Изводи из докторских дисертација Мирјане Перишић и Андреја Шоштарића*
- *Извод из мастер рада Наташе Станојковић*
- *Потврда Математичке гимназије у Београду о менторству*
- *Писмо захвалности Студенског парламента на ангажовању на пројекту Студентске праксе*
- *Потврда Универзитета Сингидунум о ангажовању на студијском програму Животна средина и одрживи развој*

5.3 Нормирање броја коауторских радова, патената и техничких решења

Сви радови др Андреје Стојића објављени након одлуке Научног већа Института за физику у Београду о предлогу за стицање претходног научног звања укључују резултате комплексних мерења и анализе података. Сви радови имају седам или мање коаутора, тако да се рачунају са пуним бројем бодова у односу на број коаутора.

5.4 Руковођење пројектима, потпројектима и пројектним задацима

У оквиру националног пројекта интердисциплинарних истраживања ИИИ 43007, под називом *Истраживање климатских промена и њиховог утицаја на животну средину – праћење утицаја, адаптација и ублажавање* руководи фазама истраживања које се односе на мерења и анализе ИОЈ и аеросола.

У периоду од 2019. до 2021. године, кандидат учествује на пројекту билатералне сарадње између Републике Србије и Републике Хрватске *Дуготрајна органохлорна једињења у мајчином млеку и њихов утицај на примарна оштећења ДНК у људским ћелијама*, на коме руководи активностима у вези са обрадом података.

Кандидат је током 2016/2017. године руководио фазама и активностима *Националног центра изузетних вредности за примену плазме у нанотехнологијама, биомедицини и екологији*, Института за физику у Београду.

Током 2018. године кандидат је био руководилац пројекта *Мапирање извора токсичних, мутагених и канцерогених испарљивих органских једињења на територији Града Београда*, финансираног од стране Зеленог фонда, Министарства заштите животне средине Републике Србије.

Прилог:

- *Извод из Годишњег извештаји Центра изузетних вредности за примену плазме у нанотехнологијама, биомедицини и екологији за 2016. годину*
- *Извод из Уговора о партнерској сарадњи за пројекат Мапирање извора токсичних, мутагених и канцерогених испарљивих органских једињења на територији Града Београда*

5.5 Активност у научним и научно-стручним друштвима

Кандидат је рецензент за часописе (рецензије након избора у претходно звање):

- *Science of the Total Environment* (2019. година),
- *Atmospheric Pollution Research* (2019. година),
- *Building and Environment* (2019. година),
- *International Journal of Environmental Research and Public Health* (2019. година),
- *Science and Technology of Nuclear Installations* (2019. година),
- *Ecotoxicology and Environmental Safety* (2018. година),
- *Fuel* (2018. година),
- *Environmental Pollution* (2017. и 2018. година),
- *Environment International* (2016. година),
- *Atmospheric Environment* (2016. година).

Кандидат је члан Асоцијације италијанских и српских научника и истраживача (AIS3).

Прилог:

- *Позиви уредника часописа за рецензију*
- *Писмо потврде регистрације чланства у Асоцијацији италијанских и српских научника и истраживача*

5.6 Утицајност научних резултата

Утицај научних резултата кандидата је приказан у секцији 5.1 овог документа. Поред тога, списак свих публикација и цитата је дат у прилогу, на основу чега се такође може закључити да су радови кандидата јасно препознати у оквиру области опште и интердисциплинарне физике.

5.7 Конкретан допринос кандидата у реализацији радова у земљи и иностранству

Др Андреја Стојић је значајно допринео сваком раду у чијој припреми је учествовао. Од 12 радова објављених у периоду након одлуке Научног већа Института за физику у Београду о предлогу за стицање претходног научног звања, сви радови су урађени у сарадњи с колегама из земље и иностранства. Кандидат је у овим радовима имао кључни допринос: на 3 рада је први аутор, на 1 раду је наведен као други аутор, на 3 рада је трећи аутор и на 3 рада последњи аутор. Током израде ових публикација, он је осмислио тему истраживања и радио на развоју одговарајућих мерних поставки и симулација, прикупљању и анализи релевантних података, развоју теоријских модела, метода и техника анализа проблема, писању радова, а такође је био у комуникацији с уредницима часописа при слању радова за објављивање.

У Институту за физику у Београду кандидат је увео нове методе у проучавање порекла, еволуције и утицаја загађујућих супстанци у атмосфери базиране на мерењима у реалном времену и примени напредних статистичких метода и вештачке интелигенције имплементиране кроз методе машинског учења и *explainable artificial intelligence* за обраду података. Знања и искуства које је стекао у теоријском моделирању, аналитичким методама и техникама анализе у области опште и интердисциплинарне физике успешно преноси млађим сарадницима у Лабораторији за физику животне средине и студентима кроз четири предмета студијског програма *Животна средина и одрживи развој* Универзитета Сингидунум, Београд.

5.8 Уводна предавања на конференцијама и друга предавања

Након претходног избора у звање, др Стојић је одржао следеће уводно предавање по позиву на конференцији:

- **A. Stojić**
  Modeling particulate matter in urban areas: Experiences of the Institute of Physics Belgrade
  The 7th International WeBIOPATR, 1-3 October, 2019, Belgrade, Serbia, M32

Поред тога, одржао је и следећа предавања на међународним конференцијама:

- **A. Stojić**, M. Perišić, G. Jovanović, S. Stanišić, N. Stanić and T. Milićević
  Parsing environmental factors which shape particulate matter pollution using explainable artificial intelligence
  The 7th International WeBIOPATR, 1-3 October, 2019, Belgrade, Serbia, M34

- **A. Stojić** and S.S. Stojić
  Concentration weighted boundary layer hybrid receptor model for analyzing particulate matter altitude distribution

The 6th International WeBIOPATR, 6-8 September, 2017, Belgrade, Serbia, M33

Прилог: Позивно писмо и програми конференција

6. ЕЛЕМЕНТИ ЗА КВАНТИТАТИВНУ ОЦЕНУ НАУЧНОГ ДОПРИНОСА КАНДИДАТА

Остварени резултати у периоду након одлуке Научног већа Института за физику о предлогу за стицање претходног научног звања дати су у табели. Према бази ISI *Web of Science*, радови кандидата укупно су цитирани 174 пута, док је број цитата без аутоцитата 128. Према бази *Scopus*, укупан број цитата је 220, док је број цитата без аутоцитата 154. Према подацима обе базе, Хиршов индекс радова кандидата је 7.

Категорија	М бодова по раду	Број радова	Укупно М бодова	Нормирани број М бодова
M13	7	5	35	35
M21a	10	1	10	10
M21	8	8	64	64
M22	5	1	5	5
M23	3	1	3	3
M24	2	1	2	2
M32	1,5	1	1,5	1,5
M33	1	12	12	12
M34	0,5	3	1,5	1,5

Поређење оствареног броја М-бодова с минималним квантитативним условима за избор у звање виши научни сарадник:

Минималан број М бодова		Услов - 150% минималног броја бодова*	Остварено (нормирано)
Укупно	50	75	**134**
M10+M20+M31+M32+M33 +M41+M42	40	60	**132,5**
M11+M12+M21+M22+M23	30	45	**82**

*** Минималан број М бодова због убрзаног покретања поступка за избор звање виши научни сарадник**

7. СПИСАК РАДОВА ДР АНДРЕЈЕ СТОЈИЋА

7.1 Монографска студија/поглавље у књизи М11 или рад у тематском зборнику водећег међународног значаја (М13)

Радови објављени након претходног избора у звање

1. Stanišić, S., **Stojić, A.**, 2020, Urban Air Pollution and Environmental Health. In: Leal Filho W., Azul A., Brandli L., Özuyar P., Wall T. (eds) Sustainable Cities and Communities. Encyclopedia of the UN Sustainable Development Goals. Springer, Cham, ISBN: 978-3-319-71061-7 https://doi.org/10.1007/978-3-319-71061-7 https://link.springer.com/referenceworkentry/10.1007/978-3-319-71061-7_120-1

2. **Stojić, A.**, Vuković, G., Perišić, M., Stanišić, S., Šoštarić, A., 2018. Urban air pollution: an insight into its complex aspects. In: A Closer Look at Urban Areas, Editor: Sahar Romero, Nova Science Publishers, NY, USA, ISBN: 978-1-63485-375-0, pp. 69-123. http://www.novapublishers.org/catalog/product_info.php?products_id=65599

3. Stanišić, S., **Stojić, A.**, Prodanović, M., 2018. Health aspects of urban life. In: A Closer Look at Urban Areas, Editor: Sahar Romero, Nova Science Publishers, NY, USA, ISBN: 978-1-63485-375-0, pp. 49-64. http://www.novapublishers.org/catalog/product_info.php?products_id=65599

4. Stanišić, S., **Stojić, A.**, Prodanović, M., 2018. Environmental concerns in Serbia – with specific regard to air-pollution and its effects on human health, Editor: Nova Science Publishers, NY, USA, ISBN: 978-1-63485-375-0, pp. 215-229. https://novapublishers.com/shop/serbia-current-issues-and-challenges-in-the-areas-of-natural-resources-agriculture-and-environment/

5. Stanišić Stojić, S., Stanišić, N., **Stojić, A.**, 2016. Short- and long-term effects of urban air pollution on cardiopulmonary and malignant death rates. In: Air Pollution: Management Strategies, Environmental Impact and Health Risks, Editor: Gerald L. Burns, Nova Science Publishers, NY, USA, ISBN: 978-1-63485-375-0. pp. 41-68. http://www.novapublishers.org/catalog/product_info.php?products_id=58708

Радови објављени пре претходног избора у звање

6. **Stojić, A.**, Stanišić Stojić, S., Mijić, Z., Ilić, L., Tomašević, M., Todorović, M., Perišić, M., 2015. Comprehensive analysis of VOC emission sources in Belgrade urban area. In: Urban and Built Environments: Sustainable Development, Health Implications and Challenges, Editor: Alexis Cohen, Nova Science Publishers, NY, USA, ISBN: 978-1-62417-735-4, pp. 55-88. https://novapublishers.com/shop/urban-and-built-environments-sustainable-development-health-implications-and-challenges/

7. Tomašević, M., Mijić, Z., Aničić, M., **Stojić, A.**, Perišić, M., Kuzmanoski, M., Todorović, M., Rajšić, S., 2013. Air quality study in Belgrade: particulate matter and volatile organic compounds as threats to human health. In: Air Pollution: Sources, Prevention and Health Effects, Editor: Rajat Sethi, Nova Science Publishers, NY, USA, ISBN: 978-1-62417-735-4, pp. 315-346. https://novapublishers.com/shop/environmental-and-agricultural-research-summaries-volume-1/

8. Aničić M., Mijić, Z., Kuzmanoski, M., **Stojić, A.**, Tomašević, M., Rajšić, S., Tasić, M., 2012. A study of airborne trace elements in Belgrade urban area: instrumental and active biomonitoring approach. In: Trace Elements: Environmental Sources, Geochemistry and Human Health, Editors: Diego Alejandro De Leon and Paloma Raquel Aragon, Nova Science Publishers, NY, USA, ISBN: 978-1-62081-401-7, pp.1-30.
   https://novapublishers.com/shop/trace-elements-environmental-sources-geochemistry-and-human-health/

7.2 Монографска студија/поглавље у књизи М12 или рад у тематском зборнику међународног значаја (М14)

Радови објављени пре претходног избора у звање

1. Mijić, Z., **Stojić, A.**, Perišić, M., Rajšić, S., Tasić M., 2012. Statistical character and transport pathways of atmospheric aerosols in Belgrade. In: Air Quality - New Perspective, Edited by Gustavo Lopez Badilla, Benjamin Valdez and Michael Schorr, Published by InTech, ISBN: 978-953-51-0674-6, pp. 199-226.
   https://www.intechopen.com/books/air-quality-new-perspective/statistical-character-and-transport-pathways-of-atmospheric-aerosols-in-belgrade
2. Mijić, Z., Rajšić, S., Žekić, A., Perišić, M., **Stojić, A.**, Tasić M., 2010. Characteristics and application of receptor models to the atmospheric aerosols research, Book chapter in Air quality edited by Ashok Kumar, ISBN 978-953-307-131-2, pp. 143-167.
   https://www.intechopen.com/books/air-quality/characteristics-and-application-of-receptor-models-to-the-atmospheric-aerosols-research

7.2 Радови у међународним часописима изузетних вредности (М21а)

Радови објављени након претходног избора у звање

1. Stanišić Stojić, S., Stanišić, N., **Stojić, A.**, 2016. Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area. Environmental Health. 15(1), 73.
   https://doi.org/10.1186/s12940-016-0164-6
   (ИФ: 3,816)

Радови објављени пре претходног избора у звање

2. **Stojić, A.**, Maletić, D., Stojić, S. S., Mijić, Z., Šoštarić, A., 2015. Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. Science of the Total Environment, 521, 19-26.
   https://doi.org/10.1016/j.scitotenv.2015.03.098
   (ИФ: 3,976)

7.3 Радови у врхунским међународним часописима (М21)

Радови објављени након претходног избора у звање

1. **Stojić, A.**, Stanić, N., Vuković, G., Stanišić, S., Perišić, M., Šoštarić, A., Lazić, L., 2019. Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition. Science of The Total Environment, 653, 140–147. https://doi.org/10.1016/j.scitotenv.2018.10.368 (ИФ: 5,589)

2. Jovanović, G., Herceg Romanić, S., **Stojić, A.**, Klinčić, D., Matek Sarić, M., Grzunov Letinić, J., Popović, A., 2019. Introducing of modeling techniques in the research of POPs in breast milk – A pilot study, Ecotoxicology and Environmental Safety, 172, 341-347. https://doi.org/10.1016/j.ecoenv.2019.01.087 (ИФ: 4,527)

3. **Stojić, A.**, Stanišić Stojić, S., 2017. The innovative concept of three-dimensional hybrid receptor modeling. Atmospheric Environment, 164, 216-223. https://doi.org/10.1016/j.atmosenv.2017.06.009 (ИФ: 3,708)

4. Šoštarić, A., Stojić, S. S., Vuković, G., Mijić, Z., **Stojić, A.**, Gržetić, I., 2017. Rainwater capacities for BTEX scavenging from ambient air. Atmospheric Environment, 168, 46-54. https://doi.org/10.1016/j.atmosenv.2017.08.045 (ИФ: 3,708)

5. Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z., **Stojić, A.**, 2017. Levels of PM_{10} bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation. Air Quality, Atmosphere and Health, 10(1), 93-103. https://doi.org/10.1007/s11869-016-0411-6 (ИФ: 2,662)

6. Stanišić Stojić, S., Stanišić, N., **Stojić, A.**, Šoštarić, A., 2016. Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. Journal of Toxicology and Environmental Health, Part A, 79(1), 17-27. https://doi.org/10.1080/15287394.2015.1101407 (ИФ: 2,731)

7. **Stojić, A.**, Stanišić Stojić, S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., Mijić, Z., 2016. Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. Environmental Science and Pollution Research, 23(11), 10722-10732. https://doi.org/10.1007/s11356-016-6266-4 (ИФ: 2,741)

8. Šoštarić, A., **Stojić, A.**, Stojić, S. S., Gržetić, I., 2016. Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system. Chemosphere, 144, 721-727. https://doi.org/10.1016/j.chemosphere.2015.09.042 (ИФ: 4,208)

Радови објављени пре претходног избора у звање

9. **Stojić, A.**, Stojić, S. S., Mijić, Z., Šoštarić, A., Rajšić, S., 2015. Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmospheric Environment, 106, 71-79.
https://doi.org/10.1016/j.atmosenv.2015.01.071
(ИФ: 3,459)

10. **Stojić, A.**, Stanišić Stojić, S., Šoštarić, A., Ilić, L., Mijić Z., Rajšić S., 2015. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environmental Science and Pollution Research, 22(17), 13137-13152.
https://doi.org/10.1007/s11356-015-4540-5
(ИФ: 2,76)

11. Mijić, Z., **Stojić, A.**, Perišić, M., Rajšić, S., Tasić, M., Radenković, M., Joksić, J., 2010. Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. Atmospheric Environment, 44(30), 3630-3637.
https://doi.org/10.1016/j.atmosenv.2010.06.045
(ИФ: 3,226)

7.4 Радови у истакнутим међународним часописима (М22)

Радови објављени након претходног избора у звање

1. Perišić M., Maletić D., Stanišić Stojić S., Rajšić S., **Stojić A.**, 2017. Forecasting hourly particulate matter concentrations based on the advanced multivariate methods. International Journal of Environmental Science and Technology, 14(5), 1047-1054. https://doi.org/10.1007/s13762-016-1208-8
(ИФ: 2,037)

Радови објављени пре претходног избора у звање

2. Stanišić Stojić, S., Ignjatović, L., Popov, S., Škrivanj, S., Đorđević, A., **Stojić, A.**, 2016. Heavy metal accumulation in wheat and barley: The effects of soil presence and liquid manure amendment. Plant Biosystems, 150(1), 104-110.
https://doi.org/10.1080/11263504.2014.976288
(ИФ: 1,39)

3. Dmitrović, S., Perišić, M., **Stojić, A.**, Živković, S., Boljević, J., Živković, J. N., Mišić, D., 2015. Essential oils of two Nepeta species inhibit growth and induce oxidative stress in ragweed (Ambrosia artemisiifolia L.) shoots in vitro. Acta Physiologiae Plantarum, 37(3), 1-15.
https://doi.org/10.1007/s11738-015-1810-2
(ИФ: 1,563)

4. Perišić, M., **Stojić, A.**, Stojić, S. S., Šoštarić, A., Mijić, Z., Rajšić, S., 2014. Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Quality, Atmosphere and Health, 8(4), 379-389.
https://doi.org/10.1007/s11869-014-0292-5
(ИФ: 1,804)

7.5 Радови у међународним часописима (M23)

Радови објављени после одлуке Научног већа о предлогу за стицање претходног научног звања

1. Todorović, M., Perišić, M., Kuzmanoski, M., **Stojić, A.**, Šoštarić, A., Mijić, Z., Rajšić, S., 2015. Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area. Journal of Environmental Science and Health, Part A, 50(13), 1351-1359.
   https://doi.org/10.1080/10934529.2015.1059110
   (ИФ: 1,276)

Радови објављени пре претходног избора у звање

2. Mijić, Z., **Stojić, A.**, Perišić, M., Rajšić, S., Tasić, M., 2012. Receptor modeling studies for the characterization of PM_{10} pollution sources in Belgrade. Chemical Industry and Chemical Engineering Quarterly, 18(4-2), 623-634. doi: 10.2298/CICEQ120104108M
   http://www.ache.org.rs/CICEQ/2012/no04-II.html
   (ИФ: 0,533)

7.6 Радови у националним часописима међународног значаја (M24)

Радови објављени после одлуке Научног већа о предлогу за стицање претходног научног звања

1. Stanišić Stojić, S., Stanišić, N., **Stojić, A.**, Džamić, V., 2016. Seasonal mortality variations of cardiovascular, respiratory and malignant diseases in the City of Belgrade. Stanovništvo, 54(1), 83-104.
   https://www.idn.org.rs/ojs3/stanovnistvo/index.php/STNV/article/download/74/65/

7.7 Предавања по позиву с међународних скупова штампана у изводу (M32)

Радови објављени након претходног избора у звање

1. **Stojić, A.**, 2019, Modeling particulate matter in urban areas: Experiences of the Institute of Physics Belgrade, The 7th International WeBIOPATR, 1-3 October, Belgrade, Serbia, pp. 67.

7.8 Саопштења с међународних скупова штампана у целини (M33)

Радови објављени након претходног избора у звање

1. **Stojić, A.**, Vuković, G., Stanišić, S., Udovičić, V., Stanić, N, Šoštarić, A. 2019. Explainable machine learning prediction of VOC in an university building microenvironment, 8th International PTR-MS Conference, February 3-8, Innsbruck, Austria, pp. 267-271.
2. **Stojić, A.**, Vuković, G., Stanišić, S., Ćućuz, V., Trifunović, D., Udovičić, V., Šoštarić, A. 2019. Multifractality of isoprene temporal dynamics in outdoor and indoor university

environment, 8th International PTR-MS Conference, February 3-8, Innsbruck, Austria, pp. 271-275.

3. Mijić, Z., Perišić, I., Ilić, L., **Stojić, A.**, Kuzmanoski, M. 2017. Air mass transport over Balkan region identified by atmospheric modeling and aerosol lidar technique, 49th International October Conference on Mining and Metallurgy, October 18-21, Bor Lake, Serbia, pp. 69-72.
4. **Stojić, A.**, Stanišić Stojić, S., 2017. Concentration weighted boundary layer hybrid receptor model for analyzing particulate matter altitude distribution. 6th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, September 6-8, Belgrade, Serbia, pp. 163-166.
5. **Stojić, A.**, Stanišić Stojić, S., Perišić, M., Mijić, Z., 2017. Multiscale multifractal analysis of nonlinearity in particulate matter time series. 6th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, September 6-8, Belgrade, Serbia, pp. 114-117.
6. Perišić, M., Vuković, G., Mijić, Z., Šoštarić, A., **Stojić, A.**, 2017. Relative importance of gaseous pollutants and aerosol constituents for identification of PM_{10} sources of variability. 6th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, September 6-8, Belgrade, Serbia, pp. 109-112.
7. Stanišić Stojić, S., **Stojić, A.**, Perišić, M., 2016. Relationship between isoprene, related gaseous pollutants and meteorological factors in an urban area. 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 26-30, Belgrade, Serbia, Vol. II, pp. 711-714.
8. Perišić, M., **Stojić, A.**, Stanišić Stojić, S., 2016. Impact of remote sources on chromium concentrations in Belgrade and the related health risk. 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 26-30, Belgrade, Serbia, Proceedings Vol. II, pp. 735-738.

Радови објављени после одлуке Научног већа о предлогу за стицање претходног научног звања

9. Stanišić Stojić, S., Stanišić, N., Šoštarić, A., **Stojić, A.**, Mladenović, S., 2015. The association between short term exposure to PM_{10} and soot and circulatory system related mortality in Belgrade area. 5th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, October 14-16, Belgrade, Serbia, pp. 211-216.
10. Stanišić Stojić, S., Stanišić, N., Šoštarić, A., **Stojić, A.**, Mladenović, S., 2015. The association between short term PM_{10} exposure and mortality caused by respiratory system diseases in Belgrade area. 5th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, October 14-16, Belgrade, Serbia, pp. 191-195.
11. Perišić, M., **Stojić, A.**, Todorović, M., Mijić, Z., Šoštarić, A., 2015. Transport contribution to $PM_{2.5}$ mass concentrations in Belgrade sub urban area. 5th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, October 14-16, Belgrade, Serbia, pp. 99-102.

12. Mijić, Z., Perišić, M., **Stojić, A.**, Kuzmanoski, M., Ilić, L., 2015. Estimation of atmospheric aerosol transport by ground based remote sensing and modeling. XIX International Eco-Conference 2015, September 23 25, Novi Sad, Serbia, pp. 375-382.

Радови објављени пре претходног избора у звање

13. **Stojić, A.**, Stanišić Stojić, S., Šoštarić, A., Mijić, Z., Perišić M., Rajšić, S., 2014. The contribution of chemical industry to ambient VOC levels in Belgrade. 12th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 22-26, 2014, Belgrade, Serbia, pp. 949-952.
14. Šoštarić, A., Perišić, M., **Stojić, A.**, Mijić, Z., Rajšić, S., 2014. Dynamics of gaseous pollutants in Belgrade urban area. 12th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 22-26, Belgrade, Serbia, Vol. I, pp. 953-956.
15. Todorović, M., Perišić, M., **Stojić, A.**, Rajšić, S., 2014. Source apportionment study in Belgrade urban area. 12th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 22-26, Belgrade, Serbia, Vol. I, pp. 929-932.
16. Šoštarić, A., **Stojić, A.**, Stanišić Stojić, S., Mijić, Z., 2014. Traffic-related VOC dynamics in Belgrade urban area. 12th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 22-26, Belgrade, Serbia, Vol. III, pp. 953-956.
17. Perišić, M., **Stojić, A.**, Mijić, Z., Todorović, M., Rajšić, S., 2013. Source apportionment of ambient VOCs in Belgrade semi-urban area. 6th International Conference on Proton Transfer Reaction Mass Spectrometry and Its Application, February 3-8, Innsbruck, Austria, pp. 204-208.
18. Perišić, M., Mijić, Z., **Stojić, A.**, 2013. Frequency analysis of PM_{10} time series and assessing source reduction for air quality compliance in Serbia. 4th WeBIOPATR Workshop Conference, October 2-6, Belgrade, Serbia, pp. 64 68.
19. Šoštarić, A., Perišić, M., **Stojić, A.**, Mijić, Z., Rajšić, S., Tasić, M., 2013. The influence of air mass origin and potential source contributions on PM_{10} in Belgrade. 4th WeBIOPATR Workshop Conference, October 2-6, Belgrade, Serbia, pp.39-43.
20. **Stojić, A.**, Perišić, M., Mijić, Z., Rajšić, S., 2011. Ambient VOCs measurements in winter: Belgrade semi-urban area. 5th International Conference on Proton Transfer Reaction Mass Spectrometry and Its Application, January 26-February 2, Innsbruck, Austria, pp. 248-251.
21. Perišić, M., **Stojić, A.**, Rajšić, S., Mijić, Z., 2010. Assessment of VOCs concentrations in Belgrade semi-urban area. 10th International Conference of Fundamental and Applied aspects of Physical Chemistry, September 21-24, Belgrade, Serbia, pp. 579-581.
22. **Stojić, A.**, Rajšić, S., Perišić, M., Mijić, Z., Tasić, M., 2009. Assessment of ambient VOCs levels in Belgrade semiurban area, 4th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, February 16-21, Obergurgl, Austria, pp. 289-293.
23. Nestorović, J., Mišić, D., **Stojić, A.**, Perišić, M., Živković, S., Šiler, B., Aničić, M., Malović, G., Grubišić, D., 2009. *In vitro* selection of nepetalactone-rich genotypes of *Nepeta rtanjensis* by using HPCL and PTR-MS. 4th International Conference on Proton

Transfer Reaction Mass Spectrometry and its Applications, February 16-21, Obergurgl, Austria, pp. 263-267.

24. Tasić, M., Mijić, Z., Rajšić, S., **Stojić, A.**, Radenković, M., Joksić, J., 2009. Source apportionment of atmospheric bulk deposition in the Belgrade urban area using positive matrix factorization. In Journal of Physics: Conference Series, IOP Publishing, April, Vol. 162, No. 1, pp. 012-018.

7.9 Саопштења с међународних скупова штампана у изводу (М34)

Радови објављени након претходног избора у звање

1. Stojić, A., Perišić, M., Jovanović, G., Stanišić, S., Stanić, N., Milićević, T., 2019, Parsing environmental factors which shape particulate matter pollution using explainable artificial intelligence, The 7th International WeBIOPATR 1-3 October, 2019, Belgrade, Serbia, pp. 34.
2. Perišić, M., Stojić, A., Jovanović, G., Stanišić, S., 2019, Receptor oriented modeling of urban particulate air pollution: source characterization and spatial distribution, The 7th International WeBIOPATR 1-3 October, 2019, Belgrade, Serbia, pp. 75.
3. Jovanović, G., Stojić, A., Perišić, M., Stanišić, S., Stanić, N., Milićević, T., 2019, Explainable relations of particulate matter and environmental factors in an urban area, The 7th International WeBIOPATR 1-3 October, 2019, Belgrade, Serbia, pp. 94.

Радови објављени пре претходног избора у звање

4. Dmitrović, S., Perišić, M., **Stojić, A.**, Živković, S., Boljević, J., Nestorović Živković, J., Aničić, N., Ristić, M., Mišić, D., 2015. The oxidative stress in Ambrosia artemisiifolia L. shoots grown in vitro induced by *Nepeta rtanjensis* and *N. cataria* essential oils. 2nd International Conference on Plant Biology (21st Symposium of the Serbian Plant Physiology Society) & COST Action FA1106 Qualityfruit Workshop, Serbian Plant Physiology Society, June 17-20, Petnica, Serbia, pp. 159.
5. Škorić, M., Todorović, S., Ristić, M., Soković, M., Glamočlija, J., Živković, S., **Stojić, A.**, Puač, N., Kanellis, A. K., 2013. In vitro culture of Cistus creticus subsp. creticus-a source of biological active compounds. 11th International Meeting on Biosynthesis, Function and Biotechnology of Isoprenoids in Terrestrial and Marine Organisms (TERPNET 2013), June 1-5, Thessaloniki, Greece, pp. 132.
6. Škorić, M., Nestorović-Živković, J., Ristić, M., **Stojić, A.**, Puač, N., Kanellis, A.K., Todorović, S., 2013. PTR MS and GC/MS analysis of volatile compounds in shoot cultures of Cistus creticus subsp. creticus. 1st International Conference on Plant Biology (20th Symposium of the Serbian Plant Physiology Society), Serbian Plant Physiology Society, July 4-7, Subotica, Serbia, pp 107.
7. **Stojić, A.**, Perišić, M., Todorović, M., Nikitović, Ž., Jotić, A., Lalić, N., Petrović, Z.Lj., 2013. Application of PTR-MS measurements of volatile organic compounds (VOC) in medical science. 15th annual conference of YUCOMAT, September 2-6, Herceg Novi, Montenegro, pp. 68.
8. **Stojić, A.**, Mijić, Z., Perišić, M., Rajšić, S., Tasić, M., 2011. Ambient VOCs measurement in Belgrade semi-urban area: winter case study. 16th European conference

on analytical chemistry Challenges in modern analytical chemistry, EUROanalysis, September 11-15, Belgrade, Serbia, pp. 102.

9. Mijić, Z., Kuzmanoski, M., **Stojić, A.**, Žekić, A. Rajšić, S., Tasić, M., 2011. Investigation of regional transport and health risk effects of metals in $PM_{2.5}$ air particulate matter in Belgrade. 3rd International WeBIOPATR Workshop & Conference, November 15-17, Belgrade, Serbia.

10. Mijić, Z., Tasić, M., Rajšić, S., **Stojić, A.**, 2011. Receptor modeling studies for the characterization of PM_{10} pollution sources in Belgrade, Proceedings of the 3rd International WeBIOPATR Workshop & Conference, November 15-17, Belgrade, Serbia.

11. Perišić, M., **Stojić, A.**, Mijić, Z., Rajšić, S., 2010. Source apportionment of volatile organic compounds in Belgrade semi-urban area. 11th European Meeting on Environmental Chemistry EMEC 11, December 8-11, Portorož, Slovenia, pp. 232.

12. **Stojić, A.**, Perišić, M., Mijić, Z., Rajšić, S., Ristić, D., 2010. Ambient VOCs measurement In Belgrade semi urban area using Proton Transfer Reaction Mass Spectrometer, 1st Center of Excellence for Food Safety and Emerging Risk (CEFSER) Workshop "Regional perspectives in food safety", 12th Danube-Kris-Mures-Tisa (DKMT) Euroregion Conference on Food, Environment and Health, Faculty of Technology, University of Novi Sad, September 14-15, Novi Sad, Serbia, CD Book of Abstracts.

13. **Stojić, A.**, Perišić, M., Mijić, Z., Rajšić, S., 2010. Proton Transfer Reaction Mass Spectrometry: ambient air VOCs measurement in Belgrade semi-urban area, 20th ESCAMPIG, July, Novi Sad, Serbia.

14. Nestorović, J., Mišić, D., Šiler, B., Živkovic, S., Malović, G., Perišić, M., **Stojić, A.**, Grubišić, D., 2010. Application of PTR-MS in detection of volatile compounds: in vitro culture of three nepeta species, 20th ESCAMPIG, July, Novi Sad, Serbia.

15. Nestorović, J., Mišić, D., Šiler, B., Živkovic, S., **Stojić, A.**, Perišić, M., Grubišić, D., 2009. PTR-MS detection of nepetalactone in shoot cultures of three Nepeta species grown under different carbohydrate source. New research in biotechnology, 2nd International Symposium, November 19-20, Bucharest, Romania, pp. 138.

16. **Stojić, A.**, Nešić, M., Mijić, Z., Novaković, V., Rajšić, S., Tasić, M., 2008. Heavy metal concentrations in streat dust and soils adjacent to roads in Belgrade, Serbia. 9th Highway and Urban Environment Symposium, June 9-11, Madrid, Spain, pp. 87.

17. Nešić, M., **Stojić, A.**, Mijić, Z., Novaković, V., Rajšić, S., 2007. First results of outdoor and indoor VOCs measurements using PTR-MS in Belgrade, Serbia, 8th European Meeting on Environmental Chemistry (EMEC8), Book of abstracts, December 5-8, Inverness, Scotland, pp. 37.

7.10 Рад у истакнутом националном часопису (М53)

Радови објављени пре претходног избора у звање

1. Mijić, Z., Tasić, M., Rajšić, S., **Stojić, A.**, 2012. Primena hibridnih receptorskih modela za ispitivanje transporta PM_{10} čestica na područje Beograda, Glasnik Hemičara, Tehnologa i ekologa Republike Srpske, 4(7), 41-48.

7.11 Саопштење са скупа националног значаја штампано у целини (М63)

Радови објављени пре претходног избора у звање

1. Perišić, M., **Stojić, A.**, Todorović, M., Mijić, Z., Rajšić, S., 2013. Analiza dinamike i transporta CO, NO_x i SO_2 u urbanoj sredini Beograda. XII Kongres fizičara Srbije, April 28-May 2, Vrnjačka Banja, Srbija, str. 444-447.
2. **Stojić, A.**, Perišić, M., Mijić, Z., Todorovic, M., Rajšić, S., 2013. Određivanje izvora emisije isparljivih organskih jedinjenja u Beogradu. XII Kongres fizičara Srbije, April 28-May 2, Vrnjačka Banja, Srbija, str. 453-456.
3. **Stojić, A.**, Perišić, M., Petrović, N., 2008. Merenje isparljivih organskih jedinjenja u realnom vremenu masenim spektrometrom (PTR-MS) Naučnostrucni skup sa međunarodnim učešćem, Zbornik radova, Institut zaštite, ekologije i informatike, Novembar 14-15, Banja Luka, Bosna i Hercegovina, str. 257-262.

7.12 Саопштења с међународних скупова штампана у изводу (М64)

Радови објављени пре претходног избора у звање

1. Stojić, S.S., **Stojić, A.**, Šoštarić, A., Mijić, Z., Todorović, M., 2015. Contribution of transported pollution to traffic-related VOC concentrations in Belgrade urban area. 7th Symposium Chemistry and Environmental Protection, June 9-12, Palić, Serbia, pg. 167-168.
2. Todorović, M., Perišić, M., **Stojić, A.**, Rajšić, S., 2013. Concentrations trend of NO, NO_2 and O_3 during the 2011 in Belgrade urban area. 6th Symposium Chemistry and Environmental Protection, May 21-24, Vršac, Serbia, pg. 320-321.
3. Perišić, M., Todorović, M., **Stojić, A.**, Kuzmanoski, M., Rajšić, S., 2013. Health risk assessment of VOCs in Belgrade semi-urban area, 6th Symposium Chemistry and Environmental Protection, May 21-24, Vršac, Serbia, pg. 378-379.
4. Nestorović, J., Mišić, D., Dević, M., **Stojić, A.**, Malović, G., Grubišić, D., 2009. PTR-MS and HPLC analysis of nepetalactone in shoots cultures of *Nepeta rtanjensis* Diklić & Milojević. XVIII Symposium of Biological Society, May 27-29, Vršac, Serbia.
5. Nešić, M., **Stojić, A.**, Mijić, Z. Rajšić, S., Tasić, M., 2008. First results of ambient VOCs measurements using PTR-MS in Belgrade. 5th Symposium Chemistry and Environmental Protection, Ed. The Serbian Chemical Society, Book of abstracts, June, 27-30, Tara, Serbia, pp. 41.

6. Nestorović, J., Mišić, D., Šiler, B., Grubišić, D., Nešić, M., **Stojić, A.**, Tasić, M., 2008. Uticaj isparljivih jedinjenja rtanjske metvice (*Nepeta rtanjensis*) na klijanje semena *Lepidum sativum*: alelopatski potencijal. IX dani lekovitog bilja, Septembar 17-20, Kosmaj, Srbija, pp. 138.

7.13 Одбрањена докторска теза (М71)

Радови објављени пре претходног избора у звање

1. **Stojić**, **A.**, 2015, Spatio-temporal Distribution of Volatile Organic Compounds and Aerosols in Troposphere: Lidar and Mass Spectrometry, Faculty of Physics, University of Belgrade.

7.14 Newsletters

1. Šoštarić, A., Mladenović, S., Stanišić Stojić, S., **Stojić, A.**, Stanišić, N., Slepčević V., 2015. Health burden of air pollutant exposure in Belgrade: a European region with high circulatory and malignant mortality rates, Newsletter, WHO Collaborating Centre for Air Quality Management and Air Pollution Control, No. 56, December 2015, pp. 3-9.

7.15 Симпозијуми

1. **Stojić**, **A.**, 2018. Principles underlying Agile approach and highly sophisticated machine learning algorithms. 1st Agile Humans Belgrade Day, October 24, Belgrade, Serbia. https://agilehumans.city/agile-humans-belgrade-day/

2. Pavlović, N., Ristić, J., Šoštarić, A., Slepčević, V., **Stojić, A.**, Stanišić Stojić, S., Stanišić, N., 2016. Analiza podataka redovnog merenja PM_{10}, O_3 i NO_2 u vazduhu i smrtnost od kardiovaskularnih i respiratornih bolesti i *Diabetes mellitusa* u Beogradu, Stručna konferencija – simpozijum „Dani Zavoda 2016. godine", sa temom: „Kvalitet vazduha – monitoring, modelovanje, unapređenje", Novembar 25, Beograd, Srbija, pp. 99-114.

Прилози

Цитираност

Web of Science InCites Journal Citation Reports Essential Science Indicators EndNote Publons Kopernio Sign In Help English

Web of Science

Clarivate Analytics

Search Tools Searches and alerts Search History Marked List

Citation report for 20 results from Web of Science Core Collection between 1996 and 2020 Go

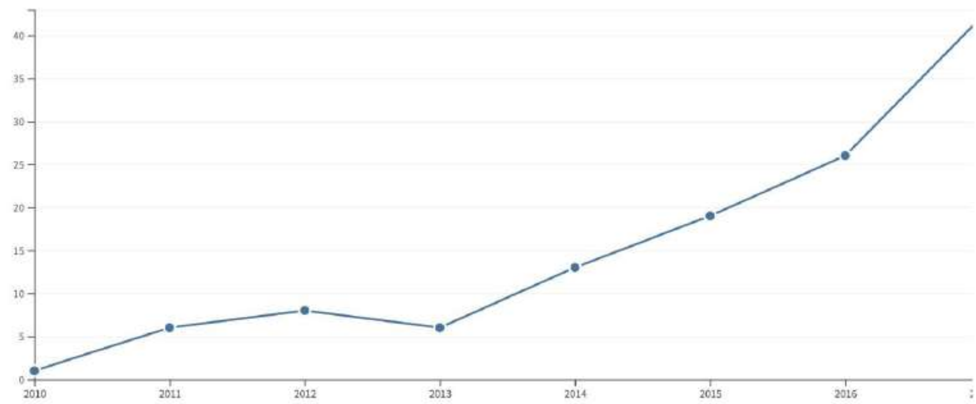
You searched for: **Article Group for:** Stojic, A. ...More

This report reflects citations to source items indexed within Web of Science Core Collection. Perform a Cited Reference Search to include citations to items not indexed within Web of Science Core Collection.

Export Data: Save to Excel File

Total Publications	h-index	Sum of Times Cited	Citing articles
20 Analyze	7	174	134 Analyze
2000 2019	Average citations per item 8.7	Without self citations 128	Without self citations 120 Analyze

Sum of Times Cited per Year



Sort by: Times Cited Date More 2 of 2

How are these totals calculated?

2016 2017 2018 2019 2020 Total Average Citations

Use the checkboxes to remove individual items from this Citation Report

or restrict to items published between 1996 and 2020 Go

								per Year
		26	42	26	27	0	174	17.40
1.	**Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade** By: Mijic, Z.; Stojic, A.; Perisic, M.; et al. ATMOSPHERIC ENVIRONMENT Volume: 44 Issue: 30 Pages: 3630-3637 Published: SEP 2010	6	6	8	8	0	63	6.30
2.	**Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia** By: Stojic, Svetlana Stanisic; Stanisic, Nemanja; Stojic, Andreja; et al. JOURNAL OF TOXICOLOGY AND ENVIRONMENTAL HEALTH-PART A-CURRENT ISSUES Volume: 79 Issue: 1 Pages: 17-27 Published: 2016	4	7	2	1	0	14	3.50
3.	**Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling** By: Stojic, A.; Stojic, S. Stanisic; Mijic, Z.; et al. ATMOSPHERIC ENVIRONMENT Volume: 106 Pages: 71-79 Published: APR 2015	3	5	1	1	0	13	2.60
4.	**Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling** By: Stojic, A.; Stojic, S. Stanisic; Sostaric, A.; et al. ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH Volume: 22 Issue: 17 Pages: 13137-13152 Published: SEP 2015	5	3	1	3	0	12	2.40
5.	**Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods** By: Stojic, Andreja; Maletic, Dimitrije; Stojic, Svetlana Stanisic; et al. SCIENCE OF THE TOTAL ENVIRONMENT Volume: 521 Pages: 19-26 Published: JUL 15 2015	2	4	2	3	0	11	2.20
6.	**RECEPTOR MODELING STUDIES FOR THE CHARACTERIZATION OF PM10 POLLUTION SOURCES IN BELGRADE** By: Mijic, Zoran; Stojic, Andreja; Perisic, Mirjana; et al. CHEMICAL INDUSTRY & CHEMICAL ENGINEERING QUARTERLY Volume: 18 Issue: 4 Pages: 623-634 Part: 2 Published: OCT-DEC 2012	2	1	1	0	0	11	1.38
7.	**Source Apportionment of Atmospheric Bulk Deposition in the Belgrade Urban Area Using Positive Matrix Factorization** By: Tasic, M.; Mijic, Z.; Rajsic, S.; et al. Conference: 2nd International Workshop on Non-Equilibrium Processes in Plasmas and Environmental Science Location: Belgrade, SERBIA Date: AUG 23-26, 2008 Sponsor(s): Serbian Acad Sci & Arts; Inst Phys; Minist Sci & Technol Serbia; Hiden Anal SECOND INTERNATIONAL WORKSHOP ON NON-EQUILIBRIUM PROCESSES IN PLASMAS AND ENVIRONMENTAL SCIENCE Book Series: Journal of Physics Conference Series Volume: 162 Article Number: UNSP 012018 Published: 2009	0	1	0	0	0	7	0.64
8.	**Levels of PM10-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation** By: Perisic, Mirjana; Rajsic, Slavica; Sostaric, Andrej; et al. AIR QUALITY ATMOSPHERE AND HEALTH Volume: 10 Issue: 1 Pages: 93-103 Published: JAN 2017	0	1	4	1	0	6	2.00

9. **Estimation of required PM10 emission source reduction on the basis of a 10-year period data** By: Perisic, Mirjana; Stojic, Andreja; Stojic, Svetlana Stanisic; et al. AIR QUALITY ATMOSPHERE AND HEALTH Volume: 8 Issue: 4 Pages: 379-389 Published: AUG 2015	2	2	0	0	0	6	1.20
10. **Comprehensive analysis of PM10 in Belgrade urban area on the basis of long-term measurements** By: Stojic, A.; Stojic, S. Stanisic; Reljin, I.; et al. Conference: International Conference on Contaminated Sediments (ContaSed-2015) Location: Ascona, SWITZERLAND Date: MAR 08-13, 2015 ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH Volume: 23 Issue: 11 Pages: 10722-10732 Published: JUN 2016	1	4	0	0	0	5	1.25

Select Page Save to Excel File

Sort by: Times Cited Date More 1 of 2

20 records matched your query of the 46,047,863 in the data limits you selected.

per Year

Use the checkboxes to remove individual items from this Citation Report

or restrict to items published between 1996 and 2020 Go

	26	42	26	27	0	174	17.40
11. **Forecasting hourly particulate matter concentrations based on the advanced multivariate methods** By: Perisic, M.; Maletic, D.; Stojic, S. S.; et al. INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCE AND TECHNOLOGY Volume: 14 Issue: 5 Pages: 1047-1054 Published: MAY 2017	0	1	1	2	0	4	1.33
12. **Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area** By: Stojic, Svetlana Stanisic; Stanisic, Nemanja; Stojic, Andreja ENVIRONMENTAL HEALTH Volume: 15 Article Number: 73 Published: JUL 11 2016	0	1	2	1	0	4	1.00
13. **Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system** By: Sostaric, A.; Stojic, A.; Stojic, S. Stanisic; et al. CHEMOSPHERE Volume: 144 Pages: 721-727 Published: FEB 2016	0	2	1	1	0	4	1.00
14. **Essential oils of two Nepeta species inhibit growth and induce oxidative stress in ragweed (Ambrosia artemisiifolia L.) shoots in vitro** By: Dmitrovic, Slavica; Perisic, Mirjana; Stojic, Andreja; et al. ACTA PHYSIOLOGIAE PLANTARUM Volume: 37 Issue: 3 Published: MAR 2015	0	0	2	2	0	4	0.80
15. **Heavy metal accumulation in wheat and barley: The effects of soil presence and liquid manure amendment** By: Stojic, S. M. Stanisic; Ignjatovic, L. M.; Popov, S.; et al. PLANT BIOSYSTEMS Volume: 150 Issue: 1 Pages: 104-110 Published: JAN 2 2016	1	1	1	0	0	3	0.75
16. **Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition** By: Stojic, Andreja; Stanic, Nenad; Vukovic, Gordana; et al. SCIENCE OF THE TOTAL ENVIRONMENT Volume: 653 Pages: 140-147 Published: FEB 25 2019	0	0	0	2	0	2	2.00
17. **Rainwater capacities for BTEX scavenging from ambient air** By: Sostaric, A.; Stojic, S. Stansic; Vukovic, G.; et al. ATMOSPHERIC ENVIRONMENT Volume: 168 Pages: 46-54 Published: NOV 2017	0	0	0	2	0	2	0.67
18. **Assessment of PM10 pollution level and required source emission reduction in Belgrade area** By: Todorovic, Marija N.; Perisic, Mirjana D.; Kuzmanoski, Maja M.; et al. JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH PART A-TOXIC/HAZARDOUS SUBSTANCES & ENVIRONMENTAL ENGINEERING Volume: 50 Issue: 13 Pages: 1351-1359 Published: NOV 10 2015	0	2	0	0	0	2	0.40
19. **The innovative concept of three-dimensional hybrid receptor modeling** By: Stojic, A.; Stojic, S. Stanisic ATMOSPHERIC ENVIRONMENT Volume: 164 Pages: 216-223 Published: SEP 2017	0	1	0	0	0	1	0.33

20.	**Introducing of modeling techniques in the research of POPs in breast milk - A pilot study** By: Jovanovic, Gordana; Romanic, Snjezana Herceg; Stojic, Andreja; et al. ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY Volume: 172 Pages: 341-347 Published: MAY 15 2019	0	0	0	0	0	0	0.00

Select Page Save to Excel File

Sort by: Times Cited Date More 2 of 2

20 records matched your query of the 46,047,863 in the data limits you selected.

Author details

< Return to search results 1 of 1 Print Email

Stojić, Andreja M.

View potential author matches

Author ID: 28168051600

http://orcid.org/0000-0002-5293-9533

Affiliation(s):

Institute of Physics, Belgrade, Serbia View more

Other name formats: Stojić, A. | Stojic, A. | Stojic, Andreja M. | Stojić, A. | Stojic, Andreja | Stojić, Andreja

Subject area: Environmental Science | Earth and Planetary Sciences | Agricultural and Biological Sciences | Medicine | Chemistry | Engineering | Social Sciences | Physics and Astronomy | Biochemistry, Genetics and Molecular Biology | Chemical Engineering | Pharmacology, Toxicology and Pharmaceutics

Profile actions

Edit author profile

Connect to ORCID

Alerts

Set citation alert

Set document alert

Save to author list

AS Andreja M. Stojić ↗

25 Documents

View Mendeley profile ↗

Documents by author

25

Analyze author output

Total citations

220 by 164 documents

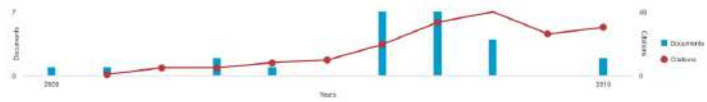
View citation overview

h-index:

7

View *h*-graph

Document and citation trends:



25 Documents | Cited by 164 documents | 40 co-authors | Topics

View in search results format > View 931 references > Sort on: Date (newest)

Export all Save all to list Set document alert Set document feed

Document title	Authors	Year	Source	Cited by
Introducing of modeling techniques in the research of POPs in breast milk – A pilot study	Jovanović, G., Romanić, S.H., Stojić, A., (...), Letinić, J.G., Popović, A.	2019	Ecotoxicology and Environmental Safety 172, pp. 341-347	0
View abstract KOBSON View at Publisher Related documents				
Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition	Stojić, A., Stanić, N., Vuković, G., (...), Šoštarić, A., Lazić, L.	2019	Science of the Total Environment 653, pp. 140-147	2

Document title	Authors	Year	Source	Cited by
View abstract KOBSON View at Publisher Related documents				
Forecasting hourly particulate matter concentrations based on the advanced multivariate methods	Perišić, M., Maletić, D., Stojić, S.S., Rajšić, S., Stojić, A.	2017	International Journal of Environmental Science and Technology 14(5), pp. 1047-1054	5
View abstract KOBSON View at Publisher Related documents				
The innovative concept of three-dimensional hybrid receptor modeling	Stojić, A., Stanišić Stojić, S.	2017	Atmospheric Environment 164, pp. 216-223	1
View abstract KOBSON View at Publisher Related documents				
Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation	Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z., Stojić, A.	2017	Air Quality, Atmosphere and Health 10(1), pp. 93-103	6
View abstract KOBSON View at Publisher Related documents				
Rainwater capacities for BTEX scavenging from ambient air	Šoštarić, A., Stanišić Stojić, S., Vuković, G., (...), Stojić, A., Gržetić, I.	2017	Atmospheric Environment 168, pp. 46-54	2
View abstract KOBSON View at Publisher Related documents				
Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area Open Access	Stanišić Stojić, S., Stanišić, N., Stojić, A.	2016	Environmental Health: A Global Access Science Source 15(1),73	5
View abstract KOBSON View at Publisher Related documents				
Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements	Stojić, A., Stojić, S.S., Reljin, I., (...), Perišić, M., Mijić, Z.	2016	Environmental Science and Pollution Research 23(11), pp. 10722-10732	7
View abstract KOBSON View at Publisher Related documents				
Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system	Šoštarić, A., Stojić, A., Stanišić Stojić, S., Gržetić, I.	2016	Chemosphere 144, pp. 721-727	4
View abstract KOBSON View at Publisher Related documents				
Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia	Stojić, S.S., Stanišić, N., Stojić, A., Šoštarić, A.	2016	Journal of Toxicology and Environmental Health - Part A: Current Issues 79(1), pp. 17-27	19
View abstract KOBSON View at Publisher Related documents				
Heavy metal accumulation in wheat and barley: The effects of soil presence and liquid manure amendment	Stanis˘ić Stojić, S.M., Ignjatović, L.M., Popov, S., (...), Đorđević, A.R., Stojić, A.	2016	Plant Biosystems 150(1), pp. 104-110	2
View abstract KOBSON View at Publisher Related documents				

Document title	Authors	Year	Source	Cited by
Short- and long-term effects of urban air pollution on cardiopulmonary and malignant death rates (Book Chapter)	Stojić, S.S., Stanišić, N., Stojić, A.	2016	*Air Pollution: Management Strategies, Environmental Impact and Health Risks* pp. 41-68	0
View abstract KOBSON Related documents				
Seasonal mortality variations of cardiovascular, respiratory and malignant diseases in the city of belgrade Open Access	Stojic, S.S., Stanišic, N., Stojic, A., Džamic, V.	2016	Stanovnistvo 54(1), pp. 83-104	2
View abstract KOBSON View at Publisher Related documents				
Assessment of PM $_{10}$ pollution level and required source emission reduction in Belgrade area	Todorovic, M.N., Perisic, M.D., Kuzmanoski, M.M., (...), Mijic, Z.R., Rajsic, S.F.	2015	Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering 50(13), pp. 1351-1359	3
View abstract KOBSON View at Publisher Related documents				
Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling	Stojić, A., Stojić, S.S., Šoštarić, A., (...), Mijić, Z., Rajšić, S.	2015	Environmental Science and Pollution Research 22(17), pp. 13137-13152	17
View abstract KOBSON View at Publisher Related documents				
Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data	Perišić, M., Stojić, A., Stanišić Stojić, S., (...), Mijić, Z., Rajšić, S.	2015	Air Quality, Atmosphere and Health 8(4), pp. 379-389	6
View abstract KOBSON View at Publisher Related documents				
Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods	Stojić, A., Maletić, D., Stanišić Stojić, S., Mijić, Z., Šoštarić, A.	2015	Science of the Total Environment 521-522, pp. 19-26	15
View abstract KOBSON View at Publisher Related documents				
Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling	Stojić, A., Stanišić Stojić, S., Mijić, Z., Šoštarić, A., Rajšić, S.	2015	Atmospheric Environment 106, pp. 71-79	17
View abstract KOBSON View at Publisher Related documents				
Comprehensive analysis of VOC emission sources in Belgrade urban area (Book Chapter)	Stojic, A., Stanišic Stojic, S., Mijic, Z., (...), Todorovic, M., Perišic, M.	2015	*Urban and Built Environments: Sustainable Development, Health Implications and Challenges* pp. 55-88	3
View abstract KOBSON Related documents				
Essential oils of two Nepeta species inhibit growth and induce oxidative stress in ragweed (Ambrosia artemisiifolia L.) shoots in vitro	Dmitrović, S., Perišić, M., Stojić, A., (...), Ristić, M., Mišić, D.	2015	Acta Physiologiae Plantarum 37(3)	8
View abstract KOBSON View at Publisher Related documents				

Document title	Authors	Year	Source	Cited by
Air quality study in belgrade: Particulate matter and volatile organic compounds as threats to human health (Book Chapter)	Tomašević, M., Mijič, Z., Aničić, M., (...), Todorović, M., Rajšič, S.	2013	*Air Pollution: Sources, Prevention and Health Effects* pp. 315-346	1
View abstract ⌄ KoBSON Related documents				
Receptor modeling studies for the characterization of PM_{10} pollution sources in Belgrade | [Primena receptorskih modela u karakterizaciji PM_{10} izvora emisije u Beogradu] Open Access	Mijić, Z., Stojić, A., Perišić, M., Rajšić, S., Tasić, M.	2012	Chemical Industry and Chemical Engineering Quarterly 18(4 II), pp. 623-634	14
View abstract ⌄ KoBSON View at Publisher Related documents				
A study of airborne trace elements in belgrade urban area: Instrumental and active biomonitoring approach (Book Chapter)	Aničić, M., Mijić, Z., Kuzmanoski, M., (...), Rajšić, S., Tasić, M.	2012	*Trace Elements: Environmental Sources, Geochemistry and Human Health* pp. 1-30	1
View abstract ⌄ KoBSON Related documents				
Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade	Mijić, Z., Stojić, A., Perišić, M., (...), Radenković, M., Joksić, J.	2010	Atmospheric Environment 44(30), pp. 3630-3637	74
View abstract ⌄ KoBSON View at Publisher Related documents				
Source apportionment of atmospheric bulk deposition in the Belgrade urban area using Positive Matrix factorization Open Access	Tasić, M., Mijić, Z., Rajić, S., (...), Radenković, M., Joksić, J.	2009	Journal of Physics: Conference Series 162,012018	6
View abstract ⌄ KoBSON View at Publisher Related documents				

Display: 50 ⌄ results per page

1

^ Top of page

Одлука о избору звање

Република Србија
МИНИСТАРСТВО ПРОСВЕТЕ, НАУКЕ И ТЕХНОЛОШКОГ РАЗВОЈА
Комисија за стицање научних звања

Број:660-01-00011/535
30.03.2016. године
Београд

ИНСТИТУТ ЗА ФИЗИКУ
ПРИМЉЕНО: 04-05-2016

Рад.јед.	Број	Арх.шифра	Прилог
0801	689/1		

На основу члана 22. става 2. члана 70. став 5. Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 110/05 и 50/06 – исправка и 18/10), члана 50. став 1. Закона о изменама и допунама Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 112/15) члана 2. става 1. и 2. тачке 1 – 4.(прилози) и члана 38. Правилника о поступку и начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача ("Службени гласник Републике Србије", број 38/08) и захтева који је поднео

Институт за физику у Београду

Комисија за стицање научних звања на седници одржаној 30.03.2016. године, донела је

ОДЛУКУ
О СТИЦАЊУ НАУЧНОГ ЗВАЊА

Др Андреј Стојић
стиче научно звање
Научни сарадник

у области природно-математичких наука - физика

О Б Р А З Л О Ж Е Њ Е

Институт за физику у Београду

утврдио је предлог број 1290/1 од 22.09.2015. године на седници Научног већа Института и поднео захтев Комисији за стицање научних звања број 1322/1 од 01.10.2015. године за доношење одлуке о испуњености услова за стицање научног звања ***Научни сарадник.***

Комисија за стицање научних звања је по претходно прибављеном позитивном мишљењу Матичног научног одбора за физику на седници одржаној 30.03.2016. године разматрала захтев и утврдила да именовани испуњава услове из члана 70. став 5. Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 110/05 и 50/06 – исправка и 18/10), члана 2. става 1. и 2. тачке 1 – 4.(прилози) и члана 38. Правилника о поступку и начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача ("Службени гласник Републике Србије", број 38/08) за стицање научног звања ***Научни сарадник***, па је одлучила као у изреци ове одлуке.

Доношењем ове одлуке именовани стиче сва права која му на основу ње по закону припадају.

Одлуку доставити подносиоцу захтева, именованом и архиви Министарства просвете, науке и технолошког развоја у Београду.

ПРЕДСЕДНИК КОМИСИЈЕ
Др Станислава Стошић-Грујичић,
научни саветник

МИНИСТАР
Др Срђан Вербић

Позивно предавање

Gmail

Andreja Stojic <[redacted]>

WeBIOPATR2019

Alena Bartonova <[redacted]> 07. септембар 2019. 18:21
Коме: Andreja Stojic <andreja@ipb.ac.rs>, Milena Jovasevic-Stojanovic <[redacted]>
Копија: Zoran Mijic <[redacted]>, Mirjana Perisic <[redacted]>

Dear Andreja, Milena,

Andreja, thank you very much for your suggested changes, and for the abstract, which from my side, I am happy to accept. I think this fits very well with the other keynotes and of course with the topics to be covered. The new title is indeed more appropriate.

From my side, I am very happy for this contribution to the WeBIOPATR, and I am looking forward to see you again in Belgrade soon.

Best regards

Alena

-----Original Message-----
From: Andreja Stojic [mailto:andreja@ipb.ac.rs]
Sent: lørdag 7. september 2019 00.40
To: Milena Jovasevic-Stojanovic <[redacted]>
Cc: Zoran Mijic <[redacted]>; Mirjana Perisic <[redacted]>; Alena Bartonova
<[redacted]>
Subject: Re: WeBIOPATR2019

Dear Milena and Alena,

first I would like to thank you for considering me as a keynote speaker and for the opportunity to present the work of our laboratory at the conference.

Please find attached the abstract of the talk "MODELING PARTICULATE MATTER IN URBAN AREAS: EXPERIENCES OF THE INSTITUTE OF PHYSICS BELGRADE".

[redacted]

Best regards,
Andreja

Institute of Physics Belgrade
Pregrevica 118, 11080 Belgrade, Serbia
http://www.ipb.ac.rs/
[Цитирани текст је сакривен]
P Please consider the environment before printing this email and attachments

The 7th International Workshop and Conference, Particulate Matter: Research and Management

WeBIOPATR2019

Belgrade, Serbia, 1st – 3th October 2019

organized by VINCA Institute of Nuclear Sciences, NILU-Norwegian Institute for Air Research and Public Health Institute of Belgrade

Dr Andreja Stojić, Assistant Research Professor
Institute of Physics 11000 Belgrade
P.O.B.68, Pregrevica 118
11080 Belgrade Serbia

Dear Dr Andreja Stojić,

We are organizing the 7th International WeBIOPATR Workshop & Conference, Particulate Matter: Research and Management and expect researchers from several countries.

The main topics of the conference are:

- ATMOSPHERIC PARTICULATE MATTER - PHYSICAL AND CHEMICAL PROPERTIES
- PARTICULATE MATTER AND HEALTH
- PARTICULATE MATTER AND REGULATORY ISSUES

The program will include key note invited lectures, oral and poster presentations. Session devoted to MSc and PhD students will be incorporated to the main program in order for the attendees to be able to gain insight into the work of the research groups involved.

We are happy that you have accepted our invitation to give presentation of an invited key-note lecture, and wish to confirm that the title of your lecture is: **"MODELING PARTICULATE MATTER IN URBAN AREAS: EXPERIENCES OF THE INSTITUTE OF PHYSICS BELGRADE".** This topic is an important complement to the traditional view on the management of particulate matter, providing new insight and knowledge. We are sure your participation will contribute to the goals, and the excellence of this meeting. We appreciate your willingness to undertake this assignment, and to participate in our workshop & conference as an invited speaker. Abstracts of your invited lecture will be published in the publication titled "Abstract of Keynote Invited Lectures and Contributed Papers" from the WeBIOPATR2019 that will be distributed during the conference. We are also kindly ask you to develop a full paper in the Proceedings from WeBIOPATR2019.

We are very much interested in your participation as invited speaker, and we are honored by your acceptance of our invitation.

Best Regards,

Cochairs of WeBOPATR2019:

Dr Milena Jovašević-Stojanović **Dr Alena Bartoňová**

WeBIOPATR 2019

The Seventh International WEBIOPATR
Workshop & Conference
Particulate Matter: Research and Management

Abstracts of Keynote Invited Lectures and Contributed Papers

Milena Jovašević-Stojanović and Alena Bartoňová, Eds

Public Health Institute of Belgrade

Belgrade 2019

ABSTRACTS OF KEYNOTE INVITED LECTURES AND CONTRIBUTED PAPERS

The Seventh International WeBIOPATR Workshop & Conference

Particulate Matter: Research and Management

WeBIOPATR 2019

1st to 3rd October, 2019

Belgrade, Serbia

Editors

Milena Jovašević-Stojanović

Alena Bartoňová

Publisher

Public Health Institute of Belgrade

Prof. Dr Dušanka Matijević, Director

Boulevar Despota Stefana 54a

Serbia, 11000 Belgrade

Printed by

Printing office of the Public Health Institute of Belgrade

Number of copies

150

ISBN 978-86-83069-56-9

www.zdravlje.org.rs

SCIENTIFIC COMMITTEE

Aleksandar Jovović, Serbia
Alena Bartoňová, Norway
Antonije Onjia, Serbia
David Broday, Israel
Dikaia Saraga, Greece
Griša Močnik, Slovenia
Ivan Gržetić, Serbia
María Cruz Minguillón, Spain
Milena Jovašević-Stojanović, Serbia
Radim J. Šrám, Czech Republic
Renata Kovačević, Serbia
Selahattin Incecik, Turkey
Slobodan Ničković, Serbia
Simone Barreira Morais, Portugal
Zoran Mijić, Serbia
Zoran Ristovski, Australia
Zorana Jovanović-Andersen, Denmark

ORGANIZING COMMITTEE

Aleksandra Stanković, Serbia
Alena Bartoňová, Norway
Andrej Šoštarić, Serbia
Anka Cvetković, Serbia
Biljana Filipović, Serbia
Branislava Matić, Serbia
Dejan Lekić, Serbia
Dragan Alavantić, Serbia
Ivan Lazović, Serbia
Jasmina Jović-Stošić, Serbia
Maja Jovanović (Secretary), Serbia
Marija Živković (Secretary), Serbia
Milena Jovašević-Stojanović, Serbia
Miloš Davidović, Serbia
Mira Aničić Urošević, Serbia
Mirjana Perišić, Serbia
Nenad Živković, Serbia
Tihomir Popović, Serbia
Vesna Slepčević, Serbia
Viša Tasić, Serbia

CONFERENCE TOPICS

1. Atmospheric Particulate Matter - Physical and Chemical Properties

   i. Sources and formation of particulate matter

   ii. Particulate matter composition and levels outdoors and indoors

   iii. Environmental modeling

   iv. Nanoparticles in the environment

2. Particulate Matter and Health

   i. Exposure to particulate matter

   ii. Health aspects of atmospheric particulate matter

   iii. Full chain approach

3. Particulate Matter and Regulatory Issues

   i. Issues related to monitoring of particulate matter

   ii. Legislative aspects

   iii. Abatement strategies

Organizers

Vinča Institute of Nuclear Sciences, Serbia

Public Health Institute of Belgrade, Serbia

NILU Norwegian Institute for Air Research, Norway

The Seventh WeBIOPATR Workshop and Conference,

Particulate Matter: Research and Management, WEBIOPATR 2019

is supported by:

Ministry of Education, Science and Technological Development of Republic of Serbia

PREFACE

The International Workshop and Conference, Particulate Matter: Research and Management – WeBIOPATR is a biennial event held in Serbia since 2007. The conference addresses air quality in general and particulate matter specifically. Atmospheric particulate matter arises both from primary emissions and from secondary formation in the atmosphere. It is one of the least well understood local and regional air pollutants, has complex implications for climate change, and is perhaps the pollutant with the highest health relevance. It also poses many challenges to monitoring.

By WeBIOPATR, we aim to link the research communities with relevance to particulate matter with the practitioners of air quality management on all administrative levels, in order to facilitate professional dialogue and uptake of newest research into practice. The workshops usually draw an audience of about 70, and attract media attention in Serbia. It enjoys support of the responsible authorities: Ministry of Education, Science and Technological Development, Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency whose sponsorship is indispensable and gratefully acknowledged. We enjoy also support of international bodies such as the WHO.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007, associated with a project funded by the Research Council of Norway. The 2nd workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. WeBIOPATR2011 was held in Beograd 14.-17. 11. 2011 and for the first time, included a dedicated student workshop. WeBIOPATR2013 was held in Beograd 2.-4. 10. 2013. It covered the traditional PM research and management issues, discussions on how to encourage citizens to contribute to environmental governance, and how to develop participatory sensing methods. WeBIOPATR2015 was held in Beograd 14.-16.10. 2015. Own sessions were devoted to sensor technologies for air quality monitoring, utilizing information and input from the EU FP7 funded project CITI-SENSE (http://co.citi- sense.eu) and the EU COST action EuNetAir (www.eunetair.it). WeBIOPATR2017, the 6th conference, was held in Beograd 6.-8.9. 2017, with a wider than before Western Balkan participation.

WeBIOPATR2019 will be held 1.-3 -10-2019 in the Mechanical Faculty, University of Belgrade. It has attracted a record 58 contributions, and is bringing together scientists from 12 countries, documenting that the issues of atmospheric pollution, with their wide implications for climate change, human health and ecosystem services, are no less important today.

We are grateful to our unrelenting national and international partners for their support for this event.

Welcome to Beograd, and have a stimulating and productive time!

Milena Jovašević-Stojanović and Alena Bartoňová

TABLE OF CONTENTS

9.1. MODELING PARTICULATE MATTER IN URBAN AREAS: EXPERIENCES OF THE INSTITUTE OF PHYSICS BELGRADE

A. Stojić
Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Serbia
andreja.stojic@ipb.ac.rs

Due to the global urbanisation that has resulted in a half of the world's population being urban at the beginning of the new millennium, we are the witnesses of both cities growth and tremendous effects the growing process has on human health, the environment, and climate. The continuous air pollution burden on the environment is dependent not only on the increasing pollutant load, but also on many processes such as pollution transport, dispersion and deposition, atmospheric chemistry, meteorological factors, and topography. This makes the environment for the unlimited set of pathways for interactions which reflects the complexity of the urban ecosystem. Moreover, the complexity of the environmental phenomenon and the depth of its interpretation, determine the complexity of the methods needed to be applied to represent the phenomena and to formalize the principles being analyzed. For these reasons, environmental research focused on root causes that shape air pollution must rely on innovative, sophisticated, and advanced modelling techniques and their hybridization (Stojić et al. 2018).

This talk systematizes analytical methods capable of contributing substantially to the contemporary perception and interpretation of the factors and processes that generate particulate matter (PM) air pollution, govern its spatio temporal dynamics, and determine its environmental fate. It will cover the experiences of the Institute of Physics Belgrade in application, utilization and development of: (1) methods for preprocessing raw data and obtaining relevant statistical distributions (Perišić et al. 2015, Stojić et al. 2015); (2) methods for determining the shares of localy generated, transported, and background pollution; (3) source apportionment methods for dominant and individual emission source characterization in broader areas; (4) machine learning methods and fluctuation analysis for capturing pollutant non-linear dynamics and their relationships with relevant environmental factors (Stojić et al. 2016); (5) explainable artificial intelligence methods for characterization of ambient conditions responsible for air pollutant spatio-temporal behaviour in the environment that shapes it (Stojić et al. 2019); (6) dispersion and three dimensional hybrid receptor models for the identification of pollution circulation patterns and its altitude distributions on various spatial scales, and characterization of remote emission sources (Stojić et al. 2017); and (7) methods for interactive results visualization.

The profound insights anticipated into the environmental processes and factors driving PM concentrations, obtained by using sophisticated and synergistic modeling, aims to provide data-driven conclusions and deepen scientific understanding of the air pollution issue. Besides the scientific community, these results could be significant for the general public and policymakers, thus providing considerable benefit to society and sustainable development.

ACKNOWLEDGMENTS

This study was performed as a part of projects no. III43007 and no. III41011, which were funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the framework of integrated and interdisciplinary research for the period 2011–2019.

REFERENCES

Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z., and Rajšić, S. (2015). Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Quality, Atmosphere & Health, 8(4), 379-389.

Stojić, A., Stojić, S. S., Šoštarić, A., Ilić, L., Mijić, Z. and Rajšić, S. 2015. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling, Environmental Science and Pollution Research, 22(17), 13137–13152.

Stojić, A., Stojić, S. S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M. and Mijić, Z. 2016. Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. Environmental Science and Pollution Research 23, 10722-10732.

Stojić, A., Stojić and S. S. 2017. The innovative concept of three-dimensional hybrid receptor modeling. Atmospheric Environment, 164, 216–223.

Stojić, A., Vuković, G., Perišić, M., Stanišić, S. and Šoštarić, A. 2018. Urban air pollution: an insight into its complex aspects. In: A Closer Look at Urban Areas, Nova Science Publishers, NY, USA.

Stojić, A., Stanić, N., Vuković, G., Stanišić, S., Perišić, M., Šoštarić, A. and Lazić, L. 2019. Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition. Science of The Total Environment, 653, 140–147.

Публикације

Публикације категорије М10

Публикације после избора у претходно звање

Springer Link

Sustainable Cities and Communities

Living Edition
| Editors: Walter Leal Filho, Anabela Marisa Azul, Luciana Brandli, Pinar Gökcin Özuyar, Tony Wall

Introduction

The problems related to the process of industrialisation such as biodiversity depletion, climate change and a worsening of health and living conditions, especially but not only in developing countries, intensify. Therefore, there is an increasing need to search for integrated solutions to make development more sustainable. The United Nations has acknowledged the problem and approved the "2030 Agenda for Sustainable Development". On 1st January 2016, the 17 Sustainable Development Goals (SDGs) of the Agenda officially came into force. These goals cover the three dimensions of sustainable development: economic growth, social inclusion and environmental protection.

The *Encyclopedia of the UN Sustainable Development Goals* comprehensively addresses the SDGs in an integrated way. The Encyclopedia encompasses 17 volumes, each one devoted to one of the 17 SDGs. This volume addresses SDG 11, namely "**Make cities and human settlements inclusive, safe, resilient and sustainable**" and contains the description of a range of terms, which allow a better understanding and foster knowledge. This book presents a set of papers on the state of the art of knowledge and practices about the numerous challenges for cities, solutions and opportunities for the future.

Concretely, the defined targets are:

- Ensure access for all to adequate, safe and affordable housing and basic services and upgrade slums
- Provide access to safe, affordable, accessible and sustainable transport systems for all, improving road safety, notably by expanding public transport, with special attention to the needs of those in vulnerable situations, women, children, persons with disabilities and older persons
- Enhance inclusive and sustainable urbanization and capacity for participatory, integrated and sustainable human settlement planning and management in all countries
- Strengthen efforts to protect and safeguard the world's cultural and natural heritage
- Significantly reduce the number of deaths and the number of people affected and substantially decrease the direct economic losses relative to global gross domestic product caused by disasters, including water-related disasters, with a focus on protecting the poor and people in vulnerable situations
- Reduce the adverse per capita environmental impact of cities, including by paying special attention to air quality and municipal and other waste management

- Provide universal access to safe, inclusive and accessible, green and public spaces, in particular for women and children, older persons and persons with disabilities
- Support positive economic, social and environmental links between urban, peri-urban and rural areas by strengthening national and regional development planning
- Substantially increase the number of cities and human settlements adopting and implementing integrated policies and plans towards inclusion, resource efficiency, mitigation and adaptation to climate change, resilience to disasters, and develop and implement, in line with the Sendai Framework for Disaster Risk Reduction 2015–2030, holistic disaster risk management at all levels
- Support least developed countries, including through financial and technical assistance, in building sustainable and resilient buildings utilizing local materials

Editorial Board

Editors and affiliations

- Walter Leal Filho (1)
- Anabela Marisa Azul (2)
- Luciana Brandli (3)
- Pinar Gökcin Özuyar (4)
- Tony Wall (5)

1. European School of Sustainability, Hamburg University of Applied Sciences, , Hamburg, Germany
2. Center for Neuroscience & Cell Biology, University of Coimbra, , Coimbra, Portugal
3. Faculty of Engineering and Architecture, Passo Fundo University Faculty of Engineering and Architecture, , Passo Fundo, Brazil
4. Istinye University, , Istanbul, Turkey
5. International Centre for Thriving, University of Chester, , Chester, UK

Bibliographic information

- Copyright Information Springer Nature Switzerland AG 2019
- Publisher Name Springer, Cham
- Online ISBN 978-3-319-71061-7
- Series Print ISSN 2523-7403
- Series Online ISSN 2523-7411

- eBook Packages Earth and Environmental Science
- Number Of Entries 68

Part of the Encyclopedia of the UN Sustainable Development Goals book series (ENUNSDG)

Springer Link

Sustainable Cities and Communities

Living Edition
| Editors: Walter Leal Filho, Anabela Marisa Azul, Luciana Brandli, Pinar Gökcin Özuyar, Tony Wall

Urban Air Pollution and Environmental Health

- Svetlana Stanišić (1) Email author (sstanisic@singidunum.ac.rs)
- Andreja Stojić (2)

1. Singidunum University, , Belgrade, Serbia
2. Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, , Belgrade, Serbia

Living reference work entry
First Online: 15 October 2019

DOI: https://doi.org/10.1007/978-3-319-71061-7_120-1

Definitions

Ambient air pollution refers to a mixture of chemical species and particulate matter originating from diverse anthropogenic and/or natural sources, as well as complex atmospheric processes.

The current growth of global population and economy mainly relies on the combustion of fossil fuels and discarding products, which leads to a rapid depletion of the planet's finite valuable resources and huge amounts of waste. As one of the results of such rapid economic growth, the world might face fossil fuel exhaustion within the next 50–100 years (Chapman 2007). The issue most closely linked to the combustion of fossil fuels is air pollution. From the pre-industrial era to the present day, shifts in anthropogenic emissions and global temperature have affected the atmospheric composition (Fang et al. 2013) to such an extent that air pollution has become an evident threat to the mechanisms which regulate life on our planet. Today, around 90% of the world's population inhabits the...

References

U

Urban Air Pollution and Environmental Health

Svetlana Stanišić[1] and Andreja Stojić[2]
[1]Singidunum University, Belgrade, Serbia
[2]Institute of Physics Belgrade, National Institute of the Republic of Serbia,
University of Belgrade, Belgrade, Serbia

Definitions

Ambient air pollution refers to a mixture of chemical species and particulate matter originating from diverse anthropogenic and/or natural sources, as well as complex atmospheric processes.

The current growth of global population and economy mainly relies on the combustion of fossil fuels and discarding products, which leads to a rapid depletion of the planet's finite valuable resources and huge amounts of waste. As one of the results of such rapid economic growth, the world might face fossil fuel exhaustion within the next 50–100 years (Chapman 2007). The issue most closely linked to the combustion of fossil fuels is air pollution. From the pre-industrial era to the present day, shifts in anthropogenic emissions and global temperature have affected the atmospheric composition (Fang et al. 2013) to such an extent that air pollution has become an evident threat to the mechanisms which regulate life on our planet. Today, around 90% of the world's population inhabits the places where air pollution levels significantly exceed the limits recommended by the World Health Organization (WHO) air quality guidelines.

The assumption that air pollutant concentrations are high in industrialized and economically developed areas with high-energy consumption per capita is the closest to people's mind. However, over the past two decades, the levels of air pollutants in modern countries have been significantly reduced. At the same time, severe air quality deterioration is observed in overpopulated areas of developing countries, as well as in rural and non-industrialized regions where biomass and low-quality coal are the principal forms of fuel (Smith 2013). For instance, people living in Asian metropoles are exposed to fine particulate matter concentrations in the range from 100 to 300 $\mu g\ m^{-3}$, which are up to 20 times higher than those commonly observed in the developed countries (Shah et al. 2013). Apart from ambient air pollution, more than three billion people worldwide rely on household fuel combustion for cooking, heating, and lightning, which makes significant effect on indoor air quality and associated premature morbidity and mortality, particularly in Africa and Asia (WHO 2019a). It should also be taken into consideration that the studies addressing air pollution and its consequences in developing regions around the globe, with the exception of studies performed in China, are still relatively scarce, due to poor surveillance data (Han and Naeher 2006).

W. Leal et al. (eds.), *Sustainable Cities and Communities*, Encyclopedia of the UN Sustainable Development Goals,
https://doi.org/10.1007/978-3-319-71061-7_120-1

Air pollution is a major contributor to mortality and is environmental hazard in urban areas. Current scientific evidence suggests that both short- and long-term exposure to even modest air pollutant levels is linked to adverse health effects, aggravation of the pre-existing health conditions and reduced life expectancy. The exposure to ambient air pollution is regarded as the ninth leading risk factor for mortality, causing about 4.2 million deaths worldwide each annum (Kurt et al. 2016). The burden of disease attributable to urban air pollution is mostly estimated in terms of deaths, due to limitations in the epidemiological database, although some studies suggest that if research referred to both mortality and morbidity, the disability-adjusted life years for cardiovascular diseases would increase by at least 20% globally (Cohen et al. 2005).

A number of studies aiming to explore the relationships between air pollution and health effects converged on the conclusion that the adverse health effects mostly follow a linear concentration-response function and can occur at levels close to background concentrations. The relative contributions of specific pollutant species to the global health burden still remain a matter of scientific debate (Stojić et al. 2018). Currently, there is no clear evidence of a threshold within the studied range of ambient pollutant concentrations below which there is no risk of morbidity and mortality, and, thus, further reduction of air pollutant concentrations is likely to bring additional health benefits (Kelly and Fussell 2015).

The governments around the globe squarely aim to decrease the amount of heat-trapping gases causing global warming, as well as the morbidity and mortality worldwide, with the least financial loss possible. In economic terms, the Environment Audit Committee has estimated that total air pollution-related health costs range between £8.5 billion and £20.2 billion per year. Although it is not possible to increase air quality without a certain decline in economic output, the trade-offs between optimizing economic and health outcomes are often mentioned and even exaggerated (Cosford et al. 2018).

The predictions reveal that, because of aging populations, health risks in many countries will rise even if the pollution levels remain constant. It has been estimated that, with no changes in air quality, mortality burden from air pollution will increase by 20–30% within the next 15 years (WHO 2019b).

Types of Air Pollutants and Their Sources

Ambient air pollution refers to a mixture of chemical species and particulate matter originating from diverse anthropogenic and/or natural sources, as well as from complex atmospheric processes. While the emissions from natural sources are more abundant, the ever-increasing reliance on fossil fuels appears to be causing more short- and long-term damage to human health and the environment, particularly in urban areas. Man-made air pollution is mostly associated with power generation, transport, agricultural emissions, industrial activities, biomass burning, and domestic heating and cooking. According to their chemical characteristics, air pollutants can be grouped into five main groups (Kampa and Castanas 2008).

Gaseous Pollutants

Gaseous pollutants include carbon, sulfur and nitrogen oxides, ozone, and volatile organic compounds. An increase in their emissions and significant deterioration of air quality that has been experienced in populated areas over the past 150 years have been confirmed by the studies investigating the sulfate and carbonaceous aerosol concentrations in Greenland ice cores and Alpine glaciers (Fischer et al. 2014). Till the middle of the twentieth century, sulfur dioxide (SO_2) and soot from fossil fuel combustion were the most abundant air pollutants in urban atmosphere. With the introduction of cleaner technologies in the industry of developed countries, the levels of SO_2 have steadily declined, but the growing traffic has given rise to nitrogen oxides (NO_x), ozone, and volatile organic compounds (VOCs) (Fenger 2009).

Vehicle exhaust is the major source of nitrogen oxide (NO) in urban areas (Stojić et al. 2015), a highly reactive air pollutant which rapidly reacts with free radicals or ozone in the atmosphere, resulting in the formation of nitrogen dioxide

(NO_2). NO_2 is an important heat-trapping gas with residence time in the atmosphere of about 170 years. At the beginning of the twentieth century, only few thousands of motor vehicles were registered in the world, mostly in the USA. Since then, the transport has developed to meet the demands of growing population, and as a result, nowadays, there are 1 billion of passenger cars traveling the streets around the world. Global participation in this expansion is governed by the economic growth and, thus, has been disproportionate. Unfortunately, numerous technological improvements, regulations of emissions in developed countries, including more rigorous standards, and the improvement of the existing ones to include non-road engines were offset by the increased number of vehicles (Chapman 2007). In addition to nitrogen oxides, carbon monoxide (CO) and carbon dioxide (CO_2) are generated through combustion processes. The significant share of CO_2 originates from vegetation decomposition, volcanic eruptions, and animals' metabolism, but emissions related to human activities mostly affect urban areas. Once emitted in the atmosphere, CO_2 contributes to greenhouse effect and has residence time of about 100 years. Recent studies have confirmed that the concentrations of CO_2 in the atmosphere are higher than they have ever been in previous 400,000 years. Regarding this, the United Nations' Intergovernmental Panel on Climate Change warned that air pollution issue is closely linked to the Earth's climate and that coal-fired electricity should no longer be a choice after 2050, if we want to keep global temperature rises to current 1.5° (Kelly and Fussell 2015).

Apart from traffic emissions, fossil fuel combustion and petrochemical industry also contribute to high levels of VOCs, a heterogeneous group of organic species with boiling points <250 °C. VOC emissions are related to both biogenic and anthropogenic sources. Biogenic emissions from forests, oceans, and soils provide the largest sources of VOCs in the global atmosphere (750–1000 Tg year^{-1}), with the emissions mainly comprised of isoprene, monoterpenes, and associated oxygenated species. However, the global anthropogenic VOC emissions (100–160 Tg year^{-1}), associated with fuel and petroleum-based products, paints, varnishes, glues, cleaners, disinfectants, pesticides, and cosmetics, are of greater concern and pose greater risks in urban areas, due to their toxicity and high local concentrations (Stojić et al. 2019). Apart from their direct impact on human health, VOCs are associated with climate change and an increase in the oxidation capability of the atmosphere. Numerous studies have underlined their importance in the formation of secondary organic aerosols, greenhouse gases, hydroxyl radical, nitrate radical, and particularly ozone. As regards the direct impact of VOCs on global warming, methane is recognized as one of the most potent greenhouse gases, with an estimated 28 to 36-fold higher global warming potential than carbon dioxide, and vice versa, VOC emissions and their environmental fates are expected to be influenced and increased by the forthcoming global warming. Finally, it should be mentioned that VOC impacts on the environment and human health are not only limited to air quality, because they are eliminated from the atmosphere through wet deposition, and once dissolved in water, these volatile species become more persistent and can be transported into groundwater. Despite the fact that the levels of other polluting species have been significantly reduced over the past few decades in developed countries, reducing the levels of VOC is still challenging. The reasons for this are associated with their enormous chemical diversity and abundance, their countless emission sources, their complex atmospheric chemistry, their insufficient funds for the establishment, and their maintenance of monitoring networks and the fact that abatement programs might have negative impact on the economic output.

Tropospheric ozone is a highly reactive gas, produced by photochemical reactions in the presence of sunlight. At ground level, ozone is detrimental to health and the environment. It has been estimated that 7–12% of the global wheat crop is affected by high ozone concentrations, with the highest damage registered in India, reaching 28% (Frumkin 2002). Because of its photochemical nature, ozone concentrations show distinct seasonal and temporal pattern. They are typically high during the summer and afternoon and low at night, in early morning, and winter (Schwartz 2004). However, at present, photochemical ozone production during winter has also been discovered in regions with oil and gas production (Helmig et al. 2014). Unlike tropospheric ozone, considered to be detrimental to human health and the environment, 30 km above the ground in the stratosphere, naturally produced ozone layer absorbs most of the Sun's ultraviolet spectrum, preventing it from reaching the planet's surface and, thus, protecting life from harmful solar radiation. Few decades ago, human emissions of chlorofluorocarbons were responsible for a significant decline in stratospheric ozone, especially above Antarctica, until the ban by the Montreal Protocol. Since 1998, ozone in the upper stratosphere has been slowly recovering from halogen-induced losses (Ball et al. 2018).

2. Heavy metals (e.g., lead, mercury, cadmium, and nickel) are natural components of the Earth's crust that enter the atmosphere through combustion, mining, and/or manufacturing facilities. They have the tendency for bioaccumulation in living tissues over time, which, in case of acute exposure, leads to intoxication, while chronic exposure can result in vital organ disorders.

Organic Pollutants

Organic pollutants refer to a toxic group of chemical species (pesticides, dioxins, furans, and polychlorinated biphenyls) that persist in the environment for a long period of time and exhibit magnified effects as they move up through the food chain.

Particulate Matter (PM)

Particulate matter refers to a complex mixture of solid and liquid particles of varying size, shape, and composition and is the most often used indicator of ambient air quality for the purpose of assessing the adverse health effects from exposure. PM is classified according to the aerodynamic particle size as follows: coarse particles (PM_{10}, particles that are less than 10 μm in diameter); fine particles ($PM_{2.5}$, particles that are less than 2.5 μm in diameter); and ultrafine particles ($PM_{0.1}$, particles that are less than 0.1 μm in diameter). Primary PM are emitted directly in the atmosphere, while secondary ones are formed through complex atmospheric reactions. Biogenic PM sources include windblown soil and dust, sea spray, and wildfires. Important anthropogenic PM emission sources refer to vehicle exhaust; burning fossil fuels or wood, for heating; power plants and industry; agriculture/waste incineration; and other physical processes, such as re-suspended road dust, wear of tire, and brake linings. In urban areas, vehicle exhaust has been considered as the most significant source of anthropogenic air pollution, typically accounting for one quarter of global CO_2 emissions and one third of fine particulate matter fraction. However, the contribution of traffic to total pollutant concentrations is highly variable and depends on weather conditions and flow densities. For instance, a research in the UK has shown that an average of 25% of particulate pollution can be associated with vehicle exhaust, although this amount can reach up to 75–80% on days with intensive traffic (O'Connell and Williams 2011).

Photochemical Smog

Photochemical smog refers to a mixture of air pollutants including ozone and peroxyacetyl nitrate that are generated when nitrogen oxides and VOCs react in the presence of sunlight. It is mostly observed as brown haze above densely populated urban regions with warm climate, during morning and afternoon hours. Cities such as Los Angeles (California, USA) and Mexico (Mexico), located in the valleys with pronounced temperature inversion, experience photochemical smog to a greater extent.

Air Pollution-Related Health Effects and Mortality

The assessment of global burden of disease is based on epidemiological cohort studies, experimental animal research, and studies exploring mechanistic pathways (Jerrett et al. 2013). Since the first evidence that linked air pollution to the increased risk of arrhythmias, myocardial infarction, stroke, chronic obstructive pulmonary disease (COPD), and other respiratory disorders, low air quality has been associated with a number of health conditions, including diabetes, kidney disease, and Alzheimer. According to the recent estimates, around 4.2 million of cardiovascular, respiratory, and malignant deaths per year globally can be attributed to air pollution (Cohen et al. 2017). More specifically, COPD, lung cancer, and ischemic heart disease with myocardial infarction are the three most represented causes, contributing with 43%, 29%, and 24% to global air pollution-related premature mortality, respectively (WHO 2019b). In order to illustrate the complexity of the issue, Holgate (2017) emphasized that in the UK 40,000 excess deaths can be associated with poor air quality annually and that society would be much more aware of its significance if this mortality was the consequence of drinking polluted water. As shown by Haque and Singh (2017), respiratory illnesses in the heavily polluted city of Kolkata (India) now exceed waterborne illness by the factor of 5.

Emerging evidence has shown that high air pollution and living near a busy road promote atherosclerosis involving multiple organs and different cell types (Bai and Sun 2016), as well as accelerate skin ageing, dementia, cognitive decline, and decline in lung function (Power et al. 2016). Even daily changes in the levels of ambient coarse and fine particulate matter have been associated with a higher risk of acute cardiovascular events, hospital admissions, and deaths (Wellenius et al. 2012). The changes in biomarkers of cardiovascular function, endothelial function and vasoconstriction, blood pressure, prothrombotic and coagulant parameters, systemic inflammatory and oxidative stress responses, and autonomic balance, following the exposure to air pollution, are registered in both young people and adult population (Brook et al. 2010). The mechanism of susceptibility is linked to the generation of reactive oxygen species, changes in antioxidant defense, and increased inflammatory responses (Krzyżanowski et al. 2005).

The effects of real-world exposures to outdoor air pollution are also strongly associated with the increase in genetic damage, mutations in both somatic and germ cells, altered gene expression, and, therefore, an increased cancer risk in adult population, while some research suggests that exposure in childhood could also contribute to the development of cancers in later life. The evidence from China shows that the number of rural residents being diagnosed with lung cancer declined by 40% after switching to stoves with chimneys in their homes (WHO 2019c).

The health impact of each air pollutant is specific. A number of scientific studies have confirmed that ambient NO_2 is a respiratory irritant that increases the risk of asthmatic exacerbations and respiratory infections and affects respiratory development, as well as the onset of pulmonary disorders in early childhood. Some epidemiological studies have also shown the relationships between NO_2 concentrations and reduced life expectancy, although it appears to be unclear whether these effects are caused by NO_2 itself or by other traffic-related and photochemically formed toxic pollutants that exhibit high spatiotemporal correlation with NO_2 (Stanišić Stojić et al. 2016a).

The main anthropogenic sources of SO_2 are combustion of sulfur-containing fossil fuels (e.g., lignite, the lowest rank of coal) and smelting of sulfur-containing ores (Stanišić et al. 2018). Controlled human studies have demonstrated that SO_2 exposure causes respiratory irritations and changes in pulmonary tissue, including increased airway resistance.

The health effects associated with exposure to CO range from subtler cardiovascular and neurobehavioral effects, being observed at lower concentrations, to unconsciousness and death, after exposure to higher concentrations of CO. Acute CO intoxication is associated with the fact that CO has 200 times higher affinity for hemoglobin binding and occurs relatively frequently. It results in flu-like syndrome, headache, dizziness, weakness, nausea, confusion, disorientation, visual disturbances, and eventually death, due to myocardial hypoxia. Another effect of CO poisoning is delayed neuropsychiatric impairment which occurs within 2–28 days after the exposure and is followed by slow resolution of neurobehavioral consequences (Raub et al. 2000).

The increase in cardiovascular mortality associated with air pollution episodes can be explained by the fact that ultrafine particles induce alveolar inflammation, thereby releasing mediators which, in susceptible individuals, cause exacerbations of the existing respiratory disorder and increase of blood coagulability (Seaton et al. 1995). In addition to their impact on circulatory and respiratory system, the WHO's International Agency for Research on Cancer classified PM as carcinogenic in 2013. The proximity of fresh PM emissions can be considered particularly detrimental to human health because particles coagulate in minutes to hours and evaporate at even faster time scales (Ban-Weiss et al. 2010). Their residence time in the atmosphere depends on their size and ranges from 10 to 100 h. While particles larger than 10 μm remain deposited in the nose or throat, particles smaller than 10 μm pose the greatest risk because they penetrate deeper into the lungs, enter the circulatory system, and later tend to be deposited in other vital organs (Stanišić Stojić et al. 2016b). In addition to particle size and exposure duration, the key determinant of potential adverse health effects is their chemical composition. A majority of studies assume that particles from different sources are equally toxic, although their toxicity varies depending on the content of black carbon, nitrates, sulfates, ammonia, and/or mineral dust. For instance, the emissions from residential fuel combustion for heating and cooking purposes in India and China are found to have an impact on premature mortality larger than average (Lelieveld et al. 2015). As regards urban areas, studies have also shown significant variations in PM chemical composition, depending on location and type of the emission source. For instance, heavy metal concentrations were higher in PM samples from Rome, whereas the PM samples collected from Amsterdam contained more magnesium (Krewski and Rainham 2007).

Health effects of VOCs are diverse. Depending on their chemical structure, dose, and length of exposure, they range from malignancy to developmental and vital organ disorder. The most hazardous are benzene, toluene, ethylbenzene and xylenes (commonly known as BTEX), styrene, 1,3-butadiene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene. Exposure to benzene increases the risk of developing malignant blood disorders; exposure to toluene causes renal tubular acidosis, while long-term exposure to styrene results in central nervous system dysfunction and peripheral neuropathy. Previous studies have shown that, after the reduction of benzene, styrene, and tetrachloroethylene concentrations in industrial and urban areas, lifetime cancer risk decreases by one order of magnitude (Lerner et al. 2014).

Higher ozone levels are associated with higher incidence and severity of respiratory symptoms, more emergency room visits and hospitalizations, and more absenteeism from school and work. While healthy people suffer adverse health effects, people with asthma and other underlying conditions are especially susceptible to ozone exposure (Frumkin 2002). Although the effects of exposure to O_3 are predominantly respiratory, adverse effects on the cardiovascular system have also been reported.

As stated above, high concentrations of each pollutant affect human health in a specific way. However, it should be taken into account that population is exposed to a complex mixture of air pollutants simultaneously, and, thus, the advanced quantifications of the air pollution-related morbidity and mortality have moved from single- to a multi-pollutant research approach. In addition to this, the environmental health research also takes into consideration the contributions of certain confounders and several other aspects, including the subject's proximity of specific emission sources, time-activity patterns, residence or work in polluted areas, as well as the subject's time spent in traffic. For instance, in the so-called street canyons and in a km-wide belt along major highways, the concentrations of all transport-related pollutants are much higher than in the areas that are not directly exposed to emissions (Krzyżanowski et al. 2005). While the majority of environmental health risk studies have been focused on urban populations, the mounting evidence suggests that rural populations are also potentially exposed to a variety of serious environmental risks from industrial facilities, mining operations, logging and timber activities, petroleum refineries, agricultural activities, incinerators, landfills, and sewage treatment facilities (Hendryx 2010).

Susceptible Categories

The extent of air pollution-related health impacts observed in urban populations is dependent not only on pollution severity and climate but also on socioeconomic factors, education, age, and underlying pathological and physiological conditions (pregnancy) (Salmond et al. 2018). Generally, the populations in highly industrialized areas, socioeconomically deprived, as well as children, pregnant women, and elderly people, appear to be more susceptible to pollution-related morbidity and mortality. Furthermore, reduced life expectancy is prevalent among individuals with pre-existing cardiovascular and respiratory conditions – i.e., asthma symptoms can be triggered by episodes of air pollution events (Stanišić Stojić et al. 2016c).

Infants represent a vulnerable population category because their immature immune and respiratory systems at birth might take 6 years to reach full functionality. The number of alveoli in human lungs increases from 24 million at birth to 257 million at the age of 4, and respiratory epithelium is not fully developed which contributes to greater permeability. Moreover, children have a larger lung surface area per kilogram of body weight, and under normal conditions, they inhale up to 50% more air per kg than adults. When compared to adults, children also spend more time outside performing the activities that increase ventilation rates, where air pollutant concentrations are generally higher.

Maternal exposure to ambient air pollution is associated with neurological development in infants and adverse birth outcomes, such as low birth weight, intrauterine growth retardation, preterm birth, and small gestational age births. Also, the current evidence shows a causal relationship between maternal air pollution exposure and respiratory deaths in the postneonatal period. Particularly, traffic-related pollution has been associated with infant mortality and the development of asthma and atopy (Šrám et al. 2005).

Cross-References

- ► Ecological Footprints
- ► Green Cities
- ► Healthy City
- ► Low Carbon City
- ► Mitigation and Adaptation to Climate Change
- ► Urban Ecological Footprints
- ► Urban Mitigation and Adaptation for Climate Change
- ► Urban Pollution and Emissions Reduction

References

Bai Y, Sun Q (2016) Fine particulate matter air pollution and atherosclerosis: mechanistic insights. Biochim Biophys Acta 1860:2863–2868

Ball WT, Alsing J, Mortlock DJ et al (2018) Evidence for a continuous decline in lower stratospheric ozone offsetting ozone layer recovery. Atmos Chem Phys 18:1379–1394

Ban-Weiss GA, Lunden MM, Kirchstetter TW et al (2010) Size-resolved particle number and volume emission factors for on-road gasoline and diesel motor vehicles. J Aerosol Sci 41:5–12

Brook RD, Rajagopalan S, Pope CA III et al (2010) Particulate matter air pollution and cardiovascular disease: an update to the scientific statement from the American Heart Association. Circulation 121:2331–2378

Chapman L (2007) Transport and climate change: a review. J Transp Geogr 15:354–367

Cohen AJ, Ross Anderson H, Ostro B et al (2005) The global burden of disease due to outdoor air pollution. J Toxicol Environ Health 68:1301–1307

Cohen AJ, Brauer M, Burnett R et al (2017) Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study. Lancet 389:1907–1918

Cosford P, Whitty C, Exley K (2018) Health matters: air pollution – sources impacts and actions. https://publichealthmatters.blog.gov.uk/2018/11/14/health-matters-air-pollution-sources-impacts-and-actions/. Accessed 10 Sept 2019

Fang Y, Mauzerall DL, Liu J et al (2013) Impacts of 21st century climate change on global air pollution-related premature mortality. Clim Chang 121:239–253

Fenger J (2009) Air pollution in the last 50 years–from local to global. Atmos Environ 43:13–22

Fischer P, Nieuwenhuijsen M, Vineis P et al (2014) Air pollution and nonmalignant respiratory mortality in 16 cohorts within the ESCAPE project. Am J Respir Crit Care Med 189:684–696

Frumkin H (2002) Urban sprawl and public health. Public Health Rep 117:201–2017

Han X, Naeher LP (2006) A review of traffic-related air pollution exposure assessment studies in the developing world. Environ Int 32:106–120

Haque MS, Singh RB (2017) Air pollution and human health in Kolkata India: a case study. Climate 5:77–93

Helmig D, Thompson CR, Evans J et al (2014) Highly elevated atmospheric levels of volatile organic compounds in the Uintah Basin, Utah. Environ Sci Technol 48:4707–4715

Hendryx M (2010) Poverty and mortality disparities in central Appalachia: mountaintop mining and environmental justice. JHDRP 4:44–53

Holgate ST (2017) Every breath we take: the lifelong impact of air pollution–a call for action. Clin Med 17:8–12

Jerrett M, Burnett RT, Beckerman BS et al (2013) Spatial analysis of air pollution and mortality in California. Am J Respir Crit Care Med 188:593–599

Kampa M, Castanas E (2008) Human health effects of air pollution. Environ Pollut 151:362–367

Kelly FJ, Fussell JC (2015) Air pollution and public health: emerging hazards and improved understanding of risk. Environ Geochem Health 37:631–649

Krewski D, Rainham D (2007) Ambient air pollution and population health: overview. J Toxicol Environ Health 70:275–283

Krzyżanowski M, Kuna-Dibbert B, Schneider J (2005) Health effects of transport-related air pollution. WHO Regional Office Europe, Copenhagen

Kurt OK, Zhang J, Pinkerton KE (2016) Pulmonary health effects of air pollution. Curr Opin Pulm Med 22:138–149

Lelieveld J, Evans JS, Fnais M et al (2015) The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature 525:367–378

Lerner JEC, Kohajda T, Aguilar ME et al (2014) Improvement of health risk factors after reduction of VOC concentrations in industrial and urban areas. Environ Sci Pollut R 21:9676–9688

O'Connell JF, Williams G (2011) Air transport in the 21st century: key strategic developments. Ashgate Publishing, Surrey

Power MC, Adar SD, Yanosky JD et al (2016) Exposure to air pollution as a potential contributor to cognitive function cognitive decline brain imaging and dementia: a systematic review of epidemiologic research. Neurotoxicology 56:235–253

Raub JA, Mathieu-Nolf M, Hampson NB (2000) Carbon monoxide poisoning – a public health perspective. Toxicology 145:1–14

Salmond J, Sabel C, Vardoulakis S (2018) Towards the integrated study of urban climate air pollution and public health. Climate 6:14–22

Schwartz J (2004) Air pollution and children's health. Pediatrics 113:1037–1043

Seaton A, Godden D, MacNee W (1995) Particulate air pollution and acute health effects. Lancet 345:176–178

Shah AS, Langrish JP, Nair H et al (2013) Global association of air pollution and heart failure: a systematic review and meta-analysis. Lancet 382:1039–1048

Smith KR (2013) Biofuels air pollution and health: a global review. Springer Science & Business Media, Berlin

Šrám RJ, Binková B, Dejmek J et al (2005) Ambient air pollution and pregnancy outcomes: a review of the literature. Environ Health Perspect 113:375–382

Stanišić Stojić S, Stanišić N, Stojić A (2016a) Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area. Environ Health. https://doi.org/10.1186/s12940-016-0164-6

Stanišić Stojić S, Stanišić N, Stojić A (2016b) Short- and long-term effects of urban air pollution on cardiopulmonary and malignant death rates. In: Burns GL (ed) Air pollution: management strategies environmental impact and health risks. Nova Science Publishers, New York

Stanišić Stojić S, Stanišić N, Stojić A et al (2016c) Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. J Toxicol Environ Health 79:17–27

Stanišić S, Stojić A, Prodanović M (2018) Environmental concerns in Serbia: focusing on air pollution and its effects on human health. In: Janev I (ed) Serbia: current issues and challenges in the areas of natural resources agriculture and environment. Nova Science Publishers, New York

Stojić A, Maletić D, Stojić SS et al (2015) Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. Sci Total Environ 521:19–26

Stojić A, Stanišić S, Perišić M et al (2018) Urban air pollution – an insight into complexity aspects health aspects of urban life. In: Romero S (ed) A closer look at urban areas. Nova Science Publishers, New York

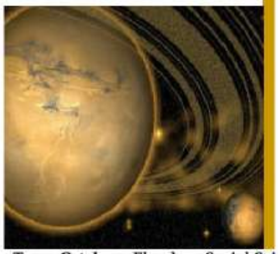
Stojić A, Stanić N, Vuković G et al (2019) Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition. Sci Total Environ 653:140–147

Wellenius GA, Burger MR, Coull BA (2012) Ambient air pollution and the risk of acute ischemic stroke. Arch Intern Med 172:229–234

WHO (2019a) How air is destroying our health. https://www.who.int/air-pollution/news-and-events/how-air-pollution-is-destroying-our-health. Accessed 3 Sept 2019

WHO (2019b) Ambient air pollution: Health impacts. https://www.who.int/airpollution/ambient/health-impacts/en/. Accessed 7 Sept 2019

WHO (2019c) Health matters air pollution. https://www.gov.uk/government/publications/health-matters-air-pollution/health-matters-air-pollution. Accessed 9 Sept 2019



ACCOUNT VIEW CART

nova science publishers

Home | Books | Series | Journals | Reference | eBooks | Information

Sales | Imprints | for Authors

Top » Catalog » Ebooks » Social Sciences » Social Sciences - General »

My Account | Cart Contents | Checkout

Quick Find

Use keywords to find the product you are looking for.
Advanced Search

What's New?

Fetal Alcohol Syndrome: Recognition, Differential Diagnosis and Long-Term Effects
$73.80

Shopping Cart

0 items

Information

Shipping & Returns
Privacy Notice
Conditions of Use
Contact Us

Notifications

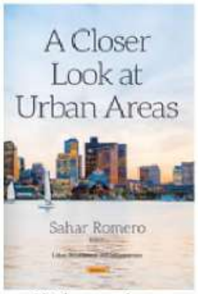
Notify me of updates to A Closer Look at Urban Areas

Tell A Friend

Tell someone you know about this product.

A Closer Look at Urban Areas

$82.00



Click to enlarge

Editors: Sahar Romero

Book Description:

Since the 'smart' component became one of the pillars of the European Union's development, many cities, particularly post-socialist ones, have perceived the smart city concept as a remedy for their problems in the economic, social or image-related spheres. *A Closer Look at Urban Areas* reviews and analyzes the implementation of the smart city concept applied in recent years in cities of the new Member States.

Due to the global phenomenon of urbanization, we are witnesses to cities' growth and the tremendous effects the growth process has on the environment and the health of populations inhabiting urban areas. Apart from numerous benefits such as opportunities for employment, entertainment, education and access to health care, the authors aim to address how urban lifestyles are also inextricably linked to numerous adverse health effects.

The increase in population, economic development, urbanization, industrialization and transport has also raised the issue of air pollution as one of the pressing concerns for contemporary society, primarily due to the harmful effects of elevated concentrations of polluting species on public health, environment and climate. Thus, the authors maintain that researching pollutant wet scavenging by atmospheric water is important for revealing the fate of air contaminants in atmospheric, terrestrial and aquatic systems. (Nova)

Special Focus Titles

01. Violent Communication and Bullying in Early Childhood Education
02. Cultural Considerations in Intervention with Women and Children Exposed to Intimate Partner Violence
03. Chronic Disease and Disability: The Pediatric Lung
04. Fruit and Vegetable Consumption and Health: New Research
05. Fire and the Sword: Understanding the Impact and Challenge of Organized Islamism. Volume 2

Table of Contents:

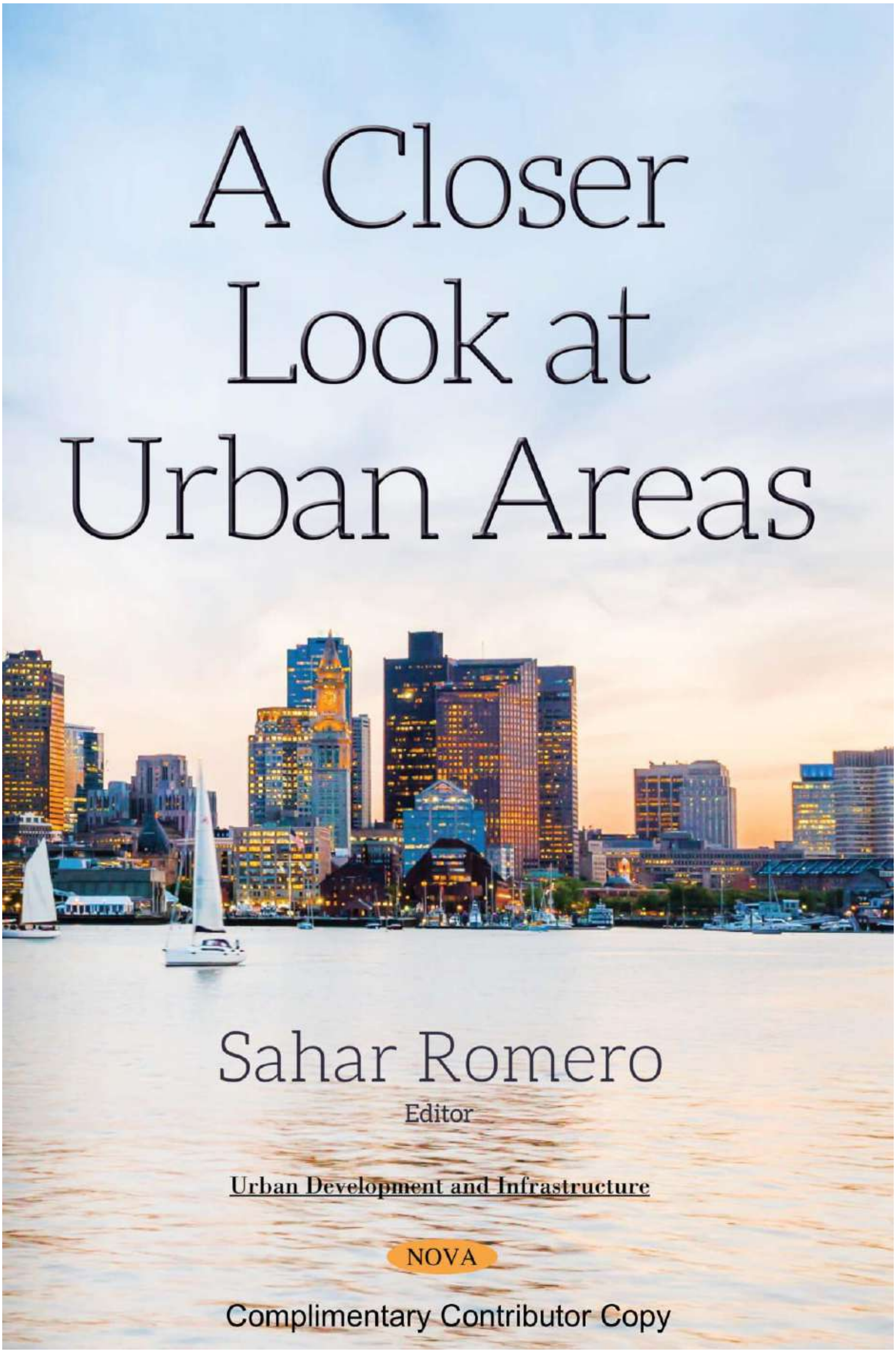
Series:
Urban Development and Infrastructure
Binding: ebook
Pub. Date: September 13, 2018
ISBN: 978-1-53614-450-5
Status: AV

Status Code	Description
AN	Announcing
FM	Formatting
PP	Page Proofs
FP	Final Production
EP	Editorial Production
PR	At Prepress
AP	At Press
AV	Available

Available Options:
Version: Download: Windows - English ▾

Add to Cart

Saturday 23 November, 2019


A Closer Look at Urban Areas
Sahar Romero
Editor
Urban Development and Infrastructure
NOVA
Complimentary Contributor Copy

A CLOSER LOOK AT URBAN AREAS

URBAN DEVELOPMENT AND INFRASTRUCTURE

Additional books and e-books in this series can be found on Nova's website under the Series tab.

URBAN DEVELOPMENT AND INFRASTRUCTURE

A CLOSER LOOK AT URBAN AREAS

SAHAR ROMERO

EDITOR

nova science publishers
New York

NOTICE TO THE READER

The Publisher has taken reasonable care in the preparation of this book, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained in this book. The Publisher shall not be liable for any special, consequential, or exemplary damages resulting, in whole or in part, from the readers' use of, or reliance upon, this material. Any parts of this book based on government reports are so indicated and copyright is claimed for those parts to the extent applicable to compilations of such works.

Independent verification should be sought for any data, advice or recommendations contained in this book. In addition, no responsibility is assumed by the publisher for any injury and/or damage to persons or property arising from any methods, products, instructions, ideas or otherwise contained in this publication.

This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.

Additional color graphics may be available in the e-book version of this book.

Library of Congress Cataloging-in-Publication Data

ISBN: ;9:/3/75836/672/7"*gDqqm+

Published by Nova Science Publishers, Inc. † New York

CONTENTS

PREFACE

Since the 'smart' component became one of the pillars of the European Union's development, many cities, particularly post-socialist ones, have perceived the smart city concept as a remedy for their problems in the economic, social or image-related spheres. *A Closer Look at Urban Areas* reviews and analyzes the implementation of the smart city concept applied in recent years in cities of the new Member States.

Due to the global phenomenon of urbanization, we are witnesses to cities' growth and the tremendous effects the growth process has on the environment and the health of populations inhabiting urban areas. Apart from numerous benefits such as opportunities for employment, entertainment, education and access to health care, the authors aim to address how urban lifestyles are also inextricably linked to numerous adverse health effects.

The increase in population, economic development, urbanization, industrialization and transport has also raised the issue of air pollution as one of the pressing concerns for contemporary society, primarily due to the harmful effects of elevated concentrations of polluting species on public health, environment and climate. Thus, the authors maintain that researching pollutant wet scavenging by atmospheric water is important for revealing the fate of air contaminants in atmospheric, terrestrial and aquatic systems.

Chapter 1 - Since the 'smart' component became one of the pillars of the European Union's development, many cities, particularly post-socialist ones, have perceived the smart city concept as a remedy for their problems in the economic, social or image-related spheres. The objective of the chapter is to review and analyze solutions in the field of implementing the smart city concept applied in recent years in cities of the new Member States. The chapter is composed of four parts. The first part presents a theoretical background of the smart city concept – its origin, principles, and rationales. The second part characterizes the European Union's approach to the implementation of the smart city idea in strategic, declarative, and programming aspects. Furthermore, specific paradoxes of being 'smart' are presented, i.e., the principles making it possible to define a city as smart. The third part includes an analysis of operations and measures taken in selected post-socialist cities as well as solutions applied in the six smart areas: smart governance (Banská Bystrica, Slovakia), smart mobility (Miskolc, Hungary), smart environment (Vrchlabí, the Czech Republic), smart economy (Dresden, Germany), smart living (Tartu, Estonia), and smart people (Lublin, Poland). The last part of the chapter, based on a multi-aspect analysis of the presented solutions, offers a catalog of recommendations for cities in the new EU Member States concerning effective implementation of the smart city concept. The catalog may be used in preparing urban development strategies, and serve as a guide for different groups of stakeholders in decision-making processes related to the implementation of 'smart' solutions or the development of new products and services.

Chapter 2 - Due to the global phenomenon of urbanization, which has resulted in half of the world's population being urban at the beginning of the new millennium, we are witnesses to both cities' growth and the tremendous effects the growth process has on the environment and the health of populations inhabiting urban areas. Apart from including numerous benefits, such as opportunities for employment and higher income, entertainment, education and access to health care, urban lifestyles are also inextricably linked to numerous adverse health effects this chapter is aimed at addressing. Rural-urban migrations have resulted in increasing numbers of overcrowded settlements, lacking the most basic infrastructure and services, i.e., slums, home to an ever-growing proportion of the world's poor. This population, living in slum conditions, and currently exceeding one billion, is continuously facing multiple threats to their health and life, primarily due to the contamination of food or water supply, poor education and healthcare, as well as communicable diseases. At the same time, urban residents of better socioeconomic status are also exposed to innumerable unfavourable effects of urban life. One of the most prominent characteristics of urban growth and sprawl is the expansion of roads, inevitably accompanied by traffic congestion and hypermobility, which result in heavy air pollution and noise. The hazards of air pollution include higher prevalence and severity of respiratory symptoms, high cardiovascular morbidity and mortality and a number of neurological inflammatory disorders, whereas short- and long-term exposure to noise has been proved to be the second most important environmental health hazard that interferes with daily activities of urban residents, by causing psychophysiological effects, impaired wellbeing, annoyance responses and behavior disorders. Furthermore, the massive road expansion also leaves its mark on both quantity and quality of green areas, which are of vital importance for not only recreational and sporting activities, but also for reducing temperature variations and absorbing carbon. The lack of green spaces, combined with hypermobility, leads to a significant percentage of urban populations having a more sedentary lifestyle, which, along with an easy access to convenience stores, is directly related to an increase in obesity in such areas. Also, scarce vegetation, in combination with dark roads and rooftop surfaces that absorb heat from sunlight, make urban areas notably warmer than their natural surroundings, particularly during the summer period. In conclusion, urbanized areas provide their residents with a myriad of possibilities enhancing the quality of life, but on the other hand, expose them to many unavoidable health hazards, the effects of which should not be neglected.

Chapter 3 - The increase in population, economic development, urbanization, industrialization and transport, has raised the issue of air pollution as one of the pressing concerns for contemporary society, primarily because of the harmful effects of elevated concentrations of polluting species on public health, environment and climate system which are still insufficiently understood. Despite the perennial intensive theoretical and experimental research, identifying and parsing the environmental factors that affect complex ecosystems with numerous inputs and outputs in subtle or severe ways, remain a challenge. The main reason lies in the fact that continuous burden on urban environment is governed not only by the increasingly intricate pollutant load, but also by pollution transport, dispersion and deposition processes, atmospheric chemistry, meteorological factors, topography, natural processes, etc. Moreover, containing not only gases, but also suspended particles and clouds, the atmosphere behaves as a colloidal medium. In this regard, researching the pollutant wet scavenging by atmospheric water is very important for revealing the environmental fate of air contaminants in atmospheric, terrestrial and aquatic systems. The development of innovative measuring and modelling techniques, as well as the exploration of new scientific approaches, methods and technologies, are already underway with the aim of studying the interrelations of air pollution and its association with geophysical parameters. Over the last years, the authors' research has been focused on the utilization and development of measurement methods capable of simultaneous real-time detection, monitoring and quantification of air pollution, as well as statistical and machine learning methods that can provide critical information regarding spatio-temporal pollutant variability and the non-linear nature of air pollution phenomena. This chapter presents the advances in machine learning application and fluctuation analysis aimed at capturing pollutant non-linear dynamics, non-stationarities and their relationships with relevant environmental factors; source apportionment methods for individual source characterization in broader areas; three-dimensional hybrid receptor modeling for the detection of pollution circulation patterns and its altitude distributions on various spatial scales; and environmental multiphase system analysis for the investigation of the mechanisms related to the pollutant particulate matter-water-gas transfer and distribution.

In: A Closer Look at Urban Areas
Editor: Sahar Romero
ISBN: 978-1-53614-449-9

Chapter 2

HEALTH ASPECTS OF URBAN LIFE

Svetlana Stanišić[1,*]***, Andreja Stojić***[2]
and Marijana Prodanović[1]
[1]Singidunum University, Belgrade, Serbia
[2]Institute of Physics Belgrade, University of Belgrade, Belgrade, Serbia

ABSTRACT

Due to the global phenomenon of urbanization, which has resulted in half of the world's population being urban at the beginning of the new millennium, we are witnesses to both cities' growth and the tremendous effects the growth process has on the environment and the health of populations inhabiting urban areas. Apart from including numerous benefits, such as opportunities for employment and higher income, entertainment, education and access to health care, urban lifestyles are also inextricably linked to numerous adverse health effects this chapter is aimed at addressing. Rural-urban migrations have resulted in increasing numbers of overcrowded settlements, lacking the most basic infrastructure and services, i.e., slums, home to an ever-growing proportion of the world's poor. This population, living in slum

* Corresponding Author Email: sstanisic@singidunum.ac.rs.

conditions, and currently exceeding one billion, is continuously facing multiple threats to their health and life, primarily due to the contamination of food or water supply, poor education and healthcare, as well as communicable diseases. At the same time, urban residents of better socioeconomic status are also exposed to innumerable unfavourable effects of urban life. One of the most prominent characteristics of urban growth and sprawl is the expansion of roads, inevitably accompanied by traffic congestion and hypermobility, which result in heavy air pollution and noise. The hazards of air pollution include higher prevalence and severity of respiratory symptoms, high cardiovascular morbidity and mortality and a number of neurological inflammatory disorders, whereas short- and long-term exposure to noise has been proved to be the second most important environmental health hazard that interferes with daily activities of urban residents, by causing psychophysiological effects, impaired wellbeing, annoyance responses and behavior disorders.

Furthermore, the massive road expansion also leaves its mark on both quantity and quality of green areas, which are of vital importance for not only recreational and sporting activities, but also for reducing temperature variations and absorbing carbon. The lack of green spaces, combined with hypermobility, leads to a significant percentage of urban populations having a more sedentary lifestyle, which, along with an easy access to convenience stores, is directly related to an increase in obesity in such areas. Also, scarce vegetation, in combination with dark roads and rooftop surfaces that absorb heat from sunlight, make urban areas notably warmer than their natural surroundings, particularly during the summer period. In conclusion, urbanized areas provide their residents with a myriad of possibilities enhancing the quality of life, but on the other hand, expose them to many unavoidable health hazards, the effects of which should not be neglected.

Keywords: urbanization, slums, traffic congestion, air pollution, noise, green areas

The Growth of Megacities and Slums

A hundred years ago, urban settlements were the centers of trade, commerce and production, and urban workers, although living in grim poverty, still had higher living standards than their rural counterparts. Occupational health hazards were very common, affecting all the residents of urban neighborhoods, and the multinational exchange of goods and services between developed countries and colonial empires facilitated the spread of communicable diseases. The widespread health hazards in urban environments were often neglected since big corporations were concerned that any acknowledgement of detrimental effects could hurt their businesses. In the decades that followed, manufacturing jobs left the urban areas of developed countries, allowing service- and information-based industries to find residence in developing regions where wages, taxes and land prices were lower, which significantly altered the urban lifestyle (Freudenberg and Galea 2008).

Over the last few decades, migration into urban centers has resulted in an ever-growing proportion of the global population living in urban areas. While a mere 5% of the world's population was urban at the beginning of the nineteenth century, the dawn of the new millennium eyewitnessed an influx of people migrating into cities, which resulted in half of the world's population living in urban areas at that point. Moreover, according to a recent report on growth by the United Nations Population Division (2014), an additional 2.5 billion people will have migrated to metropolitan areas by 2050. These rural-urban migrations have gone hand-in-hand with the rise of megacities exceeding 10 million residents (Caracci and Mezzich 2001), and recent satellite imagery research conducted by Angel (2012) has illustrated a consistent global pattern: all of the 120 sampled cities are beginning to spread outward (Campbell and Campbell 2007).

Presently, two Asian giants, China and India, account for most of the global urban population. Due to the significant growth of China's population over the past two decades, the rural-to-urban migration of more than 145 million people might be the largest one in history (Gong et al. 2016). Unlike Asia, and despite the fact that the old continent was the most urbanized region of the world for centuries, Europe is not home to any megacities at present. In the nineteenth century, London's population exceeded one million and a hundred years later, in 1910, over half of the hundred largest cities in the world were situated in the region of Europe. However, the growth and geographical distribution of urban populations worldwide have changed significantly, and in 2000, European cities comprized only 18% of the world's urban settlements, with the majority of them having slow or marginal growth (Lawrence 2013).

In addition to being centers of finance, services, entertainment, employment and culture, modern megacities are also centers of crime, violence, poverty, and inequality (Caracci and Mezzich 2001). Urban sprawl has also resulted in a rapid growth of slums – informal, overcrowded settlements, characterized by poor living conditions. Namely, apart from being exposed to inadequate housing, including, but not limited to, restricted access to safe drinking water and sanitation, environmental hazards, and inefficient waste management system (Kjellstrom and Mercado 2008), the residents of these informal urban settlements are also severely deprived of the attributes of urban life that mostly remain a monopoly of a privileged minority, such as education opportunities, child care, health services, public transportation, decent employment and security (Mercado et al. 2007). The illustrated living conditions and related specific health hazards they cause, undoubtedly contribute to unintentional injuries and exposure to lead-containing paint, allergens that might cause asthma, moisture, pests, such as fungi, rodents and insects, pesticide residues, and indoor air pollution (Matte and Jacobs 2000). Moreover, there is mounting evidence that disparity in morbidity and mortality is constantly on the increase in large metropolitan areas, with low-income populations bearing a disproportionate burden of injuries caused by sentinel events, regarded as preventable, as well as of HIV infection, tuberculosis, violence, substance abuse and asthma (Freudenberg et al. 2000). Presently, despite being potentially very hazardous to human health, slums are home to an ever-growing population of the urban poor (Vlahov et al. 2007).

URBAN MOBILITY

Adverse effects of the increased motorized transport in urban areas, in the form of e.g., air pollution, greenhouse gas emissions, noise levels, sedentary lifestyle or social isolation (Xu et al. 2010) are, beyond all doubt, phenomena to which urban residents are being continuously exposed.

The concept of hypermobility, illustrating a distinguishing feature of urban areas, has led to a significant increase in the global consumption of oil-based products, primarily in the form of petrol and diesel; moreover, it has been estimated that the urban transport sector accounts for about 22% of global energy consumption, and the percentage of global oil supplies used in the transport sector increased from 45.4% in 1973 to 61.5% in 2010 (UN habitat 2013).

Although the use of clean technologies is advocated by a significant number of governments around the globe, keeping city transport clean is still an effort, and the excessive number of vehicles in urban areas inevitably leads to air quality deterioration, as well as pollutant emissions, particularly carbon and nitrogen oxides, hydrocarbons, volatile organic compounds (Stojić et al. 2015a, 2015b, 2015c, 2015d; Šoštarić et al. 2017) and particulate matter (Stojić et al. 2016, 2017; Perišić et al. 2015, 2017a, 2017b, 2017c; Todorović et al. 2016). As a result, it has been estimated that approx. 3.2 million people died from air pollution in 2010, compared to 800,000 in 2000 (UN habitat 2013). At the same time, it has been well-documented that health hazards of air pollution include higher prevalence and severity of respiratory symptoms, high cardiovascular morbidity and mortality and a number of neurological inflammatory disorders (Stanišić Stojić et al. 2016a, 2016b, 2016c, 2016d; Frumkin 2002). Furthermore, some polluting chemical species, such as lead and volatile organic compounds from solvents, have also been proved to have significant potential to cause behavioral disturbances. All the adverse health effects of air pollution are being particularly registered in susceptible groups, i.e., elderly and very young people, the socially and financially deprived, occupationally exposed individuals and those with some underlying chronic conditions.

One of the prominent health-related issues in urban environments, frequently and justifiably associated with air pollution, is the medical condition of asthma that has become one of the leading causes of hospitalization in urban communities, with a significant increase in prevalence, morbidity and mortality over the last decade. The exposure to airborne allergens, occupational emissions and air pollution in urban areas has been evidenced to play an important role in the development and exacerbation of this chronic disorder (Asthma facts, CDC's National Asthma Control Program Grantees 2013). According to the CDC's National Health Interview Survey (2011), approx. 13% of the urban population of the USA were diagnosed with asthma, with the highest prevalence among adults of lower socioeconomic status and those with some behavioral risk factors.

A close second to the adverse health effects of deteriorating air quality is both short- and long-term exposure to noise, primarily caused by congested traffic. This is estimated to be the second most important environmental health hazard interfering with daily activities of urban residents, which results in e.g., annoyance, disturbed sleep, stress, hearing damage, hypertension and increased risk of ischemic heart disease. For instance, a nighttime noise level exceeding 40 decibels is expected to cause sleep disturbances, whereas long-term exposure to 55 decibel-noise can trigger elevated blood pressure, as well as coronary heart disease and stroke (European Commission 2016). As regards noise levels, WHO (2017) recommends less than 30 dB for good quality sleep and less than 35 dB for learning environment and cognitive performance. However, the percentage of urban populations exposed to unacceptable noise ranges from 5 to 30% in overcrowded cities (UN habitat 2013). Moreover, according to recent estimates, about 450 million people in Europe, mostly urban residents, are continuously being exposed to ambient noise levels above 55 dB(A); around 113 million are exposed to ambient noise levels above 65 dB(A), and about 9.7 million citizens are exposed to high noise levels exceeding 75 dB(A), with road traffic being the most widespread source of noise (Lawrence 2013).

In a similar vein, the study of Houthuijs et al. (2014), which aimed to investigate the health and well-being implications of road traffic, railway, aircraft and industry noise in Europe, showed there are more than 19.8 million adults annoyed by noise, with 9.1 million of them being severely affected; in addition, about 910,000 people diagnosed with hypertension and 43,000 hospital admissions registered per year, as well as approx. 10,000 premature deaths per year caused by cardiovascular disease and ischemic attacks, can be associated with noise.

Furthermore, the concept of urban hypermobility is also inextricably linked with pedestrian/vehicle conflicts and safety concerns – particularly for vulnerable and disadvantaged road users. Road traffic accidents are the ninth leading cause of death worldwide, accounting for 2.2% of mortality or 1.2 million deaths and 20-50 million people being injured each year (UN habitat 2013). Also, according to the same source, traffic accidents are the leading cause of death for the 15-29 year age group, with pedestrians and two-wheelers accounting for nearly half of all road traffic fatalities. As regards road traffic, the highest annual fatality rates (32 per 100,000 population) are registered in Africa and the Middle East. Moreover, it is also worth noting that the mean annual accident rate in developing countries (20 per 100,000 population) is almost twice that of developed countries, despite the fact that only 33% of all the registered motor vehicles are used in developing countries. For instance, it has been estimated that almost 90% of motorized travel in Mumbai is by bus or train, but approx. 10-30% of all admissions to surgical divisions in India is associated with road traffic injuries, mostly accidents at railway level crossings.

THE SHORTAGE OF GREEN SPACE AND ITS POTENTIAL EFFECTS

The expansion of roads, as an inevitable result of urbanization, involves the reallocation of open and green city spaces, which has direct effects on the quality of life of urban populations, their recreational and sporting activities, as well as carbon absorption. As a result, hypermobility, along with the indisputable lack of green areas in urban environments, the accompanying phenomena of urbanization, have resulted in a decline in the number of physically active people and increased public health burdens

(Faskunger 2013). It has been estimated that the percentage of motorized private transport ranges from 89% in the USA to 50% in Western Europe and 16% in China, whereas the percentage of people walking or cycling to work ranges from 0.3% in Atlanta to 32% in Copenhagen (Campbell-Lendrum and Corvalán 2007). The sedentary lifestyle the majority of present-day urban population lead is an evidenced risk factor for overweight, depression, osteoporosis, and diabetes, as well as cardiovascular and cerebro-vascular diseases and all-cause mortality, and according to some researchers, is comparable to hypertension, high cholesterol, diabetes, and even smoking (Northridge and Freeman 2011). Furthermore, a study that observed 30,000 people over a 14-year period has shown that cycling to work reduces the risk of mortality at a given age by 39% (UN habitat 2013). Also, in their study dealing with trade-offs between commuting time and behavioral patterns, which over time, could contribute to obesity and other deprived health outcomes, Christian (2012) explained that spending an additional 120 minutes daily commuting above average is associated with a 12% decrease in health-related activities, and that the greatest percentage of commuting time is provided by sleeping time reductions (28-35%), followed by reduced physical activity and food preparation (120 minutes of commuting takes 20.3% of time from physical activity and 5.6% from food preparation).

As regards travel decisions and the levels of physical activity in urban residents, it has been shown that the environment can have a significant influence on the decision-making process; for example, a desirable environment for bicycling would be characterized by e.g., less hilliness, higher intersection density, fewer highways and arteries, the presence of bicycle signage and traffic calming measures, as well as cyclist-activated traffic lights, more neighborhood commercial, educational, and industrial land uses, and higher population density (Winters et al. 2010). Additionally, not only is the environment a factor that could influence the level of physical activity, but some factors are also of an individual nature, e.g., ethnic group, income, or the very way residents regard the safety and pleasantness of their neighborhoods (Boslaugh et al. 2004). For all these reasons, the current scientific evidence still remains inconsistent in demonstrating links between the "walkability" of neighborhoods and physical exercise (Northridge and Freeman 2011). Moreover, one study even suggested that the tendency to use non-motorized travel remains almost unaltered regardless of the pleasantness of the environment (Krizek 2003).

The lack of physical activity, i.e., the sedentary lifestyle of urban citizens is frequently and justifiably associated with obesity prevalence. With reference to the issue, in their study aimed at exploring the link between the local environment and obesity, diet and physical activity, Jaime et al. (2011) reported that obesity prevalence is associated with a lack of parks and public sport facilities and that there is also a positive correlation between the number of specialized food markets in the neighborhood and regular fruit and vegetable intake. Similarly, some recent evidence has linked easier access to convenience stores with the increased risk of obesity (Gebauer and Laska 2011), with the risk being particularly high in food insecure low-income populations, as well as ethnic minority areas (Freedman and Bell 2009). As regards convenience stores and food availability, the study of Lucan et al. (2010) showed that, in the majority of corner stores, no fruit or vegetable snacks were available; furthermore, 96.4% of snacks were highly processed foods, of which 80.0-91.5% were classified as unhealthy. As illustrated above, the shortage of green spaces and the increased level of hypermobility, as the trademarks of urban environment and life, have led to a significantly large number of people being exposed to the risks of both insufficient physical activity and poor diet in urban areas.

In addition to these risks, scientific evidence has also suggested the physical environment can both directly and indirectly affect mental health by altering psychosocial processes. For instance, the study of Ochodo et al. (2014) reported the relationship between characteristics of the external built residential environment (walling materials used on buildings, density of dwelling units, state of street lighting, types of doors, states of roofs, and states of windows) and the risk of developing mental health disorders. In a similar vein, in their study aimed at investigating the link between urban form and depressive symptoms in Miami residents, Miles et al. (2012)

concluded that living in neighborhoods with lower housing density and larger green spaces is linked to fewer depressive symptoms, whereas living in highly populated and noisy neighborhoods can result in a larger number of such symptoms.

In conditions characterized by an excess of traffic and roads and a paucity of green spaces, increased air temperatures come as no surprise. With respect to this matter, it has been proved that the global mean temperature has increased by 1.1°C since the late nineteenth century, and the last 16 years have been the warmest since temperature measurements were introduced (Global climate change, NASA 2018). This global rise in mean temperature is particularly prominent in urban areas, where heat waves become aggravated by the heat-island effect that produces 5-11°C warmer environments compared to rural surroundings, primarily due to built structures, lowered evaporative cooling, increased heat storage, as well as low levels of green areas and vegetation (Campbell-Lendrum and Corvalán 2007). Moreover, during summer, urban areas tend to be 2-3°C warmer than their natural surroundings (Frumkin, 2016). The severity of the condition is best described via the fact that the mortality associated with heat waves in many urban centres could more than double by the 2050s, and more than triple by the 2080s (Ramin and Svoboda 2009).

CONCLUSION

At present, the world is undoubtedly witnessing the biggest ever rural-urban migrations, resulting in more than half of world's population living in urban areas. Given its pace, rates and characteristics, this process of urbanization is not only regarded as unstoppable, but also as a phenomenon with double-edged effects. On one hand, what cannot be neglected is the fact that life in metropolitan areas does include a wide spectrum of opportunities for e.g., employment, entertainment, education and access to health care; moreover, it could be said that residents of well-managed cities have never had as many services as are now available on demand. Naturally, this encourages rural-to-urban migration. On the other hand, a large number of cities are facing multiple challenges in meeting all the needs of their growing populations – and that frequently results in inadequate housing and poor infrastructure, congested roads, and a shortage of vegetation and green spaces. As a result, urban residents of both higher and lower socioeconomic status are exposed to adverse health effects of urban life. This chapter has provided an insight into some major issues related to the hazardous health effects of urban environments and lifestyles, with the aim of not only shedding light on their traits, but also raising awareness of the risks they might result in. However, it is noteworthy that well-managed urban areas, i.e., sustainable cities, having predominantly positive effects on their residents, with adequate planning and effort, should be the next step and a sought-after goal of the urbanization process.

REFERENCES

Angel, S. (2012). *Planet of cities*. Cambridge, MA: Lincoln Institute of Land Policy.

Asthma facts. (2013). *CDC's National Asthma Control Program Grantees*. Available at: https://www.cdc.gov/asthma/pdfs/asthma_facts_program_grantees.pdf.

Boslaugh, S. E., Luke, D. A., Brownson, R. C., Naleid, K. S. and Kreuter, M. W. (2004). Perceptions of neighborhood environment for physical activity: Is it "who you are" or "where you live? *Journal of Urban Health,* 81 (IV): 671-681.

Campbell, T., and Campbell, A. (2007). Emerging disease burdens and the poor in cities of the developing world. *Journal of Urban Health,* 84 (I): 54-64.

Campbell-Lendrum, D., and Corvalán, C. (2007). Climate change and developing-country cities: implications for environmental health and equity. *Journal of Urban Health,* 84 (I): 109-117.

Caracci, G., and Mezzich, J. E. (2001). Culture and urban mental health. *Psychiatric Clinics,* 24 (III): 581-593.

CDC. (2012). *National Health Interview Survey (NHIS) data: 2011 lifetime and current asthma*. Atlanta, GA: US Department of Health and Human Services.

Christian, T. J. (2012). Trade-offs between commuting time and health-related activities. *Journal of Urban Health,* 89 (V): 746-757.

European Commission. (2016). *Noise.* Available at: http://ec.europa.eu/environment/noise/health_effects_en.htm.

Faskunger, J. (2013). Promoting active living in healthy cities of Europe. *Journal of Urban Health,* 90 (I): 142-153.

Freedman, D. A., and Bell, B. A. (2009). Access to healthful foods among an urban food insecure population: perceptions versus reality. *Journal of Urban Health,* 86 (VI): 825-838.

Freudenberg, N., Silver, D., Carmona, J. M., Kass, D., Lancaster, B. and Speers, M. (2000). Health promotion in the city: a structured review of the literature on interventions to prevent heart disease, substance abuse, violence and HIV infection in US metropolitan areas, 1980–1995. *Journal of Urban Health,* 77 (III): 443-457.

Freudenberg, N., and Sandro, G. (2008). The Impact of Corporate Practices on Health: Implications for Health Policy. *Journal of Public Health Policy,* 29 (I): 86-104.

Frumkin, H. (2016). *Urban sprawl and public health*. Public health reports, Association of Schools of Public Health.

Gebauer, H., and Laska, M. N. (2011). Convenience stores surrounding urban schools: an assessment of healthy food availability, advertising, and product placement. *Journal of Urban Health,* 88 (IV): 616-622.

Global climate change. (2018). NASA. Available at: https://climate.nasa.gov/.

Gong, W., Wei, X., Liang, Y., Zou, G., Hu, R., Deng, S., Zhang, Z., Pan, J., Choi, B. C. K. and Yu, M. (2016). Urban and Rural Differences of Acute Cardiovascular Disease Events: A Study from the Population-Based Real-Time Surveillance System in Zhejiang, China in 2012. *PloS one,* 11 (XI): e0165647.

Houthuijs, D. J. M., van Beek, A. J., Swart, W. J. R. and van Kempen, E. E. M. M. (2014). *Health implication of road, railway and aircraft* *noise in the European Union: Provisional results based on the 2nd round of noise mapping*. National Institute for Public Health and the Environment, Netherlands.

Jaime, P. C., Duran, A. C., Sarti, F. M. and Lock, K. (2011). Investigating environmental determinants of diet, physical activity, and overweight among adults in Sao Paulo, Brazil. *Journal of Urban Health,* 88 (III): 567-581.

Kjellstrom, T., and Mercado, S. (2008). Towards action on social determinants for health equity in urban settings. *Environment and Urbanization,* 20 (II): 551-574.

Krizek, K. J. (2003). Residential relocation and changes in urban travel: Does neighborhood-scale urban form matter? *Journal of the American Planning Association,* 69 (III): 265-281.

Lawrence, R. J. (2013). Urban health challenges in Europe. *Journal of Urban Health,* 90 (I): 23-36.

Lucan, S. C., Karpyn, A. and Sherman, S. (2010). Storing empty calories and chronic disease risk: snack-food products, nutritive content, and manufacturers in Philadelphia corner stores. *Journal of Urban Health,* 87 (III): 394-409.

Matte, T. D., and Jacobs, D. E. (2000). Housing and health—current issues and implications for research and programs. *Journal of Urban Health,* 77 (I): 7-25.

Mercado, S., Havemann, K., Sami, M. and Ueda, H. (2007). Urban poverty: an urgent public health issue. *Journal of Urban Health,* 84 (I): 7-14.

Miles, R., Coutts, C. and Mohamadi, A. (2012). Neighborhood urban form, social environment, and depression. *Journal of Urban Health,* 89 (I): 1-18.

Northridge, M. E., and Freeman, L. (2011). Urban planning and health equity. *Journal of Urban Health,* 88 (III): 582-597.

Ochodo, C., Ndetei, D. M., Moturi, W. N. and Otieno, J. O. (2014). External built residential environment characteristics that affect mental health of adults. *Journal of Urban Health,* 91 (V): 908-927.

Perišić, M., Stojić, A., Stojić Stanišić, S., Šoštarić, A., Mijić, Z., and Rajšić, S. (2015). Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. *Air Quality, Atmosphere & Health,* 8 (IV): 379-89.

Perišić, M., Vuković, G., Mijić, Z., Šoštarić, A., and Stojić, A. (2017a). *Relative importance of gaseous pollutants and aerosol constituents for identification of PM_{10} sources of variability.* Paper presented at the sixth international WeBIOPATR workshop & conference, Serbia, Belgrade, September 6-8.

Perišić, M, Maletić, D, Stojić Stanišić, S, Rajšić, S, and Stojić, A. (2017b). Forecasting hourly particulate matter concentrations based on the advanced multivariate methods. *International Journal of Environmental Science and Technology,* 14 (V): 1047-54.

Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z., and Stojić, A. (2017c). Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation. *Air Quality, Atmosphere & Health,* 10 (V): 93-103.

Ramin, B., and Tomislav S. (2009). Health of the homeless and climate change. *Journal of Urban Health,* 86 (IV): 654-664.

Šoštarić, A., Stojić Stanišić, S., Vuković, G., Mijić, Z., Stojić, A., and Ivan G. (2017). Rainwater capacities for BTEX scavenging from ambient air. *Atmospheric Environment,* 168: 46-54.

Stanišić Stojić, S., Stanišić, N. and Andreja S. (2016a). Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area. *Environmental Health,* 15 (I): 73.

Stanišić Stojić, S., Stanišić, N., and Andreja, S. (2016b). Short- and Long-Term Effects of Urban Air Pollution on Cardiopulmonary and Malignant Death Rates, in *Air Pollution: Management Strategies, Environmental Impact and Health Risks* edited by Burns, G. L. Nova Science Publishers, Hauppauge, New York, USA.

Stanišić Stojić, S., Stanišić, N., Stojić, A., and Vladimir, Dž. (2016c). Seasonal variations of circulatory, respiratory and malignant mortality in Belgrade area [in Serbian: Sezonske varijacije smrtnosti od kardiovaskularnih, respiratornih i malignih oboljenja na području Beograda]. *Stanovništvo,* 54 (I): 83-104.

Stanišić Stojić, S., Stanišić, N., Stojić, A., and Andrej, Š. (2016d). Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. *Journal of Toxicology and Environmental Health. Part A,* 79 (I): 17-27.

Stojić, A., Maletić, D., Stanišić Stojić, S., Mijić, Z., and Andrej, Š. (2015a). Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. *Science of the Total Environment,* 521: 19-26.

Stojić, A., Stanišić Stojić, S., Mijić, Z., Šoštarić, A., and Slavica, R. (2015b). Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. *Atmospheric Environment,* 106: 71-79.

Stojić, A., Stanišić Stojić, S., Šoštarić, A., Ilić, L., Mijić, Z., and Slavica, R. (2015c). Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. *Environmental Science and Pollution Research,* 22 (XVII): 13137-13152.

Stojić, A., Stanišić Stojić, S., Mijić, Z., Ilić, L., Tomašević, M., Todorović, M., and Mirjana, P. (2015d). Comprehensive analysis of VOC emission sources in Belgrade urban area, in *Urban and Built Environments: Sustainable Development, Health Implications and Challenges*, edited by Alexis C. Nova Science Publishers, NY, USA.

Stojić, A., Stanišić Stojić, S., Perišić, M., and Zoran, M. (2017). *Multiscale multifractal analysis of nonlinearity in particulate matter time series.* Paper presented at the sixth international WeBIOPATR workshop & conference, Serbia, Belgrade, September 6-8.

Stojić, A., Stanišić Stojić, S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., and Zoran, M. (2016). Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. *Environmental Science and Pollution Research,* 23: 10722-32.

The United Nations Population Division (2014). *World Urbanization Prospects.* Available at: https://esa.un.org/unpd/wup/Publications/Files/WUP2014-Report.pdf

Todorović, M. N., Perišić, M. D., Kuzmanoski, M. M., Stojić, A. M., Šoštarić, A. I., Mijić, Z. R. and Slavica, R. F. (2016). Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area. *Journal of Environmental Science and Health, Part A,* 50: 1351-1359.

UN Habitat. (2013). *Planning and design for sustainable urban mobility: Global report on human settlements 2013.* Routledge.

Vlahov, D., Freudenberg, N., Proietti, F., Ompad, D., Quinn, A., Nandi, V. and Galea, S. (2007). Urban as a determinant of health. *Journal of Urban Health* 84, (I): 16-26.

WHO. (2017). *Data and Statistics about Noise.* Available at: http://www.euro.who.int/en/health-topics/environment-and-health/noise/data-and-statistics

Winters, M., Brauer, M., Setton, E. M. and Teschke, K. (2010). Built environment influences on healthy transportation choices: bicycling versus driving. *Journal of Urban Health,* 87 (VI): 969-993.

Xu, F., Li, J. Q., Liang, Y. Q., Wang, Z. Y., Hong, X., Ware, R. S., Leslie, E., Sugiyama, T. and Owen, N. (2010). Associations of residential density with adolescents' physical activity in a rapidly urbanizing area of Mainland China. *Journal of Urban Health,* 87 (I): 44-53.

BIOGRAPHICAL SKETCH

Svetlana Stanišić

Affiliation: Singidunum University

Education:

- 2011. PhD – Faculty of Physical Chemistry (Environmental Physical Chemistry), University of Belgrade, Serbia
- 2004. Bachelor of Dental Medicine – Faculty of Dental Medicine, University of Belgrade, Serbia

Research and Professional Experience:

- Environmental health
- Environmental monitoring and analysis
- Indoor and outdoor emission sources of air pollutants
- Effects of air pollution and extreme weather conditions on human health and mortality
- Research related to volatile organic compounds (VOC), particulate matter and inorganic gaseous pollutants and their spatio temporal distribution
- Air pollution transport (hybrid receptor models)
- Forecasting of air pollutant concentrations and their transfer to aqueous phase
- Proton-transfer-reaction mass spectrometry.

Publications from the Last 3 Years:

1. Stojić, A., Stojić, S. S., Mijić, Z., Šoštarić, A., & Rajšić, S. (2015). Spatio-temporal distribution of VOC emissions in urban area based on receptor modelling. *Atmospheric Environment*, 106, 71-79.
2. Stojić, A., Maletić, D., Stojić, S. S., Mijić, Z., & Šoštarić, A. (2015). Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. *Science of the Total Environment*, 521, 19-26.
3. Stojić, A., Stanišić Stojić, S., Šoštarić, A., Ilić, L., Mijić, Z., & Rajšić, S. (2015) Characterization of VOC sources in urban area based on PTR-MS measurements and receptor modelling. *Environmental Science and Pollution Research*, 22(17), 13137-13152.
4. Stojić, S. Stanišić Stojić, Z. Mijić, L. Ilić, M. Tomašević, Marija Todorović, and Mirjana Perišić (2015). Comprehensive Analysis of VOC Emission Sources in Belgrade Urban Area, In: *Urban and Built Environments: Sustainable Development, Health Implications and Challenges*, Editor: Alexis Cohen, Nova Science Publishers, NY, USA, ISBN: 978-1-62417-735-4, pp. 55-88.

5. Šoštarić, A., Stojić, A., Stojić, S. S., & Gržetić, I. (2016). Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system. *Chemosphere*, 144, 721-727.
6. Stanišić Stojić, S., Stanišić, N., Stojić, A., Šoštarić, A. (2016). Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. *Journal of Toxicology and Environmental Health, Part A: Current Issues*, 79(1):17-27.
7. Stojić, A., Stanišić Stojić, S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., Mijić, Z. (2016). Comprehensive analysis of PM10 in Belgrade urban area on the basis of long term measurements. *Environmental Science and Pollution Research*, 23(11), 10722-10732.
8. Stanišić Stojić, S., Stanišić, N., Stojić, A. (2016). Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area. *Environmental Health*, DOI: 10.1186/s12940-016-0164-6.
9. Šoštarić, A., Mladenović, S., Stanišić Stojić, S., Stojić, A., Stanišić, N., Slepčević, V. (2015). *Health burden of air pollutant exposure in Belgrade: a European region with high circulatory and malignant mortality rates*. WHO Collaborating Centre for Air Quality Management and Air Pollution Control, Newsletters No. 56.
10. Stanišić Stojić, S., Stanišić, N., Stojić, A. (2016) Short- and Long-Term Effects of Urban Air Pollution on Cardiopulmonary and Malignant Death Rates In: *Air Pollution: Management Strategies, Environmental Impact and Health Risks*, Editor: Gerald L. Burns, Nova Science Publishers, NY, USA, ISBN: 978-1-63485-375-0.
11. Stanišić Stojić, S., Stanišić, N., Stojić, A., Džamić, V. (2016) Sezonske varijacije smrtnosti od kardiovaskularnih, respiratornih i malignih oboljenja na području Beograda. [Seasonal variations of mortality from cardiovascular, respiratory and malignant diseases in the area of Belgrade.] *Stanovništvo*, 54(1):83-104.

12. Perišić, M., Maletić, D., Stanišić Stojić, S., Rajšić, S., Stojić, A. (2016) Forecasting hourly particulate matter concentrations based on the advanced multivariate methods, *International Journal of Environmental Science and Technology*, 14(5), 1047-1054.
13. Stojić, A., Stanišić Stojić, S. (2017) The innovative concept of three-dimensional hybrid receptor modeling, *Atmospheric Environment*, 164, 216-223.
14. Šoštarić, A., Stanišić Stojić, S., Vuković, G., Mijić, Z., Stojić, A., Gržetić, I. (2017) Rainwater capacities for BTEX scavenging from ambient air, *Atmospheric Environment*, 168, 46-54.

In: A Closer Look at Urban Areas
Editor: Sahar Romero
ISBN: 978-1-53614-449-9

Chapter 3

URBAN AIR POLLUTION: AN INSIGHT INTO ITS COMPLEX ASPECTS

Andreja Stojić[1,*], Gordana Vuković[1], Mirjana Perišić[1], Svetlana Stanišić[2] and Andrej Šoštarić[3]

[1]Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia
[2]Singidunum University, Belgrade, Serbia
[3]Institute of Public Health of Belgrade, Belgrade, Serbia

ABSTRACT

The increase in population, economic development, urbanization, industrialization and transport, has raised the issue of air pollution as one of the pressing concerns for contemporary society, primarily because of the harmful effects of elevated concentrations of polluting species on public health, environment and climate system which are still insufficiently understood. Despite the perennial intensive theoretical and experimental research, identifying and parsing the environmental factors that affect complex ecosystems with numerous inputs and outputs in subtle or severe ways, remain a challenge. The main reason lies in the

* Corresponding Author Email: andreja.stojic@ipb.ac.rs.

fact that continuous burden on urban environment is governed not only by the increasingly intricate pollutant load, but also by pollution transport, dispersion and deposition processes, atmospheric chemistry, meteorological factors, topography, natural processes, etc. Moreover, containing not only gases, but also suspended particles and clouds, the atmosphere behaves as a colloidal medium. In this regard, researching the pollutant wet scavenging by atmospheric water is very important for revealing the environmental fate of air contaminants in atmospheric, terrestrial and aquatic systems.

The development of innovative measuring and modelling techniques, as well as the exploration of new scientific approaches, methods and technologies, are already underway with the aim of studying the interrelations of air pollution and its association with geophysical parameters. Over the last years, our research has been focused on the utilization and development of measurement methods capable of simultaneous real-time detection, monitoring and quantification of air pollution, as well as statistical and machine learning methods that can provide critical information regarding spatio-temporal pollutant variability and the non-linear nature of air pollution phenomena. This chapter presents the advances in machine learning application and fluctuation analysis aimed at capturing pollutant non-linear dynamics, non-stationarities and their relationships with relevant environmental factors; source apportionment methods for individual source characterization in broader areas; three-dimensional hybrid receptor modeling for the detection of pollution circulation patterns and its altitude distributions on various spatial scales; and environmental multiphase system analysis for the investigation of the mechanisms related to the pollutant particulate matter-water-gas transfer and distribution.

Keywords: air pollution, urban environment, environmental multiphase systems, machine learning, hybrid receptor models

INTRODUCTION

The environmental impacts of urbanization and climate change are probably two of the most pressing issues modern society is facing (WHO, 2016; UN, 2016). The unpredicted rate and the diversity of urbanization, including rapid geographical expansion and population growth, industry development, the increasing need for support infrastructure, and pollution and waste generation, lead to unprecedented change in the environment which needs a deep understanding of its nature and of the responses it requires. For many key parameters, such as the variety of determinants, spatio-temporal dynamics and interconnections, urban systems are already moving far beyond the patterns which sufficient description would consider simple starting points. Micro-climates, green and built environment, the significant flows of people, energy, materials, resources, and pollutants, make the unlimited set of pathways for urban-ecosystem interactions which reflect the complexity of the urban environment.

Environmental pollution, encompassing air, water, soil, radioactive, light and thermal pollution, and noise, depends on complex interactions driven by a variety of forces embedded in numerous environmental factors. A broad spectrum of relationships being generated and operated on numerous levels, requires multiscale approach to understand the growing body of evidence on pollution impact on the environment, climate system, biodiversity and human health.

The recognition of the complexity of urban environmental factors moved analytical concepts towards a more sophisticated and synergistic modeling. An effort is made not only to identify key factors which shape the urban environment, but also to gain the convergence on the obtained facts, no matter if they are mutually complementary or in agreement.

In this respect, consideration of the air pollution issues from different viewpoints relies on the application and development of specialized methods and their assembling and hybridization for capturing pollutant statistical and spatio-temporal distributions, fluctuations, lag and cumulative effects, their interrelations and relationship with relevant environmental factors on various scales, etc. This chapter systematizes advances made in several case studies aimed at revealing some urban air pollution aspects of complexity. We place the focus on analytical tools capable of providing significant scientific information gain based on the characterization of the processes that generate pollution, govern its spatio-temporal dynamics and determine its environmental fate. Beside the application of statistical and machine learning methods for characterization of pollutant interrelations, non-linear dynamics, non-stationarities and singularities (Stojić et al., 2016, 2017a; Perišić et al., 2015, 2017a;

Todorović et al., 2016), this chapter presents their potential for air pollution forecasting (Stojić et al., 2015a; Perišić et al., 2017b), as well as for the identification of mechanisms underlying wet scavenging phenomena (Šoštarić et al., 2016; 2017). Furthermore, the source apportionment advances presented herein shift the focus from dominant sources to a large number of individual, locally specific emissions (Perišić et al., 2017a). Finally, in addition to generally accepted statistical methods for potential remote emission source identification, we present an improved air pollution transport analysis based on three-dimensional hybrid receptor models for the identification of volumetric pollution circulation patterns and pollutant altitude distributions on various spatial scales (Stojić and Stanišić Stojić, 2017).

METHODS

The data used for the analyses presented in this chapter were obtained from the Institute of Public Health Belgrade regular monitoring network and measurement campaigns conducted at sites located in Belgrade (Serbia) urban and semi-urban areas. The dataset comprises of volatile organic compound (VOC) measured at 39 molecular mases, inorganic gaseous pollutants (CO, SO_2, NO, NO_2, NO_x and tropospheric O_3), particulate matter (PM_{10} and $PM_{2.5}$) and its chemical constituents (As, Cd, Cr, Mn, Ni, Pb, BaP, Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}), rainwater physico-chemical characteristics (rain temperature, turbidity, pH, UV extinction, total organic carbon, electric conductivity, F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}), rainwater concentrations of benzene, toluene, xylene and ethylbenzene (BTEX), and meteorological parameters (wind speed and direction, relative humidity, pressure and temperature).

Statistical analyses, including bivariate polar plot and bivariate cluster (k-means clustering, grouping similar conditions together) analysis, were performed with the statistical software environment R (Team, 2014), using the Openair package (Carslaw and Ropkins, 2012). Multifractal detrended fluctuation analysis (MF-DFA) (Stojić et al., 2016) and multiscale multifractal analysis (MMA) (Stojić et al., 2017a) were used to investigate the presence of fractal behavior in complex $PM_{2.5}$ and PM_{10} time series. MMA is a generalization of the standard MF-DFA, which adds the dependence on scale, providing a broader analysis of the fluctuation properties, as well as more general and stable results (Gierałtowski et al., 2012).

Apportionment of dominant sources was obtained by the use of Unmix and Positive matrix factorization (PMF) (USEPA, 2007). The detailed descriptions of the models are presented elsewhere (Henry, 2003; Paatero, 1999). On the other hand, source apportionment of individual, locally specific emissions and information about pollutant relationships were obtained by means of the advanced bivariate polar plots coupled with pair-wise statistics applied to distinguish specific sources and to gain information about pollutant relations (Grange et al., 2016). The method includes weighted Pearson correlation, linear regression slope and Gaussian kernel to locally weight the statistical calculations on a wind speed-direction surface together with variable-scaling.

Time series decomposition into the additive components of the multiyear and seasonal trends, as well as the remainder was conducted using the Loess smoothing decomposition model (LSD) (Li et al., 2014), while hourly, daily, weekly and seasonal periodicity was analyzed by the use of Lomb-Scargle method (Ruf, 1999; Team, 2014).

Random forest (RF) and Guided regularized random forest (GRRF) were applied (Deng and Runger, 2013) for the selection of features that are most relevant for PM_{10} concentration (Stojić et al., 2016) and BTEX enrichment factor (EF) prediction (Šoštarić et al., 2017). Random forest consists of decision trees which every node represents a condition on a single variable designed to split the dataset in two parts so that similar responses end up in the same set. Variable importance, a measure based on which the optimal condition is chosen, measures how much each variable decreases the weighted impurity across the trees. GRFF uses the importance scores from a preliminary RF to guide the feature selection of regularized RF and has several advantages: it is robust and computationally efficient, it can select compact feature subsets moderating the curse of dimensionality, it avoids the effort to analyze irrelevant or redundant features, and it has competitive accuracy performance.

Machine learning algorithms used for the environmental multiphase system analyses (the relationship between EF and features that are considered most relevant for EF prediction) are implemented in Weka 3.8 (Frank et al., 2005) and include: Alternating model tree which grows an alternating model tree by minimizing squared error (Frank et al., 2015); Conjunctive rule which induces a small as possible set of rules from data that captures all generalizable knowledge within that data (Cohen, 1995); Decision stump which represents one-level decision tree (Zhao and Zhang, 2008); Decision table, a majority classifier which evaluates feature subsets using best-first search (Witten and Frank, 2016); Elastic net, a generalization of the lasso method for linear regression which uses penalization methods that introduce additional constraints into the optimization of a predictive algorithm that bias the model toward lower complexity (Zou et al., 2006); Gaussian processes which use lazy learning and a measure of the similarity between points for prediction based on collection of random variables with consistent joint Gaussian distributions (Rasmussen, 2006); IBk and IBkLG which are a types of instance-based learning (k nearest neighbors – k-NN) (Aha et al., 1991; IBkLG, 2015); Isotonic regression which implements the method based on pair-adjacent violators approach by picking the attribute that results in the lowest squared error (Witten and Frank, 2016); K* which is an instance-based classifier predicting by entropy-based distance similarity function (Cleary and Trigg, 1995); Least median squares regression which is an utilization of the existing Weka linear regression (Rousseeuw and Leroy, 2005); Linear regression method which minimizes the sum of the squared difference between the observed and the predicted values creating a line for optimal data separation (Shi and Tsai, 2002); Locally weighted learning (LWL) which uses an instance-based algorithm to assign instance weights where a linear regression model is fit based on a weighting function centered on the instance for which a prediction is to be generated (Frank et al., 2002); M5P which is based on decision trees containing a multivariate linear regression model at each node (Graczyk et al., 2009); M5 rules which generates a decision list using separate-and-conquer by building a model tree in each iteration and making the "best" leaf into a rule (Wang and Witten, 1997); Multilayer perceptron which is a feed forward neural network model with one or more hidden layers between input and output layer trained by the back-propagation algorithm that uses gradient descent to minimize error and adjust the weights to each connection between the hidden and output layer (Haykin, 1994); Pace regression which consists of a group of estimators that are either overall optimal or optimal under certain conditions, the method provably optimal under regularity conditions when the number of coefficients tends to infinity (Wang and Witten, 2002); Random forest which is an ensemble of unpruned trees, induced from bootstrap samples of the training data, using random feature selection in the tree induction process (Breiman, 2001; Zhao and Zhang, 2008); Random tree which constructs a tree that considers randomly chosen attributes at each node (Zhao and Zhang, 2008); Radial base function which is an artificial neural network which implements a normalized Gaussian radial basis function network and uses the k-means clustering algorithm to provide the basis functions and learns either a logistic regression (discrete class problems) or linear regression (numeric class problems) on top of that (Frank, 2014); REP tree which is a fast decision tree based on reduced-error pruning (with backfitting) (Kalmegh, 2015); Simple linear regression which picks the attribute that results in the lowest squared error; and SMOreg which is a Support vector machine implemented using the Sequential Minimal Optimization Regression (SMOreg) algorithm (Shevade et al., 1999).

Machine learning algorithms used for the VOC source contribution and PM_{10} concentration forecast are implemented in Toolkit for Multivariate Analysis (TMVA) (Hoecker et al., 2007) within the ROOT framework (Brun and Rademakers, 1997) and include (Stojić et al., 2015a): Boosted decision trees (BDT, BDTG); Artificial neural network Multilayer perceptron (MLP); MLP with Bayesian extension (MLPBNN); Support vector machine (SVM); Linear discriminant (LD) which provides an intermediate solution to the problem with the aim to solve relatively simple or partially nonlinear problems.; Fisher discriminant (Fisher) which determines an optimal separating function in the multivariate space of all input variables analytically for the linear case; Multidimensional probability density estimator range search (PDE-RS) which is a variant of the k-nearest neighbor, Likelihood method and function discriminant analysis (FDA) which extends the linear discriminant to moderately non-linear correlations that are fit to the training data and Function discrimination analysis with genetic algorithm converger (FDA-GA).

Trajectories used for hybrid receptor modelling were calculated 72-h backward by the use of HYSPLIT model (Draxler and Rolph, 2014) for each hour UTC above the sampling sites at the half of the planetary boundary layer (PBL) height calculated from GDAS1 using MeteoInfo (Wang, 2014), as described in Stojić et al. (2016) and Stojić and Stanišić Stojić (2017).

RESULTS AND DISCUSSION

Spatio-Temporal Dynamics

In the atmosphere, air pollutants are prone to dynamic changes which do not occur as linear or single-compartment processes due to mutual interactions of numerous factors that drive their temporal fluctuations, such as meteorological parameters, type and intensity of emission sources, etc.

Temporal Variations and Periodicity

Atmospheric pollution levels exhibit variations on different time scales, from short-term diurnal fluctuations to long-term seasonal and annual deviations. Moreover, once emitted into the atmosphere, polluting species undergo a number of physical and chemical processes including atmospheric transport and deposition at a range of local and regional scales. At a city-scale, a variety of pollution sources, meteorological regime, urban microclimate and local topography, such as building distribution and street geometry, anthropogenic heat fluxes and planetary boundary layer prominently affect the dispersion and dilution of air pollutants (Monks et al., 2009). While the studied urban areas in Belgrade (urban canyon avenue – UCA and urban boulevard – UB) are mostly affected by vehicle exhaust emissions, the suburban sites (urban industry – UI and rural industry – RI) are affected by emissions from fossil fuel burning for industry and heating purposes.

According to the results, spatio-temporal dynamics reveals annual cycle as the dominant mode of PM_{10} (Figure 1), NO and SO_2 (Figure 2) variability at each sampling location. The annual variations show pronounced winter maxima likely due to an increase of emissions from combustion processes and low PBL height, as well as the summer minima which could be attributed to the enhanced dispersion and dilution due to the expansion of daily PBL. At smaller temporal scales, a decrease of anthropogenic emissions during weekend reduces the amplitude of pollutant concentrations. Furthermore, the development and break-up of the nocturnal inversion layer, as well as the morning and afternoon rush-hour peaks shape diurnal variations, especially in an urban area.

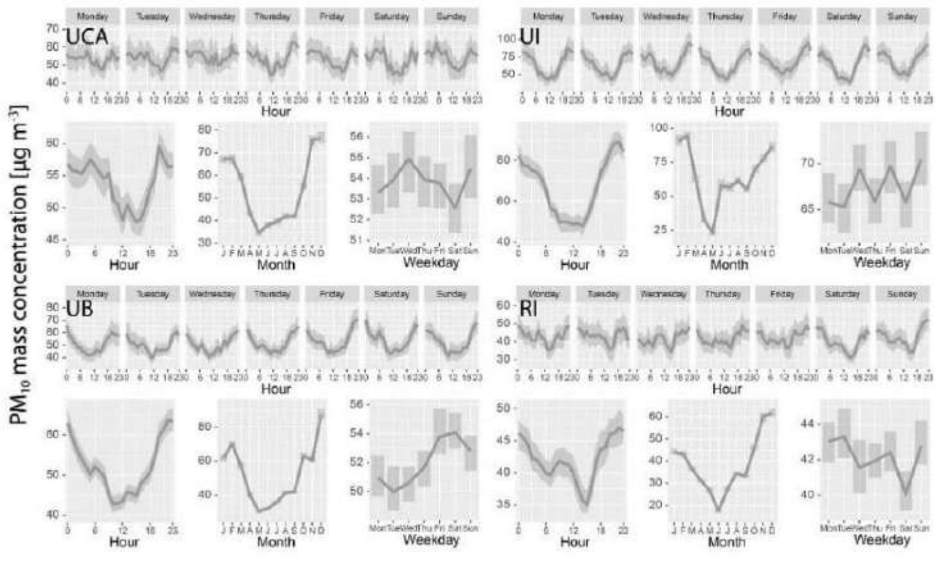


Figure 1. Daily, weekly and seasonal variations of PM_{10} mass concentrations.

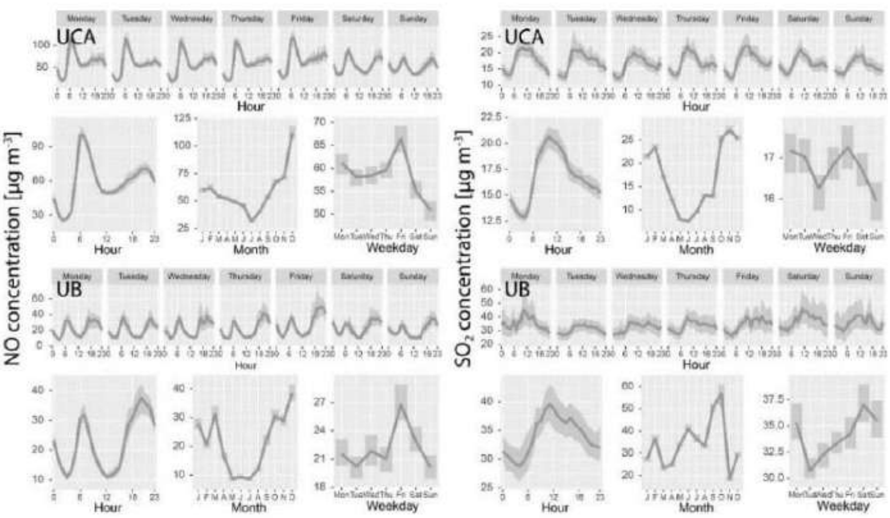


Figure 2. Daily, weekly and seasonal variations of NO and SO_2 concentrations.

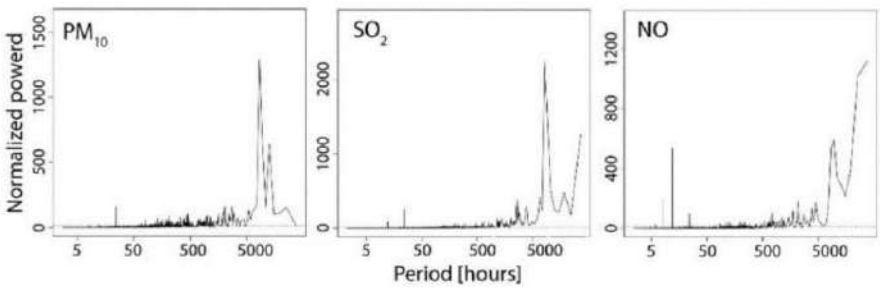


Figure 3. Lomb-Scargle periodogram.

Spectral analysis (Figure 3) indicates the importance of periodicity for the air pollution dynamics. At the scale of 12 and 24 h, 7 days and one year, the variability is mostly governed by meteorological conditions and anthropogenic emissions, while at the scales below 12 h, as in the case of NO, the additional peaks can be attributed to the local traffic-related emission sources.

Fluctuation Analysis

The constitutional characteristics of the pollutant time-series, i.e., their changes over time, could not be revealed by conventional approaches, but fractal (Mandelbrot, 1977) and Hurst rescaled analyses (Hurst, 1951;

Mandelbrot and Wallis, 1969) allow to quantify its structure via self-similarity and scale invariance. In brief, self-similarity and scale-invariance are the properties which characterize the pollutant long-term memory, i.e., fractal behavior, and the complexity of their concentrations. In other terms, the obtained results describe the effects of past patterns on future concentration or the extent to which time-series are nonrandom in behavior. The multifractal approach has been widely for the estimation of long-range correlations and forecasting of the PM_{10}, $PM_{2.5}$, NO_x, SO_2, and O_3 time-series (Windsor and Toumi, 2001; Dong et al., 2017; Plocoste et al., 2017; Stojić et al., 2017).

In our studies investigating PM_{10} and $PM_{2.5}$ time-series in Belgrade urban area (Stojić et al., 2017), the strength of multifractality was presented by the value of multifractal singularity, Q. The bigger the Q, the more the time-series is influenced by small or large fluctuations in negative or positive direction of Q interval while Q=0 reflects the absence of fluctuations and a monofractal behavior (He et al., 2017). Apart from Q, the following values of Hurst Exponent (H) were considered for searching for the time-series persistence level (Ihlen, 2012; Molino-Minero-Re et al., 2015):

- $H \geq 1.5$ represents Brown noise uncorrelated processes with infinite memory;
- H=1 is pink noise, the most well-known, firm and adaptable fractal phenomena with long memory;
- H>0.5 and H=0.5–1.5 illustrates random walk processes with long-range correlated and persistent structure;
- H=0.5 represents white noise, such uncorrelated random variables with no memory exhibited;
- H<0.5 reveals the anti-persistent increments and anti-correlated structure.

In addition, the span of multifractal singularity ($\Delta\alpha = \alpha_{max} - \alpha_{min}$) is widely used as an alternative way to study the strength of multifractality

(Stojić et al., 2016). The bigger $\Delta\alpha$ is, the stronger the multifractality degree is (He, 2017).

Both PM_{10} and $PM_{2.5}$ fluctuated nonrandom over time and were characterized by non-stationary signals with long-range dependent structure that reflects their multifractal behavior. It is shown that the source of multifractality, examined by PM time series randomization, originates both from nonlinear correlations and a fat-tailed probability distribution (Figure 4). More specifically, long-range correlated time series of PM_{10} are evident (H: 1−1.5), but their multifractality weakened over time and approached to the "healthy complex system" of pink noise (Figure 5).

As can be seen, PM_{10} patterns occasionally referred to a Brown noise (H>1.5) at temporal scales below 90 that could be associated with oscillation in emission sources that are sensitive to meteorological influences. In general, the PM_{10} persistence could be understood in terms of the steady temperature, humidity and general atmospheric circulation; the relationship between meteorological factors and PM_{10} is obvious since PM_{10} represents a mixture of microscopic solid or liquid suspended matters involved in inherent condensation and nucleation (He, 2017; Zhang et al., 2015). Furthermore, multifractal approach applied for studying PM_{10} seasonal dynamics indicated the coincidence in the maximum of autumn and winter spectra suggesting that similar sources and processes were underlying the concentrations observed in both periods (Stojić et al., 2016). Similarly, spring and summer spectra led to no significant differences in the origin of the observed PM_{10} loadings.

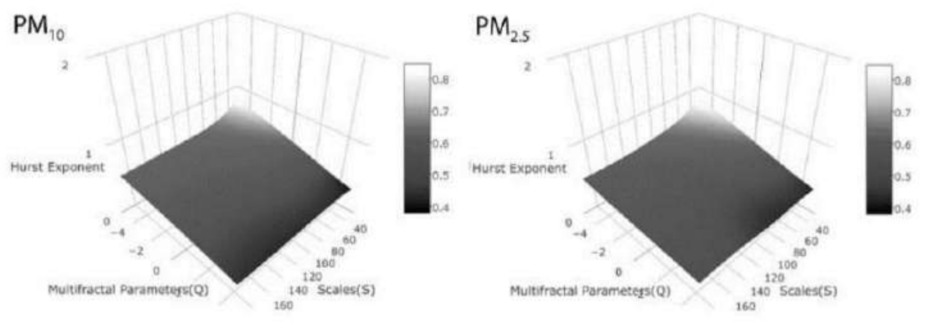


Figure 4. MMA derived Hurst surfaces for randomized PM time series.

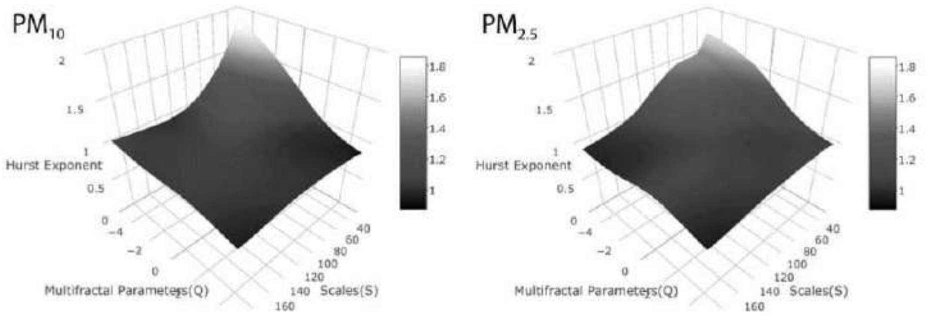


Figure 5. MMA derived particulate matter Hurst surfaces.

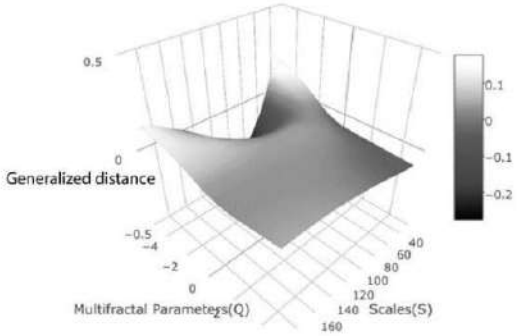


Figure 6. Generalized $PM_{10}/PM_{2.5}$ Hurst surface distance.

In accordance to PM_{10}, the $PM_{2.5}$ time series were persistent as shown by the local Hurst exponent in the interval between 1 and 1.5, but slightly affected by the concentrations occurring randomly. However, unlike PM_{10}, clear crossover was evident at the scales below 44, which corresponds to a period of about 2 days, denoting significant impact of random events that emerges at this scale. These indications support the findings of Xue et al. (2015) who reported dissimilarities among PM of different sizes in urban areas. More specifically, the authors recorded a strong multifractal nature of PM size below 5 μm, and a weak and/or monofractal stochastic behavior of PM>5 μm. In addition, generalized distance coefficient (0.069) between PM fractions Hurst surfaces exceeded the threshold value (0.065) that implies the $PM_{2.5}$ and PM_{10} time series to be considered statistically different (Figure 6); the difference is particularly pronounced in the area of small fluctuations and medium scales.

Contribution Decomposition

Concentration Decomposition

Discriminating the relative importance of background, local sources and transport processes and estimating their shares in pollutant concentrations can be considered as one of the key issues in air pollution analysis. We can assume that in urban areas, dominated by local emissions, transport and background jointly contribute to gradual variations of a concentration base level, whereas the superimposed pronounced peaks in pollutant time series occur as a result of local emissions (Figure 7).

Thereby, the differentiation between the contributions of local and remote emissions can be obtained by a two-step procedure, as described in our previous studies (Stojić et al., 2016; Stojić and Stanišić Stojić, 2017). In brief, excluding the contribution of local sources from the time series and obtaining a baseline can be performed by a number of functions available for baseline extraction (Kneen and Annegarn, 1996). Subsequently, Trajectory sector analysis (TSA) can be applied to the derived baseline to distinguish between the contributions of background and transport, and to obtain a transport time series, further used as an input for hybrid receptor modelling. In addition to TSA, background levels can be obtained by the use of 3D hybrid receptor models, which will be shown below.

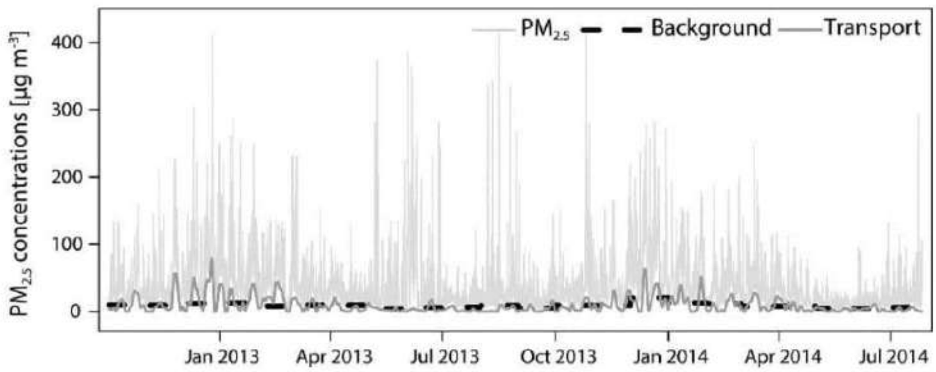


Figure 7. $PM_{2.5}$ concentration decomposition (Stojić and Stanišić Stojić, 2017).

Time Series Decomposition

Figure 8 illustrates the decomposition of PM_{10} temporal cycles indicating moderate impact of trend, significant impact of the seasonal and very large variance of the remainder components. In general, the remainder, expressed as irregularity, neither explained by the trend, nor by the seasonality, in the urban areas can be associated with anthropogenic processes which induce chemical and dynamical changes in the pollutant concentrations (Chehade et al., 2014).

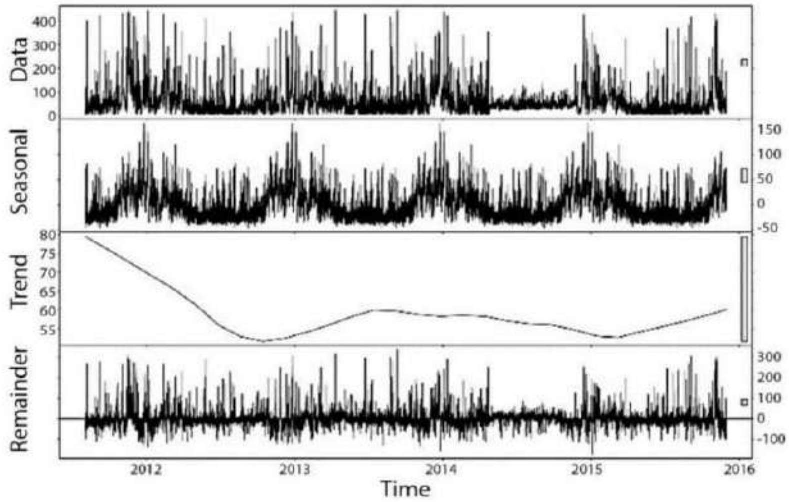


Figure 8. PM_{10} time series decomposition [μg m^{-3}].

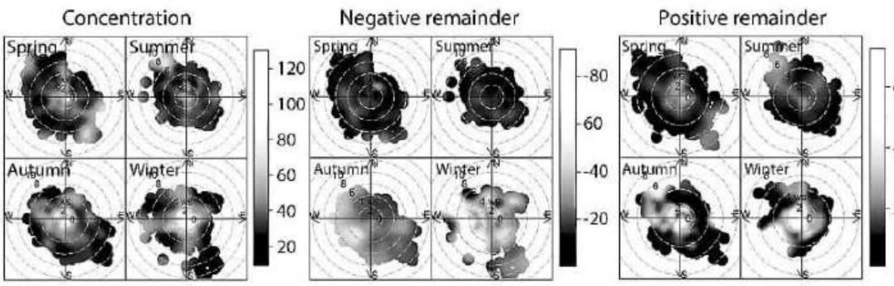


Figure 9. Bivariate polar plot of PM_{10} concentrations (left) and its remainder components: negative (middle) and positive (right) [μg m^{-3}].

To further examine their origin, the remainder shares can be subjected to the bivariate polar plot analysis, separately applied on positive and negative values. As shown in Figure 9, the episodes of the highest variations in Belgrade mainly occur during the colder part of the year – the positive ones are locally originated, or related to SW winds, while the negative ones are caused by strong NW winds.

Environmental Impacts

Local Sources

Investigating the influences of the surrounding emission sources by the use of bivariate polar plot and bivariate cluster analyses (Figure 10) reveal the dominant average contributions of the sources associated with restricted pollutant dispersion in an urban area (UCA), and by direct exposure to the emissions from the proximate industrial activities (UI and RI). At urban sites such as UB, PM_{10} concentrations tended to elevate as a result of S and SE winds during the episodes of unstable atmospheric conditions (wind speed higher than 8 m s^{-1}). Higher concentrations occur under the impact of heating plant emissions and nearby intersections with intensive traffic. Moreover, seasonal polar plots show the highest concentrations during low wind speed periods and the colder part of the year, which is expected as a result of more pronounced local emission sources and reduced advection.

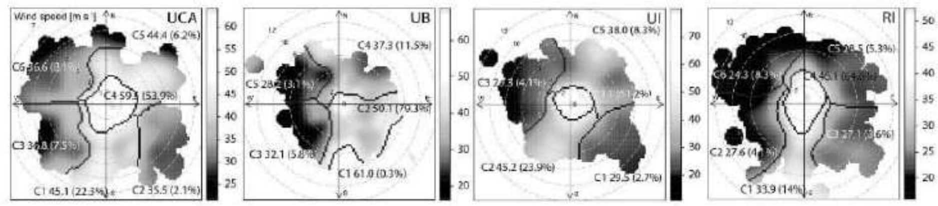


Figure 10. The relationship between PM_{10} concentrations and wind characteristics: bivariate plot (frequency [%] and average contributions [μg m^{-3}]) for the entire period in Belgrade.

Air Pollution Transport

Over the last decades, significant improvements in general hybrid receptor modeling have been made. Receptor-oriented models based on conditional probability and residence time analysis became widely accepted not only for studying dynamical processes and pollutant circulation patterns in the atmosphere, but for investigation of spatial distribution of potential emission sources and for the assessment of their impact on the receptor site without using emission inventories (Brereton and Johnson, 2012; Bycenkiene et al., 2014; Sen et al., 2016; Li et al., 2017). Hybrid receptor models consider residence time of trajectory segment endpoints in a potential source area, accounting for the above-threshold pollutant concentrations at the receptor site, as in the case of Potential source contribution function (PSCF) (Ashbaugh et al., 1985), or accounting for concentration gradients, as in the case of Concentration weighted trajectory model (CWT) (Hsu et al., 2003).

The conventional approach of hybrid receptor modelling has several drawbacks basically related to the concentration and trajectory inclusion in the model based on their representativeness. In order to obtain more realistic transport analysis, the innovative three-dimensional approach was introduced in Stojić and Stanišić Stojić, 2017. The concept relies on concentration and backward trajectory preprocessing, which enables more accurate inclusion of pollution levels in the transport model, and accounting for meteorological factors that govern the vertical distribution of air pollution, respectively.

Namely, by accounting the concentrations greater than the arbitrary chosen value (e.g., mean) it is implicitly assumed that individual peaks in the pollutant time series arise mainly as a result of transport (Kassomenos et al., 2006; Grivas et al., 2008) which may be considered appropriate only for the background sites. However, suburban and urban areas are dominated by many local emission sources implying that pronounced peaks in pollutant time series originate from local emissions and are superimposed on gradual variations of a concentration baseline level, encompassing both transport and local background contributions. The concept of concentration preprocessing which provide transport time series is described in the previous section, and the trajectory preprocessing concept will be explained in brief herein.

The lowest part of the troposphere, PBL, directly responds to surface forcing (Stull, 1988), by trapping and dispersing air pollution emitted from the ground, so the near-surface pollutant concentrations could correspond to atmospheric concentrations only within the PBL. To account PBL height fluctuations, the three-dimensional improvement of the conventional PSCF and CWT models, as well as new hybrid receptor model, Concentration weighted boundary layer (CWBL), that uses a two-dimensional grid and a PBL height as a frame of reference, are presented.

The contribution of a specific emission source to pollutant concentration at the receptor site is considered to be directly related to air mass residence time over the grid cell where the source is located (Dimitriou and Kassomenos, 2014). The probability of event A_{ij} when n trajectory endpoints fall into the ijth cell is given as:

$$P[A_{ij}] = \frac{n_{ij}}{N} \tag{1}$$

where N is the total number of endpoints (Hopke et al., 1993). However, the probability of high concentration event B_{ij}, when only a subset of m_{ij} grid cell endpoints for which the corresponding trajectories reach the receptor site when the transported concentrations are higher than the criterion value, is given as:

$$P[B_{ij}] = \frac{m_{ij}}{N} \tag{2}$$

The two-dimensional PSCF value for the ijth cell can be defined as:

$$P_{ij} = \frac{P[B_{ij}]}{P[A_{ij}]} = \frac{m_{ij}}{n_{ij}} \tag{3}$$

where the cells with higher PSCF values have a higher probability of containing emission sources.

We define three-dimensional PSCF as the ratio of a subset of m_{ijk} endpoints in the kth volume v_{ijk} of the predefined height above ijth cell for which the corresponding trajectories arrive at the receptor site when the contribution of transport to the measured concentrations are higher than the criterion value and the total number of endpoints in the *ij*th cell (n_{ij}):

$$P_{ijk} = \frac{P[B_{ijk}]}{P[A_{ij}]} = \frac{m_{ijk}}{n_{ij}} \quad (4)$$

The threshold for the selection of trajectories, which reflects the highest pollutant injection point, can be PBL height, which we consider appropriate for urban areas, or any altitude in the 3D grid map at each trajectory endpoint.

The major drawback of PSCF is related to high values that may occur as a consequence of a small number of grid cell endpoints corresponding to poor air quality at the receptor site. The problem can be overcome by the use of arbitrary weighting functions based on point count multiplied by the local PSCF (Zeng and Hopke, 1989) or by weighting trajectory endpoints (CWT) obtained by averaging estimated transport contribution at the receptor site that corresponds to the trajectories passing across the grid cell (i,j):

$$CWT_{ij} = \frac{\sum_{l=1}^{L} C_l \tau_{ijl}}{\sum_{l=1}^{L} \tau_{ijl}} \quad (5)$$

As in the case of 3D PSCF, 3D CWT for each volume cell v_{ijk} can be defined as:

$$CWT_{ijk} = \frac{\sum_{l=1}^{L} C_l \tau_{ijlk}}{\sum_{l=1}^{L} \tau_{ijl}} \quad (6)$$

where C_l is the pollutant concentration corresponding to the arrival of back trajectory l; τ_{ijl} is the number of trajectory segment endpoints in a grid cell (i,j) for back trajectory l; τ_{ijlk} is the number of trajectory segment endpoints in kth volume cell v_{ijk} for back trajectory l; L is the total number of back trajectories. As a result, the sum of altitude CWT distribution for each *ij*th cell amounts to the conventional 2D CWT solution.

Figure 11 illustrates main source regions altitude distribution that contributed to the elevated concentrations of $PM_{2.5}$ in Belgrade, while Figure 12 illustrates the altitude distribution of transported $PM_{2.5}$ concentrations and VOC industrial emissions according to CWT analysis.

Both 3D PSCF and CWT can be employed only for identification of potential source regions defined by longitude, latitude and altitude, and not for the analysis of pollutant altitude distribution along the transport pathway. For this reason, Concentration weighted boundary layer hybrid receptor model, which uses a 2D grid and a PBL height as a frame of reference, is introduced to obtain the vertical profile of pollutant concentrations above the receptor site and each grid cell along the transport pathway. The method relies on the fact that pollutant altitude distribution does not exhibit significant variation within the largest part of the PBL, except for the very top and very bottom layer (Stull, 1988; Gan et al., 2011). The CWBL value at each 2D grid cell (Figure 13) is calculated by averaging the transport contribution to pollutant concentrations that correspond to all endpoints falling into the selected cell (i,j) within the corresponding PBL heights as:

$$CWBL_{ijh} = mean(C_l^e|_{PBLH_{ijl}^e \geq h}) \tag{7}$$

where C_l^e is the concentration attributed to each endpoint e of trajectory l, and $PBLH_{ijl}^e$ refers to the PBL height at each endpoint in the moment when the air parcel passed grid cell (i, j). Figure 14 illustrates the results of CWBL-derived VOC industrial emissions altitude distribution as seen from the receptor site located in Belgrade urban area (UCA).

Moreover, CWBL is not limited to trajectory endpoint analysis – it provides pollutant altitude distribution above the receptor site (Figure 15). As can be seen, PM_{10} concentrations remained high in the ground layer of the troposphere and exhibited a rapid decline with height, reaching the minimum values for the highest PBL, which is in compliance with the aerosol altitude distribution described by Stull (1988), as well as with the findings of some recent empirical studies obtained by combining a charge-coupled device (CCD) side-scatter lidar with simultaneous ground level measurements (Tao et al., 2016).

Altitude profiles obtained by the use of CWBL provide an insight into the complexity of several factors that govern pollutant spatio-temporal distribution. Namely, PM_{10} concentrations in the ground layer are directly influenced by spatial distribution of emission sources, primarily consisting of anthropogenic emissions (Bravo-Aranda et al., 2017).

On the other hand, concentrations and residence time of particles in the upper layers are additionally affected by meteorological conditions, topography and complex atmospheric reactions, which further leads to the formation of secondary aerosols.

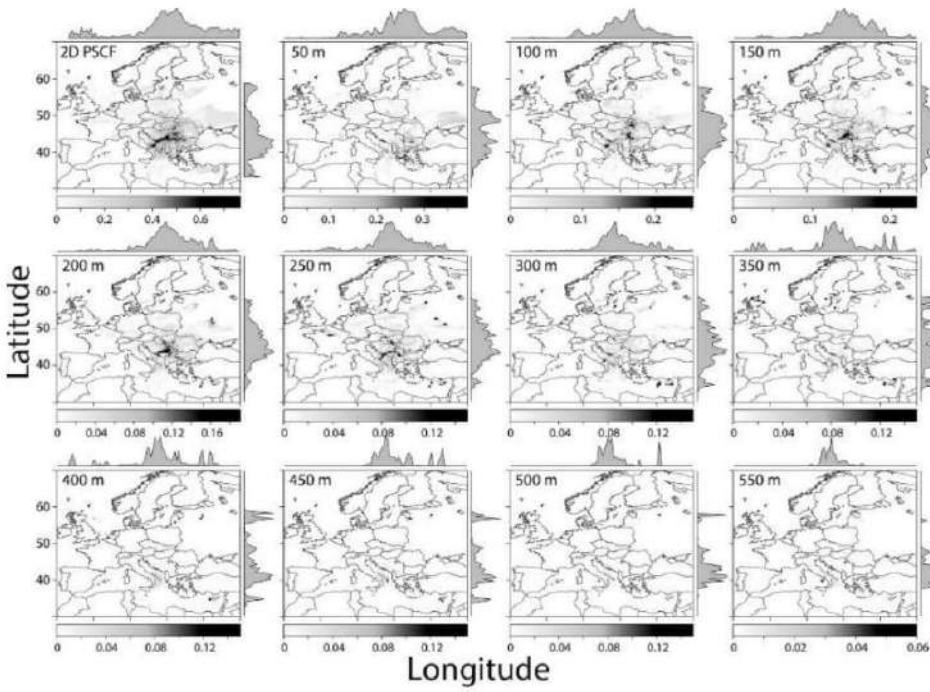


Figure 11. 2D PSCF and 3D PSCF derived maps indicating main source regions altitude distribution that contributed to the elevated concentrations of $PM_{2.5}$ in Belgrade (Stojić and Stanišić Stojić, 2017).

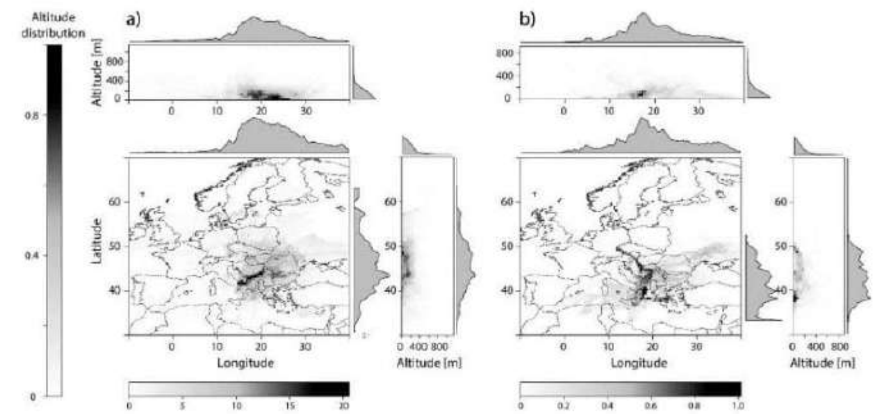


Figure 12. Two-dimensional CWT derived map for $PM_{2.5}$ [μg m^{-3}] (a), and VOC industrial emissions (average = 1) (b), and three-dimensional CWT longitudinal/latitudinal altitude distribution of pollutants during transport within the PBL (Stojić and Stanišić Stojić, 2017).

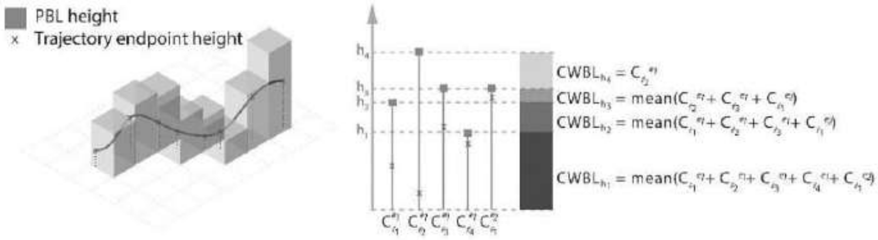


Figure 13. The concept of CWBL hybrid receptor model (left) and CWBL graphical illustration (right) (Stojić and Stanišić Stojić, 2017).

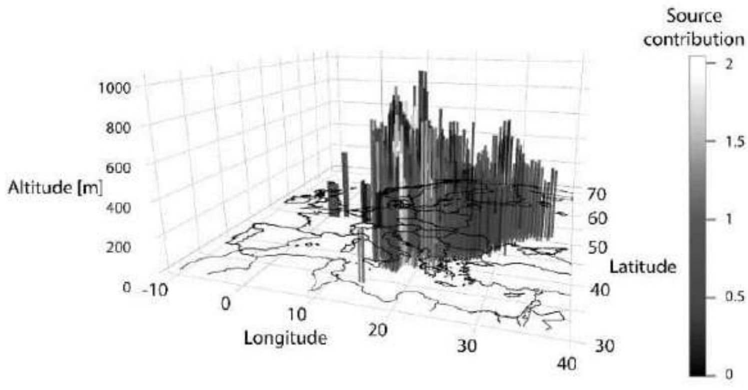


Figure 14. CWBL derived map for VOC industrial emissions (average = 1) representing its altitude distribution above the receptor site and above remote source regions as seen from Belgrade urban area (Stojić and Stanišić Stojić, 2017).

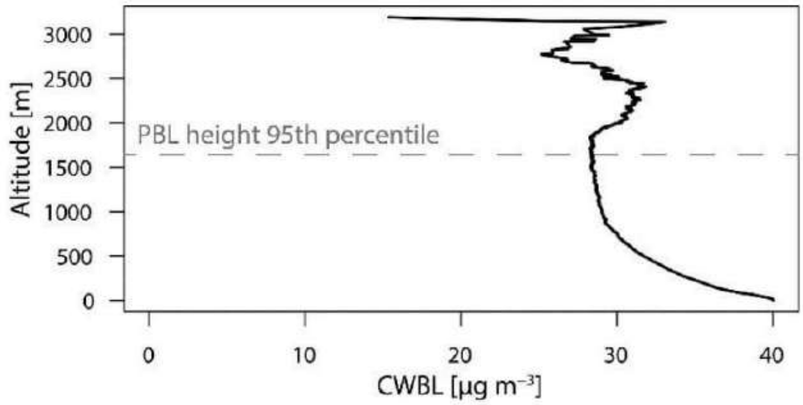


Figure 15. CWBL derived PM_{10} altitude distribution in Belgrade (Stojić et al., 2017).

Moreover, concentrations at greater heights could be representatives of regional background which cannot be measured directly (Wu et al., 2015; Han et al., 2015), so the contribution of the methods, like CWBL, which provide its assessment is of vital importance.

Environmental Multiphase Systems – Rainwater Scavenging

The relevance of rainwater in the air pollution studies is striking since it has a significant role in the spatial and temporal balancing of pollutants as well as their exchange between different environmental compartments through the process of wet deposition. Once the air pollutants are emitted into the atmosphere, they undergo atmospheric transport in particle-bound form or deposit via precipitations (rainwater, snow, fog and/or mist). The rainwater scavenges the pollutants present in the vapor/gaseous, aqueous and particulate phase involving two mechanisms: rainout (incloud scavenging) and washout (below-cloud scavenging) (Kajino and Aikawa, 2015). The rainout involves cloud condensation nuclei activation of aerosols above the cloud base, whereas washout is the collection of aerosols formed by falling hydrometeors, such as liquid precipitation in the form of rainwater. Our research regarding rainwater influences on air pollutants in urban areas focused on VOC, particularly BTEX (Šoštarić et al., 2016, 2017), which are xenobiotics widely recognized for their detrimental effects on human health and urban environment (Marć et al., 2015; Stojić et al., 2015b).

In natural environment, the incorporation of VOC in atmospheric water and their washout is a complex process, which is governed by a variety of factors. According to the available literature, the VOC uptake is primarily dependent on Henry's law constant (K_H) and consequently, on temperature and the "salting in/out" effects that are induced by different constituents of water such as dissolved salts, organic material and acids (Kampf et al., 2013; Kurtén et al., 2015; Okochi et al., 2005; Sander, 2015). The non-negligible aspects are: the VOC susceptibility to photochemical radical- and ozone-reactions as well as aerosol formation in the presence of suspended solids (Shen et al., 2013; Słomińska et al., 2014; Starokozhev et al., 2011); gas-water surface interactions including hydrogen bonding, surface adsorption and van der Waals forces (Furutaka and Ikawa, 2002; Goss, 2004; Roth et al., 2004); physico-chemical properties of the rainwater (Allou et al., 2011); as well as the sources of air masses (Mullaugh et al., 2015). To better understand the fate of BTEX in multiphase systems, our studies discussed BTEX partition and distribution in ultra-pure water and urban-environment rainwater samples by considering surface interactions (Šoštarić et al., 2016), physico-chemical properties of rainwater and meteorological parameters (Šoštarić et al., 2017). For this purpose, in-laboratory dynamic dilution system coupled with Proton Transfer Reaction Mass Spectrometer (PTR-MS), a tool for real-time measurements of VOC with high sensitivity, fast time response, and low detection limit (de Gouw et al., 2003), was used.

The following physico-chemical properties of BTEX were considered to be relevant for investigating the rainwater washout process: K_H, water solubility, octanol-water partitioning coefficient (K_{OW}), ionization potential and van der Waals surface area. Herein we will only elaborate on the parameters which were through pointed out in our experiments providing its brief theoretical background and main findings. In atmospheric chemistry, Henry's law constant is the most common way to describe the distribution of VOC in a multiphase system. There are many variants many variants of Henry's law constants, but all of them essentially represent the proportionality factor, which describes the relationship between the amount of gas dissolved in the aqueous phase and its partial pressure in the gas phase (Sander, 2015). Therefore, the distribution equilibrium of a compound could be fundamentally characterized with a unit (8) or dimensionless (9) Henry solubility:

$$K_H = \frac{C_a}{p_g} \text{ [M (mol dm}^{-3}\text{) atm}^{-1}\text{]} \tag{8}$$

$$K_H = \frac{C_g}{C_a} \tag{9}$$

where C_a is the compound concentration in the aqueous solution (refers to concentrations of less than 5–50 g L^{-1} for a compound with a molecular weight of 100 g mol^{-1}) and P_g is its partial pressure in the gas mixture (Šoštarić et al., 2017), C_g and C_a are the appropriate molar concentrations in the gas and water phases (Görgényia et al., 2002). These simplified equations could be used when reporting about measurements at constant temperatures, but for the real-world samples, it is important to introduce K_H dependence on the temperature as expressed by the alternative form of the van't Hoff equation (Sander, 2015):

$$K_H T = K_H(298.15) exp\left\{\frac{-\Delta H}{R}\left(\frac{1}{298.15} - \frac{1}{T_r}\right)\right\} \tag{10}$$

where K_H is Henry's law constant at 298.15 K for pure water, ΔH is the enthalpy change of air-water transfer, T_r is the temperature of real rainwater sample, and R is the universal gas constant (8.314 J K^{-1} mol^{-1}).

In addition to the above-described functionalities, K_H plays an essential role in quantifying the EF of VOC together with the distribution coefficient D_{OBS}, which is defined as the ratio between aqueous concentrations C_a [nM] and gas phase mixing ratios $VMRi$ [ppmV, ppbV] (Okochi et al., 2004):

$$EF = \frac{D_{OBS}}{K_H} \tag{11}$$

Our in-laboratory study indicated that D_{OBS} and EF values of BTEX significantly exceeded the value predicted by Henry's law in pure water at 25°C, independently of the pollutant water solubility, volatility and ionization potential (Šoštarić et al., 2016). Furthermore, adsorption is probably the principal phenomenon that explains the mechanisms of BTEX partitioning between the gaseous and the aqueous phase as suggested by highly positive correlation between calculated EF and parameters characterizing interfacial adsorption, such as K_{OW} and van der Waals surface. The presented laboratory experiment served as a step forward to the clarification of the phenomenon in urban-environment samples. Thereby we examined the functional dependency of BTEX enrichment factor on their gaseous concentrations, physico-chemical properties of rainwater (pH, turbidity, UV extinction, electrical conductivity, total organic carbon, anions: F^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^-, and cations: Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and meteorological parameters (temperature, relative humidity, pressure, wind speed, wind direction, and rainfall intensity/amount) during summer and autumn rainfall events (Šoštarić et al., 2017).

As assumed by Słomińska et al. (2014), BTEX concentrations in rainwater are expected to be low due to their small K_H values. However, in the Belgrade urban area, the BTEX levels, expressed by EF, are significantly above the values theoretically predicted by Henry's law constant. In addition, the BTEX enrichment was prominent during the cold part of the year that corresponds to the less intense photochemical removal and widely triggered emission sources during autumn (Figure 16). The K_H values and consequently EF for benzene, ethylbenzene and xylenes exhibited similar patterns across different altitudes; as the raindrop falls to the ground, EF decrease and *vice versa*. We note that the fluctuations between calculations using the average air and rainwater temperatures were in the range of ±20%, which suggest that the rainwater temperature measured at the ground level can serve as a good indicator of atmospheric conditions under which BTEX undergo changes. The findings support the available observations regarding the distribution of aromatic hydrocarbons between air and rainwater (Okochi et al., 2004; Sato et al., 2006) as well as between air and urban dew (Okochi et al., 2005).

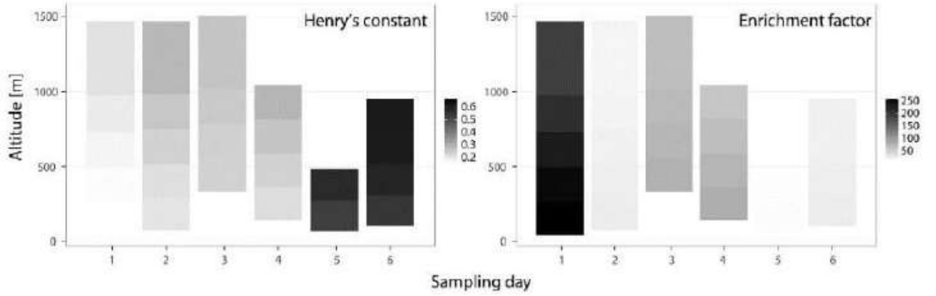


Figure 16. Toluene Henry's constant and EF altitude distributions (Šoštarić et al., 2017).

The enhanced BTEX enrichment in the rainwater samples proved to be not associated with its physicochemical properties since the significant correlation was only shown between the benzene concentrations, and F^- (-0.72) and NH_4^+ (0.83) ions. Furthermore, aromatic compounds in the gaseous form were apportioned to an Unmix-derived factor apart from the other chemical constituents with relatively high shares (99%, 44.5% and 52.2% for BTEX, respectively). Toluene, ethylbenzene and xylenes also exhibited moderate Unmix-shares together with SO_4^{2-} and NO_3^- anions, being recognized as the aerosol constituents. Beside gaseous oxides (SO_2 and NO_2), BTEX susceptibility to photo-oxidation with ozone and OH radicals along with NO_x and SO_2, is well known and leads to the formation of secondary organic aerosol (Shen et al., 2013). As enabled by on-line PTR-MS measurements (please see Šoštarić et al., 2016; 2017 for detailed explanation of the method performances), the extended BTEX exsufflation times for rainwater compared to pure water additionally suggested that not only the physico-chemical properties are affecting BTEX enhanced retention, but also the aerosol fraction have certain impact (Figure 17). The contributions of individual BTEX compounds to the aerosol formation should further be investigated as they behave differently in the atmosphere due to differences in the methyl chain substituent and the alkyl chain length, e.g., benzene is less prone to the heterogeneous reactions compared toluene and xylenes (Słomińska et al., 2014).

Finally, the interfacial adsorption is assumed to be the major mechanism that governs BTEX washout from the atmosphere, and the process is more efficient for lower gaseous concentration of pollutants. Equal surface available for smaller number of molecules and the prolonged contact time between the two phases when wind-driven raindrops were falling under a certain angle appeared to be the main contributors to such result. More specific, details/examples of environmental factors that synergistically influence spatio-temporal BTEX distribution in the multiphase system, including ambient mixing ratios, physico-chemical properties of rainwater and meteorological data are given below.

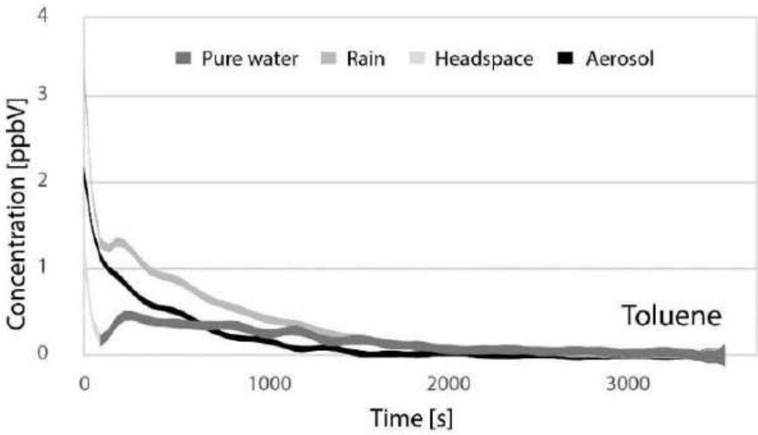


Figure 17. Toluene exsufflation from ultra-pure water and rainwater (Šoštarić et al., 2017).

Environmental Factor Interrelations

Air pollution system is a complex being influenced by multi-interrelations between various components that include numerous sources of air pollutants and the xenobiotics mutual interaction coupled with meteorological regime and atmosphere self-purification. In an open and dissipative system such as atmosphere, understanding the relevant factors and their correlations on different spatio-temporal scales are the essential task for estimation of adverse health effects and air pollution control policy (Stanišić Stojić et al., 2016b, 2016c, 2016d, 2016e). Therefore, a more meticulous attention in statistical research has been paid to the analysis of combined effects of environmental and anthropogenic factors beginning with factor analysis, principle component analysis, latent class analysis that provides information on the correlation among the investigated variables, etc. However, all these methods cannot assess the interaction of different air pollutants and the corresponding combined effects, particularly for the potential non-linear exposure-response relationship (Tonga et al., 2018).

Recent advances in modeling enabled extracting information relevant for addressing complex air pollution issues (Stojić et al., 2015a; Perišić et al., 2017a; Perišić et al., 2017c; Šoštarić et al., 2017). Machine learning is widely used methodology where non-linear associations between a target variable and a potentially unlimited number of explanatory predictors can be revealed without explicit knowledge of underlying processes by "letting the data speak for itself" (McCabe et al., 2017). In the section below, we presented the way to explore non-linear interconnections between different air pollutants using GRRF method.

Variable Importance

In addition to the usual interpretation of the effects of exposure to a single pollutant, it is crucial to understand the relationships between multi-pollutant mixtures to which people are inevitably exposed (Braun et al., 2016). In order to demonstrate how the complexity of pollutant interrelation can be esplored, we applied correlation and advanced supervised learning algorithms (GRRF) on the dataset comprising PM_{10} concentrations, its chemical constituents (As, Cd, Cr, Mn, Ni, Pb, BaP, Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}), and gaseous pollutants (CO, SO_2, NO, NO_2, NO_x, benzene, toluene, o- and m-, p-xylene) (Perišić et al., 2017a). According to the results which refer to the measurement site in the city center, the highest relative importance of As, Cd, BaP, CO and benzene as indicators of PM_{10} concentrations were observed, which is in accordance with the highest Pearson's correlation coefficients obtained between PM_{10} and its constituents: BaP (0.83), As (0.81) and Cd (0.79), as well as for CO (0.56) and benzene (0.46). The results suggest that environmental burden in urban area is mainly associated with fossil fuel combustion and that the GRRF could be considered as reliable as traditional statistical methods for exploring the potential origin of pollutants. In this analysis, inconsistency between correlation and GRRF analysis was observed for toluene which had higher importance for PM_{10} prediction than nitrogen oxides, but its correlation coefficient was among the lowest (0.25), indicating strong non-linear relationship between the two.

Source Characterization

Characterization of Dominant Sources

Widely applied receptor models Unmix and PMF, used to estimate contribution of different pollution sources in a densely populated central urban zone with heavy and slow traffic (Stojić et al., 2015a; Stojić et al., 2016), start from the assumption that in a complex pollutant mixture, species emitted from the same source are statistically interrelated. Two different datasets were considered: the first consisting of VOC (29 compounds) and five inorganic gaseous pollutants (Stojić et al., 2015a), and the second consisting of PM_{10} concentrations, its chemical constituents, and inorganic gaseous pollutants (Stojić et al., 2016).

The results of Unmix and PMF were in agreement, both showing a six-factor solution as the most feasible. Estimated source contributions were the highest for the profiles attributed to vehicle exhaust and industrial activities, followed by profiles identified as aged plums, solid fuel burning and biomass emission. Traffic-related (TR) profiles were distinguished by the highest loadings of ethylbenzene and xylenes, whereas the presence of gaseous oxides, NOx, NO_2, NO and CO, indicated the association with combustion processes. The commonly used indicator of this source category, toluene to benzene (T/B) ratio higher than 2.2 for traffic-related profiles was in a good agreement with the previously reported values for vehicle exhaust emissions (Lough et al., 2005). Also, the diurnal pattern of profile contributions reflects the variations in traffic density, with pronounced peaks in the morning and evening rush hours, and decreasing trend at the weekends (Figure 18, up). Bivariate cluster analysis for this source profile resolved dominant portion of locally generated emissions, which is expected in the urban areas with heavy, slow traffic and low ventilation (Figure 18, down).

Beside the identification of traffic emissions, both model solutions suggested gasoline evaporations, oil refinery emissions and petrochemical industry as sources with notable impacts on air quality in the studied urban area. Coupled with bivariate polar plot analysis, model results enabled the identification of the main regional industrial petrochemical complex, located only 13 km from the measurement site, as a potential source of pollutants. Regarding specific pollutants, certain shares of propylene, benzene, toluene, styrene, methacrolein, acetic acid and propionic acid produced by ethylene hydrocarboxylation characterized all profiles. As shown for the traffic emissions, minimum in daily contribution variations of all profiles was registered in morning hours, with small exceptions from the observed pattern in some cases. The minimum was followed by the increase during working hours. Furthermore, the profiles attributed to solid fuel burning was characterized by the highest contribution of SO_2, and low T/B ratios, as expected for biofuel, wood and coal burning (Johansson et al., 2004), while main contributions to aged plums were related to species with longer atmospheric lifetimes (Kwak and Baik, 2012).

According to the Unmix, four source profiles for particulate and inorganic gaseous pollutants were obtained as the most feasible model solution (Figure 19). The profile assigned to *solid fuel burning* with the highest is distinguished by the dominant shares of BaP and As. Occasional wood- and coal-burning for heating purposes during cold season in the vicinity of the receptor site was also reflected in daily variations of the profile contributions. The second profile assigned to *industrial emissions* comprised of significant shares of Cd and Pb originating from industrial activities (Pacyna, 1984). Typically for anthropogenic activities, the significant weekday/weekend differences in contributions of this profile were also observed. The profile identified as *traffic and particle resuspension* comprised high portions of EC, gaseous oxides, and soot. The seasonal pattern of particle resuspension showed decreased contribution in the cold season due to higher precipitation and snow cover, while the highest contribution was registered in summer, when the soil is dry and loose. High shares of NH_4^+, SO_4^{2-} and NO_3^- ions were apportioned to the *secondary aerosols*, with highest profile contributions during the cold season, when the concentrations of their precursors (NO_x and SO_2) typically reach their annual maximum.

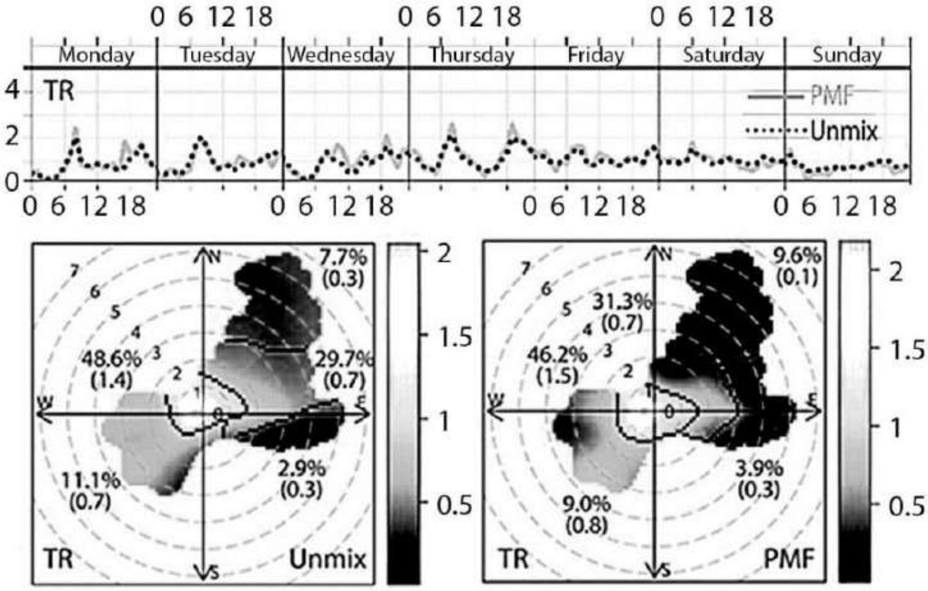


Figure 18. Diurnal dynamics (up) and relationship between source contributions and wind characteristics, together with bivariate cluster plot (percentage and average contribution) for traffic related profiles (Unmix and PMF) (down).

The presented receptor models applied at different databases have a good performance in the reproducing the dominant sources which affect air quality. In both cases, models extracted pollution associated with heating, traffic and transportation, and industrial activities as the main contributors affecting air quality in Belgrade urban area. As can be noted, additional analysis including bivariate polar plot are required for reliable identification of air pollution sources in complex urban environment.

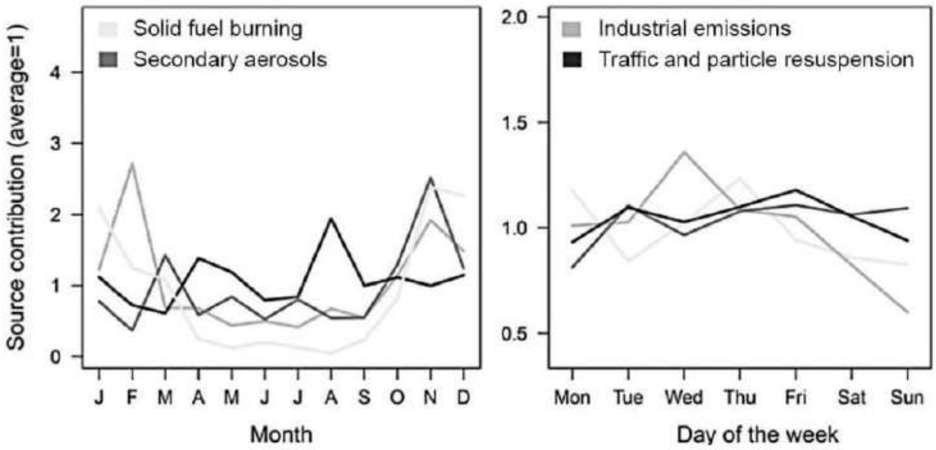


Figure 19. Monthly and weekly variations of Unmix-resolved source contributions.

Characterization of Individual Sources

In order to improve the source identification derived by receptor models and bivariate plot analysis, as well as to distinguish between individual potential emission sources based on the information of pollutant interrelationships, combined bivariate polar plot analysis and pair-wise statistics were applied. For this purpose, we used the dataset comprised of PM_{10} and gaseous pollutants (CO, benzene and toluene) concentrations observed at the sampling site in the city urban zone (Perišić et al., 2017a).

As presented in Figure 20, high correlations of PM_{10}, CO and benzene concentrations ($r \approx 0.7$) during the episodes of NW winds indicate towards several common sources of the pollutants in the vicinity of the sampling site. Moreover, the source composition obtained from slope diagrams of PM_{10} contribution to CO could be associated with various biomass combustion processes (traffic activities, heating plants and individual heating units in Belgrade urban area) (Yokelson et al., 2007).

The polar plot of the slope between PM_{10} and benzene demonstrates a similar surface pattern to the correlation polar plot (Figure 20), with maximum contributions during the periods of low wind speed. This clear and consistent PM_{10} – benzene ratio of 1:12 in the NW quadrant can be interpreted as a contribution to pollutant concentrations dominated by local traffic sources (Ielpo et al., 2014). In addition to the sources in the vicinity of the sampling site, prominent sources of the PM and toluene are located in SW, S, NE and SE directions ($r > 0.8$, wind speed > 4 m s^{-1}). Unlike sources in S and W, characterized by PM_{10} to toluene ratio of 1:1 which could be assigned to mineral oil and gas refineries, the source located in the NE is characterized by the ratio of 1:6, which indicates the impact of chemical industry, particularly production of basic organic chemicals including aromatic hydrocarbons (EPER, 2006).

Described methodology, which includes commonly used pair-wise statistics and bivariate plots, illustrate how the information on pollutant sources and processes could be enhanced by overlapping pollutant concentrations and wind characteristics. This unequivocally provides a better understanding of the relevant factors and processes in a complex urban environment.

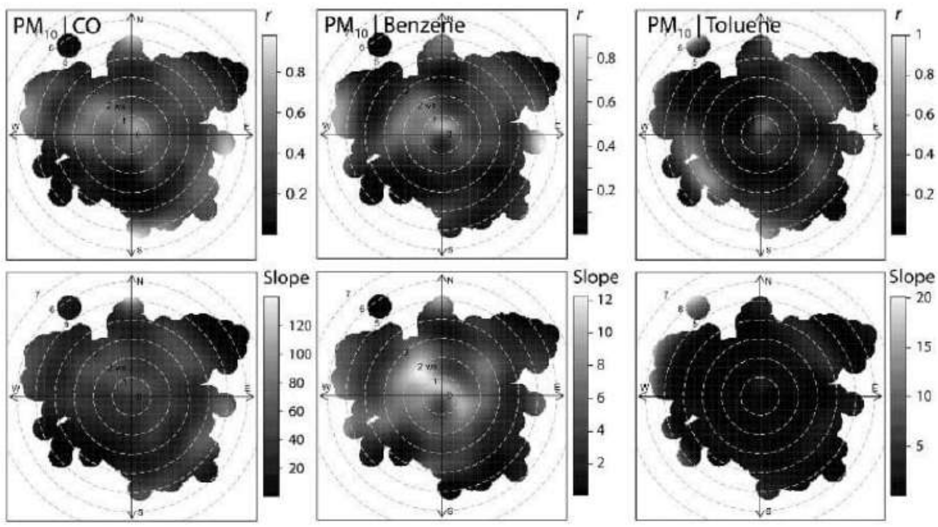


Figure 20. Bivariate polar source apportionment (Perišić et al., 2017a).

Regression Analysis, Prediction and Forecast

Nowadays, the forecasting of air pollutant concentrations in urban areas is of enormous importance given that air pollution has been a concern, particularly present in modern times due to the explosive development of urban infrastructures, industrial activities and population growth. Although forecast by itself cannot reduce the city's air pollution, a reliable and satisfactory forecast is essential as part of an air quality management system with respect to the issues of health alerts and public warnings, and as a supplement to the existing emission control programs and operational planning. Most of the research of air pollution forecasting has been initiated over the last 20 years, and it has dramatically evolved from diagnostics and empirical techniques to the latest advances in forecast resolution, more sophisticated data processing, online and statistical models along with the improvements in deterministic meteorology-chemistry approaches (Ryan, 2016). As a more economical alternative to computationally expensive and time-consuming deterministic models, the parametric or non-parametric statistical approaches to interpreting the underlying specific dependencies between pollutant concentrations and their routine prediction of accidental high concentration episodes have been investigated (Feng et al., 2015). From the numerous statistical methods reported in the literature, such as regression, artificial neural networks, fuzzy algorithms and models, multilayer perception etc., many techniques were successfully applied in forecasting air pollutants including SO_2, NO_2, CO_2, NO, CO, NO_x, $PM_{2.5}$, and PM_{10} (Bai et al., 2018; Coman et al., 2008; Domańska and Wojtylak, 2014; Hrust et al., 2009; Siwek and Osowski, 2012). In regards to the described research initiatives, our studies demonstrated successful application of various machine learning algorithms for forecasting the contributions of industry emissions and vehicle exhausts to VOC (Stojić et al., 2015a; Stanišić Stojić et al., 2016a) and PM_{10} (Perišić et al., 2017b) levels in the urban area relying on meteorological data and the concentrations of inorganic gases.

As noted previously, VOC are hazardous air pollutants that induce chronic toxicity even in small concentrations (Stojić et al. 2015b) and they commonly originate from both biogenic and anthropogenic emissions that are dominated by petrochemical industry and incomplete fossil fuel oxidation (Stojić et al., 2015c, 2015d). The abundance and spatial distribution of VOCs are mainly driven by their atmospheric lifetimes, emission intensity and meteorological factors (Liu et al., 2012). Part of our VOC-related research aimed at enhancing knowledge and understanding of pollutant variability has been focused on the assessment of the impacts which traffic- and industry-related sources have on VOC levels in urban area (Stojić et al., 2015a). Please see Stojić et al. (2015b) for detailed explanation of the VOC measurements and the basic statistics for selected pollutants, which is beyond the scope of this chapter. We employed several machine learning algorithms for classification and regression to: *i)* differentiate pollution indicators of high and low significance for the source contribution dynamics, and *ii)* forecast source contribution dynamics of the petrochemical/chemical industry (PC) and vehicle exhaust emissions (VE) relying on meteorological parameters and the concentrations of inorganic gaseous pollutants (NO_x, NO, NO_2, SO_2 and CO).

For the prediction of potentially health-damaging events of both PC and VE source contributions, extracted by Unmix and PMF receptor models, two arbitrary limits were considered: the levels above 60% as the increased level of caution and those exceeding 75% as extremely high-alarm triggering values. Among the meteorological variables, for both pollution sources, wind speed and temperature along with pressure appeared to have significant influence on source contributions in the urban canyon avenue (UCA). However, the method performances were not irrespective of input variables and the receptor model type used for the pollution profile selection. For instance, BTD method exhibited the best accuracy for VE-Unmix prediction of higher values based only on meteorological data, but not on the concentrations of the inorganic gases, whereas poorer predictions were observed for the other sources. This variability in method performances suggests that input of additional variables, which were not considered in our study, could possibly improve the method predictions. Raised to the general level, the machine learning method forecast is more precise when using Unmix-derived source contributions relying exclusively on the input data.

Discussion on the dependency of the source contributions on the examined meteorological data and inorganic gases concentrations, BDT, BDTG, MLP, LD showed the best regression performances (with absolute errors lower than 0.50), particularly when both meteorological data and inorganic gases were used as input variables (Stojić et al., 2015b). Similarly to the classification methods, regression forecasting was sensitive to the receptor model selected to derive pollution sources as well as input variables. In general, forecasting of PC-related contributions was more accurate when both meteorological data and gaseous concentrations were used, whereas higher absolute errors were recorded based on meteorological data exclusively. Nevertheless, in both cases less accurate predictions were still satisfying. In regards to the particular VOC, isoprene, MLP was selected as the best performing method with relative error of 6.94% and the correlation coefficient of 0.99% based on highly correlated VOC (1,3-butadiene, isoprene oxidation product at *m/z*71 and styrene), inorganic gases and meteorological data (Stanišić Stojić et al., 2016a). Contrary to this finding, the other machine learning methods, SMO and LR, exhibited the relative error of only 3% based on the meteorological data whereas the input of inorganic gases and other VOCs resulted in an increase in the relative error.

To conclude, the best regression methods, with relative errors starting at 6%, could provide satisfying forecasting of hourly source contributions of traffic-related VOC emissions as well as of industry-related sources, which are prone to the regional transport. Thereby, although highly dependent on the precise public meteorological forecast, the advanced machine learning methods represent a promising mean for the prediction of the episodes of dangerous pollutant concentrations.

Forecasting PM_{10} Concentrations

In the study of Perišić et al. (2017b), presented herein in brief, we evaluated the performances of machine learning methods for forecasting PM_{10} concentrations and prediction of related health-damaging events based on 5-year (2011–2015) dataset comprising hourly concentrations of PM_{10}, SO_2 and meteorological data (atmospheric pressure, temperature, humidity, wind speed and direction). Four sampling sites: urban canyon avenue (UCA; urban traffic), urban boulevard (UB; urban traffic), urban industry (UI) and rural industry (RI), were chosen from the regulatory monitoring network of air quality across the city of Belgrade to reflect substantial differences in air quality due to specifics in topography, residential structure and prevalent source of pollution.

Out of the 12 examined regression machine learning methods, BDTG and MLP with absolute and relative errors in the range between 10.6 to 24 μg m^{-3}, and 25.2 to 37.9%, respectively, appeared to be the most satisfying to interpret the relationships between PM_{10} and the SO_2 and meteorological input data. However, the prediction quality was partially affected by the site characteristics such as microclimate conditions and topography as well as by the presence of emission sources. The weakest predictability of PM_{10} levels in urban canyon avenue (UCA) is probably caused by the complexity of urban environment where the wind flow not only facilitates pollutant suspension, but also attenuates its dispersion (Vardoulakis et al., 2003). Moreover, the emission sources in the central city zone are numerous and primarily refer to traffic congestions, as well as to intense combustion processes in local fireboxes and heating plants during autumn and winter seasons. Conversely, a strong influence of a single dominant pollution source, such as an industrial facility, and the regularity of prevalent emissions on a daily, weekly and seasonal basis, led to the most accurate machine learning air quality forecast at the industrial sites, UI and RI. In addition to the regression purposes, the certain methods (BDTG and MLP) enabled reliable classification of the PM_{10} levels which require a high degree of caution (50 μg m^{-3}).

The PM_{10} time series evaluated by the machine learning regression methods correlated very well with the observed concentrations (Figure 21) at all sampling sites (RI, UB, UCA and UI). This result implied that relevant input variables were selected for the forecasting process. However, beside BDTG and MLP, the other methods exhibited the significant PM_{10} forecast errors when being used for regression compared to classification, at least based on the observed input variables that emphasize the need to investigate more appropriate variables to improve the method forecasting quality.

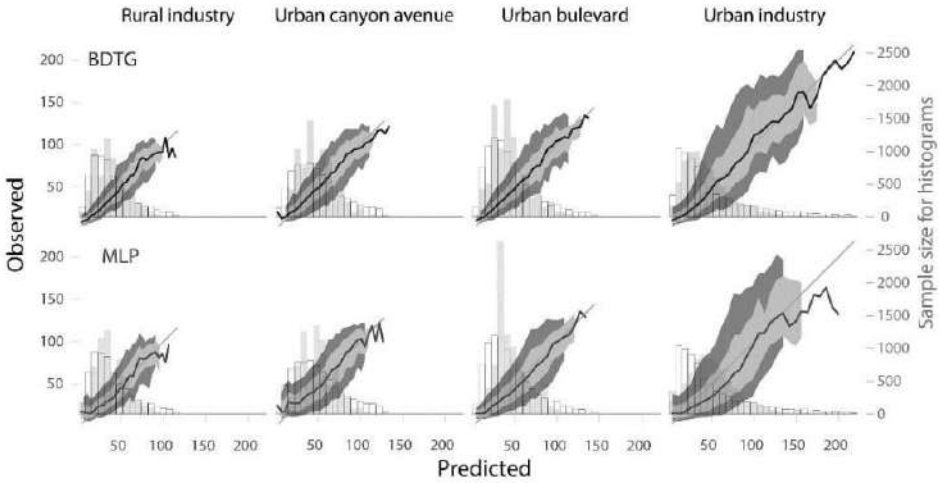


Figure 21. The comparison of the observed and best performing machine learning-predicted PM_{10} mass concentrations [μg m^{-3}] (Perišić et al., 2017b).

Finally, the presented errors for both VOC and PM forecasting in urban area suggest that the pollutant concentrations can be successfully predicted using the machine learning algorithms. What is of the utmost importance, the accurate forecasts could support the air quality management system assisting in health alerts for susceptible categories, operational planning along with reduction of regulatory monitoring expenses.

Enrichment Factor

Figure 22 illustrates an increase of EF for toluene, ethylbenzene and xylenes during summer as a function of the compound ambient gas mixing ratios (Šoštarić et al., 2017). The amplified enrichment might be associated with higher temperature during summer causing a decrease of the surface tension and favoring an interfacial adsorption (Bruant and Conklin, 2002), that has been proposed as the main mechanism for BTEX distribution in the aqueous phase (Šoštarić et al., 2016). More importantly, Figure 22 showed that higher rainwater enrichment by toluene occurred for low gaseous toluene concentrations, which is in accordance with previous studies (e.g., Sato et al., 2006).

As presented in Figure 23, higher enrichment of toluene, ethylbenzene and xylenes was mostly related to a higher wind speed at the sampling site (up to 30 m s^{-1}) and air masses coming from SW area, whereas the lowest rainwater enrichment was observed under relatively stable atmospheric conditions (wind speed<5 m s^{-1}) (Šoštarić et al., 2017). A possible explanation for this phenomenon is the prolonged contact time between the aqueous and the gaseous phases, during the period when strong wind-driven raindrops were falling obliquely. Similarly, bivariate plots revealed that gaseous organic and aerosol Unmix-derived factors were mostly associated with northern wind of moderate speed (<10 m s^{-1}), which clearly reflects their local origin.

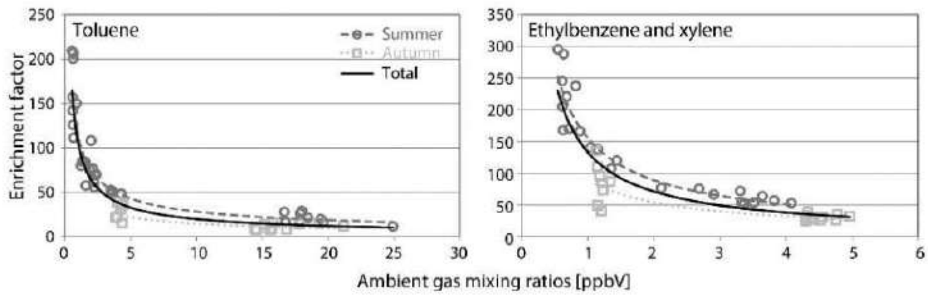


Figure 22. The relationship between T and EX enrichment factors and their gaseous concentrations (Šoštarić et al., 2017).

Feature selection uncovered the rainwater gaseous pollutant concentration and the presence of aerosol constituents to be more important for the prediction of toluene, ethylbenzene and xylenes enrichment than meteorological parameters such ambient temperature, wind speed, pressure and relative humidity. Furthermore, it became evident that BTEX concentrations associated with the ground level-emissions have higher impact on the pollutant partition to the aqueous phase than the polluted air masses coming from the greater atmospheric heights. Finally, out of the 24 examined machine learning regression methods, RF, IBk and

IBkLG provided the most accurate predictions of toluene, ethylbenzene and xylenes enrichment with relative errors of approximately 20% and correlation coefficients around 0.95 and 0.87.

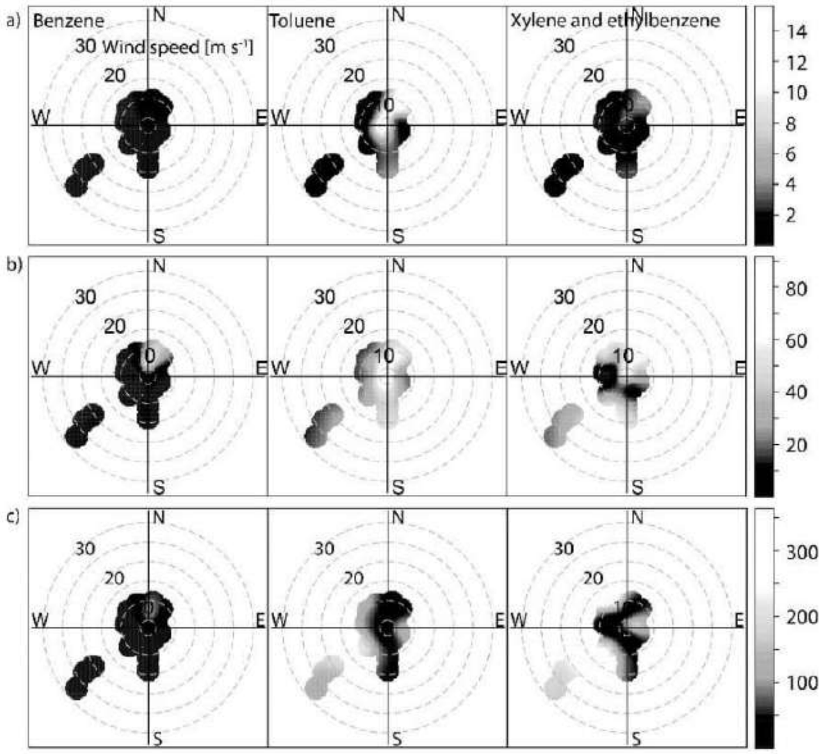


Figure 23. The relationship between BTEX air mixing ratios (ppb) (a), rain concentrations (nM) (b) and enrichment factor and wind characteristics (c) (Šoštarić et al., 2017).

Conclusion

Investigation and understanding of the coupled processes that govern the pollutant fate in a dissipative and complex system such as an atmosphere still remain a challenge for contemporary scientific community and environmental policy makers. Despite significant progress having been made, there are deep and possibly insurmountable levels of uncertainty in understanding the interconnectivity of the environmental factors, which arises from uncertainty in air pollution modeling and understanding the extent of changes in environmental factors. This chapter strives to demonstrate how a joint application of statistical tools could enable a valuable interpretation of the aspects concerning urban air complexity, and enhance the current knowledge drawn with respect to: *i)* spatio-temporal dynamics of pollutants, *ii)* decomposition of background, local and remote sources and its contribution to the pollutant levels, *iii)* three dimensional hybrid receptor modeling for the detection of pollution circulation patterns and its altitude distributions on various spatial scales, *iv)* the mechanisms governing pollutant distribution between the air-water multiphase system, *v)* source apportionment for source characterization across wider geographical area, and *vi)* possibilities for the forecasting and prediction of the pollutant non-linear interrelations. Specifically, air quality management, which aspires to the ambitious goals to face less pollution and lower risks of premature death and other serious health effects, as well as to reduce environmental damages from air pollution could greatly benefit from complementary rather than competitive assembling and hybridization of the advanced methods presented herein. Beside commonly used methods of statistical analysis and source apportionment, the improved transport and multifractal analysis presented herein could reveal specific transport pathways of pollution and support relevant industry sectors to control the pollutant release and distribution. Given the fact that timely information on occurrence of dangerous air pollutant levels is very important for prevention of hazardous health effects and implementation of early warning systems, classification and regression machine learning methods capable of supporting forecasting system of dangerous pollutant episodes depending on the meteorological regime are of high relevance in the contemporary environmental science.

REFERENCES

Aha, D. W., Kibler, D., and Albert, M. K. (1991). Instance-based learning algorithms. *Machine Learning*, 6(1), 37-66.

Allou, L., El Maimouni, L., and Le Calvé, S. (2011). Henry's law constant measurements for formaldehyde and benzaldehyde as a function of temperature and water composition. *Atmospheric Environment*, 45(17), 2991-2998.

Ashbaugh, L. L., Malm, W. C., and Sadeh, W. Z. (1985). A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. *Atmospheric Environment* (1967), 19(8), 1263-1270.

Bai, L., Wang, J., Ma, X., and Lu, H. (2018). Air Pollution Forecasts: An Overview. *International Journal of Environmental Research and Public Health*, 15(4), 780.

Braun, J. M., Gennings, C., Hauser, R., and Webster, T. F. (2016). What can epidemiological studies tell us about the impact of chemical mixtures on human health? *Environmental Health Perspectives*, 124(1), A6.

Bravo-Aranda, J. A., de Arruda Moreira, G., Navas-Guzmán, F., Granados-Muñoz, M. J., Guerrero-Rascado, J. L., Pozo-Vázquez, D., ... and Arboledas, L. A. (2017). A new methodology for PBL height estimations based on lidar depolarization measurements: analysis and comparison against MWR and WRF model-based results. *Atmospheric Chemistry and Physics*, 17(11).

Breiman, L. (2001). Random forests. *Machine learning*, 45(1), 5-32.

Brereton, C. A., and Johnson, M. R. (2012). Identifying sources of fugitive emissions in industrial facilities using trajectory statistical methods. *Atmospheric Environment*, 51, 46-55.

Bruant, R. G., and Conklin, M. H. (2002). Adsorption of benzene and methyl-substituted benzenes at the vapor/water interface. 3. Finite binary-component VHOC adsorption. *The Journal of Physical Chemistry B*, 106(9), 2232-2239.

Brun, R., and Rademakers, F. (1997). ROOT—an object oriented data analysis framework. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 389(1-2), 81-86.

Byčenkienė, S., Plauškaitė, K., Dudoitis, V., and Ulevicius, V. (2014). Urban background levels of particle number concentration and sources in Vilnius, Lithuania. *Atmospheric Research*, 143, 279-292.

Carslaw, D. C., and Ropkins, K. (2012). Openair—an R package for air quality data analysis. *Environmental Modelling and Software*, 27, 52-61.

Chehade, W., Weber, M., and Burrows, J. P. (2014). Total ozone trends and variability during 1979–2012 from merged data sets of various satellites. *Atmospheric Chemistry and Physics*, 14(13), 7059-7074.

Cleary, J. G., and Trigg, L. E. (1995). K*: An instance-based learner using an entropic distance measure. In *Machine Learning Proceedings* 1995 (pp. 108-114).

Cohen, W. W. (1995). Fast effective rule induction. In *Machine Learning Proceedings* 1995 (pp. 115-123).

Coman, A., Ionescu, A., and Candau, Y. (2008). Hourly ozone prediction for a 24-h horizon using neural networks. *Environmental Modelling and Software*, 23(12), 1407-1421.

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R. (2003). Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry. *International Journal of Mass Spectrometry*, 223, 365-382.

Deng, H., and Runger, G. (2013). Gene selection with guided regularized random forest. *Pattern Recognition*, 46(12), 3483-3489.

Dimitriou, K., and Kassomenos, P. (2014). Decomposing the profile of PM in two low polluted German cities–mapping of air mass residence time, focusing on potential long range transport impacts. *Environmental Pollution*, 190, 91-100.

Domańska, D., and Wojtylak, M. (2014). Explorative forecasting of air pollution. *Atmospheric Environment*, 92, 19-30.

Dong, Q., Wang, Y., and Li, P. (2017). Multifractal behavior of an air pollutant time series and the relevance to the predictability. *Environmental Pollution*, 222, 444-457.

Draxler, R. R., and Rolph, G. D. (2014). *HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model access via NOAA ARL*

READY. NOAA Air Resources Laboratory, Silver Spring. https://ready.arl.noaa.gov/HYSPLIT.php.

EPER. Regulation, E. P. (2006). *Regulation (EC) no. 166/2006 of the European Parliament and of the Council concerning the establishment of a European pollutant release and transfer register and amending Council Directives 91/689/EEC and 96/61.*

Feng, X., Li, Q., Zhu, Y., Hou, J., Jin, L., and Wang, J. (2015). Artificial neural networks forecasting of $PM_{2.5}$ pollution using air mass trajectory based geographic model and wavelet transformation. *Atmospheric Environment*, 107, 118-128.

Frank, E., Hall, M., and Pfahringer, B. (2002, August). Locally weighted naive bayes. In *Proceedings of the Nineteenth conference on Uncertainty in Artificial Intelligence* (pp. 249-256). Morgan Kaufmann Publishers Inc.

Frank, E., Hall, M., Holmes, G., Kirkby, R., Pfahringer, B., Witten, I., and Trigg, L. (2005). "Weka." In *Data Mining and Knowledge Discovery Handbook,* edited by Maimon, Oded and Rokach, Lior, 1305-14. Springer US.

Frank, E. (2014). *Fully supervised training of Gaussian radial basis function networks in WEKA.*

Frank, E., Mayo, M., and Kramer, S. (2015, April). Alternating model trees. In *Proceedings of the 30th annual ACM symposium on applied computing* (pp. 871-878). ACM.

Furutaka, S., and Ikawa, S. I. (2002). π-hydrogen bonding between water and aromatic hydrocarbons at high temperatures and pressures. *The Journal of chemical physics*, 117(2), 751-755.

Gan, C. M., Gross, B., Wu, Y., and Moshary, F. (2011). Application of Remote Sensing Instrument in Air Quality Monitoring. In *Air Quality Monitoring, Assessment and Management*. InTech.

Gierałtowski, J., Żebrowski, J. J., and Baranowski, R. (2012). Multiscale multifractal analysis of heart rate variability recordings with a large number of occurrences of arrhythmia. *Physical Review E,* 85(2), 021915.

Görgényi, M., Dewulf, J., and Van Langenhove, H. (2002). Temperature dependence of Henry's law constant in an extended temperature range. *Chemosphere*, 48(7), 757-762.

Goss, K. U. (2004). The air/surface adsorption equilibrium of organic compounds under ambient conditions. Critical Reviews in *Environmental Science and Technology*, 34(4), 339-389.

Graczyk, M., Lasota, T., and Trawiński, B. (2009, October). Comparative analysis of premises valuation models using KEEL, RapidMiner, and WEKA. In *International conference on computational collective intelligence* (pp. 800-812). Springer, Berlin, Heidelberg.

Grange, S. K., Lewis, A. C., and Carslaw, D. C. (2016). Source apportionment advances using polar plots of bivariate correlation and regression statistics. *Atmospheric Environment*, 145, 128-134.

Grivas, G., Chaloulakou, A., and Kassomenos, P. (2008). An overview of the PM_{10} pollution problem, in the Metropolitan Area of Athens, Greece. Assessment of controlling factors and potential impact of long range transport. *Science of the Total Environment*, 389(1), 165-177.

Han, L., Zhou, W., and Li, W. (2015). Increasing impact of urban fine particles (PM 2.5) on areas surrounding Chinese cities. *Scientific reports, 5, 12467.*

Haykin, S. (1994). *Neural networks: a comprehensive foundation.* Prentice Hall PTR.

He, H. D. (2017). Multifractal analysis of interactive patterns between meteorological factors and pollutants in urban and rural areas. *Atmospheric Environment*, 149, 47-54.

Henry, R. C. (2003). Multivariate receptor modeling by N-dimensional edge detection. *Chemometrics and intelligent laboratory systems*, 65(2), 179-189.

Hoecker, A., Speckmayer, P., Stelzer, J., Therhaag, J., Von Toerne, E., Voss, H., ... and Dannheim, D. (2015). TMVA users guide—toolkit for multivariate data analysis, *PoSACAT 040.*

Hopke, P. K., Gao, N., and Cheng, M. D. (1993). Combining chemical and meteorological data to infer source areas of airborne pollutants. *Chemometrics and Intelligent Laboratory Systems*, 19(2), 187-199.

Hrust, L., Klaić, Z. B., Križan, J., Antonić, O., and Hercog, P. (2009). Neural network forecasting of air pollutants hourly concentrations using optimised temporal averages of meteorological variables and pollutant concentrations. *Atmospheric Environment*, 43(35), 5588-5596.

Hsu, Y. K., Holsen, T. M., and Hopke, P. K. (2003). Comparison of hybrid receptor models to locate PCB sources in Chicago. *Atmospheric Environment*, 37(4), 545-562.

Hurst, H. E. (1951). Long-term storage capacity of reservoirs. *Journal of Transportation Engineering. ASCE/American Society of Civil Engineers*, 116, 770-799.

IBkLG. 2015. *Instance Based-kNN Log and Gaussian*. Computer software. Available at https://github.com/sheshas/IBkLG.

Ielpo, P., Paolillo, V., de Gennaro, G., and Dambruoso, P. R. (2014). PM 10 and gaseous pollutants trends from air quality monitoring networks in Bari province: principal component analysis and absolute principal component scores on a two years and half data set. *Chemistry Central Journal*, 8(1), 14.

Ihlen, E. A. F. E. (2012). Introduction to multifractal detrended fluctuation analysis in Matlab. *Frontiers in Physiology*, 3, 141.

Johansson, L. S., Leckner, B., Gustavsson, L., Cooper, D., Tullin, C., and Potter, A. (2004). Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. *Atmospheric Environment*, 38(25), 4183-4195.

Kajino, M., and Aikawa, M. (2015). A model validation study of the washout/rainout contribution of sulfate and nitrate in wet deposition compared with precipitation chemistry data in Japan. *Atmospheric Environment*, 117, 124-134.

Kalmegh, S. (2015). Analysis of WEKA data mining algorithm REPTree, Simple CART and RandomTree for classification of Indian news. *International Journal of Innovative Research in Science, Engineering and Technology*, 2(2), 438-446.

Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., ... and Volkamer, R. (2013). Effective Henry's law partitioning and the salting constant of glyoxal in aerosols containing sulfate. *Environmental Science and Technology*, 47(9), 4236-4244.

Kassomenos, P., Karakitsios, S., and Papaloukas, C. (2006). Estimation of daily traffic emissions in a South-European urban agglomeration during a workday. Evaluation of several "what if" scenarios. *Science of the Total Environment*, 370(2-3), 480-490.

Kneen, M. A., and Annegarn, H. J. (1996). Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* 109, 209-213.

Kurtén, T., Elm, J., Prisle, N. L., Mikkelsen, K. V., Kampf, C. J., Waxman, E. M., and Volkamer, R. (2014). Computational study of the effect of glyoxal–sulfate clustering on the Henry's law coefficient of glyoxal. *The Journal of Physical Chemistry A*, 119(19), 4509-4514.

Kwak, K. H., and Baik, J. J. (2012). A CFD modeling study of the impacts of NOx and VOC emissions on reactive pollutant dispersion in and above a street canyon. *Atmospheric Environment*, 46, 71-80.

Li, L., Qian, J., Ou, C. Q., Zhou, Y. X., Guo, C., and Guo, Y. (2014). Spatial and temporal analysis of Air Pollution Index and its timescale-dependent relationship with meteorological factors in Guangzhou, China, 2001–2011. *Environmental Pollution*, 190, 75-81.

Li, M., Zhang, Q., Kurokawa, J. I., Woo, J. H., He, K., Lu, Z., ... and Cheng, Y. (2017). MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP. *Atmospheric Chemistry and Physics*, 17(2): 935-63.

Liu, S., Wang, B., He, J., Tang, X., Luo, W., and Wang, C. (2012). Source fingerprints of volatile organic compounds emitted from a municipal solid waste incineration power plant in Guangzhou, China. *Procedia Environmental Sciences*, 12, 106-115.

Lough, G. C., Schauer, J. J., Lonneman, W. A., and Allen, M. K. (2005). Summer and winter nonmethane hydrocarbon emissions from on-road motor vehicles in the Midwestern United States. *Journal of the Air and Waste Management Association*, 55(5), 629-646.

Mandelbrot, B. B., and Wallis, J. R. (1969). Robustness of the rescaled range R/S in the measurement of noncyclic long run statistical dependence. *Water Resources Research*, 5(5), 967-988.

Mandelbrot, B. B. (1982). *The fractal geometry of nature (Vol. 1)*. New York: WH freeman.

Marć, M., Bielawska, M., Wardencki, W., Namieśnik, J., and Zabiegała, B. (2015). The influence of meteorological conditions and anthropogenic activities on the seasonal fluctuations of BTEX in the urban air of the Hanseatic city of Gdansk, Poland. *Environmental Science and Pollution Research*, 22(15), 11940-11954.

McCabe, M. F., Rodell, M., Alsdorf, D. E., Gonzalez Miralles, D., Uijlenhoet, R., Wagner, W., ... and Shi, J. (2017). The future of Earth observation in hydrology. *Hydrology and Earth System Sciences*, 21(7), 3879-3914.

Molino-Minero-Re, E., García-Nocetti, F., and Benítez-Pérez, H. (2015). Application of a time-scale local Hurst exponent analysis to time series. *Digital Signal Processing*, 37, 92-99.

Monks, P. S., Granier, C., Fuzzi, S., Stohl, A., Williams, M. L., Akimoto, H., ... and Blake, N. (2009). Atmospheric composition change–global and regional air quality. *Atmospheric Environment*, 43(33), 5268-5350.

Mullaugh, K. M., Hamilton, J. M., Avery, G. B., Felix, J. D., Mead, R. N., Willey, J. D., and Kieber, R. J. (2015). Temporal and spatial variability of trace volatile organic compounds in rainwater. *Chemosphere*, 134, 203-209.

Okochi, H., Kataniwa, M., Sugimoto, D., and Igawa, M. (2005). Enhanced dissolution of volatile organic compounds into urban dew water collected in Yokohama, Japan. *Atmospheric Environment*, 39(33), 6027-6036.

Okochi, H., Sugimoto, D., and Igawa, M. (2004). The enhanced dissolution of some chlorinated hydrocarbons and monocyclic aromatic hydrocarbons in rainwater collected in Yokohama, Japan. *Atmospheric Environment*, 38(26), 4403-4414.

Paatero, P. (1999). The multilinear engine—a table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model. *Journal of Computational and Graphical Statistics*, 8(4), 854-888.

Pacyna, J. M. (1984). Estimation of the atmospheric emissions of trace elements from anthropogenic sources in Europe. *Atmospheric Environment* (1967), 18(1), 41-50.

Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z., and Rajšić, S. (2015). Estimation of required PM10 emission source reduction on the basis of a 10-year period data. *Air Quality, Atmosphere and Health*, 8(4), 379-389.

Perišić, M., Vuković, G., Mijić, Z., Šoštarić, A., and Stojić, A. (2017). Relative importance of gaseous pollutants and aerosol constituents for identification of PM_{10} sources of variability. Paper presented at *The sixth international WeBIOPATR workshop and conference*, Serbia, Belgrade, September 6-8.

Perišić, M., Maletić, D., Stojić, S. S., Rajšić, S., and Stojić, A. (2017). Forecasting hourly particulate matter concentrations based on the advanced multivariate methods. *International journal of environmental science and technology*, 14(5), 1047-1054.

Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z., and Stojić, A. (2017). Levels of PM 10-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation. *Air Quality, Atmosphere and Health*, 10(1), 93-103.*and*

Plocoste, T., Calif, R., and Jacoby-Koaly, S. (2017). Temporal multiscaling characteristics of particulate matter PM_{10} and ground-level ozone O_3 concentrations in Caribbean region. *Atmospheric Environment*, 169, 22-35.

Rasmussen, C. E., and Williams, C. K. (2006). *Gaussian process for machine learning*. MIT press.

Roth, C. M., Goss, K. U., and Schwarzenbach, R. P. (2004). Sorption of diverse organic vapors to snow. *Environmental science and technology*, 38(15), 4078-4084.

Rousseeuw, P. J., and Leroy, A. M. (2005*). Robust regression and outlier detection* (Vol. 589). John wiley and sons.

Ruf, T. (1999). The Lomb-Scargle periodogram in biological rhythm research: analysis of incomplete and unequally spaced time-series. *Biological Rhythm Research*, 30(2), 178-201.

Ryan, W. F. (2016). The air quality forecast rote: Recent changes and future challenges. *Journal of the Air and Waste Management Association*, 66(6), 576-596.

Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, 15(8).

Sato, E., Matsumoto, K., Okochi, H., and Igawa, M. (2006). Scavenging effect of precipitation on volatile organic compounds in ambient atmosphere. *Bulletin of the Chemical Society of Japan*, 79(8), 1231-1233.

Sen, A., Ahammed, Y. N., Banerjee, T., Chatterjee, A., Choudhuri, A. K., Das, T., ... and Mandal, T. K. (2016). Spatial variability in ambient atmospheric fine and coarse mode aerosols over Indo-Gangetic plains, India and adjoining oceans during the onset of summer monsoons, 2014. *Atmospheric Pollution Research*, 7(3), 521-532.

Shen, X., Zhao, Y., Chen, Z., and Huang, D. (2013). Heterogeneous reactions of volatile organic compounds in the atmosphere. *Atmospheric environment*, 68, 297-314.

Shevade, S. K., Keerthi, S. S., Bhattacharyya, C., and Murthy, K. R. K. (2000). Improvements to the SMO algorithm for SVM regression. *IEEE transactions on neural networks*, 11(5), 1188-1193.

Shi, P., and Tsai, C. L. (2002). Regression model selection—a residual likelihood approach. *Journal of the Royal Statistical Society: Series B (Statistical Methodology)*, 64(2), 237-252.

Siwek, K., and Osowski, S. (2012). Improving the accuracy of prediction of PM_{10} pollution by the wavelet transformation and an ensemble of neural predictors. *Engineering Applications of Artificial Intelligence*, 25(6), 1246-1258.

Słomińska, M., Konieczka, P., and Namieśnik, J. (2014). The fate of BTEX compounds in ambient air. *Critical Reviews in Environmental Science and Technology*, 44(5), 455-472.

Šoštarić, A., Stojić, A., Stojić, S. S., and Gržetić, I. (2016). Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system. *Chemosphere*, 144, 721-727.

Šoštarić, A., Stojić, S. S., Vuković, G., Mijić, Z., Stojić, A., and Gržetić, I. (2017). Rainwater capacities for BTEX scavenging from ambient air. *Atmospheric Environment*, 168, 46-54.

Stanišić Stojić, S., Stojić, A., and Perišić, M. (2016). Relationship between isoprene, related gaseous pollutants and meteorological factors in an urban area. Paper presented at the *13th International Conference on Fundamental and Applied Aspects of Physical Chemistry*, Serbia, Belgrade, September 26-30.

Stojić, S. S., Stanišić, N., and Stojić, A. (2016). Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area. *Environmental Health*, 15(1), 73.

Stanišić Stojić, S., Stanišić, N., and Stojić, A. (2016). "Short- and Long-Term Effects of Urban Air Pollution on Cardiopulmonary and Malignant Death Rates," in *Air Pollution: Management Strategies, Environmental Impact and Health Risks* edited by Burns, Gerald L. Nova Science Publishers, Hauppauge, New York, USA.

Stanišić Stojić, S., Stanišić, N., and Džamić, V. (2016). Seasonal mortality variations of cardiovascular, respiratory and malignant diseases in the city of Belgrade. *Stanovništvo*, 54(1), 83-104.

Stojić, S. S., Stanišić, N., Stojić, A., and Šoštarić, A. (2016). Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. *Journal of Toxicology and Environmental Health, Part A*, 79(1), 17-27.

Starokozhev, E., Sieg, K., Fries, E., and Püttmann, W. (2011). Investigation of partitioning mechanism for volatile organic compounds in a multiphase system. *Chemosphere*, 82(10), 1482-1488.

Stojić, A., Maletić, D., Stojić, S. S., Mijić, Z., and Šoštarić, A. (2015). Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. *Science of the Total Environment*, 521, 19-26.

Stojić, A., Stojić, S. S., Mijić, Z., Šoštarić, A., and Rajšić, S. (2015). Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. *Atmospheric Environment*, 106, 71-79.

Stojić, A., Stojić, S. S., Šoštarić, A., Ilić, L., Mijić, Z., and Rajšić, S. (2015). Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. *Environmental Science and Pollution Research*, 22(17), 13137-13152.

Stojić, A., Stojić, S. S., Mijić, Z., Ilić, L., Tomašević, M., Todorović, M., and Perišić, M. (2015). Comprehensive analysis of VOC emission sources in Belgrade urban area. *Urban and built environments: sustainable development, health implications and challenges*. Nova Science, New York, ISBN, 978-1.

Stojić, A., Stojić, S. S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., and Mijić, Z. (2016). Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. *Environmental Science and Pollution Research*, 23(11), 10722-10732.

Stojić, A., Stanišić Stojić, S., Perišić, M., and Mijić, Z. (2017). Multiscale multifractal analysis of nonlinearity in particulate matter time series. Paper presented at *The sixth international WeBIOPATR workshop and conference*, Serbia, Belgrade, September 6-8.

Stojić, A., and Stojić, S. S. (2017). The innovative concept of three-dimensional hybrid receptor modeling. *Atmospheric Environment*, 164, 216-223.

Stull, R. B. (2012). *An introduction to boundary layer meteorology (Vol. 13)*. Springer Science and Business Media.

Tao, W. K., Wu, D., Lang, S., Chern, J. D., Peters-Lidard, C., Fridlind, A., and Matsui, T. (2016). High-resolution NU-WRF simulations of a deep convective-precipitation system during MC3E: Further improvements and comparisons between Goddard microphysics schemes and observations. *Journal of Geophysical Research: Atmospheres*, 121(3), 1278-1305.

Team, R. C. (2014). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria. 2013.

Todorovic, M. N., Perisic, M. D., Kuzmanoski, M. M., Stojic, A. M., Sostarić, A. I., Mijic, Z. R., and Rajsic, S. F. (2015). Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area. *Journal of Environmental Science and Health, Part A*, 50(13), 1351-1359.

Tong, Y., Luo, K., Li, R., Pei, L., Li, A., Yang, M., and Xu, Q. (2018). Association between multi-pollutant mixtures pollution and daily cardiovascular mortality: An exploration of exposure-response relationship. *Atmospheric Environment*, 186, 136-143.

UN. 2016. *The World's Cities in 2016 - Data Booklet*. http://www.un.org/en/development/desa/population/publications/pdf/urbanization/the_worlds_cities_in_2016_data_booklet.pdf. Accessed April 2018.

USEPA. Henry, R. C., and Norris, G. A. (2007). *EPA UNMIX 6.0 fundamentals and user guide*. National Exposure Research Laboratory, US Environmental Protection Agency, Research Triangle Park, NC.

Vardoulakis, S., Fisher, B. E., Pericleous, K., and Gonzalez-Flesca, N. (2003). Modelling air quality in street canyons: a review. *Atmospheric environment*, 37(2), 155-182.

Wang, Y., and Witten, I. H. (1996). *Induction of model trees for predicting continuous classes*.

Wang, Y., and Witten, I. H. (2002). Modeling for optimal probability prediction. In *Proceedings of the Nineteenth International Conference on Machine Learning*, Sydney, Australia, July (pp. 650-657).

Wang, Y. Q. (2014). MeteoInfo: GIS software for meteorological data visualization and analysis. *Meteorological Applications*, 21(2), 360-368.

Windsor, H. L., and Toumi, R. (2001). Scaling and persistence of UK pollution. *Atmospheric Environment*, 35(27), 4545-4556.

Witten, I. H., Frank, E., Hall, M. A., and Pal, C. J. (2016). *Data Mining: Practical machine learning tools and techniques*. Morgan Kaufmann.

WHO. World Health Organization. (2016). *Ambient air pollution: A global assessment of exposure and burden of disease*.

Wu, H., Zhang, Y. F., Han, S. Q., Wu, J. H., Bi, X. H., Shi, G. L., ... and Feng, Y. C. (2015). Vertical characteristics of $PM_{2.5}$ during the heating season in Tianjin, China. *Science of the Total Environment*, 523, 152-160.

Xue, Y., Pan, W., Lu, W. Z., and He, H. D. (2015). Multifractal nature of particulate matters (PMs) in Hong Kong urban air. *Science of the Total Environment*, 532, 744-751.

Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C., Crounse, J. D., Wennberg, P. O., Fisher, M. E., Wold, C. E., Campos, T. L., Adachi, K., Buseck, P. R., and Hao, W. M. (2007). Emissions from forest fires near Mexico City, *Atmospheric Chemistry and Physics* 7:5569-5584.

Zeng, Y., and Hopke, P. K. (1989). A study of the sources of acid precipitation in Ontario, Canada. *Atmospheric Environment* (1967), 23(7), 1499-1509.

Zhang, C., Ni, Z., and Ni, L. (2015). Multifractal detrended cross-correlation analysis between $PM_{2.5}$ and meteorological factors. *Physica A: Statistical Mechanics and its Applications*, 438, 114-123.

Zhao, Y., and Zhang, Y. (2008). Comparison of decision tree methods for finding active objects. *Advances in Space Research*, 41(12), 1955-1959.

Zou, H., Hastie, T., and Tibshirani, R. (2006). Sparse principal component analysis. *Journal of computational and graphical statistics*, 15(2), 265-286.

Biographical Sketch

Andreja Stojić

Affiliation: Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Serbia

Education:

- 2015 PhD – Faculty of Physics (Atomic and Molecular Physics), University of Belgrade, Serbia

- 2007 BSc – Faculty of Physics (Applied Physics and Informatics), University of Belgrade, Serbia

Research and Professional Experience:

- Environmental and data science
- Atmospheric chemistry and physics
- Environmental multiphase systems
- Air pollution spatio-temporal distribution, transport and forecast
- Environmental factors affecting human health and mortality
- Indoor and outdoor air
- Human biomonitoring
- Volatile organic compounds (VOC), persistent organic compounds (POP), aerosols and inorganic gaseous pollutants
- Proton-transfer-reaction mass spectrometry (PTR-MS)
- Environmental statistical method development
- Machine learning and statistical analysis
- R, MATLAB, Weka and Jython

Publications from the Last 3 Years:

Dmitrović, S., Perišić, M., Stojić, A., Živković, S., Boljević, J., Živković, J. N., Mišić, D. (2015). Essential oils of two Nepeta species inhibit growth and induce oxidative stress in ragweed (*Ambrosia artemisiifolia* L.) shoots in vitro. *Acta Physiologiae Plantarum,* 37(3), 1-15.

Dmitrović, S., Perišić, M., Stojić, A., Živković, S., Boljević, J., Nestorović Živković, J., Aničić, N., Ristić, M., Mišić, D. (2015). The oxidative stress in *Ambrosia artemisiifolia* L. shoots grown in vitro induced by *Nepeta rtanjensis* and *N. cataria* essential oils. *2nd International Conference on Plant Biology (21st Symposium of the Serbian Plant Physiology Society)* and COST Action FA1106 Qualityfruit Workshop, Serbian Plant Physiology Society, June 17- 20, Petnica, Serbia, pp. 159.

Mijić, Z., Perišić, I., Ilić, L., Stojić, A., Kuzmanoski, M. (2017). Air mass transport over Balkan region identified by atmospheric modeling and aerosol lidar technique, *49th International October Conference on Mining and Metallurgy*, October 18-21, Bor Lake, Serbia, pp. 69-72.

Mijić, Z., Perišić, M., Stojić, A., Kuzmanoski, M., Ilić, L. (2015). Estimation of atmospheric aerosol transport by ground based remote sensing and modeling. *XIX19th International Eco-Conference 2015*, September 23-25, Novi Sad, Serbia, pp. 375-382.

Perišić M., Maletić D., Stanišić Stojić S., Rajšić S., Stojić A. (2017). Forecasting hourly particulate matter concentrations based on the advanced multivariate methods. *International Journal of Environmental Science and Technology,* 14(5), 1047-1054.

Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z., Stojić, A. (2017). Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation. *Air Quality, Atmosphere and Health,* 10(1), 93-103.

Perišić, M., Stojić, A., Stanišić Stojić, S. (2016). Impact of remote sources on chromium concentrations in Belgrade and the related health risk. *13th International Conference on Fundamental and Applied Aspects of Physical Chemistry*, September 26-30, Belgrade, Serbia, Proceedings Vol. II, pp. 735-738.

Perišić, M., Stojić, A., Todorović, M., Mijić, Z., Šoštarić, A. (2015). Transport contribution to $PM_{2.5}$ mass concentrations in Belgrade sub urban area. *5th International WeBIOPATR Workshop and Conference Particulate Matter: Research and Management*, October 14-16, Belgrade, Serbia, pp. 99-102.

Perišić, M., Vuković, G., Mijić, Z., Šoštarić, A., Stojić, A. (2017). Relative importance of gaseous pollutants and aerosol constituents for identification of PM10 sources of variability. *6th International WeBIOPATR Workshop and Conference Particulate Matter: Research and Management*, September 6-8, Belgrade, Serbia, pp. 1-4.

Šoštarić, A., Stojić, A., Stojić, S. S., Gržetić, I. (2016). Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system. *Chemosphere,* 144, 721-727.

Šoštarić, A., Stojić, S. S., Vuković, G., Mijić, Z., Stojić, A., Gržetić, I. (2017). Rainwater capacities for BTEX scavenging from ambient air. *Atmospheric Environment,* 168, 46-54.

Stanišić Stojić, S., Ignjatović, L., Popov, S., Škrivanj, S., Đorđević, A., Stojić, A. (2016). Heavy metal accumulation in wheat and barley: The effects of soil presence and liquid manure amendment. *Plant Biosystems,* 150(1), 104- 110.

Stanišić Stojić, S., Stanišić, N., Šoštarić, A., Stojić, A., Mladenović, S. (2015). The association between short-term exposure to PM_{10} and soot and circulatory system related mortality in Belgrade area. *5th International WeBIOPATR Workshop and Conference Particulate Matter: Research and Management*, October 14-16, Belgrade, Serbia, pp. 211-216.

Stanišić Stojić, S., Stanišić, N., Šoštarić, A., Stojić, A., Mladenović, S. (2015). The association between short-term PM_{10} exposure and mortality caused by respiratory system diseases in Belgrade area. *5th International WeBIOPATR Workshop and Conference Particulate Matter: Research and Management*, October 14-16, Belgrade, Serbia, pp. 191-195.

Stanišić Stojić, S., Stanišić, N., Stojić, A. (2016). Short- and long-term effects of urban air pollution on cardiopulmonary and malignant death rates. In: *Air Pollution: Management Strategies, Environmental Impact and Health Risks,* Editor: Gerald L. Burns, Nova Science Publishers, NY, USA, ISBN: 978-1- 63485-375-0. pp. 41-68.

Stanišić Stojić, S., Stanišić, N., Stojić, A. (2016). Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area. *Environmental Health.* 15(1), 73.

Stanišić Stojić, S., Stanišić, N., Stojić, A., Džamić, V. (2016). Seasonal mortality variations of cardiovascular, respiratory and malignant diseases in the City of Belgrade. *Stanovništvo,* 54(1), 83-104.

Stanišić Stojić, S., Stanišić, N., Stojić, A., Šoštarić, A. (2016). Single and combined effects of air pollutants on circulatory and respiratory system related mortality in Belgrade, Serbia. *Journal of Toxicology and Environmental Health, Part A,* 79(1), 17-27.

Stanišić Stojić, S., Stojić, A., Perišić, M. (2016). Relationship between isoprene, related gaseous pollutants and meteorological factors in an urban area. *13th International Conference on Fundamental and Applied Aspects of Physical Chemistry*, September 26-30, Belgrade, Serbia, Vol. II, pp. 711-714.

Stojić, A., Maletić, D., Stojić, S. S., Mijić, Z., Šoštarić, A. (2015). Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. *Science of the Total Environment,* 521, 19-26.

Stojić, A., Stanišić Stojić, S. (2017). Concentration weighted boundary layer hybrid receptor model for analyzing particulate matter altitude distribution. *6th International WeBIOPATR Workshop and Conference Particulate Matter: Research and Management*, September 6-8, Belgrade, Serbia, pp. 1-4.

Stojić, A., Stanišić Stojić, S. (2017). The innovative concept of three dimensional hybrid receptor modeling. *Atmospheric Environment,* 164, 216- 223.

Stojić, A., Stanišić Stojić, S., Mijić, Z., Ilić, L., Tomašević, M., Todorović, M., Perišić, M. (2015). Comprehensive analysis of VOC emission sources in Belgrade urban area. In: *Urban and Built Environments: Sustainable Development, Health Implications and Challenges,* Editor: Alexis Cohen, Nova Science Publishers, NY, USA, ISBN: 978-1-62417-735-4, pp. 55-88.

Stojić, A., Stanišić Stojić, S., Perišić, M., Mijić, Z. (2017). Multiscale multifractal analysis of nonlinearity in particulate matter time series. *6th International WeBIOPATR Workshop and Conference Particulate Matter: Research and Management*, September 6-8, Belgrade, Serbia, pp. 1-4.

Stojić, A., Stanišić Stojić, S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., Mijić, Z. (2016). Comprehensive analysis of PM10 in

Belgrade urban area on the basis of long-term measurements. *Environmental Science and Pollution Research*, 23(11), 10722-10732.

Stojić, A., Stanišić Stojić, S., Šoštarić, A., Ilić, L., Mijić Z., Rajšić S. (2015). Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. *Environmental Science and Pollution Research*, 22(17), 13137-13152.

Stojić, A., Stojić, S. S., Mijić, Z., Šoštarić, A., Rajšić, S. (2015). Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. *Atmospheric Environment*, 106, 71-79.

Stojić, S. Stanišić, Stojić, A., Šoštarić, A., Mijić, Z., Todorović, M. (2015). Contribution of transported pollution to traffic-related VOC concentrations in Belgrade urban area. *7th Symposium Chemistry and Environmental Protection*, June 9-12, Palić, Serbia, pg. 167-168.

Todorović, M. N., Perišić, M. D., Kuzmanoski, M. M., Stojić, A. M., Šoštarić, A. I., Mijić, Z. R., Rajšić, S. F. (2015). Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area. *Journal of Environmental Science and Health*, Part A, 50(13), 1351-1359.

For books published prior to 2012, please click here (http://www.novapublishers.org/catalog/index.php).

nova science publishers (https://novapublishers.com)

$0.00 (https://novapublishers.com/cart/)

Home (https://novapublishers.com) / Shop (https://novapublishers.com/shop/) / Books (https://novapublishers.com/product-category/books/) / Social Sciences (https://novapublishers.com/product-category/books/social-sciences/) / Politics (https://novapublishers.com/product-category/books/social-sciences/politics/) / Politics of Europe (https://novapublishers.com/product-category/books/social-sciences/politics/politics-of-europe/) / Serbia: Current Issues and Challenges in the Areas of Natural Resources, Agriculture and Environment

(https://novapublishers.com/wp-content/uploads/2018/12/9781536148978-e1549988016783.jpg)

Serbia: Current Issues and Challenges in the Areas of Natural Resources, Agriculture and Environment

Igor Janev (https://novapublishers.com/writer/igor-janev/) (Editor)
Institute for Political Studies, Serbia

Series: European Political, Economic, and Security Issues (https://novapublishers.com/product-category/series/european-political-economic-and-security-issues/)

BISAC: POL058000

Binding

Hardcover X CLEAR

$230.00

Publication Date: February 2019
Status: Available
391 pages

Quantity:

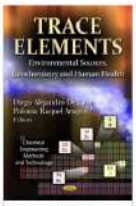
- 1 + ADD TO CART

Wishlist (/shop/serbia-current-issues-and-challenges-in-the-areas-of-natural-resources-agriculture-and-environment/?add_to_wishlist=20033)

ISBN: 978-1-53614-897-8
Categories: European Political, Economic, and Security Issues (https://novapublishers.com/product-category/series/european-political-economic-and-security-issues/), Politics of Europe (https://novapublishers.com/product-category/books/social-sciences/politics/politics-of-europe/)
Tags: 9781536150674 (https://novapublishers.com/product-tag/9781536150674/), 9781536148978 (https://novapublishers.com/product-tag/9781536148978/), politics of europe (https://novapublishers.com/product-tag/politics-of-europe/)

Details	Table of Contents	Additional Information

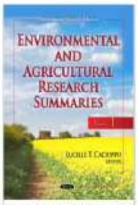
health-implications-and-challenges/)



(https://novapublishers.com/shop/trace-elements-environmental-sources-geochemistry-and-human-health/)

Trace Elements: Environmental Sources, Geochemistry and Human Health (https://novapublishers.com/shop/trace-elements-environmental-sources-geochemistry-and-human-health/)

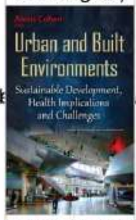
$182.00



(https://novapublishers.com/shop/environmental-and-agricultural-research-summaries-volume-1/)

Environmental and Agricultural Research Summaries. Volume 1 (https://novapublishers.com/shop/environmental-and-agricultural-research-summaries-volume-1/)

$325.00



(https://novapublishers.com/shop/urban-and-built-environments-sustainable-development-health-implications-and-challenges/)

Urban and Built Environments: Sustainable Development, Health Implications and Challenges (https://novapublishers.com/shop/urban-and-built-environments-sustainable-development-health-implications-and-challenges/)

$130.00

NOVA SCIENCE PUBLISHERS, INC.

Nova publishes a wide array of books and journals from authors around the globe, focusing on Medicine and Health, Science and Technology and the Social Sciences and Humanities.

We publish over 1,500 new titles per year by leading researchers each year, and have a network of expert authors, editors and advisors spanning the global academic community in pursuit of advanced research developments.

We invite you to browse our site to find the books or journals of particular interest to you.

Headquarters:
Nova Science Publishers, Inc.
415 Oser Avenue, Suite N
Hauppauge, NY, 11788 USA

Tel: 1-631-231-7269
Fax: 1-631-231-8175

ABOUT NOVA

About Us (https://novapublishers.com/about-us/)
Contact Us (https://novapublishers.com/contact-us/)
Catalogs (https://novapublishers.com/catalogs/)
Imprints (https://novapublishers.com/imprints/)
FAQs (https://novapublishers.com/faqs/)
Open Access (https://novapublishers.com/open-access/)
Testimonials (https://novapublishers.com/testimonials/)
Book Reviews
Our Blog (https://novapublishers.com/book-reviews/)
Newly Announced (https://novapublishers.com/blog/)
Titles (https://novapublishers.com/newly-announced-titles/)
Newly Published Titles
Proposals (https://novapublishers.com/new-titles/)
(https://novapublishers.com/proposals/)

RESOURCES FOR

Authors' Central (https://novapublishers.com/authors-central/)
Distributors and Agents (https://novapublishers.com/distributors-and-agents/)
Colleges and Universities (https://novaauthors.com/)
Librarians (https://novapublishers.com/librarians/)
Peer Review (https://novapublishers.com/peer-review-process/)
Permissions
Review (https://novapublishers.com/permissions/)
Copies (https://novapublishers.com/review-copies-and-adoptions/)
Library Copies
New Titles (https://novapublishers.com/library-copies/)
by Subject
Our (https://novapublishers.com/new-titles-by-subject/)
Authors and Editors (https://novapublishers.com/our-authors-and-editors/)
Online Books
Submit a (https://novapublishers.com/online-books/)
Book Proposal (https://novapublishers.com/submit-a-book-proposal/)
Publication Ethics and Malpractice Statement (https://novapublishers.com/publication-ethics-and-malpractice-statement/)

MY ACCOUNT

NOVA'S RECENT POSTS

Sign In or Sign Up
My Account (https://novapublishers.com/my-account/)
Track My (https://novapublishers.com/my-account/)
Order (https://novapublishers.com/track-my-order/)
My Orders (/my-account/orders/)
My Downloads (/my-account/my-downloads/)
My Support Tickets (/my-account/my-support-tickets/)
My Wishlist (https://novapublishers.com/wishlist/)

Medicine and Health Catalog Fall 2019 (https://novapublishers.com/medicine-and-health-catalog-fall-2019/)

Science and Technology Catalog Fall 2019 (https://novapublishers.com/science-and-technology-catalog-fall-2019/)

Social Sciences Fall 2019 (https://novapublishers.com/social-sciences-fall-2019/)

General Catalog Fall 2019 (https://novapublishers.com/new-books-fall-2019/)

NOVA GLOBAL

We ship internationally with the following couriers.

(/shipping-and-returns/)

NOVA A+ RATINGS

BBB Rating: A+
as of 8/18/2018
Click for Profile (https://www.bbb.org/us/ny/hauppauge/profile/publishers-book/nova-science-publishers-inc-0121-23679#sealclick)

NOVA NEWSLETTER

Sign up for the latest news from NOVA.

Yes, I would like to receive emails from Nova Science Publishers. Sign me up! (https://visitor.r20.constantcontact.com/d.jsp?llr=887t657ab&p=oi&m=1130614092667&sit=sl4ubxnmb&f=1ce061cb-2e71-4e8a-8491-7858a5c8b064)

TRUSTED & SECURED

Home (https://novapublishers.com/) Shipping and Returns (/shipping-and-returns/)
Terms of Service (/terms-of-service/) Privacy Notice (/privacy-notice/)

European Political, Economic, and Security Issues

Serbia

Current Issues and Challenges in the Areas of Natural Resources, Agriculture and Environment

Igor Janev

Editor

NOVA

Complimentary Contributor Copy

EUROPEAN POLITICAL, ECONOMIC, AND SECURITY ISSUES

SERBIA

CURRENT ISSUES AND CHALLENGES IN THE AREAS OF NATURAL RESOURCES, AGRICULTURE AND ENVIRONMENT

EUROPEAN POLITICAL, ECONOMIC, AND SECURITY ISSUES

Additional books and e-book in this series can be found on Nova's website under the Series tab.

EUROPEAN POLITICAL, ECONOMIC, AND SECURITY ISSUES

SERBIA

CURRENT ISSUES AND CHALLENGES IN THE AREAS OF NATURAL RESOURCES, AGRICULTURE AND ENVIRONMENT

IGOR JANEV
EDITOR

nova science publishers
New York

Library of Congress Cataloging-in-Publication Data

ISBN: ;9:/3/75837/289/6"*gDqqm+

Published by Nova Science Publishers, Inc. † New York

CONTENTS

PREFACE

In March 2014, Serbia was granted the candidate status for membership in the European Union. The major current challenges that Serbia faces are related to the fulfilment of the conditions for full EU membership, that include alignment of its political, legal, financial, economic, social and other systems with those in the EU. However, Serbia also faces challenges unrelated to the requirements for its accession to EU membership. Their origins are in the use of outdated production technologies, inadequate use of its natural resources and still poor infrastructure.

The present book addresses specific issues and challenges in the areas of the use of natural resources (mineral and biofuel), mining industry, sustainable agriculture and rural development, innovative agriculture production technologies accounting for the effects of climate changes. The environmental pollution issues, including their economic and societal effects, as well as the challenges of their control, are also covered in the book. Although the list of issues in the considered areas is by no means exhaustive, it nevertheless provides a good account of those that currently attract the highest interest.

In: Serbia
Editor: Igor Janev

ISBN: 978-1-53614-897-8

Chapter 9

ENVIRONMENTAL CONCERNS IN SERBIA: FOCUSING ON AIR-POLLUTION AND ITS EFFECTS ON HUMAN HEALTH

Svetlana Stanišić[1,*], Andreja Stojić[2] and Marijana Prodanović[1]
[1]Singidunum University, Belgrade, Serbia
[2]Institute of Physics Belgrade, University of Belgrade, Serbia

ABSTRACT

Given the importance of environmental issues, which are an inevitable segment of the accession negotiations between Serbia and the EU, and are already underway, this chapter aims to shed light on the major environmental problems in Serbia and their effects upon human health. Despite the progress that has been made, there are still numerous concerns regarding this matter, such as: insufficient use of renewable energy sources, waste management and disposal, detrimental anthropogenic impact and depletion of water resources, as well as the impact of greenhouse gas emissions, and, above all, increased air pollution. The lack of both environmental awareness and legal provisions has led to a rather limited use of renewable energy sources, although the country itself, with its numerous natural springs, has considerable renewable energy potential. According to data provided by the Institute of Public Health of Serbia in 2015, approx. 20.7% of drinking water samples are non-compliant, whereas one third of water samples from rural areas show faecal contamination. Air pollution can mostly be attributed to emissions from thermal power plants and the lack of facilities for the purification of exhaust gasses; the usage of lignite and low energy efficiency fuel in the energy sector; emissions from individual boiler rooms and fireboxes in households; burning agricultural land after harvest; old technologies in the industrial sector, and; the usage of old and poorly maintained vehicles. Harmful effects upon human health, resulting from the above-mentioned causes, come as no surprise; cardiovascular and malignant annual mortality rates have been among the highest in Europe over the last 15 years. Belgrade, the capital of Serbia and the second largest urban centre in the Balkans, is a significant regional traffic hub, but at the same

[*] Corresponding Author Email: sstanisic@singidunum.ac.rs.

time, is home to numerous industrial emission sources. As a result, the residents of Serbia and Belgrade are bearing the burden of all the harmful effects of air pollution that can lead to neurodevelopmental disorders, oxidative stress, anxiety, Alzheimer's and Parkinson's diseases, and many more. In conclusion, in order for Serbia to further align its practices with EU policies, a more systematic approach to environmental concerns and efficient practices are advisable.

Keywords: environment, Serbia, Belgrade, health, air pollution

INTRODUCTION

At this moment it cannot be said that Serbia is keeping pace with the European Union vis-à-vis the issues pertinent to the sphere of environmental protection successfully enough, which does represent one of the obstacles on the country's road to EU accession. However, an array of measures that require neither much effort nor costs on the part of the country could be introduced – and a closer alignment with the EU environmental *acquis* will be an unequivocal step forward. With the aim of shedding some more light on major environmental concerns Serbia is addressing at this juncture, this chapter provides an overview of both prominent environmental issues and the prospects of enhancing environmental protection practices in the country.

Serbia is one of the areas with the largest biodiversity in Europe and a country remarkable for its abundance of plant and animal species. However, air and water pollution, poor industrial waste management, tons of plastic materials being directly disposed of in uncontrolled landfills without any pre-treatment, outdated energy facilities, inefficient use of energy and an insufficient proportion of renewable energy sources within the scope of primary energy supply, still remain burning environmental issues.

While the major unresolved ecological problems are beyond the reach of scientific research currently being conducted in Serbia (Teodorović 2009), the National Strategy on the Sustainable Use of Natural Resources (Vlada Republike Srbije 2012/Government of Serbia 2012) attempted to describe the basic objectives for addressing the issues related to detrimental anthropogenic impacts on the environment, as well as the availability and depletion of natural resources in Serbia. The process of harmonising national environmental legislation and policies with the EU directives, along with the implementation of both a preventive approach to resolving environmental issues, and statutory instruments in the Republic of Serbia, are salient factors, and at the same time, major prerequisites for economic growth and development.

RENEWABLE ENERGY SOURCES

Serbia is a country endowed with extensive mineral and other renewable energy sources (RES), although the geographical distribution and structure of fossil energy resources in the country could be regarded as unfavourable: oil and gas constitute less than 1% of the country's fossil fuel energy resources, while the rest is coal, with a predominance of low-quality lignite reserves, mostly located in the Kosovo-Metohija Lignite Basin (Tešić et al. 2011). At the moment, domestic lignite, burned with the use of outdated equipment, is one of the major sources of air pollution in Serbia, and this very fact emphasises the necessity for the use of alternative, renewable and domestically available energy sources. Back in 2014, the total primary energy supply was 13.3 Mtoe, with coal contribution of at least 50%, followed by oil and its products, natural gas and RES (hydro-potential, fuel wood, pellets, briquettes, geothermal energy, etc.) (Karakosta et al. 2012). Currently, the country exploits fossil fuels for as much as 93% of its energy supply, although it has been estimated that even minor adjustments within the regulatory energy sector would lead to RES contributing to one-third of overall energy consumption. Furthermore, about 30% of Serbia's total primary energy requirements are dependent on imported energy products, which is comparable to the corresponding values in the EU. Nevertheless, a significant difference between Serbia and EU member states is noticeable within the very structure of final energy consumption, due to the large proportion of household energy consumption in Serbia; households consume more than a half of the produced electrical energy, which results in energy being distributed with significant losses.

In addition to the unfavourable structure of energy resources, accompanied by outdated technologies and inadequate maintenance of distribution network, the issues related to energy production in Serbia also include low prices, the lack of competition and excessive employment. With regard to the aforesaid, it is worth noting that the country's energy sector comprises an array of activities including examination and exploitation of energy mineral resources, efficient primary energy conversion, as well as the delivery of energy to end users. According to recent data provided by the Serbian Chamber of Commerce (2018), more than 2,500 companies, employing around 65,000 people, are registered within the energy sector. Additionally, prospective strategic partners may consider investing in the energy sector of the country to be quite risky, primarily due to political, but also commercial and financial factors (Nikolić et al. 2011).

Most countries within the EU have already endorsed initiatives to foster green technologies and RES, which could contribute to a 20% reduction in primary energy consumption by 2020; moreover, it has been estimated that there are around 3.5 million people employed in green industries in Europe. Unlike the situation in Europe, the exploitation of renewable and sustainable energy sources in Serbia is almost entirely based on large hydropower plants and non-commercial use of biomass and geothermal energy (Milenić et al. 2010). While currently insufficient to meet the growing electricity demand (Golusin et al. 2010), it was estimated that RES could potentially account for up to 50% of Serbia's primary energy production (Ivezic et al. 2013), and approximately 63% of the potential is associated with biomass exploitation. What should also be emphasised is the potential of small hydroelectric power plants and solar energy (Pekez et al. 2016), whereas, according to Tešić (2011), the percentage of geothermal energy and wind energy is less significant, comprising approx. 4 and 5% of the total RES potential.

In order to resolve the energy balance issues in a systematic manner and synchronise its practices with the requirements of ratified international contracts, Serbia has adopted some basic developmental strategies with specific goals and targets that designate the inevitability of energy resources sustainable management. Pursuant to the Energy Development Strategy of the Republic of Serbia, the main obstacles to energy efficiency improvement and the deployment of available RES include the lack of regulations for the design, construction, control and installation of devices using RES, as well as the fact that distribution system operators are not obliged to prioritise the producers using RES. At the same time, no modifications within the developmental paradigm can be implemented, due to many unresolved legal and property relations, complicated administrative procedures concerning the issuance of licenses and project approvals, and unfavourable loans, i.e., insufficiently incentive taxes, customs and other subvention systems for the use of RES. Furthermore, the lack of awareness vis-à-vis the importance of using clean technologies, both in the public and the management sectors of economic entities that operate in difficult conditions due to the economic crisis, certainly contribute to the fact that the use of RES cannot reach a high volume within a reasonable time frame.

According to Tešić et al. (2011), hydroelectricity is currently the only form of renewable energy that is accurately measured and recorded within the official Progress Report on the Implementation of the National Renewable Energy Action Plan of the Republic of Serbia (The Ministry of Mining and Energy 2016). As regards hydroelectric power, Elektroprivreda Srbije, a state-owned electric utility power company, coordinates the work of 16 hydroelectric power plants, with total power of 2,835 MW, and with Đerdap and Drina-Lim hydropower plants being the most powerful. While the current hydroelectric power production amounts to 10,200 GWh, the potential capacity is estimated at 14,200 GWh/year (Karakosta et al. 2012). For that very reason, with a view to reaching the total exploitation of natural resources, new hydroelectric power plants on the, inter alia, Drina, Lim and Velika Morava rivers are planned to be built. Unfortunately, the existing legal provisions greatly slow down the construction and use of small-scale hydroelectric power plants, since the production of electricity is defined as a matter of general interest, and due to this fact, all power plants, as potential energy producers, regardless of their capacity, are treated equally. This means that potential investors might face many bureaucracy-related obstacles they need to overcome.

With 55% of its territory being agricultural land and 25% forested territory, Serbia also has significant biomass potential. Nevertheless, the biomass market is not yet developed, and the vast majority of the produced pellets and biomass briquettes are being exported to the countries of the EU. Although the low price of coal does not motivate investors to consider biomass as an important energy source for obtaining heat energy, the production and usage of biomass residues in an unprocessed form, which is more energy-efficient and economically rational than the usage of pellets and briquettes, could be a possible means for intensifying the usage of biomass (Dodić et al. 2010).

Another eco-friendly, renewable energy resource, used for heating and electricity production in the countries of Western Europe, is biogas generated from agricultural crops, livestock residues, municipal solid waste and organic waste, under anaerobic conditions (Cvetković et al. 2015). Then again, the use of biogas as a renewable energy resource has not flourished in Serbia, primarily due to the fact that agricultural and industrial management sectors are not familiar with biogas energy production (Cvetković et al. 2014).

With a view to preserving ecological balance, as well as reducing the greenhouse effect and the use of fossil fuels, the exploitation of solar energy for the production of thermal and electrical energy is on the increase all around the globe (Pavlović et al. 2012). As cited by Pavlović et al. (2011), with an average of 277 sunny days and 2,300 sunny hours, which exceeds the European average, Serbia possesses favourable conditions for the use of solar energy. According to the same source, the average intensity of solar radiation in the Republic of Serbia ranges from 1.1 to 1.7 kWh/m^2/day in January and from 5.9 to 6.6 kWh/m^2/day in July, while the average annual solar radiation ranges from 1,200 kWh/m^2 in the northwest to 1,550 kWh/m^2 in the southeast of the country. Regrettably, despite the potential, the use of solar energy in Serbia is almost negligible at the moment.

In a similar vein, geothermal energy is another potential that should not be put aside. On the contrary, numerous thermal springs in Serbia, instead of being used merely for traditional purposes – balneology, mineral water bottling and recreation (Lund et al. 2011), could be extensively exploited. Then again, at present, both local and potential investors possess little knowledge about the possibilities of sustainable use of geothermal energy, which could replace at least 500,000 tons of the imported fossil fuels (Karakosta et al. 2012) per year, and be used for the heating of residential, public and business premises, as well as industrial applications.

Lastly, according to Zlatanović (2009), the total annual wind energy potential in Serbia is estimated at about 1,300 MWh, particularly in the region of Banat, as well as in mountain regions of the eastern and South-Eastern parts of the country (Gburčki et al. 2013). However, wind farms are regarded as a quite complex solution for renewable energy production, since they have variable effects, and it would also be necessary to invest significant efforts to balance the electrical system and sacrifice large land areas that are otherwise used for food production (Bjelić et al. 2013).

WATER POLLUTION

Vis-à-vis freshwater pollution, the largest sources of water pollution in Serbia are associated with untreated waters from industrial and municipal sewage systems, as well as from drainage water from agricultural land and landfills (Vlada Republike Srbije 2010/Government of Republic of Serbia, 2010), whereas the concentrations of heavy metals and other elements in the rivers primarily depend on location, as well as anthropogenic and agricultural activities (Dević et al. 2016).

Several hotspots of severe water pollution and sediment contamination by poly-aromatic hydrocarbons, heavy metals and polychlorinated biphenyls have been registered due to the lack of environmental legislation, lack of advanced treatment technologies and accidental spills (Teodorović 2009). The Danube River Basin receives about 80% of the wastewater from industry (Kolarević et al. 2011), and what is particularly worrying is the fact that the river water is used for the production of drinking water in a number of Serbian cities (Radović et al. 2012). The most important water polluters have proved to be the food and beverage industries, as well as the chemical industry, whereas wood, machine and textile industries are the least severe. Radović et al. (2012), in their study examining the contamination of the Danube River, have pointed out that the traces of trimethoprim, carbamazepine, metamizole metabolite and lorazepam found in the water are a result of the fact that the wastewater in Serbia is rarely treated prior to being discharged into the environment (Radović et al. 2012). In this regard, the landfills arising from the processes of mining and process industry are dominant causes of water pollution in the cities of Bor, Majdanpek, Rudnik, Veliki Majdan, Raška and Vranje. In the long history of the exploitation and processing of copper in the region of Bor, environmental pollution has been a neglected issue. In the period 1946–2000, one billion tons of coal, 650 million tons of copper, 76 million tons of Pb-Zn ore and 3.5 million tons of antimony were mined in Serbia (Draškić 2010). Unfortunately, it is common practice that, upon exploration and extraction of mineral resources, many mining sites are abandoned and contaminated mine waters freely discharged into the environment. The phenomenon was also illustrated in the study of Atanacković et al. (2013), examining the quality of mine waters from 21 abandoned mining sites.

As regards the quality of drinking water, research conducted by the Institute of Public Health of Serbia (2015) showed that out of 83,947 samples of drinking water from public supply systems in Serbia, about 20.7% were non-compliant. Among 86,427 potable water samples, 7.3% were microbiologically non-compliant, mostly for unacceptable levels of aerobic mesophilic or total coliform bacteria. In addition, the majority of non-compliant water samples found in Vojvodina, the northern region, come from groundwater that is severely burdened by the increased concentrations of humic substances, nitrates, iron, manganese and highly toxic arsenic. This is especially true in Banat, where quaternary sedimentary aquifers contain high concentrations of naturally occurring arsenic (Varsányi and Kovács 2006), while potable water samples from Central Serbia are predominantly bacteriologically contaminated. In this respect, within the Round Table on environment, air quality, water and health organised by the UN Team in Serbia (2017), it was confirmed that a significant water quality gap between rural and urban areas exists, as well as that one third of potable water samples from rural areas shows faecal contamination. The majority of drinking water sources in rural areas are insufficiently protected against septic tanks, causing a significant risk of epidemic disease outbreaks. Furthermore, the treatment of drinking water at numerous sites is inadequate, and the water supply network is worn out and in poor condition, which results in significant distribution losses.

Groundwater from a depth of 100–200 m is the major source of public water supply in the northern areas (Stauder et al. 2012). The study conducted by Jovanović et al. (2011), analysing drinking water quality in ten municipalities in Vojvodina, showed that around 63% of all water samples exceed both Serbian and European standards for arsenic drinking water concentration, due to the lack of financial and technical resources for its removal. It has been proved that long-term arsenic intake is directly associated with both malignant and non-malignant changes in nearly every organ in the body. Moreover, according to the latest reviews, there is mounting evidence of the adverse health effects of low-level arsenic exposure (Carlin et al. 2016).

Generally, it could be concluded that there is a need for water to be used in a more rational manner, as well as the need to explore hydrogeological parameters, establish groundwater reserves, and purify wastewaters with the application of strict EU standards. The National Strategy on the Sustainable Use of Natural Resources (Vlada Republike Srbije 2012/ Government of Republic of Serbia, 2012) emphasised the fact that the existing water price can cover neither the operating, maintenance and investment costs, nor the costs related to the deterioration of natural assets. Therefore, the introduction of principle of *user pays* has been suggested, with the assumption that it might lead to an increase in the awareness of both population and business management concerning the importance of water resources.

Air Pollution, Climate Change and Related Adverse Health Effects

Respirable particulate matter, ozone and inorganic gaseous pollutants comprise a global public health issue associated with a wide range of adverse effects and premature mortality

(Seinfeld and Pandis 2016). It is difficult to estimate the global consequences of air pollution, since the toxicity of particulate matter varies according to emission source. However, in 2016, about 4.2 million of deaths worldwide were associated with exposure to elevated air pollutant concentrations (WHO, 2016). In this respect, current knowledge about the issue suggests that the populations of China and India are mostly affected by emissions from residential coal and biomass combustion. In the USA, the biggest concern is related to emissions from traffic and power generation, while agricultural emissions make the largest relative contribution to the pollutant concentrations in the eastern parts of the USA, Europe, Russia and East Asia (Lelieveld et al. 2015). The WHO (2018) also emphasises the fact that up to 91% of premature death cases, resulting from air pollution, have been registered in developing countries with poor living standards – one of them being Serbia. Bearing in mind the fact that many developing countries obtain energy from energy-inefficient sources for industrial, commercial and living purposes, without the use of modern technologies designed to mitigate excessive emissions (Kurt et al. 2016), this comes as no surprise.

The reported levels of air pollutants, especially SO_2 and PM_{10} (particulate matter below 10 μm diameter), are significantly higher in Serbia than in the majority of EU member countries, with a significant number of air quality standard (AQS) exceedances, particularly in urban and suburban areas (Perišić et al. 2015, 2017a, 2017b; Todorović et al. 2015). According to Héroux et al. (2015), back in 2012, population-weighted annual mean PM_{10} concentrations in 32 countries of the European region ranged from 8.7 to 71 μg m^{-3}, with Serbia ranked fourth, behind FYR Macedonia, Turkey and Bulgaria. On a global scale, air pollutant concentrations in Serbia are higher than the values observed in wealthy countries, but similar to or lower than those registered in large industrial centres or overpopulated cities of Asia and Africa (Stojić et al. 2015a).

It has also been estimated that greenhouse gas emission in Serbia exceeds 50 tons per year. Serbia's environmental situation is a part of the European's Commission report evaluating 35 different aspects of social, economic and political life, out of which the sphere of environment has proved to be the one with most weaknesses. As of 2001, Serbia has been a member of the United Nations Framework Convention on Climate Change, whereas the Kyoto Protocol entered into force in 2008. At the same time, the country is a signatory to the Vienna Convention for the Protection of the Ozone Layer and the Montreal Protocol on Substances that Deplete the Ozone Layer (The National Strategy on the Sustainable Use of Natural Resources 2012). This implies that Serbian state authorities are not only obliged to submit national reports on a regular basis, collaborate internationally, educate and inform the public about the consequences of this phenomenon, but also to introduce clean technologies, and strengthen technical and institutional capacities for the implementation of preventive and adaptive measures.

The most polluted cities in Serbia are Belgrade, Valjevo, Užice, Bor, Smederevo, Kosjerić and Pančevo, the citizens of which are constantly exposed to high concentrations of pollutants (Stojić et al. 2015b), especially during the cold season. For instance, in Bor, an urban agglomeration with a population of 40,000, episodes of extremely high ozone concentrations occur several times a year, which result in an increased number of hospital admissions (Arsić et al. 2011).

According to the study by Stojić et al. (2015c), the number of days with average PM_{10} concentrations exceeding 50 μg m^{-3} in Belgrade ranged between 75 and 155 per year, which was higher than the AQS margin of 35 exceedances per year. The major emission sources that affect air quality in the Belgrade area include a petrochemical facility, nitric acid and fertiliser plant, oil refinery and glass industry, all located in suburbia, as well as surface lignite exploitation and thermal power stations which produce more than 50% of the electricity for the Serbian market, and all of which are just 25 to 40 km away from Belgrade. Significant emission sources are also related to both local fireboxes for heating and the district heating system, comprising 14 plants situated all throughout the city. The plants provide heating for more than 200,000 households, predominantly based on fossil fuels, such as lignite (up to 60%), natural gas and fuel oil. Furthermore, the study by Stojić et al. (2016) showed that vehicle traffic is a significant source of urban pollution throughout the whole year, due to the increasing traffic congestion, as well as the significant proportion of old and poorly-maintained vehicles.

Apart from Belgrade, other parts of Serbia likewise experience a significant burden on the environment, caused by technological obsolescence of energy systems, outdated technology and equipment in every economic sector, as well as low energy efficiency and significant reliance on sulphur-containing lignite. Over 50% of household heating in Serbia is based on solid fuels and it has to be highlighted that this is accompanied by the use of inefficient fuel combustion equipment. This leads not only to high expenses and additional electric power consumption for the purpose of reheating, but also significant emission of pollutants (Macura et al. 2014).

In terms of the effects of air pollution and climate change on human health, one should bear in mind that the population of Serbia is undergoing a process of demographic transition, characterised by old age and a high mortality rate, as well as reduced reproductive capacity and a low fertility rate. It is also worth noting that cardiovascular diseases and cancer mortality are major causes of death in the country – to be more precise, more than half of the population living in the urban areas die from cardiovascular diseases, whereas one third of deaths is due to cancer. (Stanišić Stojić et al. 2016a). What is more alarming is the fact that more than one third of deaths caused by cancer occur among the younger population (the 45-64 age group). While the detrimental impacts of air pollution on respiratory and cardiovascular diseases are well documented in the literature, there is growing evidence showing that air pollution is an important risk factor for children's health, low birth weight and preterm birth, neurodevelopmental disorders, oxidative stress, anxiety, Alzheimer's disease, and Parkinson's disease (Calderón-Garcidueñas et al. 2015, Ritz et al. 2016). Vulnerable groups include pregnant women, children, the elderly and those already suffering from chronic health preconditions, as well as people with low socio-economical backgrounds (Clark et al. 2014).

Previous research of ours investigated links between exposure to air pollutants (i.e., particulate matter, NO_2 and SO_2), and mortality caused by circulatory and respiratory diseases, on the basis of multiple-year measurements and administrative records in the Belgrade area (Stanišić Stojić et al. 2016b). There was relatively low excess risk of short-term exposure to elevated pollutant concentrations. However, the 90-day cumulative exposure was associated with the severity of health effects and with premature mortality (Stanišić Stojić et al. 2016b).

As regards the effects of climatic changes on health, individual sensitivity to high or extremely low air temperatures depends on existing chronic diseases, especially cardiovascular and respiratory, as well as adaptive capacity (Stanišić Stojić et al. 2016c). On the other hand, heavy rains and floods that have affected Serbia on several occasions over recent years create a perfect basis for the spread of infectious diseases. According to data presented by Avramović et al. (2016), the population of Belgrade is highly sensitive to both high and low temperatures, as well as flooding and drought, whereas it could be said that they are more tolerant of storms and strong winds, common phenomena in the capital of Serbia. Vulnerable groups primarily include the population with chronic diseases, but also those living in abject poverty, the homeless, as well as the elderly and persons suffering from mobility impairment.

There are several measures, the implementation of which could be effective in Serbia, and that could result in a rapid reduction of air pollutant emission. These include, but are not limited to – the introduction of environmental taxes to be levied on the import of used, polluting vehicles, electric vehicle subventions, the relocation of transit and transport from the city core, new cycling paths, and bus fleet renewal.

Other Environmental Factors Affecting Serbia

After the military operations during the conflict in the Balkans, the soil in Kosovo was enriched in depleted uranium and related fragmented species that remained buried in the ground exposed to local weather conditions. As noted by Radenković et al. (2008), almost a decade later, the depleted uranium in the contaminated study area is still 'spot' type and not widespread. In crop growing areas in the northern parts of Serbia, pesticides such as atrazine and their residues are registered in high concentrations in the soil, as well as in surface and ground waters (Gašić et al. 2002).

Owing to its unique nature, the Balkan Peninsula is characterised by a remarkable abundance of plant and animal species (Savić 2008, Bošnjaković et al. 2012). Although it is not possible to determine the exact number of living species, Serbia stands out as one of the richest areas in biodiversity in Europe, with over 1,000 plant communities, and 287 endemic Balkan species. Approximately 5.86% of Serbian territory is protected, including special nature reserves, such as Obedska pond, Ludoš Lake, Old Begej, etc. (Vlada Republike Srbije 2012/Government of Republic of Serbia, 2012). Unfortunately, illegal construction of buildings, degradation and change of land use, excessive exploitation of mineral resources and other natural resources, inadequately established communal infrastructure and functions, as well as other problems are identified in the protected areas as well.

While the quantity of solid waste generated in the urban areas might be low compared to the quantities found in industrialised countries, it does constitute a public health and environmental hazard, since the municipal management of industrial waste (waste batteries and accumulators, waste oils, polychlorinated biphenyls, pesticides, packaging, medical waste, slaughter waste, electronic waste, waste vehicles, tires etc.) remains at a low level (Prokić and Mihajlov 2012). According to the study of Vujić et al. (2010), approximately 99% of plastic materials or 269,000 tons are annually directly disposed in uncontrolled landfills, without any pre-treatment, which can be described not only as a loss of valuable resources, but also as a threat to the environment and human health.

A database of hazardous substances in the territory of Serbia was compiled in 2009, according to which there are about 600 producers conducting activities that are connected with dangerous substances. Some of the most notable include oil refineries in Pančevo and Novi Sad, chemical industries in Šabac and Barič, and thermal power plants in Obrenovac.

Environmental noise, associated with road traffic in urban areas, is widely accepted as a significant environmental factor that can result in adverse health effects and annoyance of the exposed population (Paviotti and Vogiatzis 2012). The research dealing with the cardiovascular effects of noise in Belgrade and Pančevo has shown that the systolic blood pressure is significantly higher among children from noisy residences, schools and kindergartens (Belojevic et al. 2011).

Conclusion

The present study confirms that a high level of biodiversity, and notable hydro-energy potential, along with the potentials of other natural resources, especially those in non-urbanised areas, are the major environmental advantages of Serbia. Also favourable is the fact that agricultural land in the country is not overly polluted by artificial fertilisers or pesticides, as well as the commitment that has been made by institutions with jurisdiction over environmental protection in recent years.

On the other hand, the disadvantages are mostly related to the lack of adequate strategy, currently unsustainable use of natural resources, a low level of energy efficiency within the processes of energy production, distribution and consumption, significant water and air pollution, as well as insufficient monitoring of the state of environment.

However, the most hazardous environmental threats undoubtedly include not only the lack of continuity in the activities conducted by state authorities, inefficient law enforcement, restricted budget policy, accompanied by poverty, but also the indebtedness of the country, economic stagnation, a low level of environmental awareness and continuously increasing traffic congestion.

To conclude, with a view to enhancing its EU accession prospects, Serbia should pay more attention to all the issues and practices relevant to the sphere of the environment. This would not only prove its maturity on the accession road but also its environmental awareness and care for the welfare of its citizens.

References

Arsić, Milica, Djordje Nikolić, Predrag Djordjević, Ivan Mihajlović, and Živan Živković. "Episodes of extremely high concentrations of tropospheric ozone in the urban environment in Bor-Serbia." *Atmospheric Environment* 45, no. 32 (2011): 5716-5724.

Atanacković, Nebojša, Veselin Dragišić, Jana Stojković, Petar Papić, and Vladimir Živanović. "Hydrochemical characteristics of mine waters from abandoned mining sites in Serbia and their impact on surface water quality." *Environmental Science and Pollution Research* 20, no. 11 (2013): 7615-7626.

Belojevic, Goran, Katarina Paunovic, Branko Jakovljevic, Vesna Stojanov, Jelena Ilic, Vesna Slepcevic, and Mica Saric-Tanaskovic. "Cardiovascular effects of environmental noise: research in Serbia." *Noise and Health* 13, no. 52 (2011): 217.

Bjelić, Ilija Batas, Nikola Rajaković, Boris Ćosić, and Neven Duić. "Increasing wind power penetration into the existing Serbian energy system." *Energy* 57 (2013): 30-37.

Bošnjaković, Dušica, Vladislav Ognjanov, Mirjana Ljubojević, Goran Barać, Marija Predojević, Emina Mladenović, and Jelena Čukanović. "Biodiversity of wild fruit species of Serbia." *Genetika* 44, no. 1 (2012): 81-90.

Calderón-Garcidueñas, Lilian, Randy J. Kulesza, Richard L. Doty, Amedeo D'angiulli, and Ricardo Torres-Jardón. "Megacities air pollution problems: Mexico City Metropolitan Area critical issues on the central nervous system pediatric impact." *Environmental research* 137 (2015): 157-169.

Carlin, Danielle J., Marisa F. Naujokas, Karen D. Bradham, John Cowden, Michelle Heacock, Heather F. Henry, Janice S. Lee et al. "Arsenic and environmental health: state of the science and future research opportunities." *Environmental Health Perspectives* 124, no. 7 (2016): 890.

Clark, Lara P., Dylan B. Millet, and Julian D. Marshall. "National patterns in environmental injustice and inequality: outdoor NO_2 air pollution in the United States." *PloS one* 9, no. 4 (2014): e94431.

Cvetković, Slobodan M., Tatjana S. Kaluđerović-Radoičić, Rastislav B. Kragić, and Mirjana Lj Kijevčanin. "Electricity production from biogas in Serbia-assessment of emissions reduction." *Thermal Science* 00 (2015): 189-189.

Cvetković, Slobodan, Tatjana Kaluđerović Radoičić, Bojana Vukadinović, and Mirjana Kijevčanin. "Potentials and status of biogas as energy source in the Republic of Serbia." *Renewable and Sustainable Energy Reviews* 31 (2014): 407-416.

Dević, Gordana, Sanja Sakan, and Dragana Đorđević. "Assessment of the environmental significance of nutrients and heavy metal pollution in the river network of Serbia." *Environmental Science and Pollution Research* 23, no. 1 (2016): 282-297.

Dodić, Siniša N., Vladislav N. Zekić, Vesna O. Rodić, Nedeljko Lj. Tica, Jelena M. Dodić, and Stevan D. Popov. "Situation and perspectives of waste biomass application as energy source in Serbia." *Renewable and Sustainable Energy Reviews* 14, no. 9 (2010): 3171-3177.

Draškić, D. "A Review of metallic and energetic mineral resources production in Serbia." *Mineral-resources complex of Serbia today: challenges and crossroads. Faculty of Mining and Geology, Belgrade (in Serbian). ISBN* (2010): 978-86.

Gašić, S., M. Budimir, D. Brkić, and N. Nešković. "Residues of atrazine in agricultural areas of Serbia." *Journal of the Serbian Chemical Society* 67, no. 12 (2002): 887-892.

Gburčik, Verica, Sreten Mastilović, and Željko Vučinić. "Assessment of solar and wind energy resources in Serbia." *Journal of Renewable and Sustainable Energy* 5, no. 4 (2013): 041822.

Golusin, Mirjana, Zdravko Tesic, and Aleksandar Ostojic. "The analysis of the renewable energy production sector in Serbia." *Renewable and Sustainable Energy Reviews* 14, no. 5 (2010): 1477-1483.

Héroux, Marie-Eve, H. Ross Anderson, Richard Atkinson, Bert Brunekreef, Aaron Cohen, Francesco Forastiere, Fintan Hurley et al. "Quantifying the health impacts of ambient air pollutants: recommendations of a WHO/Europe project." *International Journal of Public Health* 60, no. 5 (2015): 619-627.

Institute of Public Health of Serbia. 2015. "*Health Statistical Yearbook of Republic of Serbia.*" Accessed May 2018. http://www.batut.org.rs/download/publikacije/pub2015.pdf.

Ivezic, D., N. Djajic, and M. Zivkovic. "The potential of and barriers to renewable energy sources in Serbia." *Energy Sources, Part B: Economics, Planning, and Policy* 8, no. 2 (2013): 162-170.

Karakosta, Charikleia, Maria Flouri, Stamatia Dimopoulou, and John Psarras. "Analysis of renewable energy progress in the western Balkan countries: Bosnia–Herzegovina and Serbia." *Renewable and Sustainable Energy Reviews* 16, no. 7 (2012): 5166-5175.

Kolarević, S., Jelena Knežević-Vukčević, M. Paunović, Jelena Tomović, Z. Gačić, and Branka Vuković-Gačić. "The anthropogenic impact on water quality of the river Danube in Serbia: microbiological analysis and genotoxicity monitoring." *Archives of Biological Sciences* 63, no. 4 (2011): 1209-1217.

Kurt, Ozlem Kar, Jingjing Zhang, and Kent E. Pinkerton. "Pulmonary health effects of air pollution." *Current Opinion in Pulmonary Medicine* 22, no. 2 (2016): 138.

Lelieveld, Jos, John S. Evans, M. Fnais, Despina Giannadaki, and Andrea Pozzer. "The contribution of outdoor air pollution sources to premature mortality on a global scale." *Nature* 525, no. 7569 (2015): 367.

Lund, John W., Derek H. Freeston, and Tonya L. Boyd. "Direct utilization of geothermal energy 2010 worldwide review." *Geothermics* 40, no. 3 (2011): 159-180.

Macura, A., J. Young, and Z. Kalmar. *"Energija na drugi način: studije slučaja-Srbija.* [*Energy Other: Case Studies-Serbia*]*"* Heinrich Bőll Stiftung, Beograd (2014).

Milenić, Dejan, Petar Vasiljević, and Ana Vranješ. "Criteria for use of groundwater as renewable energy source in geothermal heat pump systems for building heating/cooling purposes." *Energy and Buildings* 42, no. 5 (2010): 649-657.

Nikolić, Dragana Makajić, Sandra Jednak, Slađana Benković, and Vladimir Poznanić. "Project finance risk evaluation of the Electric power industry of Serbia." *Energy Policy* 39, no. 10 (2011): 6168-6177.

Paviotti, Marco, and Konstantinos Vogiatzis. "On the outdoor annoyance from scooter and motorbike noise in the urban environment." *Science of the Total Environment* 430 (2012): 223-230.

Pavlović, Tomislav M., Dragana D. Milosavljević, Aleksandar R. Radivojević, and Mila A. Pavlović. "Comparison and assessment of electricity generation capacity for different types of PV solar plants of 1MW In Soko Banja, Serbia." *Thermal Science* 15, no. 3 (2011): 605-618.

Pavlović, Tomislav M., Ivana S. Radonjić, Dragana D. Milosavljević, and Lana S. Pantić. "A review of concentrating solar power plants in the world and their potential use in Serbia." *Renewable and Sustainable Energy Reviews* 16, no. 6 (2012): 3891-3902.

Pekez, J., Lj Radovanovic, E. Desnica, and M. Lambic. "The increase of exploitability of renewable energy sources." *Energy Sources, Part B: Economics, Planning, and Policy* 11, no. 1 (2016): 51-57.

Perišić, Mirjana, Andreja Stojić, Svetlana Stanišić Stojić, Andrej Šoštarić, Zoran Mijić, and Slavica Rajšić. "Estimation of required PM10 emission source reduction on the basis of a 10-year period data." *Air Quality, Atmosphere & Health* 8, no. 4 (2015): 379-389.

Perišić, Mirjana, Dimitrije Maletić, Svetlana Stanišić Stojić, Slavica Rajšić, and Andreja Stojić. "Forecasting hourly particulate matter concentrations based on the advanced multivariate methods." *International Journal of Environmental Science and Technology* 14, no. 5 (2017a): 1047-1054.

Perišić, Mirjana, Slavica Rajšić, Andrej Šoštarić, Zoran Mijić, Andreja Stojić. "Levels of PM_{10} bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation." *Air Quality, Atmosphere & Health* 10, (2017b): 93–103.

Prokić, Dunja, and Andjelka Mihajlov. "Contaminated sites. Practice of solid waste management in a developing country (Serbia)" *Environment Protection Engineering* 38, no. 1 (2012): 81-90.

Radenković, Mirjana B., Svjetlana A. Cupać, Jasminka D. Joksić, and Dragana J. Todorović. "Depleted uranium mobility and fractionation in contaminated soil (Southern Serbia)." *Environmental Science and Pollution Research* 15, no. 1 (2008): 61-67.

Radović, Tanja, Svetlana Grujić, Nikolina Dujaković, Marina Radišić, Tatjana Vasiljević, Anđelka Petković, Đulija Boreli-Zdravković, Milan Dimkić, and Mila Laušević. "Pharmaceutical residues in the Danube River Basin in Serbia–a two-year survey." *Water Science and Technology* 66, no. 3 (2012): 659-665.

Ritz, Beate, Pei-Chen Lee, Johnni Hansen, Christina Funch Lassen, Matthias Ketzel, Mette Sørensen, and Ole Raaschou-Nielsen. "Traffic-related air pollution and Parkinson's disease in Denmark: a case–control study." *Environmental Health Perspectives* 124, no. 3 (2016): 351.

Savić, Ivo R. "Diversification of the Balkan fauna: its origin, historical development and present status." *Advances in Arachnology and Developmental Biology* 12 (2008): 57-78.

Seinfeld, John H., and Spyros N. Pandis. *Atmospheric chemistry and physics: from air pollution to climate change*. John Wiley & Sons, 2016.

Serbian Chamber of Commerce. 2018. *"Struktura energetskog sektora Srbije [Structure of the energy sector of Serbia]."* Accessed April 2018. http://www.pks.rs/PrivredaSrbije.aspx?id=6&p=2&.

Stanišić Stojić, Svetlana, Nemanja Stanišić, and Andreja Stojić. "Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area." *Environmental Health* 15, no. 1 (2016b): 73.

Stanišić Stojić, Svetlana, Nemanja Stanišić, Andreja Stojić, and Vladimir Džamić. "Seasonal variations of cardiovascular, respiratory and malignant mortality in Belgrade, Serbia." *Stanovništvo*, no. 54 (2016a): 83-104.

Stanišić Stojić, Svetlana, Nemanja Stanišić, Andreja Stojić, and Andrej Šoštarić. "Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia." *Journal of Toxicology and Environmental Health, Part A* 79, no. 1 (2016c): 17-27.

Stauder, Stefan, Zoran Stevanovic, Christian Richter, Sasa Milanovic, Andra Tucovic, and Branislav Petrovic. "Evaluating bank filtration as an alternative to the current water supply from Deeper Aquifer: a case study from the Pannonian Basin, Serbia." *Water Resources Management* 26, no. 2 (2012): 581-594.

Stojić, Andreja, Svetlana Stanišić Stojić, Andrej Šoštarić, Luka Ilić, Zoran Mijić, and Slavica Rajšić. "Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling." *Environmental Science and Pollution Research* 22, no. 17 (2015b): 13137-13152.

Stojić, Andreja, Svetlana Stanišić Stojić, Irini Reljin, Milan Čabarkapa, Andrej Šoštarić, Mirjana Perišić, and Zoran Mijić. "Comprehensive analysis of PM10 in Belgrade urban area on the basis of long-term measurements." *Environmental Science and Pollution Research* 23, no. 11 (2016): 10722-10732.

Stojić, Andreja, Svetlana Stanišić Stojić, Zoran Mijić, Andrej Šoštarić, and Slavica Rajšić. "Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling." *Atmospheric Environment* 106 (2015a): 71-79.

Stojić, Andreja, Svetlana Stanišić Stojić, Zoran Mijić, Luka Ilić, Mirjana Tomašević, Marija Todorović, and Mirjana Perišić. "Comprehensive analysis of VOC emission sources in Belgrade urban area." *Urban and built environments: sustainable development, health implications and challenges. Nova Science, New York, ISBN* (2015c): 978-1.

Teodorović, Ivana. "Ecotoxicological research and related legislation in Serbia." *Environmental Science and Pollution Research* 16, no. 1 (2009): 123-129.

Tešić, Miloš, Ferenc Kiss, and Zoltan Zavargo. "Renewable energy policy in the Republic of Serbia." *Renewable and Sustainable Energy Reviews* 15, no. 1 (2011): 752-758.

The Ministry of Mining and Energy. 2016. *"Progress Report on the Implementation of the National Renewable Energy Action Plan of the Republic of Serbia."*

The Round table on environment, air quality, water and health, organized by the UN Team in Serbia. 2017. *"Serbia needs to tackle air pollution and water quality to protect health of its citizens."* Accessed April 2018. https://balkangreenenergynews.com/serbia-needs-to-tackle-air-pollution-and-water-quality-to-protect-health-of-its-citizens/

Todorović, Marija N., Mirjana D. Perišić, Maja M. Kuzmanoski, Andreja M. Stojić, Andrej I. Šoštarić, Zoran R. Mijić, and Slavica F. Rajšić. "Assessment of PM10 pollution level and required source emission reduction in Belgrade area." *Journal of Environmental Science and Health, Part A* 50, no. 13 (2015): 1351-1359.

Varsányi, Irén, and Lajos Ó. Kovács. "Arsenic, iron and organic matter in sediments and groundwater in the Pannonian Basin, Hungary." *Applied Geochemistry* 21, no. 6 (2006): 949-963.

Vlada Republike Srbije. 2010. *"Nacionalni program zaštite životne sredine."* Accessed April 2018. http://www.kombeg.org.rs/Slike/CeTranIRazvojTehnologija/2010Mart/Nacionalni%20program.pdf.

Vlada Republike Srbije. 2012. "*Nacionalna strategija održivog korišćenja prirodnih resursa."* Accessed May 2018. http://www.srbija.gov.rs/extfile/sr/170160/nacionalna_strategija_odrzivog_koriscenja_prirodnih_resursa_dobara00636_cyr.zip (In Serbian).

Vujić, Goran, Nebojša Jovičić, Milun Babić, Nemanja Stanisavljević, Bojan Batinić, and Aleksandar Pavlović. "Assessment of plastic flows and stocks in Serbia using material flow analysis." *Thermal Science* 14, no. suppl. (2010): 89-95.

WHO. 2018. *"Ambient air quality and health."* Accessed May 2018. http://www.who.int/en/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health.

Zlatanović, Miodrag. "The use of wind energy in Serbia–Natural conditions and practical policy." *Jefferson Institute, December* (2009).

Reviewed by: Gordana Vuković, gordana.vukovic@ipb.ac.rs, Institute of Physics Belgrade, University of Belgrade, 118 Pregrevica Street, 11080 Belgrade, Serbia.

BIOGRAPHICAL SKETCHES

Svetlana Stanišić, PhD

Affiliation: Singidunum University, Belgrade, Serbia

Contact: sstanisic@singidunum.ac.rs

Education: 2011. PhD – Faculty of Physical Chemistry (Environmental Physical Chemistry), University of Belgrade, Serbia; 2004. Bachelor of Dental Medicine – Faculty of Dental Medicine, University of Belgrade, Serbia

Research Topics:

- Environmental health
- Environmental monitoring and analysis
- Indoor and outdoor emission sources of air pollutants
- Effects of air pollution and extreme weather conditions on human health and mortality
- Volatile organic compounds (VOC), particulate matter and inorganic gaseous pollutants and their spatio temporal distribution
- Air pollution transport (hybrid receptor models)
- Forecasting air pollutant concentrations and their transfer to aqueous phase
- Proton-transfer-reaction mass spectrometry

Andreja Stojić, PhD

Assistant Research Professor

Affiliation: Institute of Physics Belgrade, University of Belgrade, Serbia

Education: 2015 Atomic and Molecular Physics, Faculty of Physics, University of Belgrade; 2007 Applied Physics and Informatics, Faculty of Physics, University of Belgrade

Research Topics:

- Atmospheric chemistry and physics
- Environmental multiphase systems
- Air pollution spatio-temporal distribution, transport and forecast
- Environmental factors affecting human health and mortality;
- Indoor air | Human biomonitoring
- Volatile organic compounds | Aerosols | Inorganic gaseous pollutants | Persistent organic compounds
- Meteorological factors

Marijana Prodanović, PhD

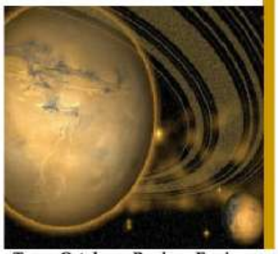
Affiliation: Singidunum University, Belgrade, Serbia

Contact: mprodanovic@singidunum.ac.rs

ACCOUNT VIEW CART

nova science publishers

Home | Books | Series | Journals | Reference | eBooks | Information
Sales | Imprints | for Authors



Top » Catalog » Books » Environment »

My Account | Cart Contents | Checkout

Quick Find

Use keywords to find the product you are looking for.
Advanced Search

What's New?

Doxycycline: Medical Uses and Effects
$82.00

Shopping Cart

0 items

Information

Shipping & Returns
Privacy Notice
Conditions of Use
Contact Us

Bestsellers

01. Weathered Crust Elution-Deposited Rare Earth Ores
02. Droughts: New Research
03. Environmental and Geographic Education for Sustainability: Cultural Contexts
04. High Diversity Forest Restoration in Degraded Areas: Methods and Projects in Brazil
05. Cleaner Technologies: Environmental Management Accounting, Investment Appraisal and Financing
06. Wetlands: Ecology, Conservation and Restoration
07. Biosocial Criminology: Challenging Environmentalism's Supremacy
08. Constructed Wetlands
09. Arid Environments and Wind Erosion
10. Cumulative Environmental Impact Assessment

Notifications

Air Pollution: Management Strategies, Environmental Impact and Health Risks

Retail Price: ~~$160.00~~

10% Online Discount
You Pay: **$144.00**

Editors: Gerald L. Burns

Click to enlarge

Book Description:

This book provides new research on the management strategies, environmental impacts and health risks of air pollution. Chapter One analyzes historical air pollution data via linear regression and the time-series technique. Chapter Two provides a spatial analysis of air pollution from road transport within urban areas and its relation to health risks. Chapter Three presents the findings on the effects of short- and long-term exposure to air pollution on death rates in Belgrade, Serbia, based on a 6-year regular pollutant monitoring and the corresponding administrative records on mortality. Chapter Four discusses how bioaerosols impact the environment, and provides methods for reducing health risks. Chapter Five reviews a case study on heavy metals air pollution of mines in the Bregalnica River Basin. (Imprint: Nova)

We've partnered with Copyright Clearance Center to make it easy for you to request permissions to reuse Nova content.
For more information, click here or click the "Get Permission" button below to link directly to this book on Copyright Clearance Center's website.

Special Focus Titles

01. Violent Communication and Bullying in Early Childhood Education
02. Cultural Considerations in Intervention with Women and Children Exposed to Intimate Partner Violence
03. Chronic Disease and Disability: The Pediatric Lung
04. Fruit and Vegetable Consumption and Health: New Research
05. Fire and the Sword: Understanding the Impact and Challenge of Organized Islamism. Volume 2

Notify me of updates to **Air Pollution: Management Strategies, Environmental Impact and Health Risks**

Tell A Friend

Tell someone you know about this product.

Table of Contents:

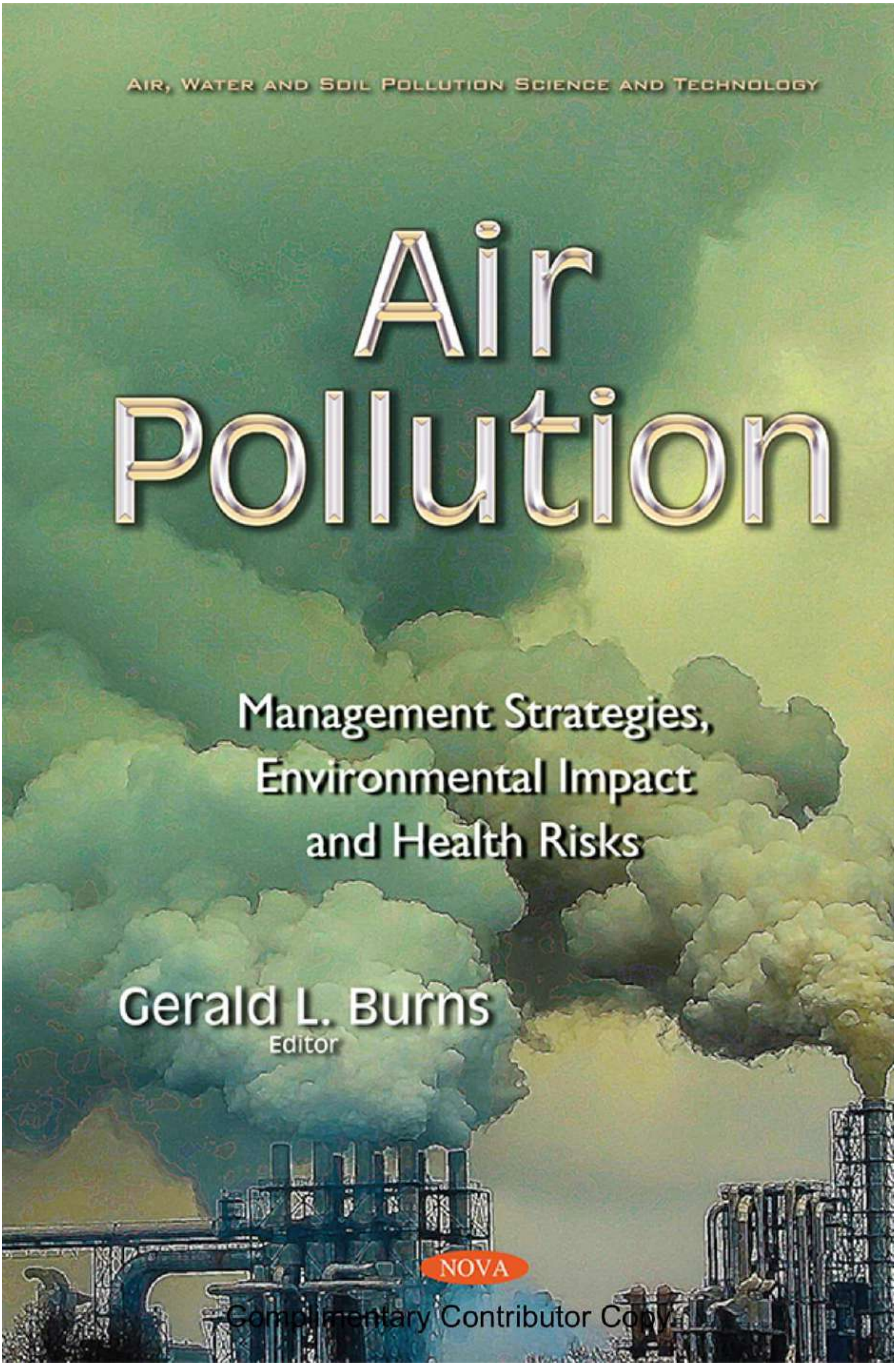
Series:
Air, Water and Soil Pollution Science and Technology
Binding: Hardcover
Pub. Date: 2016 - 3rd Quarter
Pages: 6x9 - (NBC-R)
ISBN: 978-1-63485-374-3
Status: AV

Status Code	Description
AN	Announcing

FM	Formatting
PP	Page Proofs
FP	Final Production
EP	Editorial Production
PR	At Prepress
AP	At Press
AV	Available

Add to Cart

Saturday 23 November, 2019


Air, Water and Soil Pollution Science and Technology
Air Pollution
Management Strategies, Environmental Impact and Health Risks
Gerald L. Burns
Editor
NOVA
Complimentary Contributor Copy

AIR, WATER AND SOIL POLLUTION SCIENCE AND TECHNOLOGY

AIR POLLUTION

MANAGEMENT STRATEGIES, ENVIRONMENTAL IMPACT AND HEALTH RISKS

AIR, WATER AND SOIL POLLUTION SCIENCE AND TECHNOLOGY

Additional books in this series can be found on Nova's website under the Series tab.

Additional e-books in this series can be found on Nova's website under the eBooks tab.

AIR, WATER AND SOIL POLLUTION SCIENCE AND TECHNOLOGY

AIR POLLUTION

MANAGEMENT STRATEGIES, ENVIRONMENTAL IMPACT AND HEALTH RISKS

GERALD L. BURNS
EDITOR

nova publishers
New York

Library of Congress Cataloging-in-Publication Data

ISBN: ;9:/3/856:7/597/2 (eBook)

Published by Nova Science Publishers, Inc. † New York

CONTENTS

PREFACE

This book provides new research on the management strategies, environmental impacts and health risks of air pollution. Chapter One analyzes historical air pollution data via linear regression and the time-series technique. Chapter Two provides a spatial analysis of air pollution from road transport within urban areas and its relation to health risks. Chapter Three presents the findings on the effects of short- and long-term exposure to air pollution on death rates in Belgrade, Serbia, based on a 6-year regular pollutant monitoring and the corresponding administrative records on mortality. Chapter Four discusses how bioaerosols impact the environment, and provides methods for reducing health risks. Chapter Five reviews a case study on heavy metals air pollution of mines in the Bregalnica River Basin.

Chapter 1 – Pollution data in eleven categories obtained over the 1980 – 1989 period in four highly industrialized nations (USA, UK, West Germany, The Netherlands)are examined in terms of linear regression and the time-series technique, treating time and annual population size, respectively, as explanatory variables, and the levels of polluting substances as the dependent variable. The pollution level versus time relationship can be adequately described by simple univariate linear regressions in slightly more than one half of the pollutant categories presented in the ten – year compilation of data, with acceptably high coefficients of determination (R^2). Removal of autocorrelation between adjacent residuals, based on the Durbin – Watson statistic and the concept of the lag-one autocorrelation coefficient, is illustrated in the case of two specific kinds of emission. The results underline the importance of a fully quantitative understanding of all ecologically meaningful explanatory variables in order to fully utilize the potential of the analysis in combating air pollution via preventive measures based on pertinent numerical cause – effect relationships.

Chapter 2 – This study extends the traditional research in air pollution and health risks by using spatial and temporal methods in geographical information system (GIS). The spatial interpolations are produced from point samples, which are represented by sites of monitoring stations, and by randomly generated sites with local estimates of urban air pollution by geographically weighted regression (GWR). The explanatory variables for estimates of urban air pollution, NO_2 and PM_{10}, are represented by the elevation, the distance to the nearest major road, and the ratio of the built-up area in the defined circles. The dependent variables contain annual average concentration of NO_2 and PM_{10} in Prague. The attached residuals and multiple R-squared indicate that each GWR model can partially explain the variation of concentrations in relation to the selected exploratory variables. Studying the relations between urban air pollution, such as NO_2 and PM_{10}, and lung cancer incidence are provided separately for ten districts of the city, independently for males and females. In spite of that the spatial analysis of urban air pollution on a reduced number of monitoring stations and limited available spatial datasets can be beneficial for decision-making processes, relations of the lung cancer incidence to urban air pollution indicate weak or even non-existed associations. The available datasets about the lung cancer incidence are mostly based on aggregated information for each district in the city. Thus, there is a little evidence about original sites of the lung cancer incidence, which documents many studies that are focused on assessing the public health impacts by urban air pollution. Presented spatial and temporal analysis of air pollution from road-transport within the urban areas represents a new way of research that is based on integration of urban air pollution monitoring, understanding potential human exposure, and advanced modeling tools implemented in ArcGIS. It can be used for risk assessment, decision-making processes and urban planning. It is anticipated that the use of advanced methods of exploratory spatial data analysis will bring new progress into the studied processes and new insights for urban planning and health protection.

Chapter 3 – Substantial scientific evidence suggests that exposure to even modest levels of air pollutants is associated with premature mortality. While relative contributions of pollutant species remain a matter of scientific debate, the current findings converge on the statement that short-term exposure over a period of few hours to weeks can aggravate the pre-existing health conditions, sometimes leading to a fatal outcome, whereas longer-term exposure reduces life expectancy by a few years. Susceptible groups including children and the elderly are at greater risk, as well as the people living in overpopulated low-income regions, due to being exposed to pollutant concentrations up to twenty times higher than those commonly observed in modern countries. The goal of this study is to present the findings on the effects of short- and long-term exposure to air pollution on death rates in Belgrade area (Serbia), based on the 6-year (2009-2014) regular pollutant monitoring and the corresponding administrative records on mortality. To that end, a quasi-Poisson regression model was combined with distributed lag non-linear model to examine this association after controlling for confounding variables such as temperature, seasonal trends and day of the week. The study discusses relative rates, expressed as % increase in circulatory, respiratory and malignant mortality per unit increase in daily average pollutant concentrations, together with the observed age- and gender-specific effects. According to the results, short-term exposure to elevated concentrations of PM_{10}, SO_2 and NO_2 is associated with relatively small mortality risk, whereas exposure during the last year appears to be more significant, particularly for circulatory mortality. Apart from the elderly group, severity of health effects is also observed for the male population under the age of 65. According to multiple economic indicators, Serbia is considered a developing country, even though its demographic trends are complementary with or less favourable than those typically anticipated in Western developed countries, notably due to high circulatory and malignant death rates. Poor air quality in Belgrade area is identified as an important environmental risk factor with pollutant concentrations exceeding the values observed in most European metropolis.

Chapter 4 – Bioaerosols (biological particles derived from viruses, bacteria, fungi, plants and animals) are ubiquitous in the air. This organic dust is considered to be hazardous to human health. Acute and chronic diseases are health risks associated with viable and non-viable airborne biological particles because they can be toxic, allergenic and infectious. With increasing awareness of the environmental impact of bioaerosols, which can spread easily with air currents over long distances, the development of efficient air filtration system is important for preventing health risks. Air filtration system is the most used method for controlling air pollution with bioaerosols but it is not always efficient because microbes can survive and proliferate on the surface of filters and be potential sources of diseases and allergies. Lately, many researchers have focused on improving indoor air quality by removing and inactivating biological agents. Successful methods for control and inactivation of bioaerosols include filters coated with antimicrobial nanoparticles from different plants, such as *Sophora flavescens, Euscapis japonica* or *Melaleuca* *alternifolia.* Filters coated with plant extracts have filtration efficiency from 77 to 99%, while the range for antimicrobial activity for these filters is from 14 to 100%. These natural products are considered ecological, environmentally friendly, cost–effective, less toxic (compared with inorganic nanomaterials) and efficient material for antimicrobial filter media development and can be easily applied to conventional air–conditioning systems.

Chapter 5 – Application of several moss species and attic dust for monitoring of anthropogenic impact on heavy metals air pollution in Bregalnica River Basin, Republic of Macedonia, was studied. Moss samples were reviewed for their potential to reflect heavy metals air pollution. The attention was focused on their quantification ability, underlying the metal accumulation within moss plant tissue and attic dust "historical archiving." Potential "hot spots" were selected in areas of copper mine (Bučim mine) and lead and zinc mines (Zletovo mine and Sasa mine) as main metal pollution sources in the Eastern part of the Republic of Macedonia. Continuously, dust distribution from ore and flotation tailings occurs. This results with air-introduction and deposition of higher contents of certain metals. Several moss species (*Hypnum cupressiforme*, *Homalothecium lutescens* and *Scleropodium purum*) were used as plant sampling media. Determination of chemical elements was conducted by using both instrumental techniques: atomic emission spectrometry with inductively coupled plasma (ICP-AES) and mass spectrometry with inductively coupled plasma (ICP-MS). Combination of multivariate techniques (PCA, FA and CA) was applied for data processing and identification of elements association with lithogenic or anthropogenic origin. Spatial distribution maps were constructed for determination and localizing of narrower areas with higher contents of certain anthropogenic elements. In this way influences of selected human activities in local (small scale) air pollution can be determined. Summarized data reveal real quantification of the elements distribution not only in order determination of hazardously elements distribution, but also present complete characterization for elements deposition in mines environrons.

In: Air Pollution
Editor: Gerald L. Burns
ISBN: 978-1-63485-374-3

Chapter 3

SHORT- AND LONG-TERM EFFECTS OF URBAN AIR POLLUTION ON CARDIOPULMONARY AND MALIGNANT DEATH RATES

Svetlana Stanišić Stojić[1,2*], Nemanja Stanišić[2] and Andreja Stojić[3]
[1]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia
[2]Singidunum University, Belgrade, Serbia
[3]Institute of Physics Belgrade, University of Belgrade, Belgrade, Serbia

ABSTRACT

Substantial scientific evidence suggests that exposure to even modest levels of air pollutants is associated with premature mortality. While relative contributions of pollutant species remain a matter of scientific debate, the current findings converge on the statement that short-term exposure over a period of few hours to weeks can aggravate the pre-existing health conditions, sometimes leading to a fatal outcome, whereas longer-term exposure reduces life expectancy by a few years. Susceptible groups including children and the elderly are at greater risk, as well as the people living in overpopulated low-income regions, due to being exposed to pollutant concentrations up to twenty times higher than those commonly observed in modern countries.

* Corresponding author: Email: sstanisic@singidunum.ac.rs.

The goal of this study is to present the findings on the effects of short- and long-term exposure to air pollution on death rates in Belgrade area (Serbia), based on the 6-year (2009-2014) regular pollutant monitoring and the corresponding administrative records on mortality. To that end, a quasi-Poisson regression model was combined with distributed lag non-linear model to examine this association after controlling for confounding variables such as temperature, seasonal trends and day of the week. The study discusses relative rates, expressed as % increase in circulatory, respiratory and malignant mortality per unit increase in daily average pollutant concentrations, together with the observed age- and gender-specific effects. According to the results, short-term exposure to elevated concentrations of PM_{10}, SO_2 and NO_2 is associated with relatively small mortality risk, whereas exposure during the last year appears to be more significant, particularly for circulatory mortality. Apart from the elderly group, severity of health effects is also observed for the male population under the age of 65. According to multiple economic indicators, Serbia is considered a developing country, even though its demographic trends are complementary with or less favourable than those typically anticipated in Western developed countries, notably due to high circulatory and malignant death rates. Poor air quality in Belgrade area is identified as an important environmental risk factor with pollutant concentrations exceeding the values observed in most European metropolis.

Keywords: air pollution, mortality, health effects, exposure

INTRODUCTION

The findings on toxicity and carcinogenicity of air pollutant species and their mixtures are consistent in epidemiological research, studies in experimental animals and studies of biogenic mechanisms (Jerrett et al., 2013). Ever since pre-industrial era (1860) to present days, significant changes in emissions, climate and methane concentrations have altered the atmospheric composition and led to an increase of surface ozone and $PM_{2.5}$ concentrations by 30 and 8 $\mu g\ m^{-3}$, respectively (Fang et al., 2013). The evidence from Greenland ice cores and Alpine glaciers confirmed the significant increase of sulfate and carbonaceous aerosol concentrations over the last 150 years (Fischer et al., 1998).

Current estimates of the global health burden indicate that between 3.3 and 3.7 million cardiopulmonary deaths per year can be associated with exposure to anthropogenic $PM_{2.5}$, with most cases observed in China and India

(Anenberg et al., 2010; Lelieveld et al., 2015). Lung cancer and ischemic heart disease are the two most represented causes, contributing with 12.8% and 9.4% to global premature mortality associated with $PM_{2.5}$, respectively (Evans et al., 2013). In addition to particulate matter, adverse global health effects of ozone were also estimated using satellite-based observations and extensive surface measurements. Brauer et al., (2012) concluded that between 50,000 and 270,000 premature respiratory deaths were associated globally and annually with exposure to anthropogenic ozone, whereas the findings of Silva et al., (2013) suggested that ozone-related respiratory mortality might be even higher, with up to 470,000 deaths per year. Notwithstanding the fact that the levels of particulate matter and inorganic gaseous oxides in developed countries have declined significantly over the last few decades, reducing ozone levels might be a challenge, as it is generated through a complex set of atmospheric photochemical reactions of primary pollutants.

Major emission sources in modern countries include fossil fuel combustion for industrial needs, traffic and power generation, whereas in developing countries of Asia, residential biomass burning for heating and cooking is still a matter of concern. The observed daily $PM_{2.5}$ concentrations in mega-cities of Asia, ranging from 100 to 300 µg m^{-3}, are up to twenty times higher than those commonly observed in developed countries (Shah et al., 2013). For instance, the annual average $PM_{2.5}$ concentrations of 75 µg m^{-3} in the capital city of Mongolia are mostly driven by extremely high winter concentrations (250 µg m^{-3}) due to coal and wood combustion in low-income traditional housing areas. These emissions are estimated to cause 29% of cardiopulmonary and 40% of lung cancer mortality in Ulaanbaatar, corresponding to 10% of total non-accidental death rates (Allen et al., 2013). Unfortunately, with the exception of China, the air pollution studies in Asia and developing countries worldwide are relatively scarce due to poor environmental monitoring and a paucity of mortality surveillance data. In Europe, Russia and eastern parts of the USA and Asia, agricultural sources significantly contribute to air quality deterioration (Lelieveld et al., 2015). In addition to anthropogenic pollution prevailing in urban areas, the impact of natural particles, such as mineral dust, on premature mortality should not be underestimated. According to Giannadaki et al., (2014), desert dust is associated with up to 50% of cardiopulmonary deaths in the population from twenty countries across the so-called 'dust belt' from North Africa to East Asia.

Brauer et al., (2012) reported that almost 90% of the world's population in 2005 lived in the areas with the annual mean $PM_{2.5}$ concentrations exceeding

10 μg m^{-3}, as recommended by the WHO Air Quality Guidelines. Thereby, children under the age of 5 living in low-income communities are considered the most susceptible group due to their poor nutritional status and the fact that their families lack the knowledge and resources necessary to avoid exposure. China was among the first developing countries to adopt large scale regulations on power plant emissions, which resulted in 20% reduction of infant death rates (Tanaka, 2015). The emissions related to biomass combustion also threaten public health in rural areas of developed countries. Noonan et al., (2011) reported that the single wood stove intervention in a rural area of the USA resulted in 27.6% lower $PM_{2.5}$ winter concentrations and the corresponding reduction in respiratory infections among school children. The findings of Heinrich et al., (2002) also suggested that the decreasing prevalence of non-allergic respiratory disorders in children was associated with a decline in total suspended particles and SO_2 in the eastern part of Germany after unification.

According to some projections, the number of deaths caused by exposure to air pollution could double by 2050. The fact that the exposure dose-response relationship was found to be linear down to $PM_{2.5}$ concentrations of 8 μg m^{-3} (Lepeule et al., 2012) and that modest enhancements in air quality would have health benefits, has prompted further rethinking of the current air quality guidelines. In terms of economic costs, reduction of 3.9 μg m^{-3} in mean $PM_{2.5}$ concentrations would prevent almost 8,000 cardiovascular hospitalizations and save one third of billion US dollars annually (Shah et al., 2013). Unfortunately, there is still a prevailing concern in developed countries that the financial expenditures resulting from air pollution abatement measures might outweigh the potential health benefits.

In this study, we present the findings regarding the association between PM_{10}, NO_2 and SO_2 exposure and mortality caused by circulatory, respiratory and malignant diseases in Belgrade, Serbia, based on 2009-2014 dataset. Besides the fact that PM_{10} concentrations in Belgrade area are higher than concentration measurements in other European cities (Perišić et al., 2014; Stojić et al., 2015a; Stojić et al., 2015b; Stojić et al., 2015c; Todorović et al., 2015; Šoštarić et al., 2015), recent studies have suggested that suspended particles contain high concentrations of pollutant matter, arsenic and benzo(a)pyrene, resulting from fossil-fuel combustion during winter months (Stojić et al., 2016). In order to examine both short- and long-term effects of air pollution, we used the moving average pollutant concentrations during two days (lag 01) and a year (lag Y) preceding death. The effects of air pollution on mortality follow a complex pattern across different geographic areas, depending on the population health characteristics and their technological and economic capacity to adapt, as well as due to differences in exposure level, particle composition and methodological approach. The studies that have limited their analyses to acute health effects experienced within few days upon exposure mainly emphasize the increase in death counts and hospitalizations during and immediately after pollution episodes. However, the question remains as to whether there is a critical exposure time window that is primarily responsible for the increase in death rates. The overall evidence suggests that the mortality estimates increase in magnitude as the follow-up period increases (Goodman et al., 2004).

Materials and Methods

Mortality statistics, including total (cause-of-death coding A00-R99), circulatory (I00-I99), respiratory (J00-J99) and malignant (C00-D48) mortality, were retrieved from the Institute of Public Health Belgrade (IPHB), for the period from 2009-2014. The causes of death were coded according to the International Classification of Diseases, 10th Revision, ICD-10, excluding the deaths attributed to injuries, poisoning and external causes from the overall death rate. The concentrations of PM_{10}, NO_2 and SO_2 were obtained from 7, 21 and 22 monitoring stations within the IPHB network, respectively, uniformly distributed throughout the city area. Measurements were conducted at automatic stations using beta-ray attenuation samplers (Thermo FH 62 I-R) for PM_{10} and referent sampling devices, Horiba APNA 360 and APSA 360 analyzers, for NO_2 and SO_2, respectively. At semi-automatic measuring stations, PM_{10} concentrations were determined using referent Sven Leckel samplers, whereas determination of NO_2 and SO_2 concentrations was performed based on ISO 6768:1998 (Modified Griess-Saltzman method) and ISO 6767:1990 (tetrachloromercurate (TCM)/pararosaniline method) standards, respectively. Temperature data were obtained from the Global Data Assimilation System with the spatial resolution of 1 degree.

As single-day models were reported to underestimate the cumulative effects of air pollutants on mortality (Meng et al., 2012), we specified a model which, besides temperature and other factors affecting mortality such as season, temperature and day of the week, included three categories of air pollutants: PM_{10}, NO_2 and SO_2.

The effect of temperature is shown to be both delayed in time and shifted by the so-called 'harvesting effect' – a temporal advance in deaths that would occur later in time in the absence of exposure to heat or cold (Ye et al., 2012). The harvesting effect is typically followed by a period of reduced mortality. In order to simultaneously capture the non-linear exposure-response dependencies and delayed temperature effects, we used distributed lag non-linear models (DLNM). This methodology is based on the definition of 'cross-basis,' a bi-dimensional space of functions that describes simultaneously the shape of the relationship along both the space of the predictor and the lag dimension of its occurrence (Gasparrini et al., 2010). The implementation of DLNM modeling framework (Gasparrini, 2011) is available in the statistical environment R (R Core Team, 2014). Based on the methodology presented in Gasparrini et al., (2015), we modeled the exposure-response curve with a quadratic B-spline with three internal knots placed at the 10th, 75th and 90th percentiles of the observed local temperature distribution and the lag-response curve (maximum lag up to 21 day) with a natural cubic B-spline with an intercept and three internal knots placed at equally-spaced values in the log scale. In order to control for seasonal and long-term effects, we included a natural cubic B-spline of time with 8 degrees of freedom per year. The model also included an indicator of day of the week. Finally, the effects of pollutants are included as simple moving average of their observed concentration level in 10 μg m³ over 2 (commonly referred in the literature as lag 01) and 366 (lag Y) consecutive days ending on, and inclusive of day *t*.

Accordingly, the quasi-Poisson[1] regression model is specified as follows:

$$E(Yt) = exp\{\alpha + \beta T_{t,l} + NS(time,df) + \lambda DOW_t + PM_{10t,01} + PM_{10t,Y} + O_{2t,01} + NO_{2t,Y} + SO_{2t,01} + SO_{2t,Y}\}$$

where Yt is a daily death count on day t; α is the intercept; $T_{t,l}$ is a matrix of variables obtained by the transformation of temperature, β is a vector of coefficients for $T_{t,l}$ and l is the lag day; *NS(time, df)* is the natural cubic spline of time; *DOW* and λ are dummy variables representing day of the week and the corresponding vector of coefficients, respectively.

Weekly, seasonal and annual dynamics, and trend (Pretty, 2015) of the mortality and air pollutant concentrations were analyzed using the Openair (Carslaw and Ropkins, 2012) package within the statistical software environment R (Team, 2012).

[1] Quasi-Poisson is used in order to compensate for overdispersion (i.e., residual deviance is larger than residual degrees of freedom).

RESULTS AND DISCUSSION

Seasonal Variations in Mortality and Air Pollution

During the period from 2009-2014, there were 113,430 deaths registered in Belgrade area, of which 60,407 cases (i.e., 53.25%) were attributed to circulatory diseases, 4,649 cases (i.e., 4.01%) were associated with respiratory failure, while 31,191 cases (i.e., 27.50%) were caused by malignant diseases. Annual circulatory mortality in Belgrade area over the last 15 years has been ranging between 635 to 677 per 100,000 inhabitants (Statistical Office of the Republic of Serbia, 2015). When compared with the death rates observed during the same period in Europe (Detailed Mortality Database, 2015), these values are among the highest ranking. Annual death rates caused by malignant diseases have also been extremely high over the past 15 years, ranging from 260 to 323 cases per 100,000 inhabitants. On the other hand, annual respiratory mortality, ranging from 28 to 60 cases per 100,000 inhabitants, can be considered normal in relation to the figures observed in other European countries. As regards deseasonalised trend, circulatory mortality shows stagnation (0.36%) during the observed period, whereas malignant (1.94%) and respiratory mortality (6.06%) record moderate, i.e., significant growth rates (Figure 1).

Mortality caused by circulatory and respiratory diseases exhibits a strong seasonal pattern, with highest death rates registered in February and March and minimum occurrence during summer months (Figure 2). Whereas mortality rates of the elderly population also indicate extreme seasonal variations, mortality rates of the population under the age of 65 exhibit different distribution patterns throughout the year, probably due to the effects of numerous other factors apart from air pollution. Likewise, mortality caused by malignant diseases exhibits no seasonal variations, with more than one third of deaths due to malignant diseases observed among the population younger than 65 years, which indicates poor health of Belgrade population. Unlike that, the data obtained from the Cancer Research Center in the UK for the period from 2010-2012 showed that up to 78% of such diseases were observed in the population aged 65 years and over. The health status of the population in Serbia correlates with the anticipated life expectancy. According to the Statistical Office of the Republic of Serbia (2015), it was estimated at 74.3 years, which is considerably lower than the EU-28 average value of 80.6 years (Mortality and life expectancy statistics, 2013).

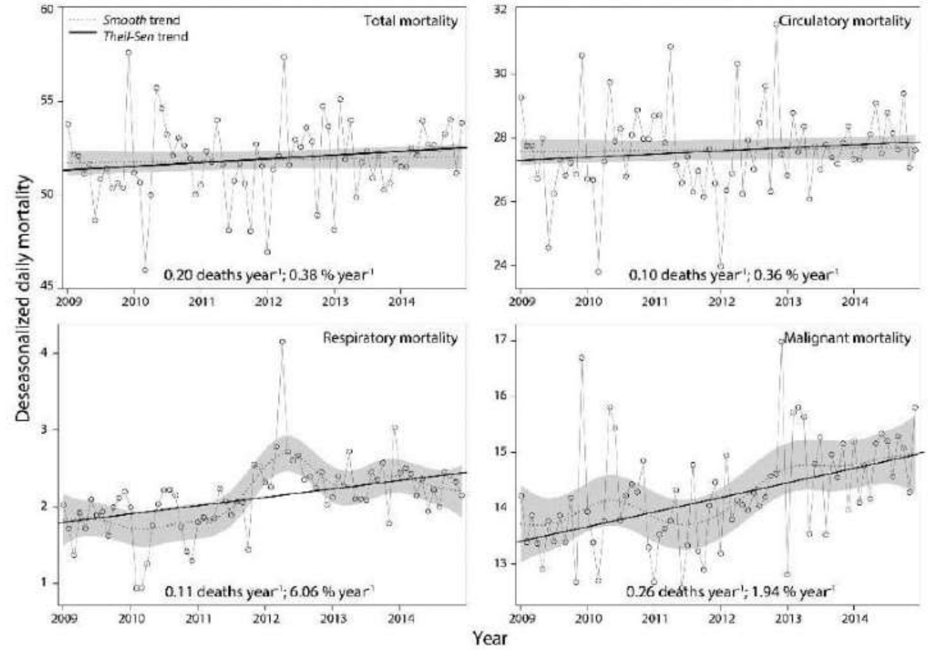


Figure 1. Mortality trend analysis in the period from 2009 to 2014.

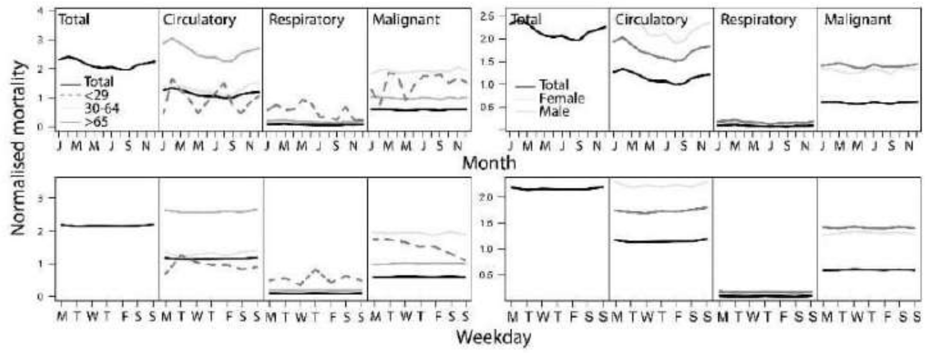


Figure 2. Mortality seasonal and weekday variations by age (left) and gender (right) in the period from 2009 to 2014.

The statistics showed that circulatory, respiratory and malignant mortality differ considerably in terms of gender structure: mortality caused by respiratory and malignant diseases was more common in male population, while circulatory mortality was prevalent in female population (Table 1).

Table 1. Mortality statistics in the period from 2009 to 2014

Mortality	Gender	Age	Mean	Sum	Min.	Max.
Total			51.84	113430	25	83
Circulatory	Total		27.61	60407	10	49
	Female	Total	3.75	32847	0	31
		<29	0.02	42	0	1
		30-64	1.02	2227	0	6
		>65	13.97	30572	3	31
		Unknown	0.00	6	0	1
	Male	Total	3.15	27560	0	22
		<29	0.02	54	0	1
		30-64	2.27	4975	0	8
		>65	10.29	22517	0	22
		Unknown	0.01	14	0	1
Respiratory	Total		2.12	4649	0	9
	Female	Total	0.23	1979	0	5
		<29	0.01	26	0	1
		30-64	0.14	301	0	3
		>65	0.75	1651	0	5
		Unknown	0.00	1	0	1
	Male	Total	0.31	2670	0	6
		<29	0.01	28	0	1
		30-64	0.21	459	0	3
		>65	1.00	2180	0	6
		Unknown	0.00	3	0	1
Malignant	Total		14.26	31191	3	29
	Female	Total	2.19	14395	0	14
		<29	0.03	64	0	2
		30-64	2.23	4886	0	9
		>65	4.32	9445	0	14
	Male	Total	2.56	16796	0	14
		<29	0.04	89	0	2
		30-64	2.61	5720	0	11
		>65	5.02	10987	0	14

Zhang et al., (2012) elaborate on the higher risk for mortality in women hospitalized with an acute myocardial infarction versus their male counterparts, relying mainly on the fact that women suffer from greater number of chronic diseases at the time of a heart attack, thus making them more susceptible to fatal outcome. Namely, previous research has shown that women were more prone to non-fatal chronic diseases throughout life, as well as to gastrointestinal and respiratory infections. Unlike them, men were generally healthier throughout life. However, their health deteriorates with age, especially vital organs (coronary and malignant diseases, emphysema, cirrhosis of the liver and chronic kidney disease), thus supporting the statement that life expectancy in men is few years shorter (Ross, Masters & Hummer, 2012). However, Salam et al., (2013) showed that, after adjusting for age, diabetes mellitus, and acute coronary syndrome, female gender remained a factor independently related to increased in-hospital mortality, thus underpinning the claim that there are other factors that could contribute significantly to greater mortality rates caused by cardiovascular diseases in women, besides age and chronic diseases.

The daily mean concentrations of PM_{10}, SO_2 and NO_2 for the entire period were 48.31, 32.68 and 15.52 µg m^{-3}, respectively. The levels of PM_{10} and SO_2 exhibited a clear seasonal pattern, with highest concentrations observed during the cold season (Figures 3 and 4). The emissions of SO_2 are predominantly associated with sulfur-rich solid fuel-burning in central heating plants and industrial facilities, whereas PM_{10} originates from a number of sources and processes, including atmospheric photochemical reactions.

As shown in Table 2, the moving average PM_{10} and SO_2 concentrations exhibit a high correlation, thus suggesting that their variations, particularly those long-term, are driven by the same anthropogenic and meteorological factors. Conversely, NO_2 concentrations exhibited pronounced weekly variations, whereas the average NO_2 values for the cold and warm season were almost identical (Stanišić Stojić et al., 2015). This could be partly explained by the fact that NO_2 levels are considered an indicator of traffic-related emissions that could be observed throughout the year.

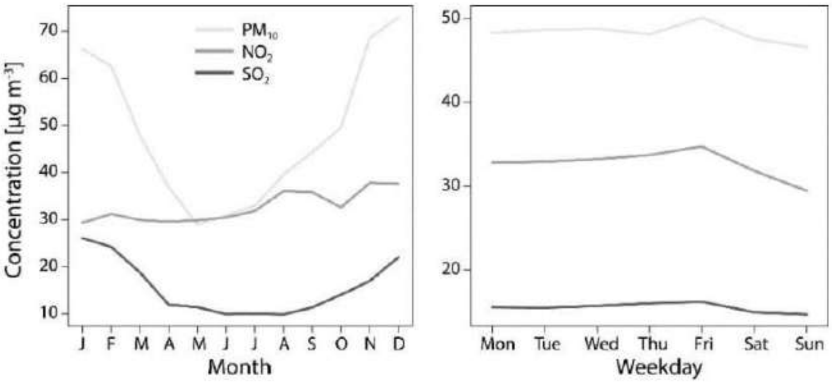


Figure 3. Pollutant seasonal and weekday variations.

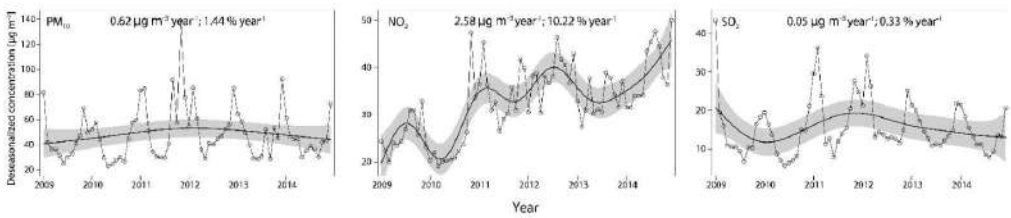


Figure 4. Pollutant trend analysis.

Complimentary Contributor Copy

As can be seen in Table 3, the number of days with average PM_{10} concentrations exceeding 50 µg m^{-3} was in the range from 75 to 155 per year, which is considerably higher than the margin of tolerance set by the Air Quality Standard (35 exceedances per year). However, the mean annual NO_2 concentrations did not exceed the target value of 40 µg m^{-3}, nor any mean daily SO_2 concentrations higher than the recommended limit of 135 µg m^{-3} could be observed.

Table 2. Correlations between pollutant species

	PM_{10} 01	PM_{10} Y	NO_2 01	NO_2 Y	SO_2 01	SO_2 Y
PM_{10} 01	1	0.15	0.51	0.08	0.71	0.18
PM_{10} Y		1	0.26	0.64	0.18	0.96
NO_2 01			1	0.37	0.43	0.24
NO_2 Y				1	0.05	0.68
SO_2 01					1	0.21
SO_2 Y						1

Table 3. Number of days with PM_{10} concentration exceeding 50 µg m^{-3} and mean annual concentrations of PM_{10}, NO_2 and SO_2 [µg m^{-3}] in the period from 2009 to 2014

Year	Number of days with PM_{10} exceedances	PM_{10}	NO_2	SO_2
2009	81	43.63	25.78	15.22
2010	75	39.73	24.69	11.93
2011	155	62.37	34.64	19.59
2012	150	52.66	38.33	17.71
2013	116	47.80	33.44	15.06
2014	90	43.66	39.22	13.60

Short-Term and Long-Term Effects of Air Pollution on Mortality

The data examined reveals that the average daily number of circulatory deaths was higher during the 15 days with highest pollutant concentrations (Table 4). Furthermore, the increase in total mortality was mostly driven by the increase in circulatory deaths, as the most prevailing type. The effects of pollution on respiratory and malignant mortality are not quite clear, probably due to long evolution and variety of malignant diseases, i.e., relatively small number of observations related to respiratory diseases and related mortality.

Table 4. Average daily number of deaths over the entire period (2009-2014) and average daily number of deaths during 15 days with highest pollutant concentrations

	Entire period	PM_{10}	NO_2	SO_2
Total	51.8	53.8	54.9	59.6
Circulatory	27.6	30.1	29.4	36.0
Respiratory	2.1	1.9	1.7	2.4
Malignant	14.2	13.9	15.5	13.1

Table 5. The estimated percentage changes in circulatory mortality due to a 10 μg m^{-3} increase in moving average pollutant concentrations during two days (lag 01) and a year (lag Y) preceding death

	<65	>65	Male	Female
PM_{10} 01	-0.001	0.074***	0.086**	0.047
	(-0.140, 0.100)	(0.019, 0.120)	(0.013, 0.150)	(-0.024, 0.100)
PM_{10} Y	0.632	0.279	-3.021	3.228*
	(-6.593, 8.329)	(-2.634, 3.252)	(-6.735, 0.803)	(-0.584, 7.144)
NO_2 01	-0.195	-0.243***	-0.268**	-0.209*
	(-0.606, 0.200)	(-0.407, 0.000)	(-0.484, 0.000)	(-0.417, 0.000)
NO_2 Y	12.708	7.824*	15.599***	2.672
	(-7.725, 37.575)	(-0.414, 16.649)	(4.057, 28.415)	(-7.235, 13.542)
SO_2 01	0.645*	0.096	0.411**	-0.052
	(-0.065, 1.308)	(-0.188, 0.300)	(0.037, 0.783)	(-0.416, 0.300)
SO_2 Y	0.763	-3.308	12.649	-14.109
	(-32.841, 51.135)	(-17.336, 13.088)	(-8.610, 38.819)	(-29.674, 4.812)
Tuesday	-11.928***	-1.947	-2.041	-4.131*
	(-19.832, -2.955)	(-5.456, 1.613)	(-6.703, 2.840)	(-8.472, 0.401)
Wednesday	-6.846	-2.962	-3.040	-3.799
	(-15.098, 2.122)	(-6.454, 0.602)	(-7.677, 1.816)	(-8.163, 0.702)
Thursday	-4.234	-3.262*	-1.830	-4.671**
	(-12.674, 4.917)	(-6.752, 0.300)	(-6.518, 3.045)	(-9.016, 0.000)
Friday	-10.374**	-0.950	-2.541	-1.762
	(-18.417, -0.995)	(-4.510, 2.737)	(-7.210, 2.327)	(-6.217, 2.840)
Saturday	0.296	-2.719	0.820	-4.947**
	(-8.439, 9.856)	(-6.215, 0.904)	(-3.950, 5.760)	(-9.273, 0.000)
Sunday	4.057	0.304	2.365	-0.542
	(-4.884, 13.769)	(-3.249, 3.977)	(-2.435, 7.358)	(-4.984, 4.081)

Table 6. The estimated percentage changes in malignant mortality due to a 10 µg m^{-3} increase in moving average pollutant concentrations during two days (lag 01) and a year (lag Y) preceding death

	<65	**>65**	**Male**	**Female**
PM_{10} 01	-0.126**	0.009	-0.001	-0.081
	(-0.248, 0.000)	(-0.076, 0.000)	(-0.098, 0.000)	(-0.184, 0.000)
PM_{10} Y	2.534	0.998	0.351	2.963
	(-3.848, 9.308)	(-3.495, 5.654)	(-4.702, 5.654)	(-2.495, 8.654)
NO_2 01	0.219	0.129	0.108	0.220
	(-0.141, 0.501)	(-0.122, 0.300)	(-0.179, 0.300)	(-0.083, 0.501)
NO_2 Y	-1.395	8.436	10.928	-2.221
	(-17.319, 17.586)	(-4.091, 22.507)	(-3.598, 27.634)	(-15.622, 13.202)
SO_2 01	0.345	0.413*	0.195	0.622**
	(-0.294, 0.904)	(-0.038, 0.803)	(-0.318, 0.702)	(0.085, 1.157)
SO_2 Y	-18.386	0.816	4.857	-16.889
	(-42.616, 16.067)	(-21.110, 28.788)	(-20.605, 38.403)	(-38.275, 11.851)
Tuesday	1.648	-0.540	-1.669	2.492
	(-6.094, 9.966)	(-5.969, 5.127)	(-7.726, 4.707)	(-4.184, 9.527)
Wednesday	1.702	3.434	2.507	3.255
	(-6.056, 10.076)	(-2.167, 9.308)	(-3.751, 9.090)	(-3.470, 10.407)
Thursday	-0.545	-0.731	-2.662	1.745
	(-8.184, 7.681)	(-6.167, 4.917)	(-8.685, 3.666)	(-4.916, 8.872)
Friday	-5.197	-0.190	-3.629	0.105
	(-12.574, 2.737)	(-5.651, 5.548)	(-9.613, 2.737)	(-6.477, 7.144)
Saturday	0.599	-1.004	-1.289	0.550
	(-7.092, 8.872)	(-6.411, 4.707)	(-7.363, 5.127)	(-6.031, 7.573)
Sunday	-3.791	0.000	-1.573	-1.011
	(-11.200, 4.185)	(-5.429, 5.654)	(-7.611, 4.812)	(-7.491, 5.866)

According to the model, no substantial change was observed in mortality immediately after air pollution episodes. Thus, a 10 µg m^{-3} increase in the average pollutant concentration is estimated to cause a negligible increase in death counts, rarely exceeding 0.5%, with statistically significant associations between PM_{10} and SO_2 and circulatory mortality in elderly and males, and SO_2 and malignant mortality in elderly and female population (Table 5 and 6). Low to moderate short-term health effects of air pollution were also reported in the extensive review of Brook et al., (2010). They concluded that the elevated $PM_{2.5}$ concentrations over 5 days led to the increase in circulatory mortality risk by 0.4% to 1.0%, even though the burden was not equally distributed within the population. Thereby, it should be taken into account that the health effects of fine particles are more severe compared to PM_{10}, because smaller diameter particles are more likely to penetrate deeply in the tracheobronchial and alveolar regions. The systematic review and meta-analysis of Shah et al.,

(2013) confirmed that heart failure hospital admissions and mortality were associated with moderate short-term increases in concentrations of particulate matter and all inorganic gaseous oxides, except for ozone.

In contrast to this, the meta-analysis including 33 time-series and case-crossover studies conducted in China, suggested that a 10 μg m^{-3} reduction in $PM_{2.5}$ concentrations would result in a considerable decrease (1.7% to 6.2%) in all-cause mortality (Shang et al., 2013). This heterogeneity in effect estimates across studies might be attributed to a number of factors, including pollutant characteristics and severity of pollution episodes in the study area. The complexity of the relationship between mortality and air pollution is driven by the fact that risk estimates can vary significantly across regions with similar characteristics, as shown in the spatial analysis for Los Angeles and New York incorporating data for 1.2 million adults from 172 U.S. urban areas (Krewski et al., 2009).

In the study aimed at investigating circulatory health effects of inorganic gaseous oxides, particulate matter and ozone, Milojević et al., (2014) used lags of 1 to 4 days and found no clear relationship between circulatory-related mortality, hospital admissions and air pollution, with the exception of $PM_{2.5}$ that was associated with arrhythmias, atrial fibrillation and pulmonary embolism, and NO_2 associated with an increased risk of myocardial infarction. Likewise, in the Danish cohort study of Raaschou-Nielsen et al., (2012), mean levels of NO_2 at the residence were also significantly associated with circulatory mortality after adjustment for potential confounders. As shown in Table 5 and Table 6, short-term exposure to NO_2 exhibited negative associations with death rates caused by circulatory and malignant diseases, which could indicate that the exposure to high NO_2 levels reaches its maximum effect upon the examined two-day period (lag 01). This assumption seems more probable when taking into account that the long-term exposure to NO_2 (lag Y) is associated with significant increase of circulatory and malignant mortality in people older than 65 years, particularly male population.

As regards long-term effects of air pollution on mortality, the herein presented results comply with the findings of Lepeule et al., (2012), suggesting that the exposure over longer period preceding death might be more significant than short-term exposure.

Thereby, the effects of PM_{10} were estimated as less significant compared to the effects of gaseous oxides (Tables 5, 6 and 7). The statistically significant associations were observed between circulatory mortality and exposure to NO_2 in elderly, particularly male population, as well as between circulatory mortality and exposure to PM_{10} in females. Similarly, the study of Chen et al., (2013), including data for three cities in Canada, suggested that long-term exposure to NO_2 was associated with a significant increase in circulatory mortality. Furthermore, Brook et al., (2010) reported a strong association between NO_2 and non-accidental mortality across 10 cities in Canada. Although these estimations cannot be ruled out, the authors assumed that NO_2 concentrations were acting as an indicator of some other variable or process. For instance, NO_2 levels exhibit high correlations in time and space with a range of toxic traffic-related species, including volatile organic compounds and polycyclic aromatic hydrocarbons, which could also contribute to the observed effects.

There isn't currently enough evidence to support the relationship between long-term exposure to air pollution and non-malignant respiratory mortality, although studies aimed at investigating short-term effects suggested that mid-term lags exceeding 40 days appear to be significant (Dimakopoulou et al., 2014). That is chiefly due to the fact that smaller incidence of respiratory mortality contributed to larger confidence intervals and larger variability of the effect estimates across studies (Hoek et al., 2013). Carey et al., (2013) investigated the relationship between individual annual exposure to air pollution and mortality in an English cohort and found a higher relative risk for respiratory deaths, which differed from most of the U.S. studies where no significant associations have been identified between particulate matter and non-malignant respiratory mortality. However, it is important to note that respiratory mortality rates in the UK were among the highest in Europe, thus leaving it an open question whether the conclusion proposed by Carey et al., (2013) can be generalized (Detailed Mortality Database, 2015).

It is reasonable to assume that the exposure-response time depends on the doze, physical and chemical properties of air pollutants, as well as the characteristics of the exposed population. Therefore, determining a unique time frame for assessing the impact of all pollutant matter might not lead to the anticipated results. As can be seen, the effects of long-term exposure to PM_{10} and SO_2 in most of the cases have the reverse effects in female and male population, which may indicate that the examined exposure time window, in this case a year preceding death, corresponded to the maximum effect in one gender group and post-harvesting effect in the other group. As previously mentioned, the post-harvesting reduction in death rates is expected to follow and balance the so-called 'harvesting effect' i.e., temporally advanced deaths of fragile population. In other words, it is possible that the effects of long-term exposure to SO_2 on circulatory mortality occurred first in females, while the reverse scenario applies for respiratory mortality.

Table 7. The estimated percentage changes in respiratory mortality due to a 10 µg m^{-3} increase in moving average pollutant concentrations during two days (lag 01) and a year (lag Y) preceding death

	<65	>65	Male	Female
PM_{10} 01	0.302	0.059	0.100	0.126
	(-0.088, 0.602)	(-0.140, 0.200)	(-0.141, 0.300)	(-0.152, 0.401)
PM_{10} Y	-2.478	-1.179	1.291	-4.278
	(-22.107, 22.018)	(-11.058, 9.746)	(-11.093, 15.373)	(-17.397, 10.849)
NO_2 01	-0.508	-0.587*	-0.453	-0.763*
	(-1.703, 0.702)	(-1.184, 0.000)	(-1.186, 0.200)	(-1.583, 0.000)
NO_2 Y	-24.294	10.727	12.785	-6.897
	(-57.938, 36.206)	(-16.360, 46.521)	(-20.223, 59.361)	(-37.108, 37.713)
SO_2 01	0.891	-0.743	-0.394	-0.467
	(-1.016, 2.737)	(-1.777, 0.300)	(-1.635, 0.803)	(-1.877, 0.904)
SO_2 Y	94.657	-15.108	-21.260	25.487
	(-40.400, 535.346)	(-51.091, 47.256)	(-60.276, 56.049)	(-41.886, 170.743)
Tuesday	-10.022	-2.139	-5.886	-0.074
	(-32.125, 19.244)	(-14.044, 11.405)	(-20.034, 10.738)	(-16.517, 19.602)
Wednesday	-10.206	-3.158	-2.238	-7.137
	(-32.277, 19.006)	(-15.014, 10.296)	(-16.852, 14.912)	(-22.724, 11.516)
Thursday	-5.439	10.014	4.007	11.761
	(-28.468, 24.982)	(-3.095, 24.857)	(-11.367, 22.018)	(-6.252, 33.109)
Friday	2.946	-4.581	0.974	-8.859
	(-21.733, 35.391)	(-16.365, 8.763)	(-14.103, 18.649)	(-24.271, 9.636)
Saturday	-10.364	-7.547	-7.624	-8.560
	(-32.425, 18.887)	(-18.979, 5.443)	(-21.617, 8.763)	(-23.932, 9.856)
Sunday	-5.048	8.611	1.462	12.723
	(-28.011, 25.232)	(-4.189, 22.998)	(-13.448, 18.887)	(-5.167, 33.910)

The current findings of gender-specific effects of air pollution on mortality are inconsistent. Chen et al., (2012) reported larger effect estimate of PM_{10} on total mortality in females than in males, which can be explained by lower smoking rate in females. In epidemiological studies, smoking is a potential confounding factor because it plays an important role in numerous pathological conditions, including malignant, lung and cardiovascular diseases. The interpretation of Chen et al., (2012) is based on the assumption that the smoking effects dominate to the extent that the exposure to air pollution may not further exacerbate the health condition. The findings of Turner et al., (2011), who examined the relationship between long-term $PM_{2.5}$ concentrations and lung cancer mortality among 188,699 lifelong never smokers, suggested that a 10 µg m^{-3} increase in mean $PM_{2.5}$ concentrations was associated with a 15-27% increase in lung cancer death rates. Conversely, the study of Pope et al., (2004) demonstrated that larger mortality risk associated with air $PM_{2.5}$ exposure is observed in smokers relative to never smokers, which they explained by additive if not synergistic impact of pollutants from smoke and ambient air.

As summarized by Solomon et al., (2012), gender might be the factor that influences susceptibility, due to the size of airways, the dose received and related particle clearance. Furthermore, it could be assumed that exposure to air pollution can be higher in male population as certain outdoor manual occupations, particularly in traditional surroundings, are more common in men, which is why more significant effects of air pollution can be expected in male population.

Aside from gender-specific health effects of air pollution, some uncertainties still remain regarding the pathophysiological mechanism of pollution-related mortality. Even though epidemiological studies are not designed to examine mechanisms, the observed time course of response might provide some information (Pope et al., 2004). For instance, it takes at least 24 hours for acute inflammatory response to develop, whereas neural response, i.e., disturbance of autonomic neural system, might be the underlying cause of myocardial infarction and vasoconstriction immediately upon exposure (Peters, 2005). During the long-term exposure, both mechanisms are present together with oxidative stress-induced DNA damage (Bräuner et al., 2007), changes in the expression of genes involved in DNA damage and repair (DeMarini, 2013) and changes in blood coagulability (Seaton et al., 1995). According to Milojević et al., (2014), the lower risk of ST elevation myocardial infarction and cerebrovascular insult and higher prevalence of non-myocardial infarction outcomes suggests that pollution-related circulatory health effects were probably more mediated by non-thrombotic pathways.

Evidence from 'Natural Experiments'

A limited number of studies investigated shifts in mortality associated with stringent environmental policies, and provided an important insight into substantial improvements in air quality and related health benefits. The study of Correia et al., (2013), based on the data from 545 USA counties, showed that a decrease in the annual average $PM_{2.5}$ concentrations over the 7-year period was associated with an increase in the mean life expectancy of 0.35 years, with the effect being pronounced in urban and densely populated areas.

The study of Clancy et al., (2002) showed that the effects of coal burning regulations in Dublin resulted in 16% and 64% declines in wintertime concentrations of SO_2 and black smoke, respectively. Accordingly, non-accidental, respiratory and circulatory deaths decreased by 5.7%, 15.5% and 10.3%, respectively. Similarly, a significant decrease of SO_2 concentrations occurred after banning sulfur-rich fuel in Hong Kong. The restrictions led to a decrease in risk for respiratory (3.9%) and circulatory (2.0%) mortality, whereas the average life expectancy increased by 20 and 41 days for females and males, respectively (Medley et al., 2002). The study conducted in Switzerland also supports the claim that long-term improvements in air quality and decreasing PM levels have beneficial effects on respiratory symptoms, including chronic cough, wheezing and breathlessness among adults (Schindler et al., 2009).

The sudden air quality deterioration caused by natural disasters or anthropogenic activities is another example of the so-called 'natural experiment' that eases concerns over confounding and exposure misclassification (Parker et al., 2008). The study of Shaposhnikov et al., (2014) investigated the combined effects of heat wave and air pollution (PM_{10} and ozone) on daily variations in death rates during wildfire in Moscow, Russia. According to the findings, with daily mean PM_{10} levels exceeding 300 $\mu g\ m^{-3}$, a steep increase in mortality risk was observed during the first two weeks, particularly for deaths related to nervous system, genitourinary and cerebrovascular diseases. The study of Chen et al., (2013) investigated the effects of China's Huai River policy that provided free coal for heating boilers in northern China cities. They showed that concentrations of total suspended particles were about 55% higher, whereas the life expectancy was about 5.5 years shorter in the North, due to the increased incidence of both circulatory and respiratory diseases.

Limitations of Epidemiological Studies

Some general limitations of epidemiological studies aimed at health risk estimation should be acknowledged. By analyzing the effects of environmental stressors, the entire population is considered equally exposed and the results obtained from a number of monitoring stations are assumed to be representative of individual exposure. More recent studies also used land regression models to derive individualized residential exposure (Jerrett et al., 2013). However, this is not realistic due to the fact that people exhibit different activity patterns and spend a significant period of time indoors (Basu and Samet, 2002). Furthermore, spatial distribution of particles and gaseous pollutants differs considerably: the concentrations of SO_2 and NO_2 are more closely related to their sources compared to PM_{10} concentrations, which are found to be relatively homogeneous over a larger area (Beelen et al., 2014). Rural areas tend to have higher death rates than metropolitan areas, which has been termed "non-metropolitan mortality penalty." Therefore, failure to control for residence in urban areas can also confound associations between air pollution and mortality (Jerrett et al., 2013).

In epidemiological analysis, indicator pollutants are the species selected to represent a mixture of hundreds of gaseous species and particles of complex physico-chemical composition (Brauer et al., 2012). However, inclusion of a single indicator pollutant in the analysis does not provide a realistic estimate, due to the fact that air pollution refers to a complex mixture of gaseous species and particles that permanently interact and undergo transformations. For instance, Janssen et al., (2011) suggest that NO_2 should not be taken as a reliable indicator of traffic due to its high background concentrations and that other species, including BC (black carbon) can better reflect health risk of combustion particles from traffic, solid fuel burning, shipping and industrial processes. They showed that an increase in life expectancy due to hypothetical traffic abatement measures was four to nine times higher when the calculation included BC compared with equivalent decrease in $PM_{2.5}$ concentrations. Furthermore, co-exposure to noise, as the potential confounding factor in traffic pollution studies, has been shown to be related to circulatory disease.

Even if each person's exposure to air pollution could be accurately determined, the pollutant concentrations would not be the only indicator of their potency. Depending on the sampling site, particulate matter exhibits significant differences in chemical composition and related toxicity. For instance, it has been shown that the carbonaceous particles derived from fossil fuel burning are more toxic than crustal material and secondary aerosols (Lelieveld et al., 2015). The presence of thousands of non-volatile and semi-volatile organic compounds in particles also remains an issue insufficiently addressed in exposure science (Solomon et al., 2012). For instance, the recent study of Raaschou-Nielsen et al., (2016) pointed out to the association between sulfur and nickel content in particles and lung cancer incidence. However, since sulfur is not known to be carcinogenic, the authors assume that it might represent a mixture of combustion-related organics or polycyclic aromatic hydrocarbons.

There is scarce evidence regarding the association between air pollution and mortality modified by socio-economic status, education and demographic factors. Krewski et al., (2000) conducted an independent re-analysis project to identify covariates that may confound previously reported relationship between air pollution and mortality. They found a significant modifying effect of education. Some studies also found significantly higher effect estimates among obese participants and those with lower educational attainment and/or socio-economic status (Brunekreef et al., 2009; Ostro et al., 2009). However, Samet et al., (2000) found no evidence that socio-economic factors, such as poverty and race, are significant modifiers of the PM_{10} effect estimates. Similar findings have also been reported by other authors.

The health effects of other environmental stressors, such as temperature, have been widely investigated. Nonetheless, a relatively small number of studies deal with the interacting effects of air pollution and extreme temperature. The study of Meng et al., (2012), including PM_{10} data from eight Chinese cities with average daily concentrations in the range from 65 to 124 $\mu g\ m^{-3}$, showed that a 10 $\mu g\ m^{-3}$ increment in PM_{10} concentrations on high temperature days corresponded to a more than doubled relative risk for air pollution-related mortality, whereas no significant effect modification was observed during cold days. Similarly, the study of Chen et al., (2015) that investigated seasonality of the pollution-attributable death rates in 17 Chinese cities, showed that relative risk associated with a 10-$\mu g\ m^{-3}$ increase in two-day average PM_{10} concentrations was highest in summer and winter months. Vanos et al., (2014) also reported significant modification of air pollution-related mortality risk by weather type and season. Namely, the estimated effect was largest during tropical days in the spring or summer. This can be explained by the temperature-related physiological stress which makes people more susceptible to the adverse effects of pollution.

In conclusion to this, air pollution commonly used in retrospective epidemiological studies is a contextual risk factor, together with temperature, which represents the living environment and explains spatial mortality variations (Sheppard et al., 2012). Nevertheless, the potential confounders are associated with individual factors, e.g., smoking, alcohol use, obesity, presence of different clinical conditions and consumption of anti-hypertensives, lipid-lowering agents, and antidiabetic agents, which also play an important role in multi-causal diseases and the observed death rates.

CONCLUSION

In this study, we discuss the effects of air pollution exposure on death rates in Belgrade, on the basis of the 6-year (2009-2014) regular pollutant monitoring and the corresponding administrative records on mortality. The poor health status of the examined population is reflected in high circulatory and malignant death rates, as well as in the fact that more than one third of malignant deaths are observed among the population younger than 65 years, and that the estimated life expectancy of 74.3 years is considerably lower than the EU average of 80.6 years. In Belgrade area, air pollution represents a significant environmental factor affecting human health. The number of days with average PM_{10} concentrations exceeding 50 μg m^{-3} during the study period was in the range from 75 to 155 per year, which is considerably higher than the margin of tolerance set out in the Air Quality Standards. According to the results, no substantial association was observed between mortality and short-term exposure: a 10 μg m^{-3} increase in the average pollutant concentration is estimated to cause a negligible increase in death counts, rarely exceeding 0.5%. Statistically significant associations were detected between PM_{10} and SO_2 and circulatory mortality in elderly and males, and SO_2 and malignant mortality in elderly and female population. However, the results further suggest that the exposure over one-year period preceding death might be more significant than short-term exposure. The elevated concentrations of NO_2 were associated with a significant increase in circulatory and malignant mortality in people older than 65 years, and particularly male population. In general, the effects of PM_{10} were estimated as less significant compared to the effects of gaseous oxides.

The health effects of air pollution follow a complex pattern across different geographic areas, depending on the population features. Even though individual studies are necessary to estimate the magnitude and trend of such relationships and to extend the current knowledge on how diverse populations respond to environmental stressors, they are mostly based on a limited data and their findings can be generalized only upon confirmation through meta-analyses. In addition, such analyses are used to summarize the results of relevant studies and reach the conclusion through a systematic approach.

ACKNOWLEDGMENTS

This paper was realized as part of projects No III43007 and No III41011 founded by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-16. The authors are thankful to the Institute of Public Health in Belgrade for providing the necessary facilities and data.

REFERENCES

Allen, RW; Gombojav, E; Barkhasragchaa, B; Byambaa, T; Lkhasuren, O; Amram, O; Takaro, TK; Janes, CR. *Air Qual Atmos Health*, 2013, 6, 137-150.

Anenberg, SC; Horowitz, LW; Tong, DQ; West, *J. Environ Health Perspect.*, 2010, 118, 1189-1195.

Basu, R; Samet, JM. *Epidemiol Rev.*, 2002, 24, 190-202.

Beelen, R; Raaschou-Nielsen, O; Stafoggia, M; Andersen, ZJ; Weinmayr, G; Hoffmann, B; Wolf, K; Samoli, E; Fisher, P; Nieuwenhuijsen, M; Vineis, P; Xun, WW; Katsouyanni, K; Dimakopolou, K; Oudin, A; Forsberg, B; Modig, L; Havulinna, AS; Lanki, T; Turunen Oftedal, B; Nystad, W; Nafstad, P; De Faire, U; Pedersen, NL; Östenson, CG; Fratiglioni, L; Penell, J; Korek, M; Pershagen, G; Eriksen, KT; Overvad, K; Ellermann, T; Eeftens, M; Peeters, P. H; Meliefste, K; Wang, M; Bueno-de-Mesquita, B; Sugiri, D; Krämer, U; Heinrich, J; De Hoogh, K; Key, T; Peters, A; Hampel, R; Concin, H; Nagel, G; Ineichen, A; Schaffner, E; Probst-Hensch, N; Künzli, N; Schindler, C; Schikowski, T; Adam, M; Phuleria, H; Vilier, A; Clavel-Chapelon, F; Declercq, C; Grioni, S; Krogh, V; Tsai, MY; Ricceri, F; Sacerdote, C; Galassi, C; Migliore, E; Ranzi, A; Cesaroni, G; Badaloni, C; Forastiere, F; Tamayo, I; Amiano, P; Dorronsoro, M; Katsoulis, M; Trichopoulou, A; Brunekreef, B; Hoek, G. *Lancet*, 2014, 383, 785-795.

Brauer, M; Amann, M; Burnett, RT; Cohen, A; Dentener, F; Ezzati, M; Henderson, SB; Krzyzanowski, M; Martin, RV; Van Dingenen, R; Van Donkelaar, A. *Environ Sci Technol.*, 2012, 46, 652-660.

Bräuner, EV; Forchhammer, L; Møller, P; Simonsen, J; Glasius, M; Wåhlin, P; Raaschou-Nielsen, O; Loft, S. *Environ Health Perspect.*, 2007, 115, 1177–1182.

Brook, JR; Burnett, RT; Dann, TF; Cakmak, S; Goldberg, MS; Fan, X; Wheeler, AJ. *J Expo Sci Env Epid.*, 2007, 17, S36-S44.

Brook, RD; Rajagopalan, S; Pope, CA; Brook, JR; Bhatnagar, A; Diez-Roux, AV; Holguin, F; Hong, Y; Luepker, RV; Mittleman, MA; Peters, A. *Circulation*, 2010, 121, 2331-2378.

Brunekreef, B; Beelen, RMJ; Hoek, G; Schouten, LJ; Bausch-Goldbohm, S; Fischer, P; Armstrong, B; Hughes, E; Jerrett, M. *Research report (Health Effects Institute)*, 2009, 139, 5-71.

Cancer Research, UK. Cancer Mortality by Age. (2015). http://www.cancerresearchuk.org/health-professional/cancer-statistics/mortality/age#heading-Zero.

Carey, IM; Atkinson, RW; Kent, AJ; Van Staa, T; Cook, DG; Anderson, HR. *Am J Respir Crit Care Med.*, 2013, 187, 1226-1233.

Carslaw, DC; Ropkins, K. *Environ Modell Softw.*, 2012, 27, 52-61.

Chen, H; Goldberg, MS; Burnett, RT; Jerrett, M; Wheeler, AJ; Villeneuve, PJ. *Epidemiology*, 2013, 24, 35-43.

Chen, R; Kan, H; Chen, B; Huang, W; Bai, Z; Song, G; Pan, G. *Am J Epidemiol.*, 2012, doi: 10.1093/aje/kwr425.

Chen, R; Peng, RD; Meng, X; Zhou, Z; Chen, B; Kan, H. *Sci Tot Environ.*, 2013, 450, 259-265.

Chen, Y; Ebenstein, A; Greenstone, M; Li, H. *PNAS*, 2013, 110, 12936-12941.

Clancy, L; Goodman, P; Sinclair, H; Dockery, DW. *Lancet*, 2002, 360, 1210-1214.

Correia, AW; Pope III, CA; Dockery, DW; Wang, Y; Ezzati, M; Dominici, F. *Epidemiology*, 2013, 24, 23-31.

DeMarini, D. M. *Mutagenesis*, 2013, 28, 485-505.

Detailed Mortality Database. World Health Organization. Regional Office for Europe. (2015). http://data.euro.who.int/dmdb/.

Dimakopoulou, K; Samoli, E; Beelen, R; Stafoggia, M; Andersen, ZJ; Hoffmann, B; Fischer, P; Nieuwenhuijsen, M; Vineis, P; Xun, W; Hoek, G. *Am J Respir Crit Care Med.*, 2014, 189, 684-696.

Evans, J; van Donkelaar, A; Martin, RV; Burnett, R; Rainham, DG; Birkett, NJ; Krewski, D. *Environ Res.*, 2013, 120, 33-42.

Fang, Y; Mauzerall, DL; Liu, J; Fiore, AM; Horowitz, LW. *Climatic Change*, 2013, 121, 239-253.

Fischer, H; Wagenbach, D; Kipfstuhl, J. *J Geophys Res Atmos.*, 1998, 103, 21927-21934.

Gasparrini, A. *J Stat Softw.*, 2011, 43, 1-20.

Gasparrini, A; Armstrong, B; Kenward, MG. *Stat Med.*, 2010, 29, 2224-2234.

Gasparrini, A; Guo, Y; Hashizume, M; Lavigne, E; Zanobetti, A; Schwartz, J; Tobias, A; Tong, S; Rocklöv, J; Forsberg, B; Leone, M. *Lancet*, 2015, 386, 369-375.

Giannadaki, D; Pozzer, A; Lelieveld, J. *Atmos Chem Phys.*, 2014, 14, 957-968.

Goodman, PG; Dockery, DW; Clancy, L. *Environ Health Perspect.*, 2004, 112, 179-185.

Heinrich, J; Hoelscher, B; Frye, C; Meyer, I; Pitz, M; Cyrys, J; Wjst, M; Neas, L; Wichmann, HE. *Epidemiology*, 2002, 13, 394-401.

Hoek, G; Krishnan, RM; Beelen, R; Peters, A; Ostro, B; Brunekreef, B; Kaufman, J. D. *Environ Health*, 2013, 12, 43-58.

Janssen, NA; Hoek, G; Simic-Lawson, M; Fischer, P; Van Bree, L; Ten Brink, H; Keuken, M; Atkinson, RW; Anderson, HR; Brunekreef, B; Cassee, FR. *Environ Health Perspect.*, 2011, 119, 1691-1699.

Jerrett, M; Burnett, RT; Beckerman, BS; Turner, MC; Krewski, D; Thurston, G; Martin, RV; van Donkelaar, A; Hughes, E; Shi, Y; Gapstur, SM. *Am J Respir Crit Care Med.*, 2013, 188, 593-599.

Krewski, D; Burnett, RT; Goldberg, MS; Hoover, K; Siemiatycki, J; Jerrett, M; Abrahamowicz, M; White, WH. Reanalysis of the Harvard Six Cities Study and the American Cancer Society Study of particulate air pollution and mortality; Health Effects Institute: Cambridge, 2000.

Krewski, D; Jerrett, M; Burnett, RT; Ma, R; Hughes, E; Shi, Y; Turner, M. C; Pope III, CA; Thurston, G; Calle, EE; Thun, MJ. Extended follow-up and spatial analysis of the American Cancer Society study linking particulate air pollution and mortality (No. 140); Health Effects Institute: Boston, 2009.

Lelieveld, J; Evans, JS; Fnais, M; Giannadaki, D; Pozzer, A. *Nature*, 2015, 525, 367-371.

Lepeule, J; Laden, F; Dockery, D; Schwartz, J. *Environ Health Perspect.*, 2012, 120, 965-970.

Medley, AJ; Wong, CM; Thach, TQ; Ma, S; Lam, TH; Anderson, HR. *Lancet*, 2002, 360, 1646-1652.

Meng, X; Zhang, Y; Zhao, Z; Duan, X; Xu, X; Kan, H. *Sci Tot Environ.*, 2012, 435, 215-221.

Milojević, A; Wilkinson, P; Armstrong, B; Bhaskaran, K; Smeeth, L; Hajat, S. *Heart*, 2014, 100, 1093-1098.

Mortality and life expectancy statistics. (2013). Eurostat, Statistics Explained. http://ec.europa.eu/eurostat/statistics-explained/index.php/Mortality_and _ life_expectancy_statistics.

Noonan, CW; Ward, TJ; Navidi, W; Sheppard, L. *Occup Environ Med.*, 2012, 69, 354-60.

Ostro, BD; Feng, WY; Broadwin, R; Malig, BJ; Green, RS; Lipsett, MJ. *Occup Environ Med.*, 2008, 65, 750-756.

Parker, JD; Mendola, P; Woodruff, TJ. *Epidemiology*, 2008, 19, 820-823.

Perišić, M; Stojić, A; Stojić, SS; Šoštarić, A; Mijić, Z; Rajšić, S. *Air Qual Atmos Health*, 2014, 1-11.

Peters A. *Toxicol Appl Pharmacol.*, 2005, 207, 477–482.

Pope, CA; Burnett, RT; Thurston, GD; Thun, MJ; Calle, EE; Krewski, D; Godleski, JJ. *Circulation*, 2004, 109, 71-77.

Pretty, R. (2015). TheilSen {openair} Tests for trends using Theil-Sen estimates. http://www.inside-r.org/packages/cran/openair/docs/TheilSen.

R Core Team. (2014). R: A Language and Environment for Statistical Computing. Vienna, Austria: R Foundation for Statistical Computing. http://www.r-project.org.

Raaschou-Nielsen, O; Andersen, ZJ; Jensen, SS; Ketzel, M; Sorensen, M; Hansen, J; Loft, S; Tjonneland, A; Overvad, K. *Environ Health.*, 2012, 11, 860-865.

Raaschou-Nielsen, O; Beelen, R; Wang, M; Hoek, G; Andersen, ZJ; Hoffmann, B; Stafoggia, M; Samoli, E; Weinmayr, G; Dimakopoulou, K; Nieuwenhuijsen, M. *Environ Int.*, 2016, 87, 66-73.

Ross, CE; Masters, RK; Hummer, RA. *Demography*, 2012, 49, 1157-1183.

Salam, A; Albinali, H; Singh, R; Asaad, N; Alqahtani, A; Al Suwaidi, J. *J Am Coll Cardiol.*, 2013, 168, 975–980.

Samet, JM; Zeger, SL; Dominici, F; Curriero, F; Coursac, I; Dockery, DW; Schwartz, J; Zanobetti, A. The national morbidity, mortality, and air pollution study. Part II: morbidity and mortality from air pollution in the United States; Health Effects Institute: Cambridge, 2000.

Schindler, C; Keidel, D; Gerbase, MW; Zemp, E; Bettschart, R; Brandli, O; Brutsche, MH; Burdet, L; Karrer, W; Knopfli, B; Pons, M. *Am J Respir Crit Care Med.*, 2009, 179, 579-587.

Seaton, A; Godden, D; MacNee, W; Donaldson, K. *Lancet*, 1995, 345, 176–178.

Shah, AS; Langrish, JP; Nair, H; McAllister, DA; Hunter, AL; Donaldson, K; Newby, DE; Mills, NL. *Lancet*, 2013, 382, 1039-1048.

Shang, Y; Sun, Z; Cao, J; Wang, X; Zhong, L; Bi, X; Li, H; Liu, W; Zhu, T; Huang, W. *Environ Int.*, 2013, 54, 100-111.

Shaposhnikov, D; Revich, B; Bellander, T; Bedada, GB; Bottai, M; Kharkova, T; Kvasha, E; Lezina, E; Lind, T; Semutnikova, E; Pershagen, G. *Epidemiology*, 2014, 25, 359.

Sheppard, L; Burnett, RT; Szpiro, AA; Kim, SY; Jerrett, M; Pope III, CA; Brunekreef, B. *Air Qual Atmos Health*, 2012, 5, 203-216.

Silva, RA; West, JJ; Zhang, Y; Anenberg, SC; Lamarque, JF; Shindell, DT; Collins, WJ; Dalsoren, S; Faluvegi, G; Folberth, G; Horowitz, LW. *Environ Res Lett.*, 2013, 8, 034005.

Solomon, PA; Costantini, M; Grahame, TJ; Gerlofs-Nijland, ME; Cassee, FR; Russell, AG; Brook, JR; Hopke, PK; Hidy, G; Phalen, RF; Saldiva, P; Sarnat, SE; Balmes, JR; Tager, IB; Özkaynak, H; Vedal, S; Wierman, SSG; Costa, DL. *Air Qual Atmos Health*, 2012, 5, 9-62.

Šoštarić, A; Mladenović, S; Stanišić Stojić, S; Stojić, A; Stanišić, N; Slepčević V. Health burden of air pollutant exposure in Belgrade: a European region with high circulatory and malignant mortality rates, Newsletters, WHO Collaborating Centre for Air Quality Management and Air Pollution Control, No. 56 - December 2015, 3-9. http://envpl.ipb.ac.rs/pages/newsletters/WHOdecember_2015_nl56_1.pdf.

Stanišić Stojić, S; Stanišić, N; Stojić, A; Šoštarić, A. *J Toxicol Environ Health A*, 2016, 79, 17-27.

Statistical Office of the Republic of Serbia. 2015. The additionally processed mortality data. Vital statistics.

Stojić, A; Stanišić Stojić, S; Mijić, Z., Ilić, L; Tomašević, M; Todorović, M; Perišić, M. In Comprehensive Analysis of VOC Emission Sources in Belgrade Urban Area, In: Urban and Built Environments: Sustainable Development, Health Implications and Challenges; Cohen, A.; Ed.; Nova Science Publishers: New York, USA, 2015c; pp. 55-88.

Stojić, A; Stanišić Stojić, S; Reljin, I; Čabarkapa, M; Šoštarić, A; Perišić, M; Mijić, Z. *Environ Sci Poll Res.*, 2016, 1-11. doi: 10.1007/s11356-016-6266-4.

Stojić, A; Stojić, SS; Mijić, Z; Šoštarić, A; Rajšić, S. *Atmos Environ.*, 2015a, 106, 71-79.

Stojić, A; Stojić, SS; Šoštarić, A; Ilić, L; Mijić, Z; Rajšić, S. *Environ Sci Poll Res.*, 2015b, 22(17), 13137-13152.

Tanaka, S. *J Health Econ.*, 2015, 42, 90-103.

Todorović, M; Perišić, M; Kuzmanoski, M; Stojić, A; Šoštarić, A; Mijić, Z; Rajšić, S. *J Environ Sci Heal A.*, 2015, 50(13), 1351-1359.

Turner, MC; Krewski, D; Pope III, CA; Chen, Y; Gapstur, SM; Thun, MJ. *Am J Respir Crit Care Med.*, 2011, 184, 1374-1381.

Vanos, JK; Hebbern, C; Cakmak, S. *Environ Pollut.*, 2014, 185, 322-332.
Ye, X; Wolff, R; Yu, W; Vaneckova, P; Pan, X; Tong, S. *Environ Health Perspect.*, 2012, 120, 19-28.
Zhang, Z; Fang, J; Gillespie, C; Wang, G; Hong, Y; Yoon, PW. *Am J Cardiol.*, 2012, 109, 1097-1103.

Публикације категорије М20

Публикације после избора у претходно звање

Ecotoxicology and Environmental Safety 172 (2019) 341–347

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Introducing of modeling techniques in the research of POPs in breast milk – A pilot study

Gordana Jovanović[a,*], Snježana Herceg Romanić[b,*], Andreja Stojić[a], Darija Klinčić[b], Marijana Matek Sarić[c], Judita Grzunov Letinić[d], Aleksandar Popović[e]

[a] Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
[b] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, PO Box 291, 10001 Zagreb, Croatia
[c] Department of Health Studies, University of Zadar, Splitska 1, 23000 Zadar, Croatia
[d] Institute of Public Health Zadar, Kolovare 2, 23 000 Zadar, Croatia
[e] Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

ARTICLE INFO

Keywords:
Persistent organic pollutants (POPs)
Parity
Age
Feature selection
Machine learning
Unmix

ABSTRACT

This study used advanced statistical and machine learning methods to investigate organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in breast milk, assuming that in a complex biological mixture, the pollutants emitted from the same source or with similar properties are statistically interrelated and possibly exhibit non-linear dynamics. The elaborated analyses such as Unmix source apportionment characterized individual source groups, while guided regularized random forest indicated the pollutant dependence on the *ortho*-chlorine atom attached to the congener's phenyl ring and mother's age. Mutual associations among PCBs were further discussed, but the results implied they were mostly not related to child delivery. PCB congeners −153, −180, −170, −118, −156, −105, and −138 appeared to be compounds of the outmost importance for mutual prediction with reference to their interrelations regarding chemical structure and metabolic processes in the mother's body. Finally, machine learning methods, which provided prediction relative errors lower than 30% and correlation coefficients higher than 0.90, suggested a possible strong non-linear relationship among the pollutants and consequently, the complexity of their pathways in the breast milk.

1. Introduction

In recent years, innovative measuring and modeling techniques, as well as new scientific approaches and methodologies have been developing with the aim of studying environmental pollutants, their spatio-temporal variability and correlated interactions. More attention in statistical research has been devoted to the correlation analysis of environmental pollutants including factor analysis, principle component analysis and latent class analysis that provides information on the relationship between investigated variables. However, all these methods cannot describe the potential non-linear exposure-response interactions of different pollutants and the corresponding combined effects (Tonga et al., 2018). Up to date advances in modeling enabled addressing the complex functional dependencies of air pollutants (Stojić et al., 2015; Perišić et al., 2017; Šoštarić et al., 2017) using machine learning as a widely accepted methodology where non-linear associations between a target variable and a potentially unlimited number of explanatory predictors can be revealed without explicit knowledge of the underlying processes by "letting the data speak for itself" (McCabe et al., 2017). Moreover, various machine learning algorithms (ML) have been initiated over the last 20 years as a more economical alternative to computationally expensive and time-consuming deterministic models dramatically evolving from diagnostics and empirical techniques to the more sophisticated data processing, online and parametric or non-parametric statistical models/approaches (Ryan, 2016). With regard to the described research initiatives, our previous studies demonstrated a successful application of ML methods for forecasting industry emission and vehicle exhaust source contributions, and PM_{10} concentrations in urban areas relying on meteorological data, or for the identification of mechanisms underlying wet scavenging phenomena (Stojić et al., 2015; Perišić et al., 2017; Šoštarić et al., 2017; Stojić et al., 2019).

This study strives to demonstrate a promising methodology for the better understanding of specific interrelations of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in breast milk and

* Corresponding authors.
E-mail addresses: gordana.vukovic@ipb.ac.rs (G. Jovanović), sherceg@imi.hr (S.H. Romanić), andreja.stojic@ipb.ac.rs (A. Stojić), darija@imi.hr (D. Klinčić), marsaric@unizd.hr (M.M. Sarić), jgrzunov@zjz-zadar.hr (J.G. Letinić), apopovic@chem.bg.ac.rs (A. Popović).

https://doi.org/10.1016/j.ecoenv.2019.01.087
Received 2 August 2018; Received in revised form 25 January 2019; Accepted 25 January 2019

the importance of their association with the mother's age and parity using ML methods and source apportionment, which start from the assumption that in a complex pollutant mixture, species emitted from the same source or with similar characteristics are statistically inter-related. OCPs and PCBs belong to the group of persistent organic pollutants (POPs) (Stockholm Convention, 2001). Four WHO surveys (1987–1989, 1992–1993, 2005–2007 and 2008–2012) were conducted to identify quantitative geographical differences in the contamination of mother's milk and in relation to safety standards (UNEP, 2013). Literature data evaluated a lot of complexities among POP interrelations in the milk samples or/and their dependence on external parameters such as mother's age and weight loss, childbirth, dietary habits and occupation (Fång et al., 2015, and references therein; Lignell et al., 2016; Polder et al., 2009; Van den Berg et al., 2006; Vigh et al., 2013). Due to chronic exposure to low concentrations of POPs and future epidemiological studies, it is important to know the impact of certain POPs as well as mixtures of POPs on human health. We believe that the modeling process can significantly contribute to this process of understanding.

Thus far, in the studies which concern the behavior of POPs in mother's milk, physiologically-based pharmacokinetic (PBPK) modeling has been widely used (e.g., Verner et al., 2009). The PBPK is mathematic representations of xenobiotic pharmacokinetics used to predict the absorption, distribution, metabolism and excretion, i.e., the pollutant fate based on physiologic and biochemical parameters of a given organism and the physicochemical properties of the selected xenobiotics (Verner et al., 2009). However, the methods that have been used in this study belongs to statistical and ML modeling which exhibit evident differences from PBPK. Briefly put, statistical and ML methods use numerical data to identify patterns in data extrapolate or interpolate data based on some best-fit, error estimates of observations, or spectral analysis of data or model generated output. On the other hand, mathematic representations, such as PBPK, determine how a system changes from one state to the next by differential equations and/or how one variable depends on the value or state of other variables by state equations. Therefore, the purpose of this paper is the statistical/ML determination of non-linear correlations, not numerical (kinetics). This is primarily a pilot study whose results should serve for further research that would involve a large number of respondents.

2. Materials and methods

2.1. Collection of samples

Breast milk samples were collected from 79 healthy mothers aged between 19 and 45, living in Zadar (Croatia). Out of the mothers, 23 were primiparae, 41 secundiparae and 15 multiparae (third child delivery). According to the results of the enclosed questionnaire, the mothers had no history of accidental or occupational exposure to the analyzed POPs. Milk was manually expressed 2–38 weeks after the birth into pre-cleaned glass bottles and stored at − 20 °C until analysis.

The samples were collected twice, in 2011 (Klinčić et al., 2016) and 2014; the second campaign was part of the WHO survey on POP levels in human milk. Before inclusion in the study, all the participants were informed about the aim and relevance of the investigation and they confirmed their participation by signing the informed consent forms. To protect the participants' privacy, all of the collected personal and clinical data and biological samples were coded and used only for the research purposes. Ethical permissions (01–745/2011 and 01–405/2014) to perform the sampling were given by the Zadar County Health Centre Ethics Committee.

2.2. Chemical analysis

The analytical procedure was described in detail in Klinčić et al. (2014). Briefly explained, two subsamples of each unfrozen milk sample (5 g) were extracted twice with a mixture of chloroform and methanol (17 ML and 10 ML; 1:1). The separated chloroform extracts were dried under a nitrogen flow, and milk fat was weighted and dissolved in *n*-hexane. Subsequently, purification was performed with sulphuric acid (5 ML) and by adsorption chromatography on a multilayer silica column with 4% diethyl-ether in *n*-hexane as a solvent. The fractionation was done using commercial tubes pre-packed with carbon (ENVI-Carb SPE tubes, 3 ML, 0.25 g, Graphitized Non-Porous Carbon, Retention Mechanism: Reversed-phase, Supelco, the USA). The analyzed organochlorine compounds were eluted with *n*-hexane/toluene (99:1) as the first fraction, reduced to dryness, and dissolved in *n*-hexane for the chromatographic analysis.

High-resolution gas chromatography with electron capture detector (s) (*CLARUS 500* chromatograph) was performed. For unambiguous determination of PCBs and OCPs, two capillary columns were used (Restek, Bellefonte, PA, USA) simultaneously (Mydlová-Memersheimerová et al., 2009): (1) 60 m × 0.25 mm, Rtx-5 film thickness of 0.25 µm, and (2) 30 m × 0.25 mm, Rtx-1701 film thickness of 0.25 µm. The column temperature was programmed from 100 °C to 110 °C at 4 °C min^{-1} (isothermally 5 min at 110 °C) and then to 240 °C at 15 °C min^{-1} (50 min isothermally at 240 °C). The carrier gas was nitrogen. The injector and detector temperatures were 250 °C and 270 °C, respectively. We used an external standard containing all of the determined pollutants for qualitative and quantitative analyses, and analyzed each sample on both columns by comparing relative retention times (Table S1, Supplementary material) and peak responses, respectively, with those in the standard, and quantified by comparing the peak responses in both the sample and standard. Only compounds identified on both columns were further processed using the average values from the columns.

2.3. The analyzed compounds and quality control

In this study we analyzed 17 PCBs: six indicator congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180), eight mono-*ortho* congeners (PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-189), PCB-60, PCB-74 and PCB170, and seven OCPs: hexachlorobenzene (HCB), α-, β-, and γ-hexachlorocyclohexanes (α-HCH, β-HCH, γ-HCH), 1,1-dichloro-2,2-di(4-chlorophenyl)ethylene (*p,p´*-DDE), 1,1-dichloro-2,2-di(4-chlorophenyl)ethane (*p,p´*-DDD), and 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (*p,p´*-DDT).

The limits of determination (LOD) were calculated as an average (N = 10) based on signal-to-noise ratio (3:1 and higher) and compound recovery.

The LODs for the analyzed compounds were 0.5 ng g^{-1} milk fat for PCB congeners, 0.1 ng g^{-1} milk fat for α-HCH and HCB, 0.2 ng g^{-1} milk fat for *p,p´*-DDE, 0.3 ng g^{-1} milk fat for β-HCH, γ-HCH and *p,p´*-DDD, and 0.6 ng g^{-1} milk fat for *p,p´*-DDT.

The method recovery and reproducibility were determined by adding a known amount of all of the analyzed compounds to the aliquots of homogenized samples before extraction (method of addition, n = 10). The recovery and reproducibility of the method were tested by spiking real human milk samples. A pool of real samples was divided into two sets, each containing seven aliquots. In each set, a known amount of all of the analyzed pollutants (between 0.5 and 5.5 ng g^{-1} milk fat, depending on the OCP compounds, and between 5 and 7.5 ng g^{-1} milk fat, depending on the PCBs) was added to five aliquots before extraction, and two aliquots were non-spiked. The recoveries of analyzed compounds were calculated after subtracting the mean levels of two non-spiked aliquots from the spiked ones. The average recoveries for PCBs ranged between 58% and 86% and for organochlorine pesticides between 59% and 92%. Method reproducibility expressed as relative standard deviation was between 6% and 22% and 7% and 24% for PCBs and OCPs, respectively. The pollutant concentrations were corrected based on their recoveries. Method blanks showed no interference with pollutants of interest.

Table 1
Descriptive statistics for organochlorine pesticide (OCPs) and polychlorinated biphenyl (PCBs) concentrations [ng g^{-1}] in the breast milk; N – the number of samples in which the analyzed compound was detected, LOD – limit of detection, Mean – average value, SD – standard deviation, Min – minimum value, and Max – maximum value.

Compound			Concentrations [ng g^{-1} milk fat]				
	N	< LOD [%]	Mean	Median	SD	Min	Max
OCPs							
α-HCH	79	/	0.2	0.1	0.2	0.2	1.5
β-HCH	79	/	1	0.4	1.1	0.1	4.8
γ-HCH	79	/	2.2	1	3.8	0.1	24.4
HCB	79	/	1.5	0.5	1.6	0.1	8
p,p´-DDE	79	/	12.6	8.1	13.2	1.5	77.8
p,p´-DDD	47	40	0.3	0.3	0.1	0.1	0.8
p,p´-DDT	79	/	3.9	0.6	5.2	0.1	23.3
indicator PCBs							
PCB – 28	36	54	1.9	1	2	0.4	10.8
PCB – 52	19	76	4.3	3.7	2.5	0.7	9.6
PCB – 101	38	52	0.3	0.2	0.4	0	2.1
PCB – 138	79	/	4.6	3.5	3.6	1.1	23.7
PCB – 153	79	/	9.4	6.4	8.2	1.2	43.6
PCB – 180	79	/	4.8	2.8	5.6	0.1	36.3
mono-ortho dl-PCBs[a]							
PCB – 105	64	19	0.6	0.5	0.5	0.1	2.3
PCB – 114	43	46	0.4	0.1	0.9	0	4
PCB – 118	74	6.3	0.8	0.6	0.6	0.1	2.7
PCB – 123	26	67	0.1	0.1	0.1	0.1	0.4
PCB – 156	68	14	0.8	0.6	0.7	0	4.2
PCB – 157	24	70	0.3	0.2	0.2	0.1	0.8
PCB – 167	64	19	0.4	0.3	0.3	0.1	1.5
PCB – 189	42	47	0.4	0.3	0.1	0.1	0.6
non-classified PCBs							
PCB – 60	10	87	0.3	0.3	0.1	0.2	0.5
PCB – 74	73	6	1.2	0.6	1.3	0	6
PCB – 170	79	/	3.2	2.1	3.5	0.6	25.6
Age	79	/	30.3	30	5.3	19	45
Birth	79	/	1.9	2	0.7	1	3

[a] *dl* – dioxin-like.

2.4. Data processing

The study processed only compounds above the LOD in at least 70% of the samples (Table 1). Thus, congeners PCB-28, PCB-52, PCB-101, PCB-114, PCB-123, PCB-157, PCB-60, and PCB-189 were not subjected to the modeling. Descriptive statistics, including basic statistics, correlation, and probability density function analysis, was complemented with linear and loess regression analyses obtained using software environment for statistical computing R (R Team, 2012). To investigate a potential dynamic of POPs concentrations, a locally weighted loess regression was used (Li et al., 2014). The method fits simple models to localized data subsets providing a function that describes the deterministic part of the variation in the data.

Guided regularized random forest (GRRF) (Deng and Runger, 2013) was applied for the selection of features (pollutants and mother's age/parity) that are most relevant to one another. The GRRF is an ensemble learning method, which guides the feature selection of regularized random forest (RRF) based on the importance scores from a preliminary RF. The method is more robust and computationally efficient than RRF. It moderates the course of dimensionality and avoids the effort to analyze irrelevant or redundant features by selecting the compact subsets of variable interactions. The variable importance presented herein was obtained by calculating the average value of 1000 model runs. Method performances were tested by 100 times replicated 10-fold cross validation.

To investigate to what extent GRRF derived the most important features (OCPs, PCBs, mother's age and childbirth) relevant for pollutant prediction, the autoWeka meta learner was implemented on 5 best predicting features (Kotthoff et al., 2016). The method search through the joint space of Weka's learning algorithms and their respective hyperparameter settings to maximize performance, using a Bayesian optimization method. All of the methods were implemented in Weka (Weka 3.8 core and Weka Sourceforge, 2016), which collects machine learning algorithms for data mining tasks such as classification, regression, clustering, association rules and visualization (Frank et al., 2005). Brief descriptions of the methods are given in Supplementary material as well as in Šoštarić et al. (2017).

For the pollutant source apportionment, Unmix (USEPA, 2007) was performed. As input variables, the maximum number of pollutants was selected according to trials and errors, which yield the most physically meaningful results. In addition, we applied GRRF to analyze the importance of Unmix derived sources.

2.5. Data presentation

In addition to the Supplementary material and Tables presented in the manuscript, we have generated a web-presentation of the results hosted at http://envpl.ipb.ac.rs/papers/18/BreastMilkPOPs/ to deliver customizable and functional Plotly's (Sievert et al., 2017) interactive figures that support and facilitate the exploratory analysis of our results. The web presentation is optimized for Chrome web browser, and it can be downloaded from the website in.zip format (approximate size 340 MB).

3. Results and discussion

3.1. Pollutant levels

Basic statistics for POP concentrations and the studied mother's parameters, age, and birth, are given in Table 1. Probability density function showed a unimodal non-normal distribution of the variables, which is right-skewed towards the lower concentrations (Fig. S1, Supplementary material). As each woman is representative for herself, we cannot consider the POP values that deviated from the most common likelihood to be extreme or atypical. The linear and loess functions similarly fit the regression curves but demonstrated an apparent inconsistency particularly pronounced in the domain of lower POP concentrations as well as between the pollutants and the maternal age and parity.

The histograms (Fig. S2a-d, Supplementary material) showed that the majority of the highest pollutant concentrations tended to occur in the milk samples of women in their thirties who had more than one childbirth. We note that this pattern is not firmly consistent and random deviations occurred. In accordance, aggregation plots (Fig. S3a-b, Supplementary material) illustrated increasing levels and shares of PCB compounds, *p,p´*-DDE, and *p,p ´*-DDD from primiparae towards multiparae. The constituents γ-HCH, p,p´-DDT, PCB-123, PCB-189, and PCB-74 deviated from the described tendency.

The results imply that birth and consequently age are important parameters influencing milk composition. As a complementary addition to the presented basic statistics, loess regression indicated prevailing dispositions of milk constituents associated with defined age categories (Fig. S4a-b, Supplementary material). We note that two categories should be approached cautiously due to the size of datasets, specifically 19–24 (N = 8) and 37–45 (N = 9) year-old women. The contaminant concentrations mainly remained unaltered regarding the age of primiparae, whereas their content exhibited specific inclines in the breast milk of multiparae (S4a-b, Supplementary material). Moreover, the variances marked with smoothing bandwidth (95% confidence interval) increased with parity indicating the complex processes that influence POP pathways in the breast milk. Since breastfeeding during lactation has been recognized as one of the most important factors for POP elimination from the maternal body, the parity factor has usually been negatively correlated with POP burden (e.g., Polder et al., 2009). However, a review of data on longitudinal changes in PCB levels during lactation highlighted their non-consistently depuration rates, which could not be confidently derived (Vigh et al., 2013). Our results concerning secundiparae showed a slight decrease of OCPs (except *p,p*´-DDD), indicator congeners, dioxin-like PCBs (-105, −118, and −156), PCB-74, and PCB-170 upon 29–30 years. Above this year interval, the pollutant levels increased and usually achieved their maximum in samples of 35-year-old mothers. These tendencies were confirmed for mothers with their third delivery only for dioxin-like PCBs and congener −74, while the other compounds exhibited exactly the opposite. Since this study was designed to represent the most likely distribution of POPs in the general population, a firm conclusion of their excretion depending on the mother's metabolism could not have been made. Concerning this issue, further research is required; the milk of the same mother after the first, second and third delivery should be sampled. The breastfeeding duration of each infant and re-entering of the pollutants during the mother's life between each breastfeeding should be considered as well. However, given that the lipid content in milk samples (1.3–8.7% or 2.1–9.6%; median = 3.8%, 4.47%) was independent of the number of births, we excluded it as a determinative cause of the differences between mothers with a second and third delivery.

3.2. Relationships among pollutants based on their concentrations and sources

The low Pearson's correlation coefficients ($r < 0.50$) and stretched density implied no or very weak linear explanatory linkage between the milk constituents and mother's conditions (Fig. S1). In addition to Pearson's correlation coefficients, widely represented as a common measure of a linear relationship between variables, we performed GRRF to supplement interpretations on the pollutant's interactions. The GRRF-derived variable importance (Table 2) implied a negligible impact of α- and β-HCH on the other investigated compounds, which is a likely consequence of their different metabolic pathway once they enter the maternal body. Regarding DDT xenobiotics, the GRRF estimated the highest relative importance of *p,p*´-DDE for the prediction of the following contaminants: PCB118 > PCB-170 > PCB−153 > PCB−180 > PCB-105 > PCB-167 > *p,p*´-DDT > PCB-138. Similarly, a prominently lower importance was observed for *p,p*´-DDT.

Out of the 17 examined congeners, GRRF recognized PCB-153, PCB-180, PCB−170, PCB−118, PCB−156, PCB−105, and PCB−138 as the most important for the mutual prediction, with a prominent influence of −153 and −180 on the others. Highly correlated predictions of the listed compounds were also confirmed using generic PBPK modeling to assess infant toxicokinetic profiles (Verner et al., 2009). The contaminants belong to non-dioxin-like/indicator (-138, −153, −180) and dioxin-like PCBs (-(-105, −118, −156)which are classified according to their toxic and biological effects. Dioxin-like PCBs resemble the reference compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which elicits AhR-mediated biochemical and toxic responses and resists in the food chain (Van den Berg et al., 2006). The chlorine atom at the *ortho* position is common to both GRRF extracted groups and PCB-170 implying that mono chlorine attached to the biphenyl ring is essential for PCB profiles in breast milk regardless of the ring coplanar structure and toxicological properties. Our results support previous conclusions (Mannetje et al., 2012; Vasios et al., 2016) who proposed the position of the halogen substitutes as suggestive for the rigidity of the molecular structure and consequently PCBs' ability to pass from blood to breast milk. The authors suggested other characteristics including lipophilicity, molecule diameter and weight, and molecular descriptors such as the number of attached halogens being less determinative for the PCB partitioning between blood serum and milk. Further studies with extensive datasets should be performed to confirm these observations for similarly structured PCB congeners such as −157, −114, and −189

Table 2
Guided regularized random forest (GRRF) derived relative variable importance [%].

	α-HCH	β-HCH	γ-HCH	HCB	*p,p*´-DDE	*p,p*´-DDD	*p,p*´-DDT	PCB-138	PCB-153	PCB-180	PCB-105	PCB-118	PCB-156	PCB-167	PCB-74	PCB-170	Mothers' age	Birth
α-HCH		4.2	28.0	17.6	3.4	3.5	3.4	4.2	2.7	2.8	11.9	4.4	3.8	8.8	25.0	6.0	3.7	2.7
β-HCH	2.0		2.5	5.3	3.2	4.2	0.9	0.5	1.2	0.5	1.5	2.2	0.7	1.7	2.5	0.4	10.7	4.8
γ-HCH	15.8	3.1		4.0	1.7	7.2	1.6	0.9	0.6	0.6	2.6	1.5	0.8	3.3	29.0	0.4	3.7	3.4
HCB	7.9	24.5	5.6		5.6	4.8	7.4	1.2	2.1	2.1	14.5	9.0	2.3	11.9	6.7	1.7	5.1	5.8
p, p´-DDE	2.0	3.3	1.7	0.9		10.1	1.9	2.0	1.9	2.7	1.4	2.8	2.0	3.0	1.7	2.0	8.7	3.9
p, p´-DDD	0.3	1.0	0.4	0.1	0.9		0.9	0.4	0.2	0.1	0.2	0.2	0.5	0.3	0.3	0.1	2.9	3.0
p, p´-DDT	4.5	8.3	3.1	11.5	5.7	15.8		5.1	4.8	6.9	11.3	8.5	5.2	12.3	5.4	5.9	3.3	6.9
PCB−138	5.9	0.8	3.3	0.3	5.3	3.9	2.5		8.0	4.7	3.3	2.3	6.0	2.1	1.2	11.4	6.6	3.2
PCB−153	4.1	3.6	1.1	1.8	11.3	8.9	8.4	22.0		17.8	5.2	10.9	14.5	4.4	0.5	14.0	4.5	5.8
PCB−180	3.8	6.5	1.0	2.6	9.5	2.8	11.3	12.4	19.4		5.0	7.4	17.4	4.2	0.8	15.7	8.5	8.4
PCB−105	15.5	4.8	8.7	20.7	7.1	5.9	13.4	4.7	9.0	8.2		27.4	10.4	14.0	9.4	6.3	3.0	7.4
PCB−118	4.3	10.3	2.2	9.8	14.7	5.2	10.8	6.8	13.6	5.7	13.5		7.7	11.1	3.0	7.5	9.0	4.3
PCB−156	2.8	6.3	1.0	2.9	9.4	7.1	11.1	17.4	12.2	19.2	5.4	3.4		9.7	1.4	17.3	3.2	8.8
PCB−167	9.9	8.6	7.3	11.5	7.1	3.3	10.3	3.8	4.8	6.6	11.3	10.6	9.7		10.4	10.6	3.0	4.8
PCB−74	17.0	4.2	32.1	7.3	1.7	5.8	5.4	1.1	0.6	0.3	7.2	3.0	0.8	7.4		0.3	3.0	3.8
PCB−170	3.6	7.3	0.9	2.4	11.5	7.3	10.1	16.7	18.4	21.4	5.3	5.5	17.6	5.5	0.7		7.7	7.1
Mothers' age	0.5	2.5	1.2	1.2	1.5	2.6	0.3	0.7	0.5	0.3	0.3	0.6	0.4	0.3	1.6	0.3		16.0
Birth	0	0.8	0.2	0.3	0.5	1.4	0.2	0.1	0	0	0.1	0.1	0.1	0.1	0.5	0	13.4	

Table 3
Unmix derived source profiles [%] and modeling statistics; RMSE − root mean square error.

Species	Source 1	Source 2	Source 3	Source 4	Mean	RMSE	Slope	Intercept	r^2	Outliers
α-HCH	10.1	36.1	39.8	14.1	0	0.03	0.97	0.01	0.95	0
β-HCH	79.6	0	0	20.4	0	0.19	0.97	0.02	0.96	1
γ-HCH	11.7	72.9	13.6	1.8	0	0.47	1	0	0.98	0
HCB	67.5	23.4	8.1	1.0	− 0.01	0.23	0.99	0.02	0.97	0
p,p´-DDE	13.3	0.4	33.0	53.3	1.68	7.57	1.24	− 4.88	0.72	1
p,p´-DDD	0	0	6.4	93.6	0.01	0.09	0.65	0.09	0.52	1
PCB − 138	0	0	52.9	47.2	0.42	1.29	0.86	0.28	0.89	1
PCB − 153	7.4	5.0	53.8	33.7	0.03	1.70	1	− 0.07	0.96	0
PCB − 180	4.4	3.6	83.1	8.9	0.03	0.53	1	− 0.05	0.99	0
PCB − 105	10.6	14.3	28.8	46.4	− 0.01	0.12	0.98	0.02	0.94	0
PCB − 118	18.3	8.4	27.0	46.3	0	0.17	1	0	0.92	1
PCB − 156	1.8	4.1	58.6	35.6	− 0.02	0.13	0.97	0.04	0.96	0
PCB − 167	13.9	12.8	28.8	44.5	− 0.01	0.08	0.96	0.02	0.92	0
PCB − 74	15.2	51.5	5.0	28.3	0.03	0.27	1.02	− 0.05	0.95	1
PCB − 170	0	4.7	80.6	14.7	0.09	0.56	0.96	0.04	0.98	0
Average contribution	16.9	15.8	34.6	32.6						

Table 4
Regression statistics: correlation coefficient (r), mean absolute (Mean Abs.), root mean square (RMSE), relative (Rel.) and relative absolute (Rel. Abs.) errors; *the compounds for which linear regression did not show satisfactory prediction.

Species	Regression method Multiple linear regression					Best performing ML classifier						
	r	Mean Abs.	RMSE	Rel. [%]	Rel. Abs. [%]	Attributes		r	Mean Abs.	RMSE	Rel. [%]	Rel. Abs. [%]
α. HCH	0.63	0.08	0.19	45.2	54.1	LWL	Linear NN Search, MLP	0.78	0.06	0.15	34.3	41.3
β. HCH	0.53	0.54	0.98	56.1	63.9	Random Forest		0.94	0.23	0.39	23.3	26.9
γ-HCH	0.66	1.6	3.05	72.5	70.7	Gaussian Processes		0.98	0.64	0.85	29.3	29
HCB	0.65	0.71	1.28	46.5	51.4	LWL	Linear NN Search, Ibk	0.99	0.08	0.15	5.1	5.7
p,p´-DDE	0.61	6.18	10.49	49.2	72.2	Attribute Selected	REPTree	0.89	4.04	5.97	32.1	47.3
p,p´-DDD	0.17	0.08	0.12	27.7	102.7	Random Forest		0.97	0.02	0.04	7.5	28.2
p,p´-DDT	0.87	1.94	2.58	49.9	46.3	Bagging	M5 Rules	0.93	1.25	1.88	32.2	30.2
PCB − 28*	0.71	1	1.59	52.6	73.4	LWL	Linear NN Search, Linear Regression	0.96	0.43	0.57	22.7	32.1
PCB − 52*	/	/	/	/	/	/		/	/	/	/	/
PCB − 101*	0.11	0.37	0.81	110.3	138.3	Additive Regression	Ibk	0.82	0.17	0.25	43.6	67.2
PCB − 138	0.93	1.04	1.38	22.5	40	LWL	Linear Regression	0.98	0.51	0.8	6.9	22.1
PCB − 153	0.93	1.73	3.38	18.4	28.4	Attribute Selected	SMOreg	0.97	1.12	1.95	12	18.7
PCB − 180	0.98	0.72	1.34	14.9	19.4	Additive Regression	SMOreg	0.99	0.52	0.79	10.8	14.4
PCB − 105	0.94	0.12	0.17	18.9	32.4	Attribute Selected	SMOreg	0.98	0.06	0.09	10	17.4
PCB − 114*	0.81	0.31	0.53	73.8	54.4	Additive Regression	M5 Rules	0.97	0.09	0.22	23.2	15.8
PCB − 118	0.89	0.2	0.28	23.3	39.7	Random Forest		0.98	0.08	0.12	9.3	15.9
PCB − 123*	0.13	0.05	0.07	33.2	92	Bagging	M5 Rules	0.95	0.02	0.02	16.3	36.5
PCB − 156	0.95	0.14	0.21	18.3	30	LWL	Linear NN Search, SMOreg	0.98	0.1	0.15	13.1	21.9
PCB − 157*	/	/	/	/	/	/		/	/	/	/	/
PCB − 167	0.92	0.09	0.12	20.9	36.8	Random Forest		0.99	0.03	0.05	7.8	13.9
PCB − 189*	0.46	0.13	0.19	36.4	130.6	LWL	Linear NN Search, MLP	0.84	0.05	0.07	17.4	52.7
PCB − 60*	/	/	/	/	/	/		/	/	/	/	/
PCB − 74	0.87	0.4	0.67	34	41.9	Attribute Selected	MLP	0.96	0.24	0.36	20.4	25.5
PCB − 170	0.97	0.43	0.8	13.2	20	LWL	Linear Regression	0.99	0.25	0.35	7.7	12.0

whose concentrations in this study were lower than the LOD.

In addition, GRRF proposed a slight influence of the mother's age on the PCB and OCP composition of the milk regardless of the first, second or third child delivery. The compounds associated with this importance were β-HCH, *p,p´*-DDE, PCB-138, PCB-180, PCB-118, PCB-156 and PCB-170, whose interrelations are discussed above.

Unmix differentiated four factors, i.e., source profiles (Table 3), with high determination (> 0.90) and correlation (> 0.90) coefficients. The highest attributions of β-HCH (78%) and HCB (67%), and γ-HCH (73%) characterized the first and the second factor (Source 1 and 2), respectively, thereby representing the POPs mainly generated as by-products of lindane (United Nations Environment, 2017). The overall highest shares (approximately 30%) were allocated to the third and fourth factor. The "heavy" hexa- to hepta-chloro occupational congeners (Seegal et al., 2011): PCB-180 (83%), PCB-170 (81%), PCB-156 (59%), PCB-153 (54%), and PCB-138 (53%), which have a higher half-life than the "light" ones, moderately contributed to the third factor (Source 3). The fourth factor (Source 4) was recognized as a metabolic pathway of *p,p´*-DDT due to the highest shares of *p,p´*-DDD (93%), *p,p´*-DDE (53%), and partially belongs to the "light" tetra- to penta-chloro congeners PCBs (around 46%). These results are in accordance with the mutual associations of pollutants selected by GRRF. In addition, GRRF did not recognize a noticeable relationship between Unmix derived profiles and the mother's age (Table 3).

Ratios of Unmixed-derived source contributions are likely to be consistent throughout the maternal lifespan, which is reasonable considering the life expectancy of the pollutants (Fig. 5Sa-b, Supplementary material). We note that each source represents a specific

Table 5
Regression statistics: correlation coefficient (r), mean absolute (Mean Abs.), root mean square (RMSE), relative (Rel.) and relative absolute (Rel. Abs.) errors for maternal age and parity.

	GRRF atribute selection				Unmix derived source contributions			
	Mothers' age	Mothers' age with Birth	Birth	Birth with Mothers'age	Mothers' age	Mothers' age with Birth	Birth	Birth with Mothers'age
Best performing ML classifier	Additive Regression (K*)	Random Forest	Additive Regression (Desicion Stump)	SMOreg	Random Sub Space (Ibk)	LWL (Linear NN Search, Random Forest)	Bagging (IBk)	Ibk
r	0.98	0.88	0.77	0.96	0.69	0.78	0.9	1
Mean Abs.	0.49	2.08	0.4	0.09	3.07	2.54	0.23	0
RMSE	0.97	2.6	0.45	0.2	3.83	3.17	0.28	0
Rel. [%]	1.6	6.9	21.1	4.6	10.4	8.6	14.8	0
Rel. Abs. [%]	11.7	49.7	76.5	16.8	77.2	63.8	44.4	0

mixture of the pollutants grouped according to similar chemical structure or behavior that has been discussed in the previous paragraph. Highly chlorinated congers are less susceptible to elimination mechanisms compared to the more volatile OCPs, which results in their continuously increased levels in the milk of older mothers. Despite this, pronounced ratios of 500:0 and 400:0 for Source 1: Source 3 and Source 1: Source 2, respectively, occurred in the milk samples of mothers in their mid-twenties; but this should be approached cautiously due to the small number of samples studied herein.

Given the representative range of maternal ages due to the size of dataset, the ratio of HCH to DDT compounds and heavy PCB congeners mainly remains unaltered with age and number of born children (Fig. 5Sa-b, Supplementary material). Ratios among the congeners, which were recognized to be functionally dependent, showed changeable signature and maximums between first-time mothers and multiparae. Loess regression of Unmix derived source contributions (Fig. S4c, Supplementary material) supported these results. The source contributions varied among the ages of primiparae and secundiparae, whereas the shares of Sources 1, 2 and 3 prominently increased in the samples of the mothers with third child delivery. This observation supports the conclusions of Hooper et al. (2007), who emphasized that breast-feeding does not substantially reduce PCBs in the milk samples of primiparae and indicated no markedly lower fetal and lactational exposures for the second or third child. However, these indications need further investigation since some studies reported that pregnancy, lactation, and consequently, parity, are factors that reduce POP concentrations in the maternal body. For example, Schecter et al. (1998) reported that prenatal blood contains higher concentrations of POPs than postpartum maternal blood, while Waliszewski et al. (2002) observed that the colostrum has higher levels of POPs than mature milk.

The multiple linear regression (MLR) showed that the method could provide predictions of PCB-138, PCB-153, PCB-180, PCB-105, PCB-118, PCB-167 and PCB-170, based on the other congeners with relative errors ranging from 20% to 40%, and correlation coefficients higher than 0.90 (Table 4). GRRF and Unmix analyses derived specific joining for all of these compounds. We note that these findings should be approached only as indications and not as absolute phenomena due to our limited dataset. In cases when MLR did not reveal a satisfactory prediction, the other ML methods based on GRRF feature selection showed better performances (Table 4), confirming prominent non-linear relationships between pollutants, and emphasizing the possible complexity of their interactions. Specifically, RF, Gaussian Processes and LWL using IBk can provide predictions of β-HCH, γ-HCH and HCB, respectively, with relative errors lower than 30% and high correlation coefficients ($r > 0.90$). The calculations for *p,p´*-DDT and its metabolites could thus be explained. Moreover, given the MLR-extracted congeners and accuracy metrics, *r* and the relative absolute error, LWL, Attribute Selected Classifier and Additive Regression (SMOreg) appeared to be superior to MLR.

Apart from a description of a functional dependency of the pollutants on each other, ML methods such as Additive Regression (K*, $r = 0.98$, relative error = 1.6%) based on GRRF attribute selection could be proposed as the best performing classifiers to link maternal age and milk composition, whereas dependence on birth showed poorer results (Table 5). Conversely, the prediction of maternal parity was more accurate when we employed Bagging on Unmix derived source contribution (IBk, $r = 0.90$, relative error = 14.8%).

4. Conclusion

Understanding the causative occurrence of POPs in breast milk represents a topic of global significance because of their continuous impact on human health, particularly sensitive sub-populations such as women and children. In this study, we employed different ML methods and a source apportionment model to estimate the OCP and PCB interrelations as well as their dependence on the mother's age and child delivery rather than to provide spatio-temporal interpretations of data and a toxicology risk assessment. This study revealed changeable POP ranges in the milk of primiparae and multiparae. Regression ML methods showed a reliable prediction among the pollutants for which GRRF feature selection and Unmix analyses resolved correlated profiles emphasizing the importance of the constitutional descriptors of congeners, such as the number and position of the attached chlorine. The proposed analyses could serve as a promising methodology for future investigations in the epidemiology in the context of human's health. However, we note that the presented results need further verification with extensive datasets and in terms of POP physiological and metabolic pathways as well as genotoxicological effects.

Acknowledgments

The authors are grateful to the Croatian Science Foundation (Project OPENTOX, No. 8366) and the Ministry of Education and Science of the Republic of Serbia (Projects No. III43007 and III41011). We wish to thank all the staff of the Zadar County Health Center, Community, and Primary Health Care, for their assistance in the sampling of human milk.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2019.01.087.

References

Deng, H., Runger, G., 2013. Gene selection with guided regularized random forest. Pattern Recognit. 46, 3483–3489.
Fång, J., Nyberg, E., Winnberg, U., Bignert, A., Bergman, Å., 2015. Spatial and temporal trends of the Stockholm Convention POPs in mothers' milk — a global review.

Environ. Sci. Pollut. Res. 22, 8989–9041.

Frank, E., Hall, M., Holmes, G., Kirkby, R., Pfahringer, B., Witten, I.H., Trigg, L., 2005. Weka. Data Mining and Knowledge Discovery Handbook 1305–1314 Springer, US.

Hooper, K., She, J., Sharp, M., Chow, J., Jewell, N., Gephart, R., Holden, A., 2007. Depuration of polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) in breast milk from California first-time mothers (primiparae). Environ. Health Perspect. 115, 1271–1275.

Klinčić, D., Herceg Romanić, S., Matek Sarić, M., Grzunov, J., Dukić, B., 2014. Polychlorinated biphenyls and organochlorine pesticides in human milk samples from two regions in Croatia. Environ. Toxicol. Phar. 37, 543-552.

Klinčić, D., Herceg Romanić, S., Brčić Karačonji, I., Matek Sarić, M., Grzunov Letinić, J., Brajenović, N., 2016. Organochlorine pesticides and PCBs (including dl-PCBs) in human milk samples collected from multiparae from Croatia and comparison with primiparae. Environ. Toxicol. Pharmacol. 45, 74–79.

Kotthoff, L., Thornton, C., Hoos, H.H., Hutter, F., Leyton-Brown, K., 2016. Auto-WEKA 2.0: Automatic model selection and hyperparameter optimization in WEKA. J. Mach. Learn. Res. 17, 1–5.

Li, L., Qian, J., Ou, C.Q., Zhou, Y.X., Guo, C., Guo, Y., 2014. Spatial and temporal analysis of Air Pollution Index and its timescale-dependent relationship with meteorological factors in Guangzhou, China, 2001–2011. Environ. Pollut. 190, 75–81.

Lignell, S., Winkvist, A., Bertz, F., Rasmussen, K.M., Glynn, A., Aune, M., Brekke, H.K., 2016. Environmental organic pollutants in human milk before and after weight loss. Chemosphere 159, 96–102.

Mannetje, A.'t., Coakley, J., Jochen, M.F., Harden, F., Toms, L.M., Douwes, J., 2012. Partitioning of persistent organic pollutants (POPs) between human serum and breast milk: a literature review. Chemosphere 89, 911–918.

McCabe, M.F., Rodell, M., Alsdorf, E.D., Miralles, G.D., Uijlenhoet, R., Wagner, W., Lucieer, A., Houborg, R., Verhoest, N.E.C., Franz, E.T., Shi, J., Gao, H., Wood, F.E., 2017. The future of Earth observation in hydrology. Hydrol. Earth Syst. Sci. 21 (3879–14).

Mydlová-Memersheimerová, J., Tienpont, B., David, F., Krupcík, J., Sandra, P., 2009. Gas chromatography of polychlorinated biphenyl congeners on an extremely efficient nonselective capillary column. J. Chromatogr. A 1216, 6043-6062.

Perišić, M., Maletić, D., Stanišić Stojić, S., Rajšić, S., Stojić, A., 2017. Forecasting hourly particulate matter concentrations based on the advanced multivariate methods. Int. J. Environ. Sci. Tech. 14, 1047–1054.

Polder, A., Skaare, J.U., Skjerve, E., Løken, K.B., Eggesbø, M., 2009. Levels of chlorinated pesticides and polychlorinated biphenyls in Norwegian breast milk (2002–2006), and factors that may predict the level of contamination. Sci. Total Environ. 407, 4584–4590.

Ryan, F.W., 2016. The air quality forecast rote: recent changes and future challenges. J. Air Waste Manag. Assoc. 66 (6), 576–596.

Schecter, A., Kassis, I., Papke, O., 1998. Partitioning of dioxins, dibenzofurans, and coplanar PCBs in blood, milk, adipose tissue, placenta and cord blood from five American women. Chemosphere 37, 1817–1823.

Seegal, R.F., Fitzgerald, E.F., Hills, E.A., Wolff, M.S., Haase, R.F., Todd, A.C., Parsons, P., Molho, E.S., Higgins, D.S., Factor, S.A., Marek, K.L., Seibyl, J.P., Jennings, D.L., McCaffrey, R.J., 2011. Estimating the half-lives of PCB congeners in former capacitor workers measured over a 28-year interval. J. Expo. Sci. Environ. Epidemiol. 21, 234–246.

Sievert, C., Parmer, C., Hocking, T., Chamberlain, S., Ram, K., Corvellec, M., Despouy, P., 2017. plotly: Creat. Interact. Web Graph. via plotly. js. R. Package Version 4. 6. 0.

Stockholm Convention, 2001. Stockholm Convention for Persistent Organic Pollutants. Available at: ⟨http://chm.pops.int/⟩. Accessed date: December 2017.

Stojić, A., Stanić, N., Vuković, G., Stanišić, S., Perišić, M., Šoštarić, A., Lazić, L., 2019. Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition. Sci. Total Environ. 653, 140–147.

Stojić, A., Maletić, D., Stojić, S.S., Mijić, Z., Šoštarić, A., 2015. Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. Sci. Total. Environ. 521, 19–26.

Šoštarić, A., Stanišić Stojić, S., Vuković, G., Mijić, Z., Stojić, A., Gržetić, I., 2017. Rainwater capacities for BTEX scavenging from ambient air. Atmos. Environ. 168, 46–54.

Team, 2012. R: A Lang. Environ. Stat. Comput. ⟨http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf⟩.

Tonga, Y., Luo, K., Runkui, L., Lu, P., Ang, L., Mingan, Y., Qun, X., 2018. Association between multi-pollutant mixtures pollution and daily cardiovascular mortality: an exploration of exposure-response relationship. Atmos. Environ. 186, 136–143.

United Nations Environment, 2017. The 16 New POPs, An introduction to the chemicals added to the Stockholm Convention on Persistent Organic Pollutants by the Conference of the Parties. Available at: ⟨http://chm.pops.int/⟩. Last (accessed November 2017).

United Nations Environment Programme, 2013. Results of the global survey on concentrations in human milk of persistent organic pollutants by the United Nations Environment Programme and the World Health Organization, Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants, Sixth meeting, Geneva, 28 April–10 May.

United States Environmental Protection Agency (USEPA), 2007. EPA Unmix6.0 Fundamentals and User guide. USEPA Office of Research and Development.

Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223–241.

Vasios, G., Kosmidi, A., Kalantzi, O.-I., Tsantili-Kakoulidou, A., Kavantzas, N., Theocharis, S., Giaginis, C., 2016. Simple physicochemical properties related with lipophilicity, polarity, molecular size and ionization status exert significant impact on the transfer of drugs and chemicals into human breast milk. Expert Opin. Drug Metab. Toxicol. 11, 1273–1278.

Verner, M.-A., Ayotte, P., Muckle, G., Charbonneau, M., Hadad, S., 2009. A physiologically based pharmacokinetic model for the assessment of infant exposure to Persistent organic pollutants in Epidemiologic studies. Environ. Health Perspect. 117, 481–487.

Vigh, É., Colombo, A., Benfenati, E., Håkansson, H., Berglund, M., Bódis, J., Garai, J., 2013. Individual breast milk consumption and exposure to PCBs and PCDD/Fs in Hungarian infants: a time-course analysis of the first three months of lactation. Sci. Total Environ. 449, 336–344.

Waliszewski, S.M., Aguirre, A.A., Infanzon, R.M., Siliceo, J., 2002. Persistent organochlorine pesticide levels in maternal blood serum, colostrum, and mature milk. Bull. Environ. Contam. Toxicol. 68, 324–331.

Weka Sourceforge, 2016. ⟨http://weka.sourceforge.net/packageMetaData⟩, Accessed date: June 2016.

Science of the Total Environment 653 (2019) 140–147

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition

Andreja Stojić [a,*], Nenad Stanić [b], Gordana Vuković [a], Svetlana Stanišić [b], Mirjana Perišić [a], Andrej Šoštarić [c], Lazar Lazić [d]

[a] Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Pregrevica 118, 11000 Belgrade, Serbia
[b] Singidunum University, Danijelova 32, 11000 Belgrade, Serbia
[c] Institute of Public Health Belgrade, Despota Stefana 54, 11000 Belgrade, Serbia
[d] Faculty of Physics, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

HIGHLIGHTS

- XGBoost and SHAP methods were applied to investigate TEX air – rainwater partition.
- XGBoost relative errors were below 20% when evaluating variable relationships.
- Air TEX concentrations, rainwater and air temperature govern TEX distribution.
- Ion rainwater concentrations and wind speed occasionally impact TEX transfer.

GRAPHICAL ABSTRACT

Figure: FEATURE IMPACT ON RAINWATER TOLUENE

ARTICLE INFO

Article history:
Received 3 September 2018
Received in revised form 25 October 2018
Accepted 27 October 2018
Available online 30 October 2018

Editor: Jianmin Chen

Keywords:
Multiphase system
Wet deposition
BTEX
Machine learning
XGBoost
SHAP

ABSTRACT

Current research suggests that, apart from photochemical reactions, toluene, ethylbenzene and xylene (TEX) removal from ambient air might be affected by atmospheric precipitation, depending on the concentrations and water solubility of the compounds, Henry's law, physico-chemical properties of the water, as well as the frequency and intensity of precipitation events. Nevertheless, existing knowledge of the role that wet deposition plays in biogeochemical cycles of volatile species remains insufficient, and this topic requires more scientific effort to be explored and understood. In this study, we employed the eXtreme Gradient Boosting tree ensemble for revealing TEX transfer from ambient air to rainwater, and applied a novel SHapley Additive exPlanations feature attribution framework to examine the relevance of the monitored parameters and identify key factors that govern wet deposition of TEX. According to the results, main impacts, including ambient air TEX concentrations, and rainwater and air temperatures, and occasional, but less important impacts, including wind speed, air pressure, turbidity, and total organic carbon, NO_3^-, Cl^- and K^+ rainwater concentration, shaped TEX partition between gaseous and aqueous phases during rain events.

1. Introduction

The behavior and distribution of volatile organic compounds (VOCs) in ambient air and atmospheric precipitation has attracted considerable

* Corresponding author.
E-mail address: andreja.stojic@ipb.ac.rs (A. Stojić).

https://doi.org/10.1016/j.scitotenv.2018.10.368
0048-9697/© 2018 Elsevier B.V. All rights reserved.

scientific attention over recent years, due to the abundance and environmental effects of VOCs, as well as their evidenced toxic and carcinogenic nature (Stojić et al., 2015). Theoretically, the partition of volatile species between the gaseous and aqueous phases in the atmosphere might be described by Henry's law and an enrichment factor (EF) (Kampf et al., 2013; Kurtén et al., 2015; Okochi et al., 2005; Sander, 2015). However, some empirical findings suggest the process of wet deposition appears to be more complex and also dependent on other factors, including physico-chemical properties of atmospheric water and surrounding air, as well as on the rainwater dissolved aerosols containing VOCs (Šoštarić et al., 2017). Therefore, the important topic of air pollutant deposition requires more scientific effort to be explored and understood.

Over recent years, the application of artificial intelligence implemented in machine learning has become evident in the field of environmental science, and supported by the great availability of high-dimensional data. Nevertheless, tremendous advances in prediction of air pollutant distribution and behavior in the environment remained somewhat limited and underexploited due to the fact that complex models' performances and interpretability are in apparent conflict (Alvarez-Melis and Jaakkola, 2018a, 2018b). While the best explanation of a simple model is the model formulation itself, understanding and correctly interpreting models parameterized with a large number of variables, such as random forest or an extreme gradient boosting machine (XGBoost), can be challenging (Staniak and Biecek, 2018). Likewise, a single simple decision tree is easy to interpret, but ensembles of hundreds and thousands of trees, which would have superior predictive capabilities, are not interpretable (Tan et al., 2016).

Although some authors consider the tendency to explain complex models with a single point-wise approach too optimistic (Alvarez-Melis and Jaakkola, 2018a, 2018b), simple approximations provide valuable insight into understanding causality, features that drive the model's prediction, the prediction's accuracy and finally, provide opportunities for robust validation procedures and model improvement (Fong and Vedaldi, 2017). In other words, interpretation methods have been developed to shed light on scientific problems where human intuition and domain knowledge are often limited (Montavon et al., 2017). The goal of current interpretation methods which are able to mimic the behavior of machine learning algorithm is not to explain the logical concept behind the black box, but to provide feasible reasons for the choice of a particular instance (Guidotti et al., 2018). As shown by Lundberg et al. (2018), current interpretation frameworks lead to inconsistent results and often contradictory explanations for machine learning algorithms. Therefore, Lundberg and Lee (2017a) recently developed SHAP (Shapley Additive exPlanations), an additive feature attribution method, which they showed has a unique solution in the class of explanation models aimed at post-hoc interpreting machine learning methods, and which is more aligned with human intuition. Unlike approaches that provide a specific global predictor, the SHAP framework provides an explanation of the tree ensemble's overall behavior in the form of particular feature contributions. As well as other methods for interpreting machine learning predictions, SHAP is becoming increasingly popular as a tool in predicting natural and social phenomena. For instance, the recent study of Janizek et al. (2018) combined SHAP and an XGBoost tree-based approach to predict and explain the synergy of novel drug combinations for precision cancer treatment.

Our previous studies were aimed at exploring the contribution of atmospheric precipitation on benzene, toluene, ethylbenzene and xylene (BTEX) removal from ambient air and mechanisms of BTEX partition between aqueous and gaseous phases through field experiments and laboratory simulations (Šoštarić et al., 2016, 2017). In this study, we used the SHAP algorithm to obtain a more detailed insight into the factors that govern toluene, ethylbenzene and xylene (TEX) environmental distribution and transfer from ambient air to rainwater. Beside the accuracy and consistency of the results achieved by SHAP analysis, the present study reveals in which respect the predictors affected the investigated variables.

2. Materials and methods

A detailed description of the sampling and measurement campaign, as well as the obtained dataset used in this study, is given in our previous paper (Šoštarić et al., 2017). In brief, TEX concentrations in air and rainwater were measured simultaneously during several rain events in the summer and autumn of 2015 in a suburban residential area in Belgrade, Serbia, where there were a number of local TEX emission sources, mainly solvent-related or winter-active fireboxes. The measurements were obtained by proton transfer reaction mass spectrometry (Standard PTR-quad-MS, Ionicon Analytic GmbH, Innsbruck, Austria). Beside TEX concentrations, the dataset contained rainwater physico-chemical parameters including major inorganic anions (F^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^-), dissolved cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}), total organic carbon (TOC), electrical conductivity (EC), UV extinction, turbidity (NTU), pH, rainwater temperature and meteorological parameters (rain intensity, wind speed and direction, pressure, humidity and temperature).

Regression analysis by means of XGBoost was implemented for estimating the relationships between TEX rainwater concentrations and EFs on one hand, and TEX ambient air concentrations, and physico-chemical and meteorological parameters, on the other (Chen and Guestrin, 2016). Gradient boosting is a technique implemented in a complex prediction model by iterative combinations of ensembles of weak prediction models into a single strong learner. Regarding decision trees, gradient boosting builds a sequential series of smaller trees, where each tree tries to complement each other and correct for the residuals in the predictions made by all previous trees (Sheridan et al., 2016). XGBoost is a general-purpose supervised machine learning method achieving high accuracy in a wide range of practical applications, usually outperforming random forests, support vector machines and deep learning neural networks. In this study we used Python (Python Software Foundation) XGBoost implementation (XGBoost Python Package). The dataset was split into stratified training (80%) and validation (20%) sets. Hyperparameter tuning was implemented using a brute-force grid search and stratified cross-validation that was replicated ten times. The best performing values were used for the final model.

The ability to accurately interpret a model's prediction supports deeper understanding of the process being modeled. A widely accepted interpretation approach is the Single tree approximation, which induces a single tree as a comprehensive global predictor that approximates the concept represented by the algorithm, covers the highest possible number of correct training examples, and minimizes the error of the remaining examples. The Decision Rules is another commonly used understandable method for extracting and refining the set of rules, and which capture only the most significant clauses without duplicating information from the trained models. Furthermore, the Feature Importance and Saliency Mask methods are designed to identify the smallest patch which exposes most clearly the central properties of the dataset and removal of which would affect the error of the model significantly (Dabkowski and Gal, 2017). There are also other currently employable interpretation methods, the description of which is beyond the scope of this brief summary.

Nowadays, a variety of statistical tools including tree-based modeling packages can be implemented to compute a measure of feature importance and provide information regarding the features that govern a model's prediction. Unlike the conventional attribution methods, such as those implemented in gradient boosting machines and random forests, which are not individualized for each prediction and because of this, are prone to inconsistency, the SHAP method offers uniquely consistent and locally accurate attribution values (Lundberg et al., 2018). Based on unification and additive attribution algorithms, SHAP values attribute to each feature the change in the expected model prediction when conditioning on that feature (Lundberg and Lee, 2017a). SHAP overcomes the main drawback of inconsistency, suppressing the possibility of underestimating the importance of a feature with a certain attribution value.

The SHAP runs from exponential to $O(TLD^2)$ for unbalanced trees and $O(TL \log^2 L)$ for balanced trees, where T is the number of trees, L is the maximum number of leaves in any tree, and D is the maximum depth of any tree (Lundberg and Lee, 2017b). The idea of the polynomial time algorithm for SHAP values instead of an exponential time algorithm is to recursively keep track of what proportion of all possible subsets flow down into each tree leaf. The exponential reduction in complexity provides alternatives to traditional partial dependence and feature importance plots (Friedman et al., 2001), termed SHAP dependence and SHAP summary plots, respectively. Namely, since they are individualized feature attributions unique to every prediction, SHAP values enable better capture of interaction effects. Unlike partial dependence plots, which represent the dependency of a model on a subset of features with all other features fixed, SHAP dependence plots capture a feature's attributed importance, and changes as the feature's value varies. Moreover, contrary to standard partial dependence plots which only produce lines, SHAP dependence plots capture interaction effects in the model, representing them as vertical dispersion. The combination of SHAP dependence plots and SHAP interaction and SHAP main effect values (representing the impact of a feature after all interaction effects have been removed) can reveal global interaction patterns which could not be identified otherwise. In this paper we used supervised clustering based on SHAP feature attributions, SHAP summary plots and partial SHAP dependency and interaction plots to explore the interaction effects between relevant factors.

3. Results and discussion

The role of different forms of atmospheric water in TEX's environmental fate is still an issue of scientific research. In theory, the capacity of rainwater to scavenge TEX could be determined by a distribution coefficient, Henry's law constant, and the ratio of these two factors (defined as EF, Supplementary material). However, existing studies dealing with wet deposition of volatile species and their transfer from gaseous to aqueous phases are not only scarce, but produced contradictory evidence and conclusions (Okochi et al., 2005; Sato et al., 2006; Allou et al., 2011).

In general, BTEX concentrations in water are expected to be low due to the small Henry's law constant values of aromatic compounds. However, Delzer et al. (1996) were among the first to show that, in spite of their low solubility, toluene and total xylenes were the most frequently detected volatiles in urban stormwater. In the study that compared shallow groundwater BTEX concentrations with the values estimated on the basis of their atmospheric concentrations, assuming Henry's law constant at 15 °C, the authors reported that the observed BTEX concentrations in water samples were higher than expected (Baehr et al., 1999). Furthermore, those authors claimed that BTEX presence in shallow groundwater is directly related to their atmospheric concentrations only at estimated aqueous levels below 0.1 μg L^{-1}. Some years later, Okochi et al. (2004, 2005) also reported the concentrations of volatile species in rainwater and dew exceeded the values predicted by Henry's law. In addition to this, the laboratory study of Sato et al. (2006) demonstrated that dissolved organic compounds, including humic acids, might act as co-solvents, enhancing VOC transfer to atmospheric water. Finally, our recent findings (Šoštarić et al., 2016, 2017) confirmed that levels of BTEX in both deionized water in laboratory simulations and rainwater exceeded theoretically calculated values of BTEX transfer between phases. Moreover, our studies contributed to the existing knowledge by elaborating how meteorological conditions govern BTEX partition, as well as by exploring the relationships between the wet deposition process, the main inorganic constituents of rainwater, and rainwater's physico-chemical properties (pH, EC, NTU, UV extinction and TOC).

In contrast to this, Mullaugh et al. (2015) propose the wet deposition process is of less significance for the removal of aromatic hydrocarbons from the lower layers of the atmosphere due to the high volatility, hydrophobic nature and relatively short atmospheric lifetimes of the compounds. Furthermore, the authors identified that rainfall intensities and amounts were not controlling factors for BTEX concentrations in the rainwater, as the results presented herein have also confirmed.

An XGBoost tree-based method was successfully employed for exploring nonlinear relationships between rainwater TEX concentrations and EFs based on TEX concentrations in ambient air, rainwater physico-chemical properties and meteorological conditions during rain events. As can be seen in Table 1, the predicted/observed calculated relative errors were below 20%, while the correlation coefficients exceeded 0.93. The gain XGBoost F score, as one of the indicators of feature importance (Fig. 1), suggested that the ambient air TEX concentrations appeared to be far the most important predictors of toluene deposition in rainwater. Additionally, XGBoost weight scores showed that TOC and wind direction might also affect toluene rainwater concentrations. In contrast to this, the cover feature attribution score showed that a number of other factors, including wind speed, rain intensity, air and rainwater temperature, TEX ambient air concentrations, and concentrations of rainwater constituents, such as Na^+, SO_4^{2-}, K^+, Ca^{2+} and Cl^- could be influential attributes for rainwater scavenging of toluene.

Similarly, inconsistent results and highly variable XGBoost F scores were registered for ethylbenzene and xylenes (Fig. 1, Supplementary material). As noted by Lundberg et al. (2018), the commonly employed interpretations of XGBoost methods provide contradicting conclusions on the relevance of examined features for prediction of TEX rainwater concentrations and EFs.

According to the results, the mean SHAP value distribution (Figs. 2, S1 and S2, Supplementary material) and supervised clustering analysis (Fig. 3) demonstrated the way ambient air TEX concentrations, together with rainwater and air temperatures, governed the process of TEX wet deposition and rainwater enrichment. These were also impacted by contributions from TOC, wind speed, air pressure, NTU and NO_3^-, NO_2^-, Na^+, Cl^- and K^+ concentrations. As indicated by the long-tailed distribution to the right (Fig. 2), increased toluene concentrations in rainwater were mainly associated with high ambient air TEX concentrations (ranging from 14.4 to 24.9 ng g^{-1} and from 3.4 to 5.0 ng g^{-1} for toluene and ethylbenzene/xylenes, respectively) and NO_3^- concentrations (Fig. 3). The relationship between toluene and nitrates was particularly evident (represented by significant red feature cluster attributions) when the nitrate ion concentrations exceeded 2 mEq L^{-1}, as well as during NW/N wind episodes (Fig. 3), probably being associated with the arrival of polluted air masses which resulted in higher NO_3^- concentrations in rainwater. Moreover, these species could be emitted from the common pollution sources, such as fossil fuel burning and traffic exhaust. Under stable atmospheric conditions with wind speed below 5 m s^{-1}, NO_3^- concentrations dropped below 2 mEq L^{-1}, and the relationship of NO_3^- to toluene transfer to rainwater weakened (as indicated by blue cluster attributions; Fig. 3). On the other hand, ethylbenzene and xylenes transfer to rainwater

Table 1
XGBoost performance.

Variable	Predicted/observed		
	Correlation	Absolute error	Relative error [%]
Rainwater toluene [nM]	0.94	9.73	17
Rainwater ethylbenzene/xylenes [nM]	0.94	5.80	11
Toluene enrichment factor	0.97	7.59	17
Ethylbenzene/xylenes enrichment factor	0.93	16.57	20

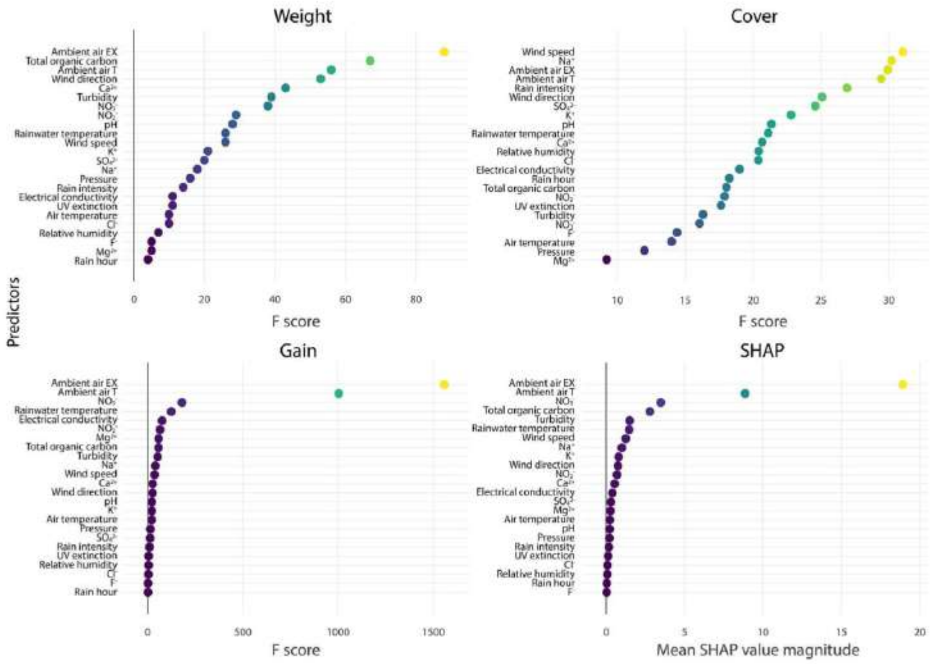


Fig. 1. Importance score comparisons for rainwater toluene concentrations.

was additionally affected by meteorological conditions (rainwater temperature, wind speed and direction, as well as air pressure in a few rainfall events) and TOC (Fig. S2). Unsurprisingly, increased air and rainwater temperatures, which cause the solubility of gases to decrease, as well as high wind speed and air pressure negatively affected ethylbenzene/xylenes transfer to rainwater (Figs. 2 and 3). Namely, high wind speed leads to enhanced dispersion of volatile species and short-lasting contact between gaseous and aqueous phases during rain events.

The fact that other features including Na^+, K^+, Cl^- and NO_2^- concentrations, as well as NTU and UV extinction were arranged in non-gradually decreasing order of importance to the left suggests that they could also occasionally exhibit some impact on TEX rainwater

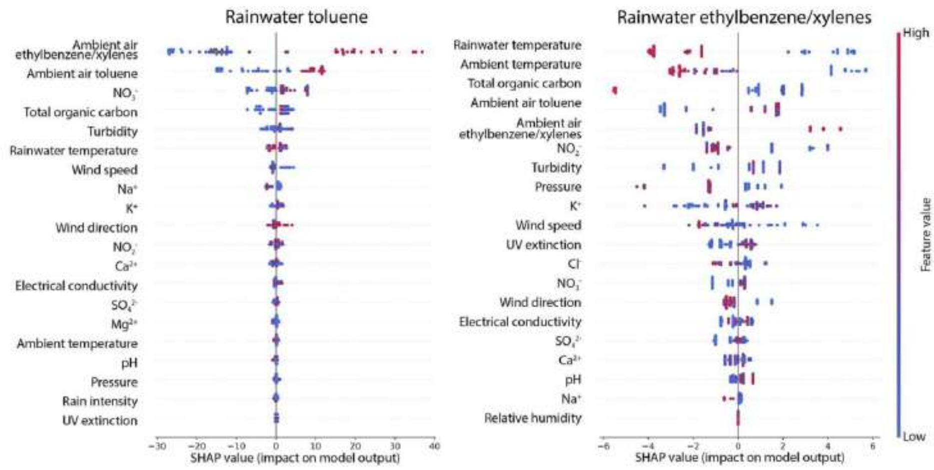


Fig. 2. SHAP summary plots of toluene and ethylbenzene/xylene concentrations in rainwater.

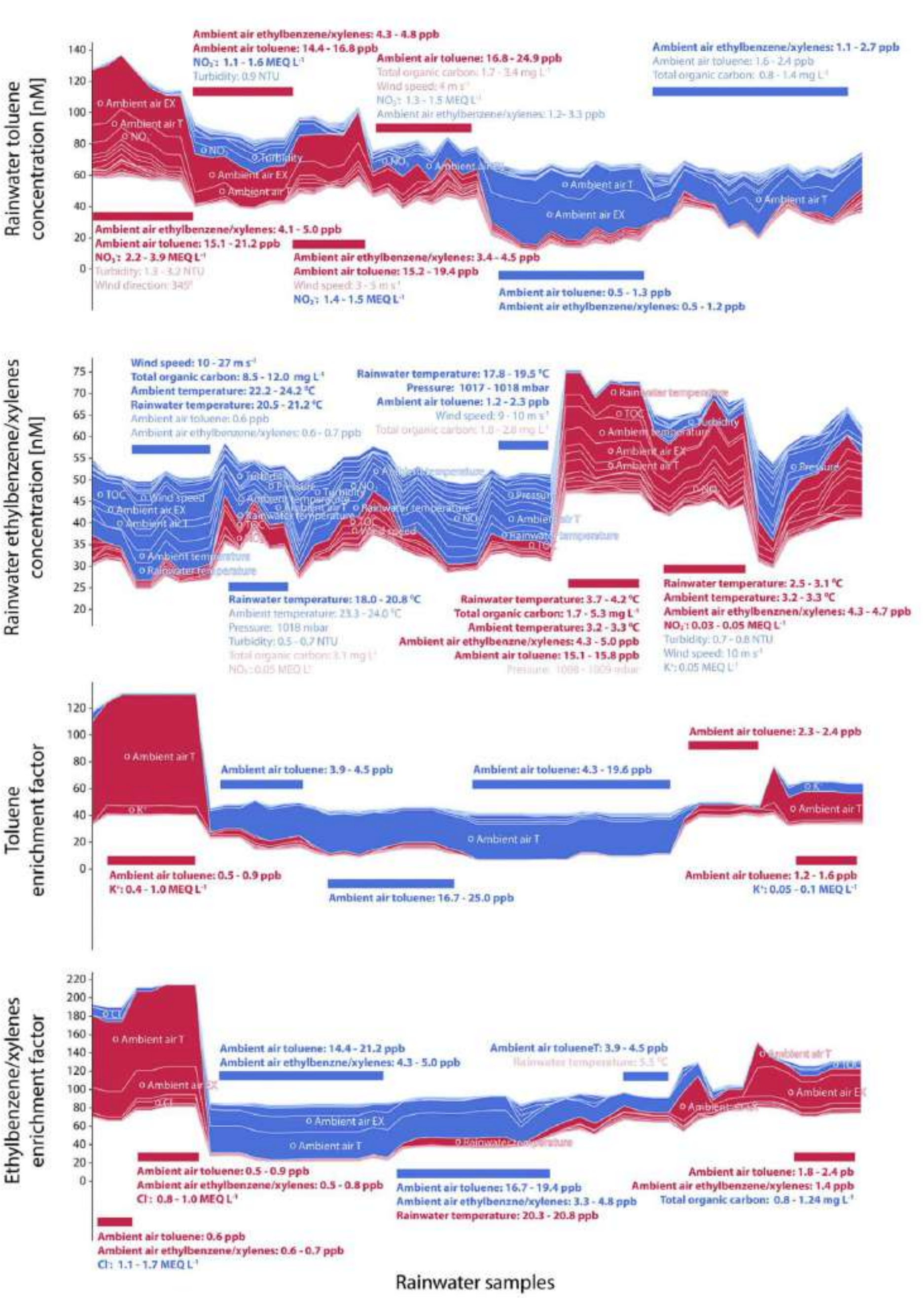


Fig. 3. SHAP supervised clustering: rainwater toluene and ethylbenzene/xylene concentrations and enrichment factors (features present in all the samples in a cluster are represented in bold).

concentrations (Figs. 2 and 3, S4–S40). Theoretically, the impact of Na^+, K^+ and Cl^- presence on gas behavior in aqueous solution can be explained by the salting out effect. This effect refers to the observation that the solubility of gases in a single or mixed electrolyte solution is decreased compared to that in pure water under the same conditions (Sander, 2015). As shown by Allou et al. (2011), Henry's constants for formaldehyde and benzaldehyde in 35 g L^{-1} NaCl salt solution were 27–66% and 12–21% lower, respectively, than the corresponding values in deionized water. While our results mostly comply with this theoretical background, in a few cases, increases of Na^+, K^+ and Cl^- concentrations in rainwater were associated with higher TEX transfer to rainwater, and correspondingly, higher Henry's constant values (Figs. S4–S40).

Diverse properties of the compounds themselves control the distribution of toluene and ethylbenzene/xylenes between environmental compartments. These properties include differences in solubility, volatility and other physicochemical properties, and the fact that ethylbenzene/xylenes are more chemically inert than toluene due to longer alkyl chain and methyl substitutions (Odermatt, 1994). Thereby, the diversity of properties is reflected in both the diversity of identified features that control TEX distribution and SHAP values which are an order of magnitude higher for toluene than for ethylbenzene/xylenes, as can be seen in Fig. 2.

Besides exhibiting an inverse relationship with TEX solubility, rainwater temperature decline is accompanied with less intense molecular vibrations, increasing the tendency of water molecules to form hydrogen bonds, so lowering the concentration of H^+ ions, and therefore, increasing the pH. Furthermore, this basification is associated with lower acid-base dissociation of chemical species that produce SO_4^{2-}, NO_3^- and NO_2^- and which originate from the gaseous oxides SO_2 and NO_x, and/or their acidic products (Wang et al., 2015). In compliance with this, during several rainfall events with neutral to alkaline rainwater (Fig. S5, S6, S25 and S26), TEX transfer to rainwater was favored, particularly under stable atmospheric conditions (wind speed <6 m s^{-1}) when limited wind-induced dispersion of particles and/or gas enabled prolonged contact between gaseous and aqueous phases. It is also worth mentioning that TEX scavenging by rainwater was more pronounced immediately after the rain began, *i.e.* during the first 1–2 h of a rain event (Fig. S6 and S26).

Intense UV extinction can be considered a good indicator of conjugated systems, which can refer to the presence of monoaromatic volatile species. However, the almost negligible associations between the TEX concentrations and UV extinction, as well as TOC, suggest the UV factor could be associated with the occurrence of VOC in rainwater in general, rather than particularly with toluene and/or ethylbenzene/xylenes (Figs. S5, S9, S21, S29). Similar conclusions can be drawn for turbidity and electrical conductivity. For example, the highest TEX rainwater concentrations were associated with lower NTU values (1 to 3), *i.e.* the highest TEX transfer from ambient air to rainwater occurred in cases when rainwater contained negligible amounts of particulate matter that theoretically should enhance TEX transfer (Figs. 3 and S5, S9, S21, S25). Therefore, the observed relationship between NTU, EC and TEX deposition in rainwater is rather indirect, probably caused by the presence of ions and/or suspended particles in rainwater and the aforementioned salting out effect (Figs. S12, S15, S37, S39). What is common to all parameters (TOC, UV, EC and NTU) is that their maximum values were associated with high wind speed (20–30 m s^{-1}) and wind direction below 250°, during the intensive summer rainfall events, probably because intense wind enhances air transport and suspension of organic and inorganic particles in rainwater. Otherwise, in the majority of observations, W, NW and N winds predominated, which corresponded to lower feature values (Figs. S13, S17, S36, S38) and presumably smaller impacts of local pollutant sources that has been confirmed in our previous study (Šoštarić et al., 2017).

As shown by SHAP interaction plots and zero SHAP values (Figs. S18, S40, S72, S73, S76), the TEX deposition process in rainwater is independent of mutual interactions between the physico-chemical parameters of rainwater. On the other hand, the interactions between ambient air toluene and ethylbenzene/xylene concentrations or meteorological conditions were noticeable for toluene transfer to rainwater, although with significantly lower impact on the model output in the SHAP dependence plot, as indicated by the lower SHAP values. The conjoint interdependencies of the examined features (SHAP values: ambient air ethylbenzene/xylenes−NO_3^- (−4 to 6); ambient air ethylbenzene/xylenes−NTU (−3 to 3); ambient air toluene−TOC (−2 to 2); ambient air toluene−wind direction (−0.5 to 1.5); ambient air ethylbenzene/xylenes−EC (−0.5 to 1.5); ambient air ethylbenzene/xylenes−NO_2^- (−1.5 to 1.5); ambient air toluene−ambient air ethylbenzene/xylenes (−3 to 1); ambient air ethylbenzene/xylenes− rainwater temperature (−3 to 1); ambient air toluene−NO_3^- (−1 to 1)) appeared to have a slight/moderate impact on toluene rainwater concentrations, whereas the rest were irrelevant for the toluene wet deposition process (Figs. 4, and S18, S72). We also speculate that the interconnections among the following feature pairs: ambient air toluene−NTU (−1.5 to 2), K^+–air temperature (−2 to 2), rainwater temperature–air pressure (−3 to 2), K^+–NO_2^- (−0.4 to 1), K^+–ambient air ethylbenzene/xylenes (−0.4 to 1), NO_2^-−NO_3^- (−0.4 to 1), rainwater temperature–TOC (−0.75 to 1), K^+–NTU (−1 to 1), K^+−ambient air toluene (−1 to 1), K^+–EC (−1 to 1), wind speed–Cl^- (−1.5 to 1), ambient air ethylbenzene/xylenes–NO_2^- (−1.5 to 0.5), wind speed–UV extinction (−0.6 to 0.8), wind speed–Ca^{2+} (−0.6 to 0.8), ambient temperature–NO_2^- (−1.5 to 0.5) and ambient temperature–NO_3^- (−0.4 to 0.4) could be of interest for further investigations of ethylbenzene/xylenes transfer to rainwater (Figs. S40, S73).

The results revealed that toluene enrichment factor (EF_T) variations were governed primarily by the dependencies of ambient air toluene concentrations on the other variables (SHAP = 80, Figs. S41–S44), together with the significantly lower impact of rainwater constituents and their associations with K^+ (6), pH (1), NO_2^- (0.10), Cl^- (0.5), TOC (0.4), rainwater ethylbenzene/xylenes (0.4) and toluene (0.2) concentrations, as well as with meteorological parameters: rainwater (2) and ambient air (0.75) temperature, and air pressure (4) (Figs. S45–S53). The conjoint interdependences of the noted variables (SHAP values: ambient air toluene–K^+: up to 6; ambient air toluene−rainwater temperature: up to 1; ambient air toluene−air pressure: up to 1) appeared to have a slight influence on EF_T values, whereas other interrelations could be considered irrelevant due to their zero SHAP values (Figs. S54, S74, S77).

It is important to add that high SHAP vales characterizing mainly lower air and rainwater toluene concentrations were accompanied by increases in TOC, NTU values and concentrations of polar species (Figs. S42 and S43). These polar species are heterogeneous products of fossil fuel burning and traffic emission compounds (K^+ and NO_2^-), but they are also precursors of secondary organic aerosols (NO_2^-). These findings could be expected since K^+ and NO_2^- ions are more soluble than aromatic hydrocarbons, which lack the capability of forming strong hydrogen bonds with polar water molecules. Secondly, TOC and NTU are indicators of particulate matter presence in rainwater, and these solid particles are able to modify gaseous-aqueous TEX partition by creating new solid-liquid interfaces. In these three-phase systems, suspended particles, which can originate from urban aerosols, diesel soot or mineral dust, are able to reduce the gaseous and aqueous levels of toluene and ethylbenzene/xylenes by 10% to 20%, respectively (Starokozhev et al., 2011). In addition, the reduced amounts of TEX in rainwater could be a consequence of heterogeneous reactions of NO_2 which are facilitated by particulate cations, and result in large amount of particulate nitrite (Wang et al., 2015).

The SHAP results, which shape the prediction of ethylbenzene/xylene enrichment factor (EF_{EX}) in rainwater depending on TOC (2), UV extinction (0.4), and NTU (0.3), were complementary to those obtained for EF_T, and illustrate the ethylbenzene and xylene partition in the three-phase system. Regarding the meteorological conditions, the most influential were rainwater temperature and air pressure, whereas

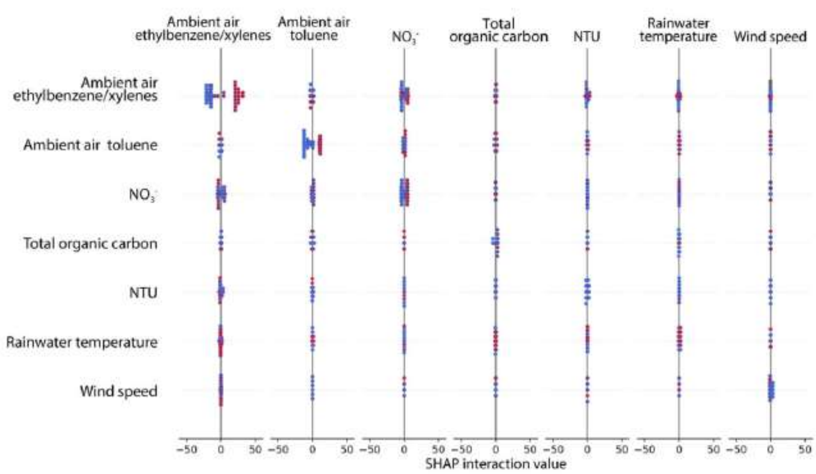


Fig. 4. SHAP interaction summary plot of the most important features for rainwater toluene prediction.

air temperature and wind characteristics were found to be insignificant for describing EF_{EX} in rainwater. As discussed in detail for EF_T, we noted that interrelationships among pressure and the other variables, as well as between the following pairs of variables: Cl^-—ambient air toluene, K^+–rainwater ethylbenzene/xylenes, K^+–ambient air/rainwater toluene, TOC–ambient air toluene, TOC–gaseous ethylbenzene/xylenes and NTU–rainwater temperature could be of interest for further investigations that would require new measurements and larger datasets (Figs. S71, S75, S78).

4. Conclusions

Elevated ambient concentrations of toluene, ethylbenzene and xylene as a result of anthropogenic activities in urban areas are an issue of scientific and practical concern due to their impacts on both the environment and human health. Due to the fact that advances in machine learning have resulted in numerous applications of complex algorithms for predicting environmental processes and concentrations of pollutant species in environmental samples, it is critical researchers gain insight into the way such algorithms arrive at their predictions. Recently, several methods for interpretable approximations of sophisticated models have been developed, with the focus on producing *a posteriori* explanations and introducing simpler formulations able to capture the input-output behavior and preserve certain key features. In this study, the extreme gradient boosting tree-based method was successfully employed (with relative errors lower than 20%) for predicting TEX concentrations and corresponding enrichment factors in rainwater, based on their concentrations in ambient air and rainwater, physico-chemical properties of rainwater and meteorological conditions. Furthermore, a novel feature attribution framework was applied to examine the relevance of the monitored parameters for the modeled predictions, and enabled insight into the main factors that govern deposition of TEX in rainwater, while overcoming the usually inconsistent and contradictory interpretations derived from commonly applied machine learning algorithms. As the modeling showed, ambient air TEX concentrations, and rainwater and air temperatures were the main features that shaped TEX partition between gaseous and aqueous phases during rain events. Occasional, but far less important impacts were assigned to wind speed, air pressure, turbidity, and total organic carbon, NO_3^-, Cl^- and K^+ rainwater concentrations, whereas the impacts of other measured parameters proved to be negligible. Moreover, the current knowledge on TEX deposition in rainwater would benefit from further in-depth exploration of the interaction effects between the examined features.

Acknowledgments

This paper was realized as part of projects No III43007, No III41011 and OI176013, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia No III43007, No III41011 and OI176013 for the period 2011-18, and was supported by the Institute of Public Health Belgrade, Serbia.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.10.368.

References

Allou, L., El Maimouni, L., Le Calvé, S., 2011. Henry's law constant measurements for formaldehyde and benzaldehyde as a function of temperature and water composition. Atmos. Environ. 45 (17), 2991–2998. https://doi.org/10.1016/j.atmosenv.2010.05.044.
Alvarez-Melis, D., Jaakkola, T.S., 2018a. Towards robust interpretability with self-explaining neural networks. arXiv:1806.07538 (arXiv preprint).
Alvarez-Melis, D., Jaakkola, T.S., 2018b. On the robustness of interpretability methods. arXiv:1806.08049 (arXiv preprint).
Baehr, A.L., Stackelberg, P.E., Baker, R.J., 1999. Evaluation of the atmosphere as a source of volatile organic compounds in shallow groundwater. Water Resour. Res. 35 (1), 127–136. https://doi.org/10.1029/1998WR900030.
Chen, T., Guestrin, C., 2016. Xgboost: A scalable tree boosting system. In: August (Ed.), Proceedings of the 22nd ACM SIGKDD International Conference on Knowledge Discovery and Data Mining. ACM, pp. 785–794 https://doi.org/10.1145/2939672.2939785.
Dabkowski, P., Gal, Y., 2017. Real time image saliency for black box classifiers. Advances in Neural Information Processing Systems , pp. 6967–6976. arXiv:1705.07857v1.
Delzer, G.C., Zogorski, J.S., Lopes, T.J., Bosshart, R.L., 1996. Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991–95. USGS Water-Resources Investigations Report, pp. 96–4145 https://doi.org/10.3133/wri964145.
Fong, R.C., Vedaldi, A., 2017. Interpretable explanations of black boxes by meaningful perturbation. arXiv:1704.03296 (arXiv preprint).
Friedman, J., Hastie, T., Tibshirani, R., 2001. The Elements of Statistical Learning. Vol. 1 (10). Springer series in statistics, New York, NY, USA 978-0-387-84858-7.
Guidotti, R., Monreale, A., Turini, F., Pedreschi, D., Giannotti, F., 2018. A survey of methods for explaining black box models. arXiv:1802.01933 (arXiv preprint).
Janizek, J.D., Celik, S., Lee, S.I., 2018. Explainable Machine Learning Prediction of Synergistic Drug Combinations for Precision Cancer Medicine. bioRxiv, p. 331769.
Kampf, J.C., Waxman, M.E., Slowik, G.J., Dommen, J., Pfaffenberger, L., Praplan, P.A., Prévôt, S.H.A., Baltensperger, U., Hoffmann, T., Volkamer, R., 2013. Effective Henry's law

partitioning and the salting constant of glyoxal in aerosols containing sulfate. Environ. Sci. Technol. 47, 4236–4244. https://doi.org/10.1021/es400083d.

Kurtén, T., Elm, J., Prisle, L.N., Mikkelsen, V.K., Kampf, J.C., Waxman, M.E., Volkamer, R., 2015. Computational study of the effect of glyoxal-sulfate clustering on the Henry's law coefficient of glyoxal. J. Phys. Chem. A 119, 4509–4514. https://doi.org/10.1021/jp510304c.

Lundberg, S.M., Lee, S.I., 2017a. A unified approach to interpreting model predictions. Advances in Neural Information Processing Systems, pp. 4765–4774. arXiv:1705.07874v2.

Lundberg, S.M., Lee, S.I., 2017b. Consistent feature attribution for tree ensembles. arXiv:1706.06060 (arXiv preprint).

Lundberg, S.M., Erion, G.G., Lee, S.I., 2018. Consistent individualized feature attribution for tree ensembles. arXiv:1802.03888 (arXiv preprint).

Montavon, G., Samek, W., Müller, K.R., 2017. Methods for interpreting and understanding deep neural networks. Digital Signal Process. 73, 1–15. https://doi.org/10.1016/j.dsp.2017.10.011.

Mullaugh, K.M., Hamilton, J.M., Avery, G.B., Felix, J.D., Mead, R.N., Willey, J.D., Kieber, R.J., 2015. Temporal and spatial variability of trace volatile organic compounds in rainwater. Chemosphere 134, 203–209. https://doi.org/10.1016/j.chemosphere.2015.04.027.

Odermatt, J.R., 1994. Natural chromatographic separation of benzene, toluene, ethylbenzene and xylenes (BTEX compounds) in a gasoline contaminated ground water aquifer. Org. Geochem. 21 (10–11), 1141–1150. https://doi.org/10.1016/0146-6380(94)90076-0.

Okochi, H., Sugimoto, D., Igawa, M., 2004. The enhanced dissolution of some chlorinated hydrocarbons and monocyclic aromatic hydrocarbons in rainwater collected in Yokohama, Japan. Atmos. Environ. 38 (26), 4403–4414. https://doi.org/10.1016/j.atmosenv.2004.03.053.

Okochi, H., Kataniwa, M., Sugimoto, D., Igawa, M., 2005. Enhanced dissolution of volatile organic compounds into urban dew water collected in Yokohama, Japan. Atmos. Environ. 39 (33), 6027–6036. https://doi.org/10.1016/j.atmosenv.2005.05.025.

Python Software Foundation, d. Python language reference, version 3.6. Available at. http://www.python.org, Accessed date: June 2018.

Sander, R., 2015. Compilation of Henry's law constants (version 4.0) for water as solvent. Atmos. Chem. Phys. 15 (8), 4399–4981. https://doi.org/10.5194/acp-15-4399-2015.

Sato, E., Matsumoto, K., Okochi, H., Igawa, M., 2006. Scavenging effect of precipitation on volatile organic compounds in ambient atmosphere. Bull. Chem. Soc. Jpn. 79 (8), 1231–1233. https://doi.org/10.1246/bcsj.79.1231.

Sheridan, R.P., Wang, W.M., Liaw, A., Ma, J., Gifford, E.M., 2016. Extreme gradient boosting as a method for quantitative structure–activity relationships. J. Chem. Inf. Model. 56 (12), 2353–2360. https://doi.org/10.1021/acs.jcim.6b00591.

Šoštarić, A., Stojić, A., Stojić, S.S., Gržetić, I., 2016. Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system. Chemosphere 144, 721–727. https://doi.org/10.1016/j.chemosphere.2015.09.042.

Šoštarić, A., Stojić, S.S., Vuković, G., Mijić, Z., Stojić, A., Gržetić, I., 2017. Rainwater capacities for BTEX scavenging from ambient air. Atmos. Environ. 168, 46–54. https://doi.org/10.1016/j.atmosenv.2017.08.045.

Staniak, M., Biecek, P., 2018. Explanations of model predictions with live and breakdown packages. arXiv:1804.01955 (arXiv preprint).

Starokozhev, E., Sieg, K., Fries, E., Püttmann, W., 2011. Investigation of partitioning mechanism for volatile organic compounds in a multiphase system. Chemosphere 82, 1482–1488. https://doi.org/10.1016/j.chemosphere.2010.11.033.

Stojić, A., Stojić, S.S., Šoštarić, A., Ilić, L., Mijić, Z., Rajšić, S., 2015. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ. Sci. Pollut. Res. 22 (17), 13137–13152. https://doi.org/10.1007/s11356-015-4540-5.

Tan, H.F., Hooker, G., Wells, M.T., 2016. Tree space prototypes: another look at making tree ensembles interpretable. arXiv:1611.07115 (arXiv preprint).

Wang, L., Wen, L., Xu, C., Chen, J., Wang, X., Yang, L., ... Zhang, Q., 2015. HONO and its potential source particulate nitrite at an urban site in North China during the cold season. Sci. Total Environ. 538, 93–101. https://doi.org/10.1016/j.scitotenv.2015.08.032.

XGBoost Python Package, d. . Available at. https://github.com/dmlc/xgboost/tree/master/python-package, Accessed date: June 2018.

Atmospheric Environment 164 (2017) 216–223

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

The innovative concept of three-dimensional hybrid receptor modeling

A. Stojić [a], S. Stanišić Stojić [b,*]

[a] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
[b] Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia

HIGHLIGHTS

- Three-dimensional PSCF and CWT for identification of source altitude distribution.
- New hybrid receptor model for pollutant altitude distribution along transport pathway.
- Refined approach for more realistic representation of source distribution.
- Potential $PM_{2.5}$ source regions were registered in Romania, Bulgaria and Bosnia.
- Pollutant time series preprocessing to make models applicable for urban sites.

ARTICLE INFO

Article history:
Received 6 January 2017
Received in revised form
25 May 2017
Accepted 4 June 2017
Available online 6 June 2017

Keywords:
PSCF
CWT
Three-dimensional hybrid receptor models
$PM_{2.5}$
VOC

ABSTRACT

The aim of this study was to improve the current understanding of air pollution transport processes at regional and long-range scale. For this purpose, three-dimensional (3D) potential source contribution function and concentration weighted trajectory models, as well as new hybrid receptor model, concentration weighted boundary layer (CWBL), which uses a two-dimensional grid and a planetary boundary layer height as a frame of reference, are presented. The refined approach to hybrid receptor modeling has two advantages. At first, it considers whether each trajectory endpoint meets the inclusion criteria based on planetary boundary layer height, which is expected to provide a more realistic representation of the spatial distribution of emission sources and pollutant transport pathways. Secondly, it includes pollutant time series preprocessing to make hybrid receptor models more applicable for suburban and urban locations. The 3D hybrid receptor models presented herein are designed to identify altitude distribution of potential sources, whereas CWBL can be used for analyzing the vertical distribution of pollutant concentrations along the transport pathway.

1. Introduction

Air mass trajectory analysis has been widely used to study dynamical processes and pollutant circulation patterns in the atmosphere. Over the last few decades, a variety of statistical tools have been developed and applied for analyzing a large set of trajectories, including general hybrid receptor models that are focused on the behavior of ambient pollutant at the point of impact (Hopke, 2003). The receptor-oriented models based on conditional probability and residence time analysis, such as potential source contribution function (PSCF) and concentration weighted trajectory (CWT), have been used in numerous air pollution studies to investigate the spatial distribution of potential emission sources and assess their impact on single receptor location without using emission inventories (Brereton and Johnson, 2012; Byčenkienė et al., 2014; Sen et al., 2016; Li et al., 2017). PSCF relates residence time of trajectory segment endpoints in a potential source area with the above-threshold pollutant concentrations at the receptor site (Ashbaugh et al., 1985). However, because PSCF has difficulties distinguishing strong sources from moderate sources, it was modified into the CWT (Hsu et al., 2003) which has the additional ability to determine the relative significance of potential sources by calculating concentration gradients.

The conventional approach to hybrid receptor modeling has several drawbacks. To our knowledge, the concept of hybrid receptor modeling estimates the relative importance of transport

* Corresponding author. Danijelova 32, 11010 Belgrade, Serbia.
E-mail address: sstanisic@singidunum.ac.rs (S. Stanišić Stojić).

http://dx.doi.org/10.1016/j.atmosenv.2017.06.009
1352-2310/

processes without respecting the differences between background and urban receptor locations. Therefore, we propose time series preprocessing to make hybrid receptor models more applicable for suburban and urban sites, where the pollutant concentrations are dominated by local emissions. Another disadvantage of the conventional approach is that computing the trajectories for predefined arbitrary chosen heights at the receptor site does not necessary yield a realistic representation of pollutant transport pathways because it overlooks the fact that the redistribution of emitted pollutant species occurs dominantly at the lowest 100 to 3000 m of the atmosphere, a part known as planetary boundary layer (PBL). According to Stull (1988), pollutant ambient concentrations exhibit a significant decrease with height because the species emitted or generated near ground are mostly trapped and concentrated within the PBL, whereas free atmosphere concentrations remain low. Therefore, in this study we considered the PBL height fluctuations for more realistic evaluation of source-receptor relationships in air pollution analysis, not only at the receptor site, but also at each segment along the transport pathway. Given that non-PBL transport of pollutants is relatively rare (Langford et al., 2015), but observed for certain cases, such as intercontinental transport and Arctic Haze, the current approach of computing the trajectories for predefined heights, as described in the work of Cheng et al. (1993), is more appropriate for these occasions.

In order to obtain a more realistic description of transport processes, we introduce the innovative approach to air pollution transport analysis based on backward trajectories, which accounts for meteorological factors that govern the vertical distribution of pollutant concentrations and appreciates the differences between background and urban locations. To that end, a three-dimensional (3D) improvement of the conventional PSCF and CWT models, as well as new hybrid receptor model that uses a 2D grid and a PBL height as a frame of reference are presented.

2. Air pollutant transport phenomena

Discriminating the relative importance of background, local sources and transport processes for pollutant concentrations at the sampling site is one of the key issues in air pollution analysis. The conventional concept of hybrid receptor modeling takes into account the concentrations greater than the arbitrary chosen criterion value (e.g. mean or median concentrations), thereby assuming that individual peaks in the pollutant time series are mainly observed as a result of regional or long-range pollutant transport (Kassomenos et al., 2006; Grivas et al., 2008). While this approach may be considered appropriate for background sites where sudden rise in concentrations can be almost exclusively observed as a result of transport, it may fail for suburban and urban locations. Conversely, we assume that in suburban and urban areas, dominated by a number of local emission sources, transport and background jointly contribute to gradual variations of a concentration base level, whereas the superimposed pronounced peaks in pollutant time series are registered as a result of local emissions (Fig. 1a). Following this logic, differentiation between the contributions of local and remote emission sources was obtained by a two-step procedure that was described in our previous studies (Stojić et al., 2015a, 2016).

In brief, for excluding the contribution of local sources from the time series, baseline. rollingBall from the "baseline" package (Kneen and Annegarn, 1996) in statistical software R (Team R.C., 2013) was chosen out of a number of functions available for baseline extraction. Subsequently, Trajectory Sector Analysis (TSA) was applied to the derived baseline to distinguish between the contribution of background and transport, and the obtained transport time series were further used as input data for hybrid receptor models.

The potential concept of 3D PSCF analysis has been recently proposed by Kim et al. (2016). As defined in this study, an air parcel passing through a cell with an emission source was considered to be unaffected by pollution if it passes at an altitude higher than the arbitrary threshold of up to 3000 m. Therefore, the authors calculated the PSCF by simply ignoring the segment endpoints above the chosen threshold value. However, as previously mentioned, the troposphere extends from the ground up to 11 km, but only the lowest part or the PBL is directly influenced by the underlying surface and responds to surface forcing (Stull, 1988). As the pollutants emitted from the ground are dominantly trapped and dispersed within the PBL by turbulent mixing under favorable meteorological conditions, the near-surface pollutant concentrations registered at the receptor site could correspond to atmospheric concentrations only within the PBL height. In compliance with this, the previous studies (Gan et al., 2011) that used the community multiscale air quality (CMAQ) modeling system to simulate the emission, transport, transformation and deposition of atmospheric pollutants have shown that pollutant concentrations rapidly decrease in the vicinity of the PBL (Fig. 1b). The PBL height exhibits diurnal variations in a broad range from several tens to several thousands of meters, and therefore, the 3D analysis that relies on a set of trajectories obtained for a single predefined height does not adequately address the issue of pollutant transport. Unlike the study of Kim et al. (2016), as well as other studies that use the conventional hybrid receptor models, the transport analysis presented herein accounts for hourly PBL height fluctuations by including the trajectories based on their representativeness. Namely, the dynamic calculation of trajectories was performed within the PBL at the receptor site. The trajectories with endpoints exceeding PBL height for 20–50% depending on height (due to uncertainty in the PBL height determination, according to Seidel et al., 2012) were excluded from the analysis. Additionally, due to the emergence of significant turbulences within the PBL, trajectories can be quite curved, and disruption can occur at the bottom level, which is often the case for small height-trajectories above the receptor site. Such trajectories were excluded from the analysis as they do not properly represent transport.

2.1. 3D PSCF

The contribution of a specific source to pollutant concentrations at the receptor site is considered to directly correspond to air mass residence time over the region where the source is located (Dimitriou and Kassomenos, 2014). The endpoints along the trajectory separated by a specific time period are used to calculate air mass residence time for each grid cell. As described by Hopke et al. (1993), if N is the total number of trajectory endpoints, the probability that n trajectory endpoints fall into the ijth cell (n_{ij}) is given as:

$$P[A_{ij}] = \frac{n_{ij}}{N} \quad (1)$$

If we assume that the same ijth cell contains a subset of m_{ij} endpoints for which the corresponding trajectories arrive at the receptor site when the transported concentrations are higher than the predefined criterion value (e.g. mean value), the probability of high concentration event B_{ij} is given by:

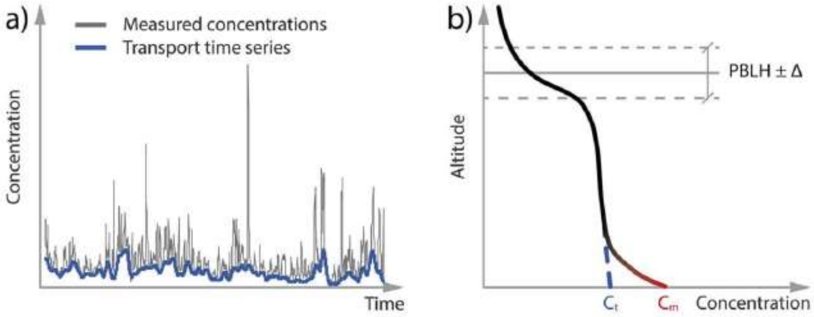


Fig. 1. Transport time series obtained by the use of baseline extraction and TSA-derived background reduction (a), and pollutant concentration vertical distribution and the contribution of transport (Ct) to the measured concentrations (Cm) at the receptor site (b, based on Stull, 1988).

$$P[B_{ij}] = \frac{m_{ij}}{N} \quad (2)$$

The 2D PSCF value for the *ij*th cell is defined as:

$$P_{ij} = \frac{P[B_{ij}]}{P[A_{ij}]} = \frac{m_{ij}}{n_{ij}} \quad (3)$$

where the cells with high PSCF values have a high possibility of containing emission sources.

The major limitation of 2D PSCF analysis is related to exceptionally high values that may occur from the situation where grid cells containing few trajectory endpoints are associated with poor air quality at the receptor site. In order to eliminate grid cells with insufficient trajectory coverage, Zeng and Hopke (1989) have introduced the arbitrary weighting function based on point count multiplied by the local PSCF that we used as:

$$w = \begin{cases} 0.25, & N < 0.5s \\ 0.5, & 0.5s \le N < s \\ 0.75, & s \le N < 2s \\ 1, & N \ge 2s \end{cases} \quad (4)$$

where s refers to the average number of endpoints per cell.

Unlike the previous 3D PSCF concept, based on a single threshold value which is estimated to reflect the highest injection point (Kim et al., 2016), the threshold for the selection of trajectories herein was PBL height data at each trajectory endpoint. In general, in the 3D grid map, PSCF vertical distribution can be defined as the ratio of a subset of m_{ijk} endpoints in the kth volume cell v_{ijk} of the predefined height (Fig. 2a, c) for which the corresponding trajectories arrive at the receptor site when the contribution of transport to the measured concentrations exceeds the pre-specified criterion value and the total number of endpoints in the *ij*th grid cell (n_{ij}):

$$P_{ijk} = \frac{P[B_{ijk}]}{P[A_{ij}]} = \frac{m_{ijk}}{n_{ij}} \quad (5)$$

2.2. 3D CWT

In the CWT, each grid cell (i,j) receives a weighted concentration obtained by averaging estimated transport contribution at the receptor site that corresponds to the trajectories passing across the cell:

$$CWT_{ij} = \frac{\sum_{l=1}^{L} C_l \tau_{ijl}}{\sum_{l=1}^{L} \tau_{ijl}} \quad (6)$$

By including the altitude, a CWT for each volume cell v_{ijk} can be defined as:

$$CWT_{ijk} = \frac{\sum_{l=1}^{L} C_l \tau_{ijlk}}{\sum_{l=1}^{L} \tau_{ijl}} \quad (7)$$

where C_l - is the pollutant concentration corresponding to the arrival of back trajectory l; τ_{ijl} is the number of trajectory segment endpoints in a grid cell (i,j) for back trajectory l; τ_{ijlk} is the number of trajectory segment endpoints in kth volume cell v_{ijk} for back trajectory l; L is the total number of back trajectories.

As a result, the sum of 3D CWT values for each *ij*th cell amounts to the score derived by the use of conventional 2D CWT solution.

The approach presented herein can be applied for the development of other trajectory ensemble models, such as 3D simplified quantitative transport bias analysis (sQTBA) and 3D residence time weighted concentration (RTWC), and such ideas have already been contemplated.

2.3. Concentration weighted boundary layer (CWBL)

While the 3D hybrid receptor models can be employed for identification of potential source regions defined by longitude, latitude and altitude, they cannot be used for analyzing the vertical distribution of pollutant concentrations along the transport pathway (Fig. 2a, c). In this study, we propose a new hybrid receptor model, the concentration weighted boundary layer (CWBL), which uses a 2D grid and a PBL height as a frame of reference in order to obtain the vertical profile of pollutant concentrations above each grid cell. The method is based on the fact that pollutant concentrations do not exhibit significant variations within the largest part of the PBL, except for the very top and very bottom layer, the latter being severely affected by ground emissions (Stull, 1988; Gan et al., 2011). In this procedure, the estimated contribution of transport to pollutant concentrations measured at the receptor site is attributed to all volume cells within the PBL at each endpoint location along the corresponding trajectory that arrives at the receptor site (Fig. 2b).

As presented in Fig. 2d, the CWBL value at each 2D grid cell over the observation period is calculated by averaging the transport

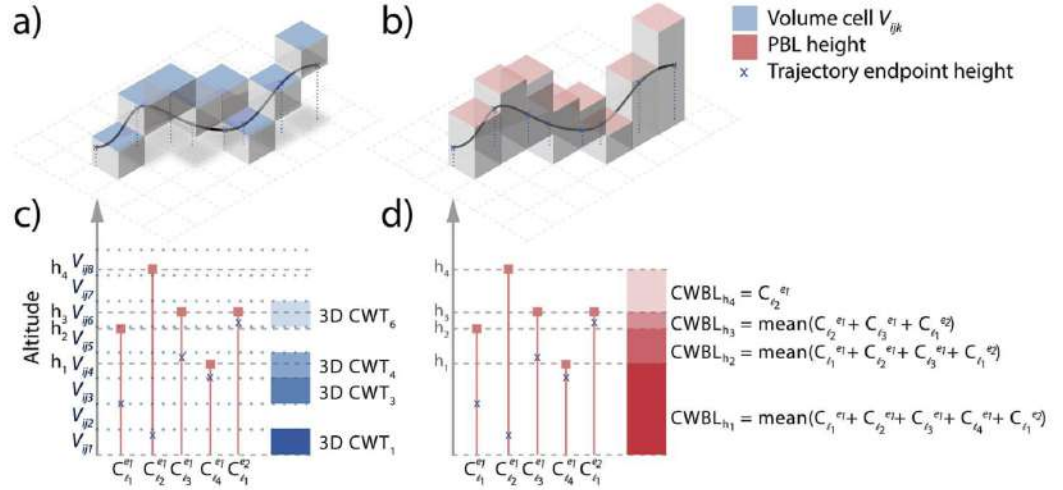


Fig. 2. The concept of 3D PSCF and CWT (a), and CWBL (b) analysis and 3D CWT$_k$ (c) and CWBL graphical interpretation (d). The threshold for the selection of trajectories was PBL height at each trajectory endpoint location.

contribution to pollutant concentrations that correspond to all endpoints falling into the selected cell (i,j) within the corresponding PBL heights, as follows:

$$CWBL_{ijh} = mean\left(C^{e}_{l|PBLH^{e}_{ijl} \geq h}\right) \tag{8}$$

where C^e_l is the concentration attributed to each endpoint e of trajectory l, and $PBLH^e_{ijl}$ refers to the PBL height at each endpoint in the moment when the air parcel passed grid cell (i, j).

As for other hybrid receptor models, the CWBL values can be down-weighted when the number of the endpoints corresponding to a grid cell is less than two or three times of the average number (Zeng and Hopke, 1989).

3. Materials and methods

In order to examine the performance of the 3D hybrid receptor models and CWBL, $PM_{2.5}$ mass concentrations observed in Belgrade urban area during 2013 and industrial VOC emissions derived by the use of positive matrix factorization (PMF) on the basis of VOC and inorganic gaseous pollutant concentrations, measured in Belgrade urban area from January to March 2014, were used. $PM_{2.5}$ concentrations were determined by the use of automatic beta attenuation sampler, whereas VOC concentrations were measured by the use of proton transfer reaction mass spectrometry (PTR-MS). The measurement procedures and uncertainties, together with the obtained data and basic statistics are presented in Stojić et al. (2015a, 2015b, 2016).

As explained in the previous section, the preprocessing of the pollutant time series included the exclusion of the local emissions contribution by the use of a frequency differentiated non-linear digital filtering algorithm implemented in the function baseline. rollingBall of the Baseline package (Kneen and Annegarn, 1996) of the statistical software environment R (Team R.C., 2013). Afterwards, the contribution of transport was estimated by subtracting the average monthly background contribution from the derived baseline, as described in Stojić et al. (2015a, 2016).

The conventional TSA procedure according to Zhu et al. (2011) implies that the trajectory directions are predefined by several sectors that are numbered clockwise, with sector 1 from due north. This procedure was slightly modified. Namely, by rotating sector grid by 1° in a clockwise direction, we searched for the distribution in which the minimum of the transported pollution was apportioned to a certain sector. Thereby, the sector was considered for further analysis only if it had sufficient trajectory coverage, *i.e.* contained at least 50% of the trajectories it would contain if the total number of back trajectories arriving at a receptor site would be evenly apportioned between all sectors. The main advantage of such approach is that it enables background contribution to be identified on the basis of the area with the lowest relative contribution of transport, avoiding this least-polluted area to be divided among sectors by the predefined geospatial grid overlaid onto the receptor region (Fig. S1, Supplementary material).

For a more precise description of the pollution plume, it is necessary to use the larger number of trajectories calculated for the larger number of heights above the receptor site, but still below the PBL height (Stojić et al., 2015a). In this study, the trajectories were dynamically calculated for 30, 50 and 70% of the PBL height at the receptor site every hour UTC each day by the use of the HYSPLIT model (Stein et al., 2015) and the Opentraj package (Opentraj, 2015) of the statistical software R. As explained in the previous section, hybrid receptor modeling included only the representative trajectories within the PBL not reaching the ground level (GL). In the case that the central trajectory (at 50% of PBL height above the receptor site) reached GL or exceeded PBL at defined number of endpoints, all three trajectories were excluded from the analysis because the condition that vertical profiles of pollutant concentrations remain relatively constant for a considerable part of the PBL was probably not met. If only the lowest of the three trajectories reached GL, its height would be gradually increased by 1 m till the level at which it could be avoided. Similarly, if the highest trajectory exceeded the

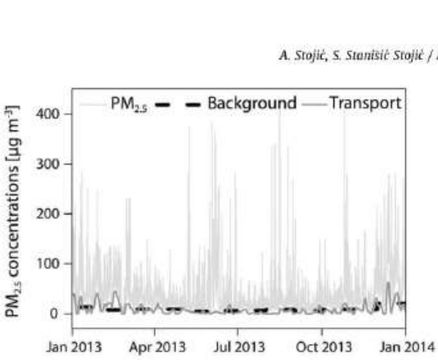


Fig. 3. $PM_{2.5}$ concentrations measured at the receptor site, TSA-derived background and transport contributions.

PBL height, the PBL height at the receptor site used for back trajectory calculation would be gradually decreased by 1 m till the PBL exceedance at each endpoint could be avoided, *i.e.* till the entire trajectory could remain within PBL at each endpoint. Thereby, for the purpose of the transport analysis presented herein, three trajectories were always assigned to the corresponding concentrations.

Different statistical approaches to computing trajectories and their sources of error are summarized by Stohl (1998). In this study, we used 72 h-back trajectories since they offer a good compromise between synoptic scale transport and positional errors. A compilation of trajectory uncertainties shows that the minimum absolute horizontal transport deviation (AHTD) of trajectories after three days of travel typically does not exceed 500 km. According to Sofowote and Dempsey (2015), the HYSPLIT determines the direction from which air masses reach the site with an error of 15–30% of the total travel distance. In general, Sofowote et al. (2014) explained that the ensemble presented herein has the best performance with large datasets since they average out the random errors associated with trajectories.

The PBL height at each trajectory endpoint was calculated using GDAS1 (Global Data Assimilation System, 2015) and MeteoInfo software (Wang, 2014).

The plots presented in this paper were produced by the use of 'raster', 'rasterVis', 'mapdata' and 'maptools' (Lamigueiro, 2014), 'openair' (Carslaw and Ropkins, 2012) and 'plotly' (Plotly, 2015) packages of the statistical software R.

4. Results and discussion

The discrimination between the contributions of local and remote emission sources and assessment of their impact on the receptor site was obtained by the previously described procedure that included the segregation of transport time series and the selection of representative trajectories according to inclusion criteria.

4.1. Segregation of the transport time series

Fig. 3 illustrates the use of baseline. rollingBall for the extraction of baseline from the $PM_{2.5}$ time series.

Further, TSA was applied to the derived baseline to differentiate between the contribution of background and transport, and the obtained transport time series were further used as input data for hybrid receptor models. According to the results of particle related trajectory analysis, the variations of background contribution estimates do not exceed 10%, depending on the sector distribution.

4.2. Trajectory selection

As previously explained, the trajectories with endpoints exceeding the PBL height, as well as a number of small height-trajectories that were curved and thus, reached the ground level, were excluded from the analysis. The percentage of representative trajectories for the defined number of endpoints over the study period are presented in Table S1, Supplementary material. As can be seen, even if trajectories reach ground level and exceed the PBL height in up to 10 endpoints, not more than 50% of trajectories shall remain representative. The Interactive plot 1 (Supplementary file 1) displays more clearly the ratio between the representative trajectories (maximum 2 endpoints reaching ground level, 3 exceeding the PBL height) and those not meeting these criteria (Fig. S2, Supplementary material).

As shown in Fig. 4, different spatial distribution of potential emission sources and assessment of their impact on the receptor site is obtained as a result of concentration time series preprocessing and trajectory selection. Discernible hot spots over Bosnia, Romania and Bulgaria appeared more clearly after applying the proposed procedure.

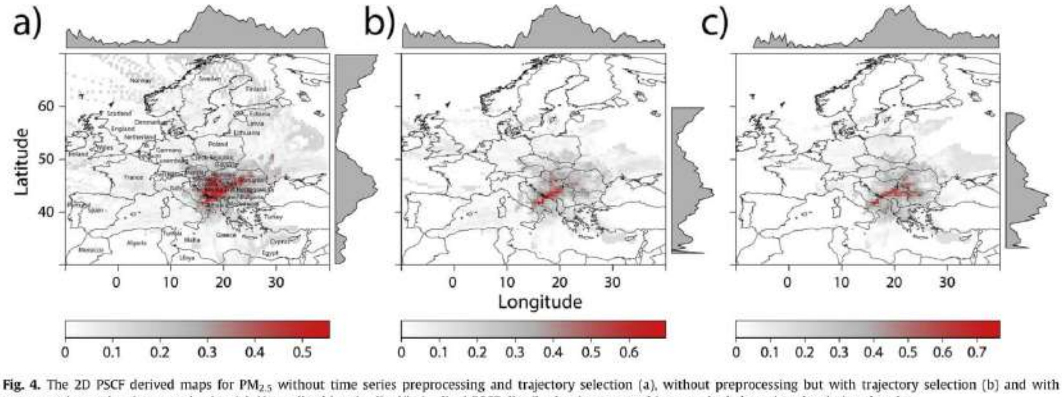


Fig. 4. The 2D PSCF derived maps for $PM_{2.5}$ without time series preprocessing and trajectory selection (a), without preprocessing but with trajectory selection (b) and with preprocessing and trajectory selection (c). Normalized longitudinal/latitudinal PSCF distribution is presented in grey-shaded portions bordering the plots.

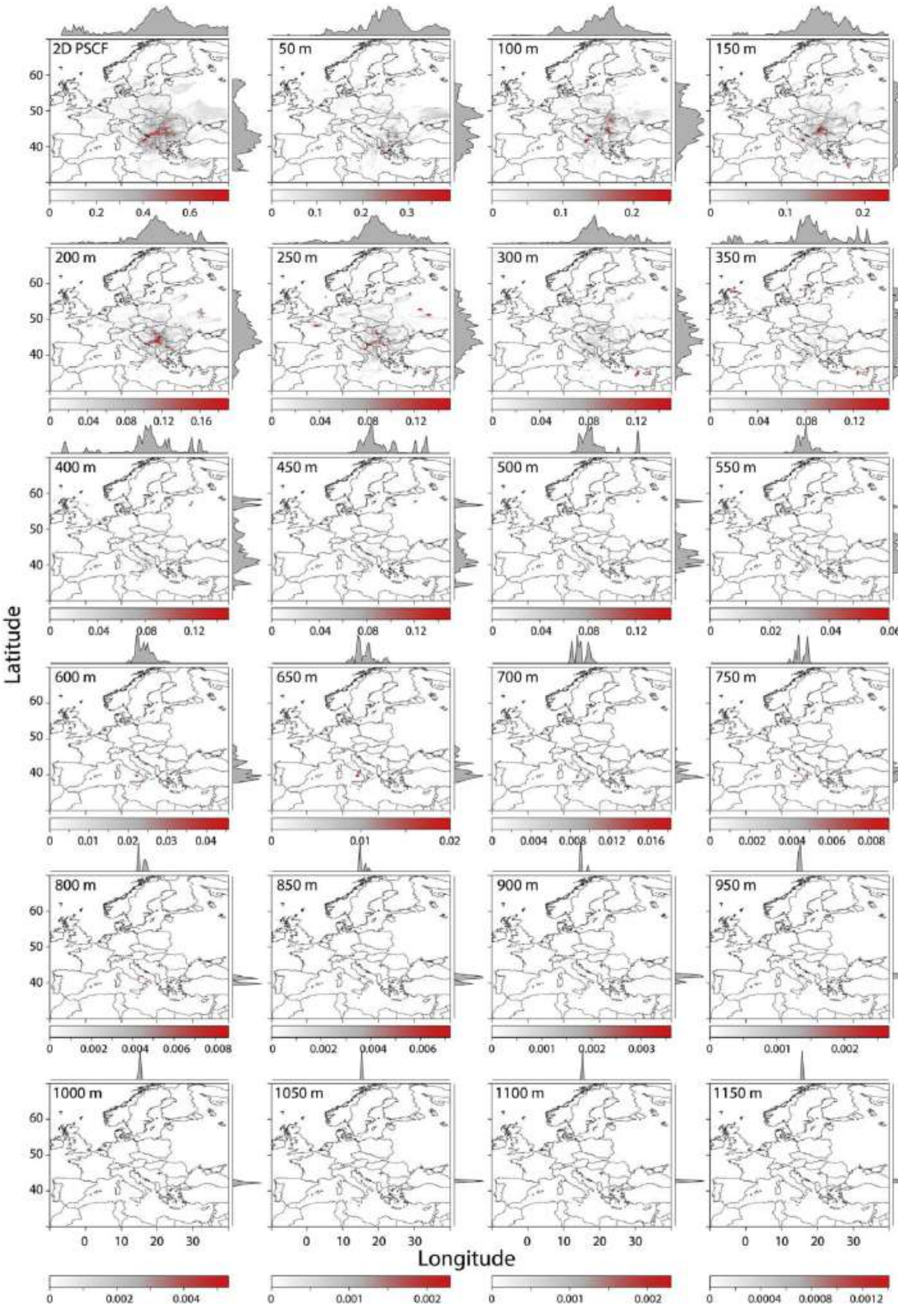


Fig. 5. 2D PSCF and 3D PSCF derived maps.

4.3. 3D hybrid receptor models

4.3.1. 3D PSCF

Fig. 5, Fig. S3 (Supplementary material) and Interactive plot 2 (Supplementary file 2) display the main source regions that contributed to the elevated concentrations of $PM_{2.5}$ in Belgrade, according to the results of 3D PSCF analysis. In the 3D solution, the data were calculated over altitude slices of 50 m up to the maximal trajectory height within the PBL. Horizontal slices clearly depict the potential heights at which air mass flow occurred: the highlighted grid cells being densely distributed over the source regions in the lower troposphere suggest that the significant pollutant transport mostly occurred at altitudes in the range from 100 to 250 m above ground level, which can be well observed in Interactive plot 3 (Supplementary file 3) and Fig. S4.

4.3.2. 3D CWT

Fig. 6 illustrates the distribution of transported $PM_{2.5}$ concentrations and VOC industrial emissions according to the 2D CWT and 3D CWT.

The CWT values can also be down-weighted when the number of endpoints corresponding to a grid cell is less than two or three times of the average number.

4.3.3. CWBL

The results of CWBL are shown in Fig. 7 and Interactive plot 4 (Supplementary file 4). As can be seen, the altitude distribution of VOC industrial emissions over the grid cells is clearly depicted. Additionally, using the CWBL as multireceptor model, by including a large dataset obtained from a number of sampling sites, could be even more predictive in identifying potential transport pathways. It is important to note that CWBL is not limited to trajectory endpoint analysis, but it also provides pollutant altitude distribution above the receptor site.

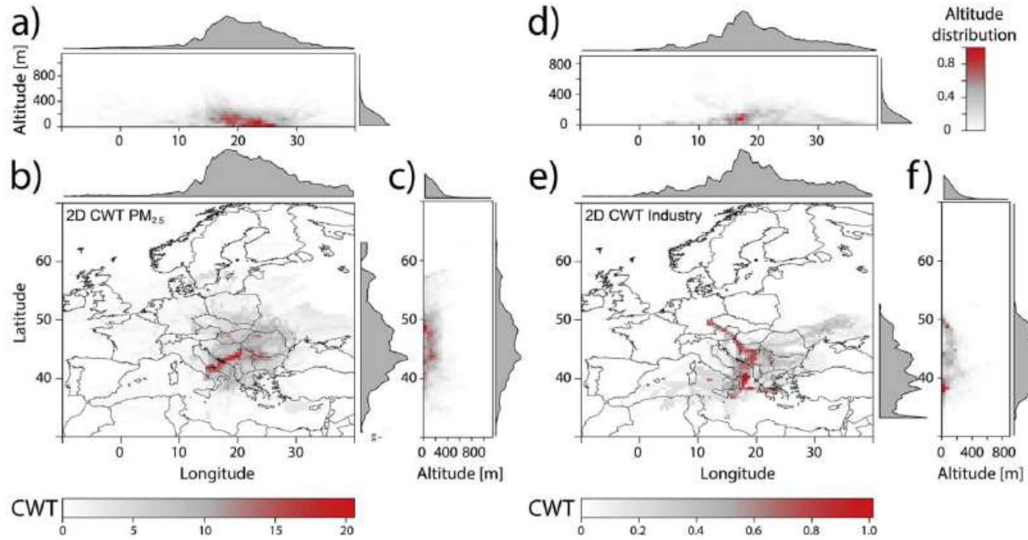


Fig. 6. 2D CWT derived map for $PM_{2.5}$ [μg m^{-3}] (b), and VOC industrial emissions (average = 1) (e), and 3D CWT longitudinal/latitudinal altitude distribution of pollutants during transport within the PBL (a, c, d, e).

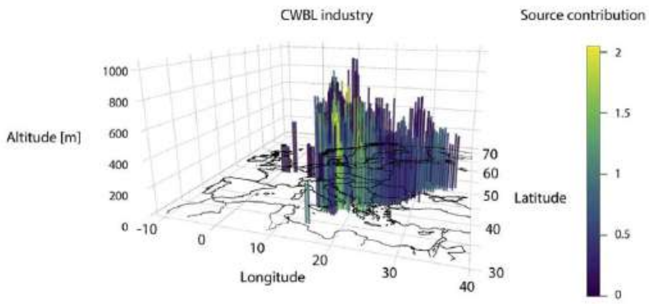


Fig. 7. CWBL derived map for VOC industrial emissions (average = 1) representing its continual altitude distribution above the receptor site, as well as above remote source regions, starting from the ground level to the maximum PBL height at each grid cell.

5. Conclusions

Significant improvements have been made over the last decades in the mathematical modeling of pollutant dispersion in the atmosphere, and as a result, general hybrid receptor models including PSCF and CWT have become widely accepted tools for identifying emission sources and transport patterns affecting the receptor site. In this study, we presented the modified approach to air pollution transport analysis, which enables more realistic discrimination between the relative importance of background, local sources and transport processes for pollutant concentrations at the receptor site, as well as the selection of representative trajectories for further analysis. Depending on the conditions at the receptor site, the selection and inclusion of the trajectories can be conducted in a number of ways, including the one presented herein. Additionally, we presented the concept of 3D hybrid receptor modeling that can be employed for more realistic estimation of source contributions to the receptor site (3D PSCF and 3D CWT) and for analyzing the vertical distribution of pollutant concentrations along the transport pathway (CWBL). Further research is needed to examine other functions for data preprocessing and trajectory data inclusion, as well as to explore the full potential of 3D hybrid receptor models and compare the outcome with the results of dispersion models or emission inventories. Also, future methodological enhancements of hybrid receptor models are expected, as there is a substantial need for their application nowadays.

Funding

This study was performed as part of the projects Grant No III43007 and No III41011, which were supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011–2017.

Acknowledgements

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model used in this publication, as well as the Openair Project. The authors wish to thank the anonymous reviewers for their comments and suggestions, which led to an improvement to the presentation of this work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.06.009.

References

Ashbaugh, L.L., Malm, W.C., Sadeh, W.Z., 1985. A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. Atmos. Environ. (1967) 19 (8), 1263–1270.

Byčenkienė, S., Plauškaitė, K., Dudoitis, V., Ulevicius, V., 2014. Urban background levels of particle number concentration and sources in Vilnius, Lithuania. Atmos. Res. 143, 279–292.

Brereton, C.A., Johnson, M.R., 2012. Identifying sources of fugitive emissions in industrial facilities using trajectory statistical methods. Atmos. Environ. 51, 46–55.

Carslaw, D.C., Ropkins, K., 2012. Openair—an R package for air quality data analysis. Environ. Model. Softw. 27, 52–61.

Cheng, M.D., Hopke, P.K., Zeng, Y., 1993. A receptor-oriented methodology for determining source regions of particulate sulfate observed at Dorset, Ontario. J. Geophys. Res. Atmos. 98 (D9), 16839–16849.

Dimitriou, K., Kassomenos, P., 2014. A study on the reconstitution of daily PM 10 and PM 2.5 levels in Paris with a multivariate linear regression model. Atmos. Environ. 98, 648–654.

Gan, C.M., Gross, B., Moshary, F., Wu, Y., 2011. Application of Remote Sensing Instrument in Air Quality Monitoring. INTECH Open Access Publisher.

Grivas, G., Chaloulakou, A., Kassomenos, P., 2008. An overview of the PM 10 pollution problem, in the Metropolitan Area of Athens, Greece. Assessment of controlling factors and potential impact of long range transport. Sci. total Environ. 389 (1), 165–177.

Global Data Assimilation System (2015) https://www.ready.noaa.gov/gdas1.php. Accessed: 10th November, 2016.

Hopke, P.K., Gao, N., Cheng, M.D., 1993. Combining chemical and meteorological data to infer source areas of airborne pollutants. Chemom. Intelligent Laboratory Syst. 19 (2), 187–199.

Hopke, P.K., 2003. Recent developments in receptor modeling. J. Chemom. 17 (5), 255–265.

Hsu, Y.K., Holsen, T.M., Hopke, P.K., 2003. Comparison of hybrid receptor models to locate PCB sources in Chicago. Atmos. Environ. 37 (4), 545–562.

Kassomenos, P., Karakitsios, S., Papaloukas, C., 2006. Estimation of daily traffic emissions in a South-European urban agglomeration during a workday. Evaluation of several "what if" scenarios. Sci. total Environ. 370 (2), 480–490.

Kim, I.S., Wee, D., Kim, Y.P., Lee, J.Y., 2016. Development and application of three-dimensional potential source contribution function (3D-PSCF). Environ. Sci. Pollut. Res. 1–9.

Kneen, M.A., Annegarn, H.J., 1996. Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 109, 209–213.

Lamigueiro, O.P., 2014. Displaying Time Series, Spatial, and Space-time Data with R. CRC Press.

Langford, A.O., Senff, C.J., Alvarez, R.J., Brioude, J., Cooper, O.R., Holloway, J.S., Lin, M.Y., Marchbanks, R.D., Pierce, R.B., Sandberg, S.P., Weickmann, A.M., 2015. An overview of the 2013 Las Vegas Ozone Study (LVOS): impact of stratospheric intrusions and long-range transport on surface air quality. Atmos. Environ. 109, 305–322.

Li, L., Yan, D., Xu, S., Huang, M., Wang, X., Xie, S., 2017. Characteristics and source distribution of air pollution in winter in Qingdao, eastern China. Environ. Pollut. 224, 44–53.

Opentraj (2015) https://cran.r-project.org/web/packages/opentraj/opentraj.pdf. Accessed: 10th November, 2016.

Plotly, 2015. Plotly Technologies Inc. Collaborative Data Science. Montréal, QC. https://plot.ly.

Seidel, D.J., Zhang, Y., Beljaars, A., Golaz, J.C., Jacobson, A.R., Medeiros, B., 2012. Climatology of the planetary boundary layer over the continental United States and Europe. J. Geophys. Res. Atmos. 117 (D17).

Sen, A., Ahammed, Y.N., Banerjee, T., Chatterjee, A., Choudhuri, A.K., Das, T., Deb, N.C., Dhir, A., Goel, S., Khan, A.H., Mandal, T.K., 2016. Spatial variability in ambient atmospheric fine and coarse mode aerosols over Indo-Gangetic plains, India and adjoining oceans during the onset of summer monsoons, 2014. Atmos. Pollut. Res. 7 (3), 521–532.

Sofowote, U., Dempsey, F., 2015. Impacts of forest fires on ambient near–real–time PM 2.5 in Ontario, Canada: meteorological analyses and source apportionment of the July 2011–2013 episodes. Atmos. Pollut. Res. 6 (1), 1–10.

Sofowote, U.M., Rastogi, A.K., Debosz, J., Hopke, P.K., 2014. Advanced receptor modeling of near–real–time, ambient PM 2.5 and its associated components collected at an urban–industrial site in Toronto, Ontario. Atmos. Pollut. Res. 5 (1), 13–23.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. Bull. Am. Meteorological Soc. 96 (12), 2059–2077.

Stohl, A., 1998. Computation, accuracy and applications of trajectories—a review and bibliography. Atmos. Environ. 32 (6), 947–966.

Stojić, A., Stanišić Stojić, S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., Mijić, Z., 2016. Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. Environ. Sci. Pollut. Res. 23 (11), 10722–10732.

Stojić, A., Stojić, S.S., Mijić, Z., Šoštarić, A., Rajšić, S., 2015b. Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos. Environ. 106, 71–79.

Stojić, A., Stojić, S.S., Šoštarić, A., Ilić, L., Mijić, Z., Rajšić, S., 2015a. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ. Sci. Pollut. Res. 22 (17), 13137–13152.

Stull, R.B., 1988. Mean boundary layer characteristics. In: An Introduction to Boundary Layer Meteorology. Springer, Netherlands, pp. 1–27.

Team R. C, 2013. R: a Language and Environment for Statistical Computing.

Wang, Y.Q., 2014. MeteoInfo: GIS software for meteorological data visualization and analysis. Meteorol. Appl. 21 (2), 360–368.

Zeng, Y., Hopke, P.K., 1989. A study of the sources of acid precipitation in Ontario, Canada. Atmos. Environ. (1967) 23 (7), 1499–1509.

Zhu, L., Huang, X., Shi, H., Cai, X., Song, Y., 2011. Transport pathways and potential sources of PM10 in Beijing. Atmos. Environ. 45 (3), 594–604.

Atmospheric Environment 168 (2017) 46–54

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Rainwater capacities for BTEX scavenging from ambient air

A. Šoštarić [a, *], S. Stanišić Stojić [b], G. Vuković [c], Z. Mijić [c], A. Stojić [c], I. Gržetić [d]

[a] Institute of Public Health Belgrade, Bulevar Despota Stefana 54a, 11000 Belgrade, Serbia
[b] Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia
[c] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
[d] Faculty of Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia

HIGHLIGHTS

- Potential of rainwater for BTEX scavenging from ambient air was examined.
- BTEX concentrations in rain samples exceeded the theoretically predicted values.
- BTEX retention could be associated with BTEX aerosol fraction.
- Random forest and instance based algorithms provide reliable enrichment predictions.
- Gas mixing ratios, rainwater characteristics and meteorology affect BTEX distribution.

ARTICLE INFO

Article history:
Received 14 March 2017
Received in revised form
15 August 2017
Accepted 18 August 2017
Available online 23 August 2017

Keywords:
BTEX
Wet deposition
Rain
PTR-MS
Multivariate methods
Unmix

ABSTRACT

The contribution of atmospheric precipitation to volatile organic compound (VOC) removal from the atmosphere remains a matter of scientific debate. The aim of this study was to examine the potential of rainwater for benzene, toluene, ethylbenzene and xylene (BTEX) scavenging from ambient air. To that end, air and rainwater samples were collected simultaneously during several rain events that occurred over two distinct time periods in the summer and autumn of 2015. BTEX concentrations in the gaseous and aqueous phases were determined using proton transfer reaction mass spectrometry. The results reveal that the registered amounts of BTEX in rainwater samples were higher than those predicted by Henry's law. Additional analysis, including physico-chemical characterization and source apportionment, was performed and a possible mechanism underlying the BTEX adsorption to the aqueous phase was considered and discussed herein. Finally, regression multivariate methods (MVA) were successfully applied (with relative errors from 20%) to examine the functional dependency of BTEX enrichment factor on gaseous concentrations, physico-chemical properties of rainwater and meteorological parameters.

1. Introduction

Benzene, toluene, ethylbenzene and the three xylene isomers, frequently referred to as BTEX, constitute a group of aromatic hydrocarbon species of particular environmental interest, commonly associated with the petrochemical industry and incomplete fossil fuel oxidation (Stojić et al., 2015a, 2015b). Besides being important photochemical precursors for tropospheric ozone and secondary organic aerosols (SOA) (Chatani et al., 2015), these hazardous air pollutants cause chronic toxicity even in small concentrations (Stojić et al., 2015c). According to the IARC data, benzene is recognized as a significant public health threat and classified as group I carcinogen, ethylbenzene is a suspected IIB carcinogen, while both toluene and the xylene isomers belong to group III neurotoxins (WHO, 1986, 1993, 1997; Durmusoglu et al., 2010).

In the atmosphere, volatile species are distributed between the gaseous, aqueous and particle phase (Matsumoto et al., 2010). In their biogeochemical cycle, it is believed that the role of atmospheric water is quite prominent, but this issue is still subject to continuous scientific debate (McNeill et al., 2012). The concentrations of BTEX in various forms of atmospheric water depend on various factors including their ambient gas mixing ratios, water solubility and Henry's law constant, frequency and intensity of precipitation events (Balla et al., 2014), gas-water surface interactions (Raja and Valsaraj, 2004), content and concentrations of other species in atmospheric water (Okochi et al., 2005; Sato et al.,

* Corresponding author.
E-mail address: andrej.sostaric@zdravlje.org.rs (A. Šoštarić).

http://dx.doi.org/10.1016/j.atmosenv.2017.08.045
1352-2310/

2006; Allou et al., 2011), as well as the origin of air masses (Mullaugh et al., 2015). Previous studies, which primarily focused on wet deposition of BTEX and their partition between gaseous and aqueous phases, were relatively scarce and provided contradictory conclusions.

In the study aimed at investigating the capacity of rainwater for wet scavenging of BTEX, Okochi et al. (2004) reported that the concentrations of species detected in rain samples were higher than those predicted by Henry's law, and concluded that atmospheric precipitation might play significantly greater role in removing BTEX from ambient air than previously thought. Thereby, the observed supersaturation was assumed to be associated with the presence of surface-active agents in rain droplets, whereas the rainfall intensity appeared to be of negligible importance. Accordingly, our previous study confirmed a significant enrichment of BTEX in the aqueous phase in a dynamic equilibrium system designed to resemble the interactions between the gaseous and water phase during rainfall (Šoštarić et al., 2016). Conversely, recent findings of Mullaugh et al. (2015) indicate that BTEX were not efficiently scavenged from the atmosphere by wet deposition processes. Furthermore, the authors concluded that light-mediated reactions with OH· or nitrogen radicals remain the major atmospheric sink for BTEX. Nonetheless, it should be noted that this research was not based on the ambient air measurements, but it mainly relied on the previously published BTEX data from similar locations.

In order to better understand the fate of volatile species in atmospheric, terrestrial and aquatic systems, the present study examines the contribution of rainwater to wet scavenging of atmospheric BTEX, as well as the mechanisms related to their air-water distribution transfer.

2. Materials and methods

A total of 53 sample pairs of air and rainwater samples were collected simultaneously during several rain events that occurred over two distinct time periods in the summer and autumn season of 2015. The sampling was performed at the Institute of Physics (Belgrade, Serbia; 44°49′ N, 20°28′ E), located in the vicinity of the Danube river, in the suburban residential area, with a number of local fireboxes active during the heating season.

Rainwater sampling was performed using a custom-built precipitation collector with the effective sampling area of 9 m^2. The steep collecting panels (45°) were designed to reduce rainfall retention time and minimize possible BTEX volatilization. Such large sampling area enabled collecting a vast number of samples per each rain event. The panels were thoroughly rinsed with 18 MΩ ultrapure water (ELGA PURELAB maxima system) prior to each sampling campaign, and the rinsing water was collected and analyzed as a field blank control sample. No target compounds were detected in the field blank control samples. The samples were collected and stored directly into brown glass bottles of 1 300 mL. All bottles were washed with detergent, thoroughly rinsed with ultrapure water and dried in an oven for 2 h at 105 °C to remove any trace of contamination. During the sampling, the bottles were filled to the top to avoid headspace, and the sampling duration and sample temperature were recorded. Since sampling equipment enables collection of large volumes of rainwater within a short period, the last sample in each sampling campaign was collected in the bottle of 2600 mL and was split into two standard aliquots. The first aliquot was analyzed immediately, whereas the other one was examined after all other samples to determine whether the BTEX levels changed over time. No difference could be observed in the obtained quantity of double samples (Table S1, Supplementary material).

BTEX concentrations in both gas and water phases were measured using proton transfer reaction mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria), whose detailed description is given elsewhere (Lindinger et al., 1998). Since PTR-quad-MS is not capable of distinguishing isobaric ions, the signal detected at m/z 107 referred to C_8 aromatic hydrocarbons, ethylbenzene, o-, m-, and p-xylene. Signals detected at m/z 79 and m/z 93 referred to benzene and toluene, respectively (Warneke et al., 2003).

The air samples were collected as a side flow from a 1/8-inch teflon tube sampling line through which ambient air was drawn at the flow rate of about 50 L min^{-1} to ensure short residence. The sample inlet was located 6 m above ground level with a sampling angle of 360°. Drift tube parameters included: pressure, ranging from 2.04 to 2.14 mbar; temperature, 60 °C; voltage, 600 V; E/N parameter, 145 Td providing reaction time of 90 μs? The count rate of $H_3O^+H_2O$ was 3–8% of the $9.2 \cdot 10^6$ counts s^{-1} count rate of primary H_3O^+ ions. PTR-MS calibration was performed before and after each sampling campaign using an external standard five-point calibration, ranging from 0 to 26 ppbV, 0–25 ppbV and 0–80 ppbV for B, T and EX, respectively. For this purpose, 2.5 ppmV mixture of BTEX (BTEX in nitrogen, Messer Group GmbH) was diluted with high-purity synthetic air (CH free, Messer Group GmbH) by means of HORIBA ASGU 370-P system.

Determination of BTEX concentrations in rainwater was performed immediately after each sampling campaign. A liter of each unfiltered rainwater sample was transferred to the gas washing bottle (GWB) and purged out with synthetic air at a flow rate of 1L min^{-1}. Rainwater filtration was avoided due to potential adsorption of species on the filter. The GWB output was connected with PTR-MS inlet via T-piece, and further analytical procedure, calibration and data processing were conducted as described in Šoštarić et al. (2016). In brief, PTR-MS signal obtained during exsufflation was subject to baseline fitting. The exsufflation time was determined for each sample as the interval required for equilibrium to be achieved (t_{eq}). The obtained exsufflation time was used for determining the amounts of target compounds retained in the analyzed rainwater samples. The aqueous concentrations of analyzed species were calculated by multiplying the obtained amounts by the conversion factor (3.25; 3.83 and 4.41 for B, T and EX, respectively). The detection limits (DL) in rainwater were determined using HC free air and calculated as 10 nM, 10 nM and 20 nM for B, T and EX, respectively. The remaining portion of each rainwater sample was transferred to a 300-mL bottle and stored at 4 °C until further analysis, which included determination of the major inorganic anions (F^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^-), dissolved cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}), total organic carbon, electrical conductivity, UV extinction, turbidity and pH, in accordance with the standard methods (US EPA 300.1:1993, EN ISO 14911:1998, ISO 8 245:1999, EN 27888:1993, SMEWW 19th method 5 910 B, US EPA 180.1:1993, EN ISO 10523:2008, respectively). More details of the methods and equipment applied for physico-chemical analysis conducted on rainwater samples are presented in Supplementary material.

In order to determine the extent to which Henry's law constant (K_H) describes BTEX distribution between the gaseous and aqueous phase, distribution coefficients (D_{OBS}) were calculated for each sample pair and each species, as the ratio of the corresponding experimentally derived rainwater concentrations in nM (C_R) and ambient gas phase mixing ratios in ppbV (p_g):

$$D_{OBS} = C_R/p_g \ \left(M\ atm^{-1}\right) \quad (1)$$

Furthermore, the enrichment factors (EF) were calculated as the ratio of D_{OBS} and K_H.

Considering the K_H temperature dependence, EF were calculated using temperature corrected K_HT for each rain sample by means of the following equation (Sander, 2015):

$$K_HT = K_H(298.15)exp\left\{\frac{-\Delta H}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad (2)$$

where K_H is the Henry's law constant at 298.15 K for pure water, ΔH is the enthalpy change of air-water transfer, T is the rainwater temperature, and R is the universal gas constant (8.314 J K^{-1} mol^{-1}). Furthermore, to assess the representativeness of ground level conditions for the atmospheric conditions during rainfall, K_HT and EF altitude profiles were calculated using the temperature profiles obtained from GDAS1 (Global Data Assimilation System, 2015), by replacing the rainwater temperature value by the temperature at the corresponding altitude.

Meteorological parameters during rain events (precipitation (accumulated rainfall, rain current and peak intensity, and the duration of a rain event), wind speed and direction, pressure, humidity and temperature) were measured by Vaisala Weather Transmitter WXT530 Series. Cloud information, including cloud height and type, was obtained from the airport "Nikola Tesla", Belgrade, ICAO code LYBE, located 8.9 km SSW from the sampling site.

The relationships between enrichment factors (EF), physicochemical characteristics and wind characteristics (wind speed and direction) were examined using the bivariate polar plot analyses (Carslaw and Beevers, 2013) implemented in the Openair package (Carslaw and Ropkins, 2012) within the statistical software environment R (Team, 2012).

The neutralization factors (NF) were calculated based on the study of Moreda-Piñeiro et al. (2014), Tiwari et al. (2016) and references therein in order to examine the potential of the cations to balance the rainwater acidic components:

$$[NF_{Ca^{2+}}] = \frac{[nssCa^{2+}]}{NO_3^- + [nssSO_4^{2-}]} \quad (3)$$

$$[NF_{Mg^{2+}}] = \frac{[nssMg^{2+}]}{NO_3^- + [nssSO_4^{2-}]} \quad (4)$$

$$[NF_{NH_4^+}] = \frac{[NH_4^+]}{NO_3^- + [nssSO_4^{2-}]} \quad (5)$$

$$[NF_{K^+}] = \frac{[nssK^+]}{NO_3^- + [nssSO_4^{2-}]} \quad (6)$$

To calculate the non-sea salt fraction of any particular ion (*nss*), we assumed that all Na originated from marine sources, and used it as a referent element. The nss contribution is given as:

$$[nss - X]_i = [X_i] - [Na^+]_i \left[\frac{[X]}{Na^+}\right]_{sea\ salt} \quad (7)$$

where $[nss - X]_i$ is the nss concentration of the selected ion in the sample *i*, $[X_i]$ is the total concentration of the ion X measured in the rainwater sample *i*, $[Na^+]$ is the total concentration of Na^+ measured in the rainwater sample, and $[[X][Na^+]^{-1}]_{seasalt}$ is the reference ratio determined in the seawater.

Potential remote source regions that might affect the observed BTEX mixing ratios were identified using HYSPLIT-derived 72-h back trajectories (Draxler and Rolph, 2014). The trajectories were computed for each hour UTC a day before and during each rain event, above the sampling location at the half of the planetary boundary layer height calculated from GDAS1 using MeteoInfo (Wang, 2014), as described in Stojić et al. (2016) and Stojić and Stanišić Stojić (2017).

Rainwater source apportionment was performed using Unmix (USEPA, 2007). The maximum number of species selected as input variables was chosen using the trial and error with the overall aim of yielding the most physically meaningful results. For concentrations below the DL, a value equal to the half of the DL was used.

Guided regularized random forest (GRRF) was applied (Deng and Runger, 2013) for the selection of features that are most relevant for EF. Random forest (RF) consists of a number of decision trees which every node represents a condition on a single variable designed to split the dataset in two parts so that similar response values end up in the same set. Variable importance measures how much each variable decreases the weighted impurity across all tress, a measure based on which the optimal condition is chosen. GRFF uses the importance scores from a preliminary RF to guide the feature selection of regularized random forest (RRF), and has several advantages as follows: it is more robust and computationally efficient than RRF, varSelRF and LASSO logistic regression; it can select compact feature subsets moderating the curse of dimensionality; it avoids the effort to analyze irrelevant or redundant features; and it has competitive accuracy performance. Variable importance presented herein was obtained by calculating the average value of 2000 GRRF runs. The appropriate number of trees was determined to assure out-of-bag error convergence. Method performance was tested by 100 times replicated 10-fold cross validation.

To analyze the relationship between EF and features that are considered most relevant for EF prediction, the following 24 regression MVA methods implemented in Weka 3.8 (Hall et al., 2009) were applied: Alternating Model Tree, Conjunctive Rule, Decision Stump, Decision Table, Elastic Net, Gaussian Processes, IBk, IBkLG, Isotonic Regression, K*, Least Median Squared, Linear Regression, Locally Weighted Learning, M5P, M5 Rules, Multilayer Perceptron, Pace Regression, Random Forest, Random Tree, Radial Base Function (RBF) Network, RBF Regressor, REP Tree, Simple Linear Regression and SMOreg Support Vector Machine. A brief description of the methods, including functions (neural network, support vector machine, etc.), clustering techniques, rules and trees, is provided in Supplementary material. Method performance was tested by 10 times replicated 10-fold cross-validation.

3. Results and discussion

Light showers, with occasional thunderstorms, constituted a considerable part of summer rain events. Scattered and broken clouds in the form of cumulonimbus or towering cumulus were observed at the height of 400–1 000 m. In the autumn campaign, the vast majority of rain events were light and sporadically followed by mist. Scattered clouds were registered at levels below 300 m, whereas broken clouds were observed from 100 to 900 m.

As expected, both aqueous and gaseous BTEX concentrations were higher during the cold part of the year. Lower BTEX concentrations in summer can be attributed to intense photochemical removal and washout effects associated with more sunny and rainy days (Lee et al., 2002), whereas higher concentrations of BTEX in autumn can be associated with individual combustion fireboxes widely spread in the vicinity of the sampling site. Furthermore, aqueous B concentrations in summer were below DL.

As can be seen in Fig. 1, each rain event was associated with air

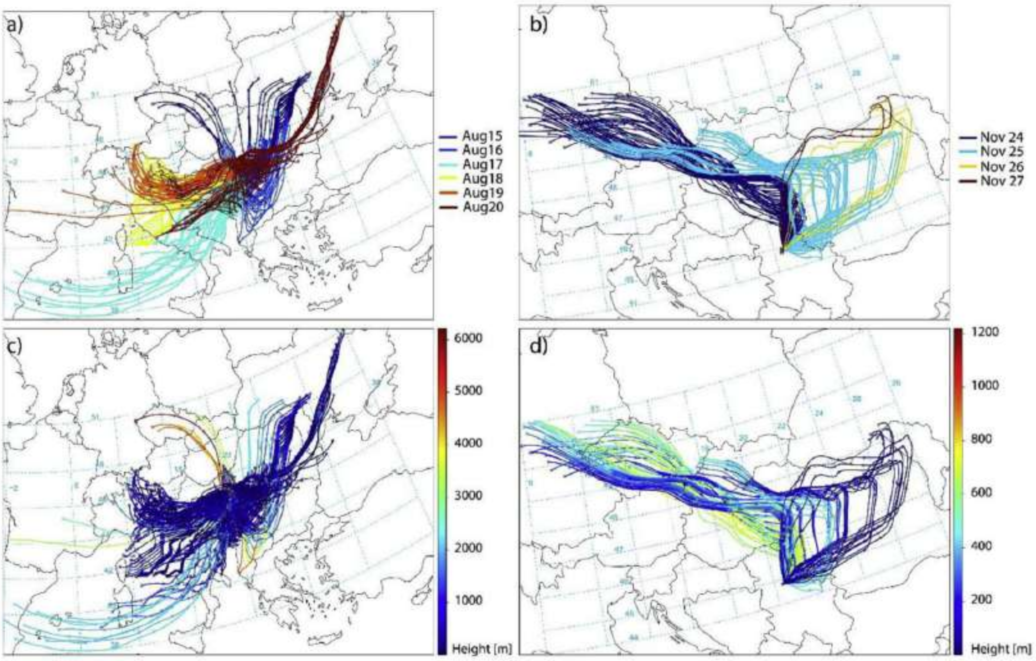


Fig. 1. Back trajectories a day before (August 15 and November 24) and during summer (a) and autumn (b) rain events and corresponding trajectory heights (c, d).

masses coming from different source regions and heights. During summer rain events, air flows from all directions were followed by significant variations in physico-chemical properties of rainwater, whereas N and NE air masses in autumn were associated with a more uniform rainwater composition. Gaseous concentrations of volatile species, particularly B, were relatively stable during rain events, which can be explained by the fact that the sampling site was dominated by local BTEX sources.

3.1. Physico-chemical characteristics of rainwater

Basic statistics for all rainwater parameters and BTEX concentrations is given in Table S2, Supplementary material. The average rainwater pH was 6.01, while the turbidity was below 10 NTU, indicating that the samples contained moderate amounts of suspended particles from the atmosphere. As illustrated in Fig. S1, conductivity, as well as high concentrations of most ions (SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, K^+ and Na^+) were influenced by the high-speed SW wind (20–30 m s^{-1}), while only NH_4^+ concentrations were increased with the wind of moderate speed (10 m s^{-1}) from NE direction.

The rainwater pH varied from 3.70 to 8.20 with the volume weighted mean of 6.01, which is mainly due to scavenging of alkaline species (Ca^{2+} and SO_4^{2-}). The average pH value is also close to the 5-year-mean (6.1) obtained as a part of the regular air quality monitoring in Belgrade. The contribution of SO_4^{2-} to the rainwater acidity was confirmed by ($Cl^- + NO_3^-$) and (SO_4^{2-}) ratio below 1 (Tiwari et al., 2016). As shown, Ca^{2+} was the dominant neutralization component, followed by NH_4^+, Mg^{2+} and K^+, with mean of 77%, 14%, 7% and 2.3%, respectively.

As shown in Fig. S2, significant correlations were observed as follows: > 0.80 (NO_3^- – SO_4^{2-}, NH_4^+ – aq. B, NH_4^+ – gas. B, NH_4^+ – EF_B); 0.70–0.80 (F^- – SO_4^{2-}, F^- – NO_3^-, F^- – aq. B, F^- – gas. B, F^- – EF_B, K^+ – Na^+); and 0.60–0.70 (NO_3^- – Mg^{2+}, SO_4^{2-} – Mg^{2+}, SO_4^{2-} – EF_{EX}, Na^+ – Mg^{2+}). Furthermore, high correlations were noted between aq. And gas. BTEX concentrations (≥0.80), as well as between aq. EX and aq. B (0.67) and aq. T (0.67), suggesting that these species might share the common source.

As can be seen in Tables S3, S4 and S5, four factors were derived using Unmix. With high contributions of volatile BTEX species (99%, 44.5% and 52.2%) and a relatively high share of UV extinction (33.3%), the first factor was recognized as organic compounds in the gaseous form. The second factor, characterized by the highest contribution of TOC (71.6%) and turbidity (79.7%), represented the solid fraction dissolved in the atmospheric water. Significant shares of K^+ (58.0%), SO_4^{2-} (42.2%) and NO_3^- (31.3%) were also apportioned to this factor, as a result of fossil fuel burning and traffic exhaust (Rao et al., 2016; Tiwari et al., 2016). The high shares of crustal-related elements, Na^+ (61.8%) and Mg^{2+} (61.4%), were apportioned to the third factor (Cao et al., 2008; Sapek, 2014). Moderate to significant shares (>30%) of all species except Na^+, K^+ and B were apportioned to the fourth factor, being recognized as the aerosol fraction. Apart from gaseous oxides (SO_2 and NO_2), which react with ozone and OH· radicals in the presence of Ca^{2+} and Mg^{2+} (Seinfeld and Pandis, 2006), BTEX are susceptible to photo-oxidation that can also lead to SOA formation. BTEX reactions include oxidation with ozone and OH·, but also with NO_x and SO_2, which results in multi-functional oxy products that are further deposited onto the existing aerosol or initiate the formation of SOA by self-nucleation. BTEX behave differently in the atmosphere due to differences in the methyl chain substituent and the alkyl chain length. Benzene is considered being extremely stable compared to T and EX (Słomińska et al., 2014), and it is less susceptible to the heterogeneous reactions and formation of SOA in the atmosphere.

The contributions of the gaseous organic- and aerosol-related factors were mostly associated with N wind of moderate speed (<10 m s^{-1}), which clearly reflects their local origin, while the solid- and crustal-related factors were associated with the air masses from SW direction and high wind speed (20–30 m s^{-1}) (Fig. S3). The contribution of the factor assigned to aerosols declined during rain events due to wet deposition, while similar behavior was not observed for other factors.

TEX air mixing ratios and rain concentrations decreased during the first 2 h of the rainfall, but tend to rise afterwards probably as a result of rainfall intensity decrease (Fig. S4, Supplementary material). The highest TEX enrichment, caused by air mixing ratio decrease, was detected during the second hour. Typical washout effect was observed for source contributions related to the rain-water aerosol and solid components, and was less pronounced for crustal factor. Unlike TEX, only a slight decrease in benzene air mixing ratios was noticeable, which is reflected in a constant EF_B increase.

3.2. BTEX distribution between gaseous and aqueous phases

The exsufflation time required for the equilibrium to be achieved was different for rainwater samples and ultrapure water, which suggests that physico-chemical properties and BTEX content distributed between different phases have certain impact on the adsorption to the aqueous phase (Fig. 2, left). However, the correlations were registered only between the concentrations of B, and F^- (−0.72) and NH_4^+ (0.83) (Fig. S2, Supplementary material). The impact of rainwater physico-chemical properties on the BTEX retention was further examined by insufflating 2 ppbV of BTEX in 10 pre-exsufflated rainwater samples, as described in our previous paper (Šoštarić et al., 2016). The results showed slightly longer exsufflation periods for rainwater samples compared to the pure water, indicating that physico-chemical properties are not the main contributor to the extended retention in the rainwater. The comparative qualitative analysis of rainwater and ultrapure water exsufflation time series obtained by real-time PTR-MS measurements showed that different capacities for BTEX retention can be mainly associated with BTEX aerosol fraction (Fig. 2, right).

Generally, due to very small K_H values of aromatic compounds, BTEX concentrations in rainwater are expected to be low (Słomińska et al., 2014). However, according to the results, EF values were in the range from 61 to 128, from 8 to 209, and from 25 to 295 for B, T and EX, respectively, indicating that the BTEX amounts in the aqueous phase significantly exceeded the theoretically predicted levels. Both lower and higher EF values have been reported in the literature. According to the studies dealing with the distribution of chlorinated hydrocarbons and monocyclic aromatic hydrocarbons between air and rainwater, EF ranged from 2.4 to 34 for BTEX (Okochi et al., 2004; Sato et al., 2006), whereas the study of Valsaraj et al. (1993) reported several hundred to a thousand-fold enrichment of hydrophobic organic compounds in fog samples. The enhanced BTEX transfer to urban dew water was also shown by Okochi et al. (2005), with the reported EF values ranging from 7.87 to 20.2. Furthermore, Fries et al. (2007) showed that the concentrations of aromatic hydrocarbons including ethylbenzene, xylenes and 1,2,4-trimethylbenzene, have been significantly lower in rain (15–53 ng L^{-1}) than in snow (71–2 200 ng L^{-1}). In the later study,

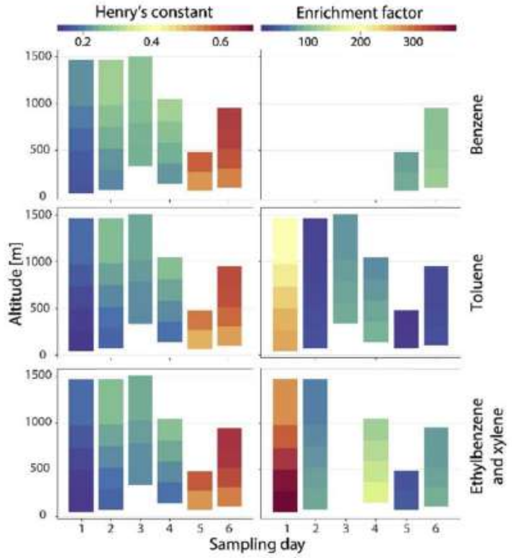


Fig. 3. Henry's constant and EF BTEX altitude distributions.

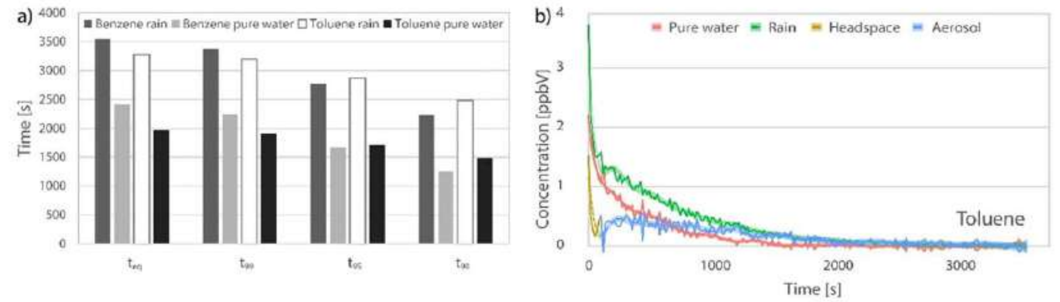


Fig. 2. The time required to reach equilibrium (t_{eq}) and 99, 95 and 90% quantity of benzene and toluene to be exsufflated (left), and toluene exsufflation from ultra-pure water and rainwater (right).

Fries et al. (2008) found that in-cloud scavenging could be a possible explanation for the occurrence of VOC in fallen snow.

Fig. 3 illustrates the K_H and EF altitude distribution for BTEX. It should be mentioned that K_H and EF for B and EX exhibit the similar pattern. As can be seen, K_H and consequently EF, change as the raindrop falls to the ground. K_H values calculated using the average temperature on the path of the raindrop differ ±20% from those obtained using the rainwater temperature. Such agreement indicates that the rainwater temperature measured at the ground level is a good indicator of atmospheric conditions under which reactions with BTEX takes place. Moreover, in the study of Lin et al. (2011), it was concluded that, at higher altitudes in locations with dominant local sources, VOC concentrations were generally lower, and hence, higher K_H values would not be expected to affect C_R, nor calculated values of D_{OBS} and EF.

As suggested by the field studies (Valsaraj et al., 1993; Goss, 1994; Okochi et al., 2004; Starokozhev et al., 2009), as well as the laboratory experiments (Bruant and Conklin, 2000, 2002; Raja et al., 2002; Raja and Valsaraj, 2004; Šoštarić et al., 2016), the interfacial adsorption might be the major mechanism associated with the enhanced VOC transfer to the aqueous phase.

Some previous studies have examined the composition of atmospheric water and the impact of different species, including nitric acid, anionic and nonionic surfactants, as well as the impact of salinity and pH on air-water VOC distribution (O'Sullivan et al., 1996; Vane and Giroux, 2000; Sato et al., 2006; Allou et al., 2011). The supersaturation of VOC in rain samples was explained by decreased rainwater polarity associated with the presence of different organic compounds (Sato et al., 2006). The presence of colloidal organic matter with its large binding capacity for many hydrophobic species was found in fog droplets (Valsaraj et al., 1993). Similarly, in the study of Okochi et al. (2005), the enhanced dissolution of VOC species in urban dew compared to rainwater was explained by the fact that dew forms near the ground and contain more humic-like substances that could lead to a decrease in water surface tension and consequently result in higher VOC enrichment.

The present study considers several factors that could contribute to BTEX enrichment in rainwater, including BTEX concentrations, rainwater physico-chemical properties, rainfall intensity, air masses origin, meteorological conditions and adsorption at the air/water interface.

As regards the physico-chemical characteristics of rainwater, only F^- and SO_4^{2-} can be considered important for the prediction of EF_B (−0.73) and EF_{EX} (0.62), respectively. The latter indicates that SO_2-rich coal burning emissions are also a significant source of EX, while the results for B should be taken with caution due to the small data size.

Higher rainwater T enrichment was mostly observed for low gaseous T concentrations, high TOC (8–12 mg L^{-1}) and turbidity (Supplementary file 1), although the strict link between rainwater enrichment and gaseous concentrations cannot be established. The exsufflation dynamics (Fig. 2) and the EF values suggest that prolonged BTEX retention could also be attributed to the adsorption to aerosol fraction. We have considered T partitioning, not only because T concentrations were in a relatively broad range, but also because of the significant number of samples collected in both seasons with comparable concentrations, despite the fact that similar findings were observed for the rainwater enrichment with EX (Supplementary file 2). As can be observed in Fig. 4 and Table S6 of the Supplementary material, higher T enrichment was mostly associated with a higher wind speed at the sampling site (up to 30 m s^{-1}) and air masses coming from SW area, whereas the lowest rainwater enrichment was registered under relatively stable atmospheric conditions (ws < 5 m s^{-1}). Similar associations were also observed for EX. Higher rainwater enrichment could be the result of the prolonged contact time between the aqueous and the gaseous phases, when strong wind-driven raindrops were falling obliquely.

According to GRRF results (Table S7, Supplementary material), physico-chemical rainwater properties and gaseous T concentrations appear to be of greater importance than meteorological factors for predicting T and EX rainwater enrichment. Furthermore, these findings also indicate that ground level gaseous concentrations have higher impact on the transfer of species to the aqueous phase than the polluted air masses coming from greater atmospheric heights.

Out of 24 examined MVA regression methods, some of which were previously successfully applied for prediction of PM_{10} and VOC emissions (Stojić et al., 2015d; Perišić et al., 2017), it has been shown that RF, IBk and IBkLG can provide predictions of EF_T and EF_{EX} based on the variables of the highest importance derived by GRRF with relative errors of approx. 20%, *i.e.* 27%, and correlation coefficients around 0.95 and 0.87, respectively (Table 1). Conversely, the prediction of EF_T and EF_{EX} based on Unmix derived source contributions was less accurate (K*: 36.3% relative error and correlation coefficient 0.79). As can be concluded, functional description of EF_T and EF_{EX} can be based on certain rainwater properties and gaseous T concentrations. In addition to ambient and rainwater B concentrations, EF_B is affected by meteorological conditions (sample and ambient temperature and Rh), but these results should be taken with caution due to the small B data size.

Fig. 5 represents EF for T and EX as a function of their ambient gas phase mixing ratios. As can be seen, EF values increased in summer, due to ambient air temperature, which is one of the most important factors for the decrease of the surface tension leading to enhanced interfacial adsorption (Bruant and Conklin, 2000, 2002). Another important feature of Fig. 5 is the power functional dependence of EF on ambient gas phase mixing ratios, as adsorption processes are generally more efficient for lower adsorbate concentrations and are characterized by the power functions. These findings are in compliance with the findings of Sato et al. (2006) who showed that rainwater enrichment is especially significant for the species with lower atmospheric concentrations.

4. Conclusions

The transfer of BTEX and other VOC from the atmosphere to various forms of atmospheric water is an important process that affects the global transport of air pollutants, environmental fate and enables the transfer of these species to terrestrial and aquatic systems. The purpose of this study was to investigate the scavenging potential of rainwater and consider the potential mechanisms and factors associated with this phenomenon.

As shown, BTEX concentrations observed in the aqueous phase exceeded the theoretically predicted values. Given that the interfacial adsorption is assumed to be the major mechanism underlying the enhanced rain scavenging of BTEX, the removal process was observed to be more efficient for lower gas mixing ratios, mainly due to equal surface available for smaller number of molecules and the prolonged contact time between the two phases when wind-driven rain drops were falling obliquely. Accordingly, theoretical predictions are probably more accurate in the area of larger gaseous concentrations, whereas in the case of lower concentrations, transfer to the aqueous phase is often underestimated. Furthermore, the results of the presented regression multivariate analysis suggest that multiple factors determine the spatio-temporal BTEX distribution in the environmental multiphase system, including ambient mixing ratios, physico-chemical properties of rainwater and meteorological data. More specifically, the functional description of EF_T and EF_{EX} can be based on certain rainwater properties.

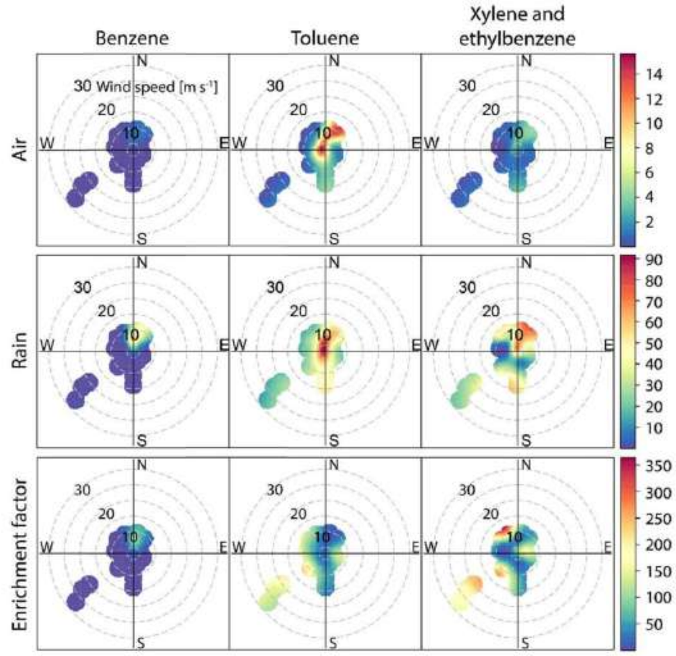


Fig. 4. The relationship between BTEX air mixing ratios (ppb), rain concentrations (nM) and enrichment factor and wind characteristics.

Table 1
MVA method performance comparison for enrichment factor prediction based on the measured parameters and Unmix-derived source contributions: absolute error, relative error and correlation coefficient (r).

Method	EF_T						EF_{EX}					
	Measured parameters			Unmix derived source contributions			Measured parameters			Unmix derived source contributions		
	Abs. error	Rel. error	r	Abs. error	Rel. error	r	Abs. error	Rel. error	r	Abs. error	Rel. error	r
Alternating Model Tree	18.5	34.8	0.88	40.8	76.4	0.67	33.8	42.0	0.78	59.2	111.0	0.53
Conjunctive Rule	26.1	48.9	0.64	32.0	59.9	0.40	39.2	48.7	0.55	43.4	81.2	0.41
Decision Stump	25.5	47.8	0.57	29.3	54.9	0.46	36.4	45.2	0.57	39.4	73.8	0.45
Decision Table	17.8	33.3	0.85	25.3	47.4	0.68	33.9	42.1	0.71	44.8	83.9	0.46
Elastic Net	15.2	28.5	0.88	22.3	41.9	0.77	29.4	36.5	0.74	38.6	72.4	0.62
Gaussian Processes	16.1	30.2	0.88	21.9	41.0	0.79	30.6	38.0	0.72	41.0	76.8	0.60
IBk	11.6	21.7	0.95	20.6	38.5	0.79	22.4	27.8	0.89	31.9	59.8	0.68
IBkLG	11.6	21.7	0.95	20.6	38.5	0.79	22.4	27.8	0.89	31.9	59.8	0.68
Isotonic Regression	13.7	25.7	0.93	31.4	58.9	0.54	34.9	43.3	0.62	39.5	74.0	0.58
K*	11.9	22.3	0.92	19.4	36.3	0.79	22.0	27.4	0.87	31.0	58.1	0.68
Least MedSq	17.4	32.7	0.87	35.6	66.8	0.67	52.7	65.4	0.29	47.4	88.8	0.50
Linear Regression	15.5	29.1	0.89	22.7	42.5	0.78	30.8	38.2	0.74	39.0	73.2	0.61
LWL	15.9	29.7	0.91	26.7	50.0	0.72	35.5	44.1	0.70	39.4	73.9	0.53
M5P	13.9	26.1	0.91	21.6	40.5	0.78	29.7	36.9	0.74	40.4	75.7	0.60
M5Rules	15.0	28.1	0.90	22.9	42.9	0.74	30.8	38.3	0.74	42.2	79.1	0.59
Multilayer Perceptron	17.7	33.1	0.92	24.2	45.4	0.80	37.5	46.5	0.74	49.5	92.7	0.55
Pace Regression	15.9	29.8	0.88	22.7	42.6	0.77	30.1	37.4	0.74	38.6	72.4	0.62
Random Forest	11.6	21.7	0.95	22.5	42.2	0.76	27.8	34.5	0.76	34.9	65.4	0.62
Random Tree	13.8	25.9	0.89	28.6	53.7	0.59	32.8	40.8	0.67	41.7	78.1	0.54
RBF Network	29.9	56.0	0.45	30.4	57.0	0.65	44.8	55.7	0.49	52.8	98.9	0.40
RBF Regressor	14.7	27.6	0.91	23.6	44.2	0.78	28.1	34.9	0.83	40.9	76.6	0.56
REP Tree	13.9	26.1	0.91	22.5	42.1	0.72	36.9	45.8	0.58	42.0	78.8	0.43
Simple Linear Regression	29.9	56.1	0.49	30.3	56.7	0.55	34.3	42.7	0.71	40.5	75.8	0.61
SMOreg	14.7	27.5	0.88	21.5	40.3	0.79	28.8	35.8	0.75	39.0	73.2	0.61

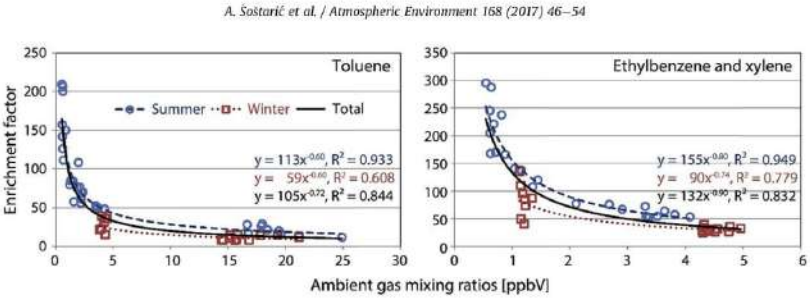


Fig. 5. The relationship between T and EX enrichment factors and their gaseous concentrations.

On the other hand, it has been shown that EF_B is affected by meteorological conditions (sample and ambient temperature, and Rh), as well as B ambient and rainwater concentrations (however, these results should be interpreted with caution due to the small B data size).

Acknowledgments

This paper was realized as part of projects No III43007 and No III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011–17, and was supported by the Institute of Public Health of Belgrade, Serbia.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.08.045.

References

Allou, L., El Maimouni, L., Le Calve, S., 2011. Henry's law constant measurements for formaldehyde and benzaldehyde as a function of temperature and water composition. Atmos. Environ. 45, 2991–2998.

Balla, D., Papageorgiou, A., Voutsa, D., 2014. Carbonyl compounds and dissolved organic carbon in rainwater of an urban atmosphere. Environ. Sci. Pollut. Res. 21, 12062–12073.

Bruant Jr., R.G., Conklin, M.H., 2000. Dynamic determination of vapor/water interface adsorption for volatile hydrophobic organic compounds (VHOCs) using axisymmetric drop shape analysis: procedure and analysis of benzene adsorption. J. Phys. Chem. B 104, 11146–11152.

Bruant Jr., R.G., Conklin, M.H., 2002. Adsorption of benzene and methyl-substituted benzenes at the vapor/water interface. 3. finite binary-component VHOC adsorption. J. Phys. Chem. B 106, 2232–2239.

Cao, J.J., Chow, J.C., Watson, J.G., Wu, F., Han, Y.M., Jin, Z.D., An, Z.S., 2008. Size-differentiated source profiles for fugitive dust in the Chinese Loess Plateau. Atmos. Environ. 42, 2261–2275.

Carslaw, D.C., Beevers, S.D., 2013. Characterising and understanding emission sources using bivariate polar plots and k-means clustering. Environ. Model. Softw. 40, 325–329.

Carslaw, D.C., Ropkins, K., 2012. Openair - an R package for air quality data analysis. Environ. Model. Softw. 27, 52–61.

Chatani, S., Matsunaga, S.N., Nakatsuka, S., 2015. Estimate of biogenic VOC emissions in Japan and their effects on photochemical formation of ambient ozone and secondary organic aerosol. Atmos. Environ. 120, 38–50.

Deng, H., Runger, G., 2013. Gene selection with guided regularized random forest. Pattern Recognit. 46, 3483–3489.

Draxler, R.R., Rolph, G.D., 2014. HYSPLIT (HYbrid Single-particle Lagrangian Integrated).

Durmusoglu, E., Taspinar, F., Karademir, A., 2010. Health risk assessment of BTEX emissions in the landfill environment. J. Hazard. Mater 176, 870–877.

Fries, E., Starokozhev, E., Haunold, W., Jaeschke, W., Mitra, S.K., Borrmann, S., Schmidt, M.U., 2007. Laboratory studies on the uptake of aromatic hydrocarbons by ice crystals during vapor depositional crystal growth. Atmos. Environ. 41, 6156–6166.

Fries, E., Sieg, K., Püttmann, W., Jaeschke, W., Winterhalter, R., Williams, J., Moortgat, G.K., 2008. Benzene, alkylated benzenes, chlorinated hydrocarbons and monoterpenes in snow/ice at Jungfraujoch (46.6 N, 8.0 E) during CLACE 4 and 5. Sci. Total Environ. 391, 269–277.

Global Data Assimilation System, 2015. https://www.ready.noaa.gov/gdas1.php. (Accessed 27 December 2015).

Goss, K.U., 1994. Predicting the enrichment of organic compounds in fog caused by adsorption on the water surface. Atmos. Environ. 28, 3513–3517.

Hall, M., Frank, E., Holmes, G., Pfahringer, B., Reutemann, P., Witten, I.H., 2009. The WEKA data mining software: an update. SIGKDD Explor 11, 10–18.

Lee, S.C., Chiu, M.Y., Ho, K.F., Zou, S.C., Wang, X., 2002. Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong. Chemosphere 48, 375–382.

Lin, C.C., Lin, C., Hsieh, L.T., Chen, C.Y., Wang, J.P., 2011. Vertical and diurnal characterization of volatile organic compounds in ambient air in urban areas. J. Air Waste. Manag. Assoc. 61, 714–720.

Lindinger, W., Hansel, A., Jordan, A., 1998. On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). Medical applications, food control and environmental research. Int. J. Mass Spectrom. Ion. Process 173, 191–241.

Matsumoto, K., Matsumoto, K., Mizuno, R., Igawa, M., 2010. Volatile organic compounds in ambient aerosols. Atmos. Res. 97, 124–128.

McNeill, V.F., Grannas, A.M., Abbatt, J.P., Ammann, M., Ariya, P., Bartels-Rausch, T., Domine, F., Donaldson, D.J., Guzman, M.I., Heger, D., Kahan, T.F., 2012. Organics in environmental ices: sources, chemistry, and impacts. Atmos. Chem. Phys. 12, 9653–9678.

Moreda-Piñeiro, J., Rodríguez, E.L., Pérez, C.M., Heras, G.B., Carou, I.T., Mahía, P.L., Lorenzo, S.M., Rodríguez, D.P., 2014. Influence of marine, terrestrial and anthropogenic sources on ionic and metallic composition of rainwater at a suburban site (Northwest Coast of Spain). Atmos. Environ. 88, 30–38.

Mullaugh, K.M., Hamilton, J.M., Avery, G.B., Felix, J.D., Mead, R.N., Willey, J.D., Kieber, R.J., 2015. Temporal and spatial variability of trace volatile organic compounds in rainwater. Chemosphere 134, 203–209.

O'Sullivan, D.W., Lee, M., Noone, B.C., Heikes, B.G., 1996. Henry's law constant determinations for hydrogen peroxide, methyl hydroperoxide, hydroxymethyl hydroperoxide, ethyl hydroperoxide, and peroxyacetic acid. J. Phys. Chem. 100, 3241–3247.

Okochi, H., Sugimoto, D., Igawa, M., 2004. The enhanced dissolution of some chlorinated hydrocarbons and monocyclic aromatic hydrocarbons in rainwater collected in Yokohama. Jpn. Atmos. Environ. 38, 4403–4414.

Okochi, H., Kataniwa, M., Sugimoto, D., Igawa, M., 2005. Enhanced dissolution of volatile organic compounds into urban dew water collected in Yokohama. Jpn. Atmos. Environ. 39, 6027–6036.

Perišić, M., Maletić, D., Stojić, S.S., Rajšić, S., Stojić, A., 2017. Forecasting hourly particulate matter concentrations based on the advanced multivariate methods. Int. J. Environ. Sci. Technol. 14, 1047–1054.

Raja, S., Valsaraj, K.T., 2004. Adsorption and transport of gas-phase naphthalene on micron-size fog droplets in air. Environ. Sci. Technol. 38, 763–768.

Raja, S., Yaccone, F.S., Ravikrishna, R., Valsaraj, K.T., 2002. Thermodynamic parameters for the adsorption of aromatic hydrocarbon vapors at the gas–water interface. J. Chem. Eng. Data 47, 1213–1219.

Rao, P.S.P., Tiwari, S., Matwale, J.L., Pervez, S., Tunved, P., Safai, P.D., Srivastava, A.K., Bisht, D.S., Singh, S., Hopke, P.K., 2016. Sources of chemical species in rainwater during monsoon and nonmonsoonal periods over two megacities in India and dominant source region of secondary aerosols. Atmos. Environ. 146, 90–99.

Sander, R., 2015. Compilation of Henry's law constants (version 4.0) for water as solvent. Atmos. Chem. Phys. 15, 4399–4981.

Sapek, B., 2014. Calcium and magnesium in atmospheric precipitation, groundwater and the soil solution in long-term meadow experiments. J. Eleme 19, 191–208.

Sato, E., Matsumoto, K., Okochi, H., Igawa, M., 2006. Scavenging effect of precipitation on volatile organic compounds in ambient atmosphere. Bull. Chem. Soc. Jpn. 79, 1231–1233.

Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric Chemistry and Physics: from Air Pollution to Climate Change, second ed. J. Wiley & Sons, New York.

Šoštarić, A., Stojić, A., Stanišić, S.S., Gržetič, I., 2016. Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system. Chemosphere 144, 721–727.

Starokozhev, E., Fries, E., Cycura, A., Püttmann, W., 2009. Distribution of VOCs

between air and snow at the Jungfraujoch high alpine research station, Switzerland, during CLACE 5 (winter 2006). Atmos. Chem. Phys. 9, 3197–3207.
Stojić, A., Stanišić Stojić, S., 2017. The innovative concept of three-dimensional hybrid receptor modeling. Atmos. Environ. 164, 216–223.
Stojić, A., Stanišić, S.S., Šoštarić, A., Ilić, L., Mijić, Z., Rajšić, S., 2015a. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ. Sci. Pollut. Res. 22, 13137–13152.
Stojić, A., Stojić, S.S., Mijić, Z., Ilić, L., Tomašević, M., Todorović, M., Perišić, M., 2015b. Comprehensive analysis of VOC emission sources in Belgrade urban area. Urban Built Environ. 55–88.
Stojić, A., Stojić, S.S., Mijić, Z., Šoštarić, A., Rajšić, S., 2015c. Spatio-temporal distribution of VOC emissions in urban area based on receptor modelling. Atmos. Environ. 106, 71–79.
Stojić, A., Maletić, D., Stojić, S.S., Mijić, Z., Šoštarić, A., 2015d. Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. Sci. Total. Environ. 521, 19–26.
Stojić, A., Stanišić, S.S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M., Mijić, Z., 2016. Comprehensive analysis of PM10 in Belgrade urban area on the basis of long term measurements. Environ. Sci. Pollut. Res. 23, 10722–10732.
Słomińska, M., Konieczka, P., Namieśnik, J., 2014. The fate of BTEX compounds in ambient air. Crit. Rev. Env. Sci. Tec. 44, 455–472.
Team, 2012. R: a language and environment for statistical computing. http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf (Accessed 4 December 2015).
Tiwari, S., Hopke, P.K., Thimmiah, D., Dumka, U.C., Srivastava, A.K., Bisht, D.S., Rao, P.S.P., Chate, D.M., Srivastava, M.K., Tripathi, S.N., 2016. Nature and sources of ionic species in precipitation across the Indo-Gangetic Plains, India. Aerosol Air Qual. Res. 16, 943–957.
USEPA, 2007. EPA Unmix 6.0 Fundamentals and User Guide. USEPA Office of Research and Development.
Valsaraj, K.T., Thoma, G.J., Reible, D.D., Thibodeaux, L.J., 1993. On the enrichment of hydrophobic organic compounds in fog droplets. Atmos. Environ. 27, 203–210.
Vane, L.M., Giroux, E.L., 2000. Henry's law constants and micellar partitioning of volatile organic compounds in surfactant solutions. J. Chem. Eng. Data 45, 38–47.
Wang, Y.Q., 2014. MeteoInfo: GIS software for meteorological data visualization and analysis. Meteorol. Appl. 21, 360–368.
Warneke, C., De Gouw, J.A., Kuster, W.C., Goldan, P.D., Fall, R., 2003. Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method. Environ. Sci. Technol. 37, 2494–2501.
WHO, 1986. Toluene Environmental Health Criteria, vol. 52. WHO (International Programme on Chemical Safety).
WHO, 1993. Benzene Environmental Health Criteria, vol. 150. WHO (International Programme on Chemical Safety).
WHO, 1997. Ethylbenzene Environmental Health Criteria, vol. 186. WHO (International Programme on Chemical Safety).

Environ Sci Pollut Res
DOI 10.1007/s11356-016-6266-4

RESEARCH ARTICLE

Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements

A. Stojić[1] · S. Stanišić Stojić[2] · I. Reljin[3] · M. Čabarkapa[3,4] · A. Šoštarić[5] · M. Perišić[1] · Z. Mijić[1]

Received: 23 September 2015 / Accepted: 8 February 2016

Abstract In this study, we investigated the impact of potential emission sources and transport pathways on annual and seasonal PM_{10} loadings in an urban area of Belgrade (Serbia). The analyzed dataset comprised PM_{10} mass concentrations for the period 2003–2015, as well as their chemical composition (organic/elemental carbon, benzo[a]pyrene, As, Cd, Cr, Mn, Ni, Pb, Cl^-, Na^+, Mg^{2+}, Ca^{2+}, K^+, NO_3^-, SO_4^{2-}, and NH_4^+), meteorological parameters, and concentrations of inorganic gaseous pollutants and soot for the period 2011–2015. The combination of different methods, such as source apportionment (Unmix), ensemble learning method (random forest), and multifractal and inverse multifractal analysis, was utilized in order to obtain a detailed description of the PM_{10} origin and spatio-temporal distribution and to determine their relationship with other pollutants and meteorological parameters. The contribution of long-range and regional transport was estimated by means of trajectory sector analysis, whereas the hybrid receptor models were applied to identify potential areas of concern.

Keywords PM_{10} · Source apportionment · Multifractal · Inverse multifractal · TSA · Transport

Responsible editor: Gerhard Lammel

Electronic supplementary material The online version of this article (doi:10.1007/s11356-016-6266-4) contains supplementary material, which is available to authorized users.

✉ A. Stojić
andreja.stojic@ipb.ac.rs

[1] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

[2] Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia

[3] Faculty of Electrical Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11120 Belgrade, Serbia

[4] Singidunum University, Danijelova 32, 11010 Belgrade, Serbia

[5] Institute of Public Health Belgrade, Bulevar Despota Stefana 54, 11000 Belgrade, Serbia

Introduction

In recent years, the issue of particulate matter (PM) pollution has drawn considerable attention, mostly because of its adverse effects on human health and the environment (Cheng et al., 2013). Numerous epidemiological and toxicological studies have shown that there is a causal relationship between PM_{10} (with an aerodynamic diameter of less than 10 μm) exposure and both circulatory and respiratory system-related mortality (Pinheiro et al., 2014; Perez et al., 2015). Even though the World Health Organization updated air quality guidelines for daily mean PM_{10} levels of 50 μg m^{-3} (WHO, 2005), the reports concede that there is little evidence of the threshold at which no adverse health effects would be expected (Buekers et al., 2011). Apart from their detrimental impact on human health, PM_{10} affect climate by scattering and absorbing solar radiation and by serving as nuclei for cloud formation (Wang et al., 2015).

Unlike the previous PM_{10} studies in the Western Balkans that were limited in scope and time, the herein presented findings are based on long-term data. This study utilizes a combination of analytical methods that have enabled a more comprehensive understanding and interpreting of the results and provided a more accurate description of the PM_{10} spatio-temporal distribution and their relationship with other pollutants and meteorological conditions. Besides generally accepted analytical methods, this paper also presents an improved

Published online: 18 February 2016

approach to long-range and regional transport and elaborates on the possibility of implementing multifractal and inverse multifractal analysis, which further enhanced the overall quality of conclusions drawn herein.

Study area

The measurements were conducted at the Institute of Public Health Belgrade (44° 49′ N, 20° 28′ E), located along a broad boulevard in a densely populated central urban zone with heavy and slow traffic (Stojić et al., 2015a). Multi-storey buildings on both sides of the street limit air dispersion to a certain extent and thus increase the likelihood of air pollutant accumulation under stagnant synoptic conditions (Jorba et al., 2013). In the vicinity of the measurement site, in the NE area, extends a 150-year-old park (Botanical Garden) representing a diverse plant collection within the 5-acre area. The Port of Belgrade is situated along the Danube River, approximately 800 m in the same direction, with intense freight and passenger shipping and vivid commercial activities. The pulp and paper industry is located 3 km further, with the annual production of 75,000 t of packaging paper. The N and NE suburban area of Belgrade located about 7–13 km from the measurement site is home of several industrial facilities, including the petrochemical and chemical industry, oil refinery, nitric plant, and glass industry.

The climate in Serbia is moderate continental, with an average annual temperature of 11.7 °C and relative humidity of 69.5 %. The prevailing wind in the city is Koshava blowing from the SE/ESE direction, usually for 2–3 days continuously, thus increasing the horizontal dispersion and dilution of pollutants at ground-level (Rajšić et al., 2004).

Materials and methods

The analyzed dataset comprised daily (2003–2015) and hourly (2011–2015) PM_{10} mass concentrations obtained by means of referent Sven Leckel and beta-ray attenuation (Thermo FH 62-IR) samplers, respectively. The chemical characterization of PM_{10} samples collected during the period 2011–2015 included daily concentrations of benzo[a]pyrene (BaP), trace metals (As, Cd, Cr, Mn, Ni, and Pb), ions (Cl^-, Na^+, Mg^{2+}, Ca^{2+}, K^+, NO_3^-, SO_4^{2-}, and NH_4^+), and elemental/organic carbon determined by the use of referent methods: gas chromatography mass spectrometry (GC-MS, Agilent GC 6890 MSD 5975), inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500), ion chromatography (Metrohm 761 Compact IC), and Automatic Semi-continuous Field-Deployable Thermal/Optical OCEC Carbon Aerosol Analyzer (Sunset Laboratory Inc.), respectively. Thermal-optical analysis was employed for determination of OC/EC, as described in Karanasiou et al. (2011), according to the thermal protocol EUSAAR 2 (Cavalli et al., 2010). Additionally, daily soot concentrations (refers to a carbon-rich material formed by incomplete combustion of fossil fuels and biomass) were obtained by the use of Pro Ekos device based on ISO 9835:1993 standard. Hourly concentrations of inorganic gaseous pollutants (NO_x, NO_2, NO, SO_2, and CO) were obtained by the use of referent sampling devices (Horiba APNA 360, APSA 360, and APMA 360). Meteorological parameters (wind speed and direction, pressure, humidity, and temperature) were determined by Lufft WS500-UMB Smart Weather Sensor. The accuracy and precision of detection methods are provided in Online Resource, Tables 1 and 2.

Daily, weekly, seasonal, and annual dynamics, trend (Pretty, 2015), and periodicity were analyzed using the Openair (Carslaw and Ropkins, 2012) and Lomb (Ruf, 1999) packages within the statistical software environment R (Team, 2012). The relationships between pollutant concentrations and wind characteristics were examined using the bivariate polar plot, bivariate cluster, and conditional bivariate probability function (CBPF) analyses within the Openair package. Bivariate polar plot was used to analyze the joint wind speed/wind direction dependence of air pollutant concentrations in order to obtain directional information on potential sources (Carslaw and Beevers, 2013). To identify and group features of similar characteristics in bivariate polar plots which correspond to different source types, bivariate cluster analysis (k-means clustering) was applied. CBPF, as an extension of the commonly used conditional probability function (Ashbaugh et al., 1985) to the bivariate case, was used to estimate the probability that the measured concentration occurs in cells defined by ranges of wind direction and wind speed (Uria-Tellaetxe and Carslaw, 2014). The bivariate case provides more information on the type of sources by presenting important dispersion characteristic information. By considering the intervals of concentrations herein presented as percentile ranges, significantly more source information can be revealed, because different source types have different wind speed dependencies. The principal uncertainty of bivariate plot analysis is estimated to be small due to great number of data points per wind direction/wind speed cell.

The temporal variations of pollutant concentrations were also analyzed by the use of the multifractal approach that enlightens the local fluctuations of the scaling properties of a measure, herein defined as pollutant concentration (Vehel, 1998; Reljin et al., 2000). The calculated multifractal spectra (INRIA, software Fraclab) confirmed the non-linear behavior of pollutant time-series. Legendre spectrum estimator was chosen as the most efficient, providing errors below 0.1 % (−60 dB mean squared error (MSE)) compared with theoretically calculated spectrum in the case of infinitely long time series. The inverse multifractal analysis (Reljin et al., 2000) was used to examine the distribution characteristics within

PM_{10} dataset. The scaling exponent $f(\alpha)$ was calculated based on the Hölder exponent α, and the shape and the extension of the $f(\alpha)$-curve was considered to determine where the existing fluctuations in distribution occur. The Hölder exponent α describes the local variability of time series data at some point in time, while the multifractal spectrum $f(\alpha)$ represents the probability distribution of the local Hölder exponent. Beam width, as an important parameter determining histogram-based inverse multifractal spectrum, was adjusted to one order of magnitude less than time series length, providing negligible error below −60 dB MSE.

Several runs of Unmix (USEPA, 2007) were performed to obtain the appropriate number of source profiles. The maximum number of species selected as input variables was chosen using the trial and error with the general goal of yielding the most physically meaningful results. A value equal to the half of the method detection limit (DL) for each variable was used for concentrations below the DL.

The relative importance of each measured variable and meteorological parameter was determined using the random forest (RF) method (Liaw and Wiener, 2002) within the statistical software environment R. The analysis enabled a better insight into PM_{10} sources, as well as amendment of receptor model results, particularly in the cases of variables that were excluded from the analysis due to bad fitting. The appropriate number of trees was determined to assure out-of-bag error convergence, an unbiased internal error estimate of the prediction error. Since the variable interactions stabilize at a slower rate than error, in this way, the sufficient number of trees was selected to stabilize the error and avoid overfitting.

The analysis of regional and long-range PM_{10} transport was performed for the period 2005–2015 using several models and 72-h air mass back trajectories. The contribution of local, background, and transported pollution to the observed concentrations was determined using trajectory sector analysis (TSA) on the basis of average monthly contribution of local background data calculated according to Stojić et al. (2015a). A more precise description of pollution plume requires including the greater number of trajectories calculated for the larger number of heights above the receptor site, but still below planetary boundary layer (PBL) height, because vertical profiles of pollutant concentrations are relatively constant for a significant part of the PBL (Stull, 1988). Contrary to our previous studies that relied on the representative trajectories obtained for the set of predefined heights and their clusterization for providing a description of pollution plume, the current study presents the description of pollution plume based on dynamical calculation of trajectories within the PBL. Namely, the transport analysis performed as proposed herein is enhanced in two respects. Firstly, the inclusion of hourly fluctuations of the PBL height at the receptor site is enabled, which was not possible when using predefined heights. Secondly, the inclusion of trajectories calculated from wind field eliminates the error that would emerge from clusterization of representative trajectories. The trajectories were dynamically calculated for 30, 50, and 70 % of PBL height at the receptor site every hour UTC each day by the use of HYSPLIT model (Draxler and Rolph, 2014) and the Opentraj package (Opentraj, 2015). Quite curved trajectories that reached the ground level (GL) were excluded from the analysis since they do not represent transport from a sector in an adequate way (around 18 %). The exclusion was applied in the following cases: (1) if the central trajectory (at 50 % of PBL height above the receptor site) reached GL at any moment, all three trajectories were excluded from the analysis because the condition that vertical profiles of pollutant concentrations remain relatively constant for a considerable part of PBL was probably not met; (2) if only the lowest of the three trajectories reached GL, its height would be gradually increased by 1 m at the receptor site till the level at which it could be avoided. Thereby, for the purpose of transport analysis, three trajectories were always assigned to the corresponding concentrations.

The PBL height and all meteorological field parameters included in GDAS1 (Global Data Assimilation System, 2015) were calculated using MeteoInfo software (Wang, 2014). Furthermore, trajectory cluster analysis (TCA), potential source contribution function (PSCF) and concentration weighted trajectory (CWT) hybrid receptor models (Hsu et al., 2003) were applied according to Stojić et al. (2015b) to identify potential sources of non-local origin.

Results and discussion

Time series analysis

After the exclusion of unreliable data resulting from equipment malfunction, a total of 94.4 % of daily and 78.2 % of hourly PM_{10} values were analyzed (Online Resource, Table 3). According to the results, the mean annual PM_{10} concentrations ranging from 29.98 to 60.51 $\mu g\ m^{-3}$ exceeded the EU AQS limit of 40 $\mu g\ m^{-3}$ (Directive 2008/50/EC) during the period from 2003–2007 and 2011–2015. Thereby, the number of daily limit exceedances was in the range from 37 to 151 per year. The highest concentrations registered during winter and autumn months, with average values of 63.98 and 52.05 $\mu g\ m^{-3}$, respectively, were associated with the emissions from thermal plants and local fireboxes, as well as with low PBL height, low wind speed (2 $m\ s^{-1}$), and other atmospheric conditions in the cold season. All this further resulted in reduction of vertical pollutant transport and dispersion. Accordingly, the most polluted months were January (68.36 $\mu g\ m^{-3}$) and November (66.32 $\mu g\ m^{-3}$), while the lowest mean values were observed in May (31.17 $\mu g\ m^{-3}$) and June (34.16 $\mu g\ m^{-3}$). Lower PM_{10} concentrations during spring and summer months

(37.52 μg m^{-3} and 35.92 μg m^{-3}, respectively) were mostly associated with an increase of the PBL height and strong N/NW winds which assist the aeration of the city causing pollutant dispersion at ground level. Higher precipitations during the warmer part of the year could also reduce PM_{10} concentrations by wet deposition and wetting of the road surface, which affects particle resuspension (Barmpadimos et al., 2011). Furthermore, the reduced traffic emissions in vacation season could also partly contribute to the observed concentrations.

Despite the growing number of in-use vehicles over the last two decades, a decreasing trend in the mean annual concentrations of 3.7 μg m^{-3} year^{-1} (6.4 % year^{-1}) during the period 2003–2010 (60.51 to 29.98 μg m^{-3}, respectively) could be associated with extensive works on thermal systems. These include elimination of over 1000 boiler rooms that consumed heavy oil, diesel fuel, or sulfur-containing coal and instead of which the district heating facilities were built (Fig. 1). Furthermore, a new technology of ash and slag transport was introduced and reconstruction of electrostatic precipitators was conducted at Nikola Tesla power plant complex. This facility is located about 40 km away from Belgrade and produces more than 50 % of electricity for the Serbian market (Perišić et al., 2014). It should also be noted that the monthly mean values in 2008 and 2010 were lower than 30 μg m^{-3} for 7 months in a row, which could be partly attributed to reconstruction of major roads and highway, diversion of freight traffic to the ring-road around Belgrade, and reduced traffic intensity in the city center. Following the significant rise from 29.98 μg m^{-3} (2010) to 59.25 μg m^{-3} (2011), the mean annual concentrations continued to gradually increase by 3.1 μg m^{-3} year^{-1} (6.3 % year^{-1}) till 2015. The multifractal characteristics of PM_{10} time series for two periods, before and after January 1, 2011, were analyzed and shown in Fig. 2. The broader parabola represents the latter period with emission events resulting in higher variability of concentrations. We assume that the observed increase in concentrations over the last 5 years could be attributed to the emergence of new strong emission sources and re-activation of the previously existing ones, i.e., increase in urban traffic flow, outdated technologies, and insufficient investment in heating facilities and industry sector.

Throughout the entire period, the annual PM_{10} weekend-weekday difference amounted up to 22 % (5.2 % average), thus indicating considerable variations in anthropogenic activities and their contribution to the observed concentrations. As

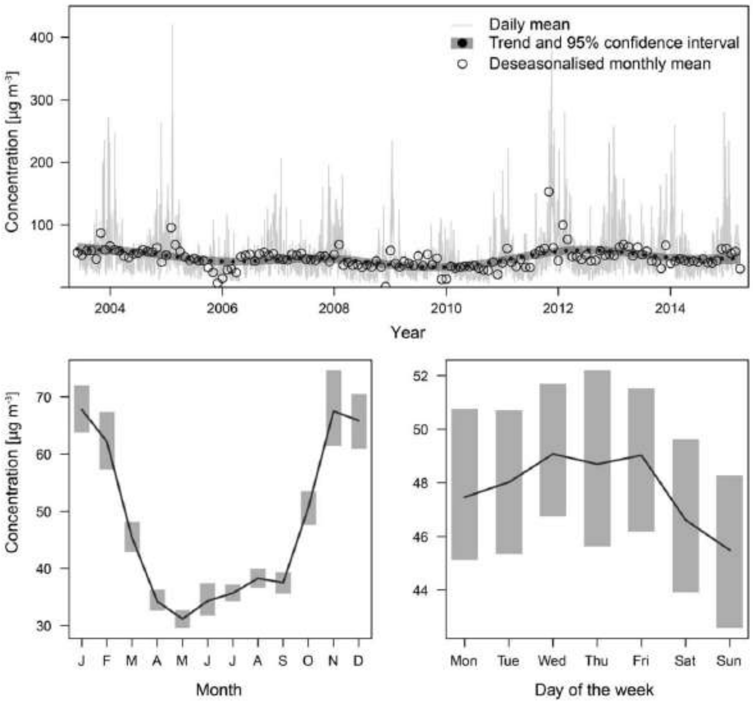


Fig. 1 PM_{10} mass concentrations time series and trend (*above*), monthly and weekly variations (*below*)

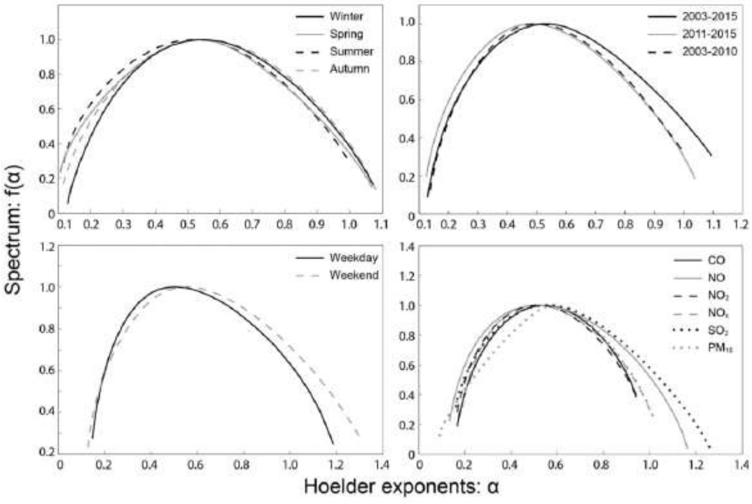


Fig. 2 Multifractal spectra of PM_{10} seasonal (*left, above*), weekday/weekend (*left, below*) variations 2003–2015, PM_{10} concentrations observed in different periods (*right, above*), and all measured pollutant concentrations 2011–2015 (*right, below*)

can be seen in the multifractal diagram (Fig. 2), the observed difference in the position and shape of parabolas suggests that lower concentrations during the weekend were spread along a broad range of values, probably due to the absence of strong emission sources. Conversely, weekdays were mainly characterized by higher concentrations contributing significantly to the total observed concentrations. The noticeable weekly periodicity of gaseous oxides (CO, NO_x, and NO) over the last 5 years points to the role of combustion processes in air quality deterioration (Online Resource, Fig. 1). The weekday-weekend effect was less pronounced during the winter period as significant portion of anthropogenic contribution in cold season is associated with fuel combustion for heating purposes.

The relationship between meteorological conditions and PM_{10} levels was examined by Rost et al. (2009), who drew the conclusion that the absence of precipitation, along with low values of mixing-layer height, exerts the biggest impact, resulting in high near-surface concentrations, especially in winter. According to the results of the random forest model (Online Resource, Tables 4 and 5), PBL height was the most important meteorological variable for predicting pollutant concentrations, followed by lifted index, as a measure of atmospheric stability (Lee et al., 2014). Diurnal autumn pattern exhibited a steady daytime maximum as a result of the pollutant accumulation in the shallow daily boundary layer (322 m), with smaller morning peak (7:00 a.m.–8:00 a.m.) and flattened increase in the evening hours (4:00 p.m.–7:00 p.m.) reflecting the rush hour congestion (Online Resource, Fig. 2). The expansion of the boundary layer to 548 m, together with the lower rate of secondary particles formation due to relatively high and persistent cloud cover (64 %) and low insolation, led to somewhat lower PM_{10} daytime loadings in winter. Winter diurnal pattern revealed that high concentrations remained constant till late evening hours, which can probably be attributed to the extended heating period during the coldest months. The observed pollutant levels displayed similar diurnal patterns in the spring and summer: the pronounced midday minimum reflecting the seasonal evolution of boundary layer (1186 and 1256 m, respectively) was followed by a rapid increase in late afternoon hours to the level which remained fairly constant over the night. The observed summer noontime peak (12:00 a.m.–3:00 p.m.) can be associated with photochemical formation of secondary aerosol particles. Multifractal approach was applied for the purpose of analyzing seasonal dynamics (Fig. 2). The coincidence in the maxima of autumn and winter spectra indicates that similar sources and processes were lying behind the concentrations registered in both periods. Likewise, the clusterization of spring and summer spectra led to similar conclusions, i.e., there were no significant differences in the origin of the observed PM_{10} loadings during the warmer period of the year.

There is good agreement between the results of bivariate cluster and trajectory sector analysis, indicating that approximately 51.7 % (cluster C5, Fig. 3), and 54.7 % of the PM_{10} loadings, respectively, were associated with the local emission sources from the surrounding area. The measured concentrations are extremely seasonally dependent (Online Resource, Fig. 3), and pollution indicates clear weekday/weekend variations regardless of the source direction. This supports the statement that PM_{10} sources in the vicinity of the measurement site are predominantly of anthropogenic origin (Online Resource, Fig. 4). The CBPF plot in the percentile ranges from

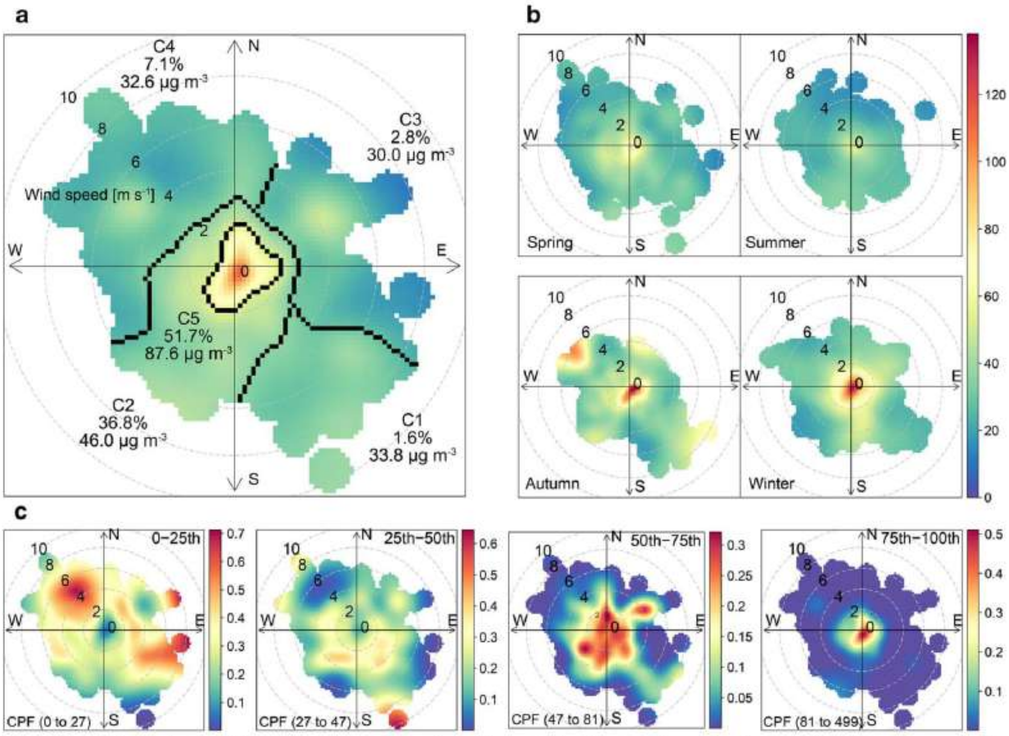


Fig. 3 The relationship between PM_{10} mass concentrations and wind characteristics: bivariate cluster plot (frequency (%) and average contribution (μg m^{-3})) **(a)**, seasonal variations (μg m^{-3}) **(b)**, and CBPF plot in four range of percentiles **(c)**

25 to 50 revealed relative contribution of polluted plumes from N/NE area, which can be assigned to the Port of Belgrade and the suburban area with a number of industrial facilities, as well as the impact of S city area with frequent daily traffic congestions (Fig. 3). The sources of moderate strength distributed around the measurement site can be associated with vehicle exhaust and thermal plant emissions, whereas the plot above the 75th percentiles revealed the dominance of local traffic-related emissions, probably particle resuspension and solid fuel burning in residential fireboxes.

According to the inverse multifractal analysis (Online Resource, Fig. 5), the significant portion (75.7 %) of hourly PM_{10} concentrations corresponds to $f(\alpha)$ values ranging from 0.34 to 0.44 (Fig. 4), which are related to the maximum of the derived spectrum. The related events are associated with emission sources situated in the vicinity of the measurement site, which highlights the dominance of local sources in Belgrade urban area. The lowest and highest α values (0.78–0.98 and 1.25–1.65) correspond to singularities, i.e., high pollutant concentrations that are in sharp contrast to those observed immediately before and after. As could be expected, the singularities corresponding to high concentrations mostly occurred with low wind speed during winter (48.0 %) and autumn (26.1 %). Alternatively, the singularities associated with extremely low concentrations (2.6 %) are registered during the warmer period of the year (71.3 %) and related to stronger winds which assist the aeration of the city and cause pollutant dispersion. Low PM_{10} loadings in winter months were mostly associated with S/SW and E/SE winds with speed over 2 m s^{-1}.

Chemical composition and source apportionment

Compared to the results of several studies aimed at chemical characterization of PM_{10} particles in European cities (Hueglin et al., 2005; Heal et al., 2005; Querol et al., 2008) and Air quality in Europe—2014 report (European Environmental Agency, 2014), the average concentrations of Mn, Ni, Cd, and Pb were lower, whereas the concentrations of As and Cr were higher, probably due to low-grade coal combustion (Bencko 1997) and, in the case of Cr, due to solvent usage in the surrounding industrial facilities and local laboratories at the Institute of Public

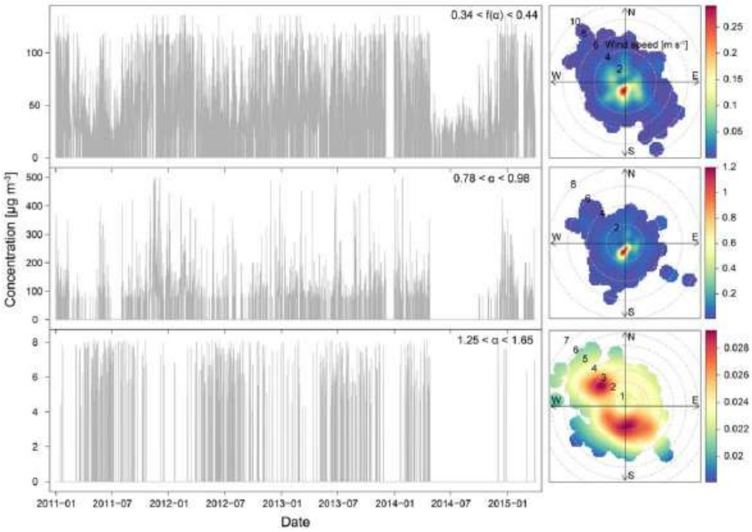


Fig. 4 Singularities derived by inverse multifractal analysis (*left*) and singularity concentration and frequency of occurrence product (*right*) for the most frequent (*above*), highest (*middle*), and lowest (*below*) concentrations ($\mu g\ m^{-3}$)

Health (Online Resource, Table 6 and Fig. 6). Nevertheless, BaP, as an indicator of carcinogenic polycyclic aromatic hydrocarbons, remains one of the main concerns, with concentrations (1.69–4.62 ng m^{-3}) significantly exceeding the WHO-estimated reference level of 0.12 ng m^{-3}, as well as the target value of 1 ng m^{-3} set forth in the Directive 2004/107/EC. Generally, the levels of BaP have increased in Europe since 2003, driven by wood and coal burning for domestic heating. Our results also indicate that the concentrations of BaP and As increased 17 and 5 times on average, respectively, during the heating season (October 1–April 1). Furthermore, the concentrations of NH_4^+ and SO_4^{2-} ions were significantly higher than those reported by Lenschow et al. (2001) and Pandolfi et al. (2011), thus indicating high secondary aerosols contribution to PM_{10} loadings in the canyon avenue with restricted pollutant dispersion. Higher levels were also observed for Cl^-, probably due to the use of cleaning and disinfecting agents at the Institute of Public Health, as well as due to the emissions from the paper and pulp industry.

A total of 254 daily mean concentrations of OC, EC, inorganic gaseous oxides, soot, benzo[a]pyrene (BaP), As, Cd, Cl^-, Pb, NH_4^+, SO_4^{2-}, and NO_3^- were used for source apportionment. After evaluating the results obtained, the most feasible model solution was chosen. The resolved source profiles are presented in Table 1, together with their estimated contributions to the overall PM_{10}, while the absolute profiles and the stability of the solution are provided in Online Resource, Table 7.

The profile assigned to solid fuel burning (SFB) with related contribution of 29.8 % is distinguished by dominant shares of BaP (97.5 %) and As (67.2 %) and significant portions of OC, SO_2, CO, NO_3^-, and soot. In urban environments, solid fuel burning is considered the major

Table 1 Unmix-resolved source profiles (%)

Species	Solid fuel burning	Industrial emissions	Secondary aerosols	Vehicle derived and particle resuspension
OC	49.7	15.8	9.2	25.2
EC	18.6	12.6	9.7	59.1
NO_x	18.5	23.1	0	58.3
NO_2	15.6	14.5	12.8	57.1
NO	24.9	26.9	0	48.2
SO_2	32.0	17.4	10.3	40.4
CO	36.7	10.1	11.8	41.3
Soot	28.4	16.4	20.1	35.1
As	67.2	15.3	6.1	11.4
Cd	7.0	86.0	6.9	0
Cl^-	19.8	3.2	30.9	46.2
Pb	11.8	66.4	16.7	5.1
NH_4^+	8.9	17.5	73.5	0
NO_3^-	27.2	8.2	49.6	15.0
SO_4^{2-}	12.9	17.6	52.1	17.4
BaP	97.5	0	2.5	0
Average contribution	29.8	21.9	19.5	28.7

source of BaP (European Environmental 2013; Khalil and Rasmussen, 2003). Similarly, the sources of As are mainly associated with burning of coal and wood treated with arsenic-containing preservatives (Department for Environment, Food and Rural Affairs DEFRA and Environmental Agency 2002). Not surprisingly, SFB profile contribution displayed a distinct seasonal pattern (Fig. 5), as well as negative correlation with temperature (−0.59), and significant correlation with SO_4^{2-} and OC concentrations (0.66 and 0.86). Even though SO_4 ions are mostly associated with photochemical formation of secondary aerosols in summer, high level of SO_4 ions in cold season could be attributed to high concentration of their precursor, SO_2.

The profile assigned to industrial emissions (IE), accounting for 21.9 % of the observed concentrations, comprised significant shares of Cd (86.0 %) and Pb (66.4 %). In addition to fossil fuel burning, the major sources of Cd are non-ferrous metal production and solid waste incineration, whereas the sources of Pb include lead smelters, as well as iron and steel industry (Pacyna, 1984). The weekday-weekend difference was observed as a result of working activities, whereas the seasonal pattern of IE profile corresponded to annual PBL variations, with higher contributions in winter season.

The high shares of NH_4^+ (73.5 %), SO_4^{2-} (52.1 %), and NO_3^- (49.6 %) ions were apportioned to the profile attributed to secondary aerosols (SA), with estimated contribution of 19.5 %. The formation of NH_4NO_3 and $(NH_4)_2SO_4$ is highly non-linear and time dependent (Mysliwiec and Kleeman, 2002), involving gas-phase precursors emitted from traffic and non-mobile combustion processes (Almeida et al., 2005). Previous studies reported enhanced photochemical formation of $(NH_4)_2SO_4$ in summer due to intense insolation and higher precipitation and a reverse trend of NO_3^- with a maximum contribution in the winter season (Hasheminassab et al. 2013; Hailin et al., 2008; Aldabe et al., 2011). Nevertheless, our study reveals that the highest contributions of all species were registered in the cold season, together with maximum concentrations of their precursors, SO_2 and NO_x. No significant weekly and seasonal variations in SA profile contribution were observed, probably due to specific conditions within the canyon avenue with limited pollutant dispersion.

The profile identified as vehicle derived and particle resuspension (VD/PR) represented a relatively high contribution of total observed pollution (28.7 %) and comprised high portions of EC, gaseous oxides, and soot. As regards seasonal dynamics, resuspension and airborne fraction of wear particles were decreased with higher precipitation and snow cover, whereas the highest levels of profile contribution were registered in summer, when the soil is dry and loose. The weekday-weekend difference was negligible, since in the urban street, vehicle traffic is not solely restricted to working days (Fig. 5).

The presented conclusions of source apportionment are in good agreement with the RF results, as the pollutants being relevant for prediction of each other were apportioned to the same source profile. It is worth noting that the importance of inorganic gaseous pollutants, as indicators of PM_{10} concentrations, was not highly ranked due to the fact that significant portion of PM_{10} originates from processes other than combustion. The difference in their behavior is verified using the multifractal approach. By analyzing multifractal dimensions of datasets, the typical parabola-like diagrams for all spectra were obtained, with a notable difference between the shapes. These findings suggest that the PM_{10} concentrations and inorganic gaseous pollutants were affected by different emission sources and environmental processes (Fig. 2). The regular parabola observed for PM_{10} spectra reflects the multiplicative process with the absence of dominant factors that could be easily determined. On the other hand, the parabolic shapes for other pollutants are distorted and shifted to the left, thus indicating that their concentrations were affected by fewer sources and/or additive processes.

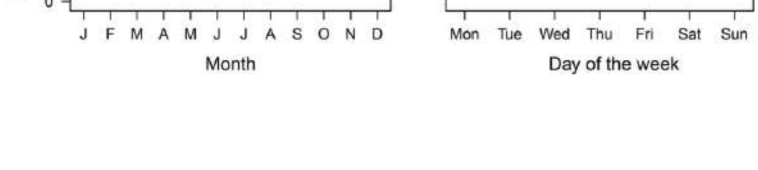


Fig. 5 Monthly and weekly variations of Unmix-resolved source contributions

Transport analysis

According to the results of the TSA for the period 2005–2015, the shares of transport, background, and local sources in total mixing ratios amounted to 15.0, 30.3, and 54.7 %, respectively. The estimated annual contribution of locally emitted pollutants was in the range from 18.9 to 38.0 μg m^{-3} (33.5–70.0 %), which clearly reflects their dominance in the stagnant conditions in the canyon avenue with limited dispersion. The decrease in PM_{10} concentrations until 2010 was observed as a result of decrease in contributions of local sources (0.9 μg m^{-3} year^{-1}, 4.5 % year^{-1}) and background level (2 μg m^{-3} year^{-1}, 8.1 % year^{-1}). This probably occurred as a result of extensive works on thermal systems within the Belgrade area, as previously mentioned. The contribution of local emissions in the period after January 1, 2011, doubled (from 16. to 33.4 μg m^{-3}), reaching its maximum in 2013 (38.0 μg m^{-3}) (Online Resource, Fig. 7). The same goes for transport contribution (from 12.5 to 22.2 %), which was estimated to 13.5 μg m^{3} on average.

According to the results of the trajectory cluster analysis (Fig. 6), highly polluted air masses from NE/E regions, W, and S (clusters C4, C5, C6, and C1) mostly affected the receptor site over the entire period, whereas the impact of N and NW air flows (clusters C2 and C3) was assessed to be considerably lower. The contribution of each cluster during the entire period is shown in Online Resource, Fig. 8. Both TCA and TSA results show that the contribution of transport pollution exhibited pronounced seasonal variations, with the highest values observed in autumn.

The results of PSCF and CWT analysis reveal that the measurement site was influenced by strong regional sources located in E and S/SW areas, as well as by polluted air flows from distant W/SW and E/NE areas (Fig. 6). Depending on the seasonal fluctuations in meteorological conditions and PBL height, transport contributions exhibited significant variations, with the highest values recorded during the cold season (Online Resource, Fig. 8).

In winter months, Belgrade area was affected by regional and long-range PM_{10} transport coming from the entire Europe, except for Spain, Great Britain, and Scandinavian countries, with potentially most important sources being located in NE, in Baltic countries and the Russian Federation (Online Resource, Fig. 9). During the summer season, the effects of sources located in southern Italy and the area surrounding the Black Sea could be observed. In autumn, the air flows from E region exerted the highest impact on the measurement site, whereas the effects of air masses arriving from Greece and North Africa, with occasional Saharan desert dust intrusions, prevailed throughout the spring (Pérez et al., 2006).

Conclusions

The aim of the study was to analyze PM_{10} spatio-temporal distribution and their relationship with other pollutants and meteorological conditions based on the long-term data from an urban area. The information on emission source types and locations, seasonal alternation of dominant sources, dispersion of pollutants in time and space, and the impact of metrological variables have been obtained relying on the results of the use and combinations of several models. The results of analyses, no matter if they are mutually complementary or in agreement, support the assumptions and conclusions based on which it is possible to design abatement strategies. Besides generally accepted methods, such as statistical analysis and source apportionment, the authors presented an improved transport analysis based on TSA, PSCF and CWT, and multifractal and inverse multifractal analysis, which have considerably enhanced the overall quality of conclusions drawn herein.

The mean annual concentrations exhibited a significant increase in 2011, and continued to rise gradually over next years. Such tendency can be mainly associated with the emergence of new strong emission sources and re-activation of the previously existing ones. The results of bivariate cluster and trajectory sector analyses are in agreement, both showing that locally emitted pollution had the highest impact on air quality in Belgrade urban area. By the use of Unmix, four source profiles were resolved, out of which solid fuel burning was associated with highest estimated contribution of 29.8 %. The

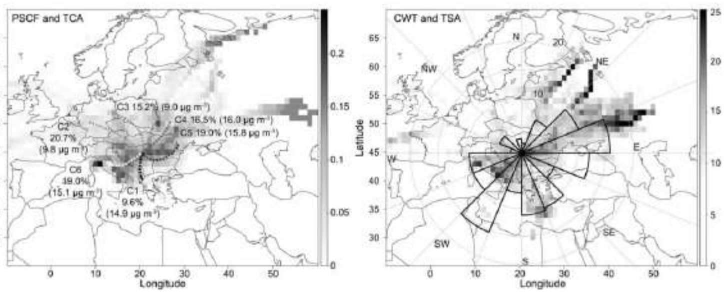


Fig. 6 PSCF and TCA (*left*) and CWT and TSA (μg m^{-3}) (*right*) resolved maps

impact of wood- and coal-burning for heating purposes is also reflected in high benzo[a]pyrene concentrations, thus significantly exceeding the WHO estimated reference level. Multifractal analysis also points to diversity of PM_{10} sources, as opposed to inorganic gaseous oxides originating from fewer sources. The transport pathways associated with western, eastern, and southern air masses appeared to have a considerable bearing on the pollution budget in Belgrade. The control of solid fuel burning for heating operations and implementation of clean technologies in industry sector might be the principal objective for the solution of the issue affecting the air quality at receptor area.

Acknowledgments This study was performed as part of the projects No. III43007 and No. III41011, which were founded by the Ministry of Education, Science, and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011–2016.

References

Aldabe J, Elustondo D, Santamaría C, Lasheras E, Pandolfi M, Alastuey A et al (2011) Chemical characterisation and source apportionment of PM2. 5 and PM10 at rural, urban and traffic sites in Navarra (North of Spain). Atmos Res 102:191–205

Almeida SM, Pio CA, Freitas MC, Reis MA, Trancoso MA (2005) Source apportionment of fine and coarse particulate matter in a sub-urban area at the Western European Coast. Atmos Environ 39: 3127–3138

Ashbaugh LL, Malm WC, Sadeh WZ (1985) A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. Atmos Environ 19:1263–1270

Barmpadimos I, Hueglin C, Keller J, Henne S, Prévôt ASH (2011) Influence of meteorology on PM_{10} trends and variability in Switzerland from 1991 to 2008. Atmos Chem Phys 11:1813–1835

Bencko V (1997) Health aspects of burning coal with a high arsenic content: the central Slovakia experience. In: Calderon RL, Chappell WR (eds) Abernathy CO. Arsenic, Springer Netherlands, pp 84–92

Buekers J, Stassen K, Panis LI, Hendrickx K, Torfs R (2011) Ten years of research and policy on particulate matter air pollution in hot spot Flanders. Environ Sci Policy 14:347–355

Carslaw DC, Beevers SD (2013) Characterising and understanding emission sources using bivariate polar plots and k-means clustering. Environ Modell Softw 40:325–329

Carslaw DC, Ropkins K (2012) Openair—an R package for air quality data analysis. Environ Modell Softw 27:52–61

Cavalli F, Viana M, Yttri KE, Genberg J, Putaud JP (2010) Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos Meas Tech 3:79–89

Cheng Z, Jiang J, Fajardo O, Wang S, Hao J (2013) Characteristics and health impacts of particulate matter pollution in China (2001–2011). Atmos Environ 65:186–194

Department for Environment, Food and Rural Affairs (DEFRA) and Environmental Agency (2002) Contaminants in soil: collation of toxicological data and intake values for humans. Arsenic (R&D Publication), Bristol

Draxler RR, Rolph GD (2014) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model access via NOAA ARL READY. NOAA Air Resources Laboratory, Silver Spring, http://ready.arl.noaa.gov/HYSPLIT.php

European Environmental Agency (2013) Air quality in Europe—2013 report, Luxembourg, http://www.eea.europa.eu/publications/air-quality-in-europe-2013. Accessed: 21st May, 2015

European Environmental Agency (2014) Air quality in Europe—2014 report, Luxembourg, http://www.eea.europa.eu/publications/air-quality-in-europe-2014. Accessed: 21st May, 2015

Global Data Assimilation System (2015) https://www.ready.noaa.gov/gdas1.php. Accessed: 20th May, 2015.

Hailin W, Zhuang Y, Ying W, Yele S, Hui Y, Zhuang G, Zhengping H (2008) Long-term monitoring and source apportionment of PM 2.5/ PM 10 in Beijing, China. J Environ Sci 20:1323–1327

Hasheminassab S, Daher N, Schauer JJ, Sioutas C (2013) Source apportionment and organic compound characterization of ambient ultrafine particulate matter (PM) in the Los Angeles Basin. Atmos Environ 79:529–539

Heal MR, Hibbs LR, Agius RM, Beverland IJ (2005) Total and water-soluble trace metal content of urban background PM 10, PM 2.5 and black smoke in Edinburgh, UK. Atmos Environ 39:1417–1430

Hsu YK, Holsen TM, Hopke PK (2003) Comparison of hybrid receptor models to locate PCB sources in Chicago. Atmos Environ 37:545–562

Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H (2005) Chemical characterisation of PM2. 5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland. Atmos Environ 39:637–651

INRIA, software Fraclab, A fractal analysis toolbox for signal an image processing. http://fraclab.saclay.inria.fr/works/biomedical

Jorba O, Pandolfi M, Spada M, Baldasano JM, Pey J, Alastuey A et al (2013) Overview of the meteorology and transport patterns during the DAURE field campaign and their impact to PM observations. Atmos Environ 77:607–620

Karanasiou A, Diapouli E, Cavalli F, Eleftheriadis K, Viana M, Alastuey A, Querol X, Reche C (2011) On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols. Atmos Meas Tech 4:2409–19

Khalil MAK, Rasmussen RA (2003) Tracers of wood smoke. Atmos Environ 37:1211–1222

Lee YK, Otkin JA, Greenwald TJ (2014) Evaluating the accuracy of a high-resolution model simulation through comparison with modis observations. J Appl Meteorol Clim 53:1046–1058

Lenschow P, Abraham HJ, Kutzner K, Lutz M, Preuß JD, Reichenbächer W (2001) Some ideas about the sources of PM_{10}. Atmos Environ 35:S23–S33

Liaw A, Wiener M (2002) Classification and regression by random forest. R news 2(3):18–22

Mysliwiec MJ, Kleeman MJ (2002) Source apportionment of secondary airborne particulate matter in a polluted atmosphere. Environ Sci Technol 36:5376–5384

Opentraj (2015) https://cran.r-project.org/web/packages/opentraj/opentraj.pdf. Accessed: 27th May, 2015.

Pacyna JM (1984) Estimation of the atmospheric emissions of trace elements from anthropogenic sources in Europe. Atmos Environ (1967) 18:41–50

Pandolfi M, Gonzalez-Castanedo Y, Alastuey A, Jesus D, Mantilla E, de la Campa AS et al (2011) Source apportionment of PM_{10} and $PM_{2.5}$ at multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions. Environ Sci Pollut R 18:260–269

Pérez C, Nickovic S, Baldasano JM, Sicard M, Rocadenbosch F, Cachorro VE (2006) A long Saharan dust event over the western Mediterranean: Lidar, Sun photometer observations, and regional dust modeling. J Geophys Res-Atmos (1984–2012), 111(D15). doi:10.1029/2005JD00657

Perez L, Grize L, Infanger D, Künzli N, Sommer H, Alt GM, Schindler C (2015) Associations of daily levels of PM_{10} and NO_2 with emergency hospital admissions and mortality in Switzerland: trends and missed prevention potential over the last decade. Environ Res 140:554–561

Perišić M, Stojić A, Stojić SS, Šoštarić A, Mijić Z, Rajšić S (2014) Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Qual Atmos Health 8(4):379–389

Pinheiro SDLLD, Saldiva PHN, Schwartz J, Zanobetti A (2014) Isolated and synergistic effects of PM_{10} and average temperature on cardiovascular and respiratory mortality. Rev Saude Publ 48:881–888

Pretty R (2015) TheilSen {openair} Tests for trends using Theil-Sen estimates, http://www.inside-r.org/packages/cran/openair/docs/TheilSen. Accessed: 15th August, 2015

Querol X, Alastuey A, Moreno T, Viana MM, Castillo S, Pey J et al (2008) Spatial and temporal variations in airborne particulate matter (PM 10 and PM 2.5) across Spain 1999–2005. Atmos Environ 42:3964–3979

Rajšić SF, Tasić MD, Novaković VT, Tomašević MN (2004) First assessment of the PM10 and PM2.5 particulate level in the ambient air of Belgrade City. Environ Sci Pollut R 11:158–164

Reljin I, Reljin B, Pavlović I, Rakočević I (2000) Multifractal analysis of gray-scale images. In Electrotechnical Conference, 2000. MELECON 2000. 10th Mediterranean, Vol. 2, IEEE, pp. 490-493.

Rost J, Holst T, Sahn E, Klingner M, Anke K, Ahrens D, Mayer H (2009) Variability of PM10 concentrations dependent on meteorological conditions. Int J Environ Pollut 36:3–18

Ruf T (1999) The Lomb-Scargle periodogram in biological rhythm research: analysis of incomplete and unequally spaced time-series. Biol Rhythm Res 30:178–201

Stojić A, Stojić SS, Šoštarić A, Ilić L, Mijić Z, Rajšić S (2015a) Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ Sci Pollut R. 22(17):13137–13152

Stojić A, Stojić SS, Mijić Z, Šoštarić A, Rajšić S (2015b) Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos Environ 106:71–79

Stull RB (1988) An introduction to boundary layer meteorology. Springer, London

Team RC (2012) R: a language and environment for statistical computing. http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf. Accessed: 10th June, 2015.

Uria-Tellaetxe I, Carslaw DC (2014) Conditional bivariate probability function for source identification. Environ Modell Softw 59:1–9

USEPA (2007) EPA Unmix 6.0 fundamentals and user guide. USEPA Office of Research and Development, http://archive.epa.gov/heasd/documents/web/pdf/unmix-6-user-manual.pdf. Accessed: 1st August, 2015

Véhel JL (1998) Introduction to the multifractal analysis of images. Fractal Image Encoding and Analysis 159:299–341

Wang YH, Liu ZR, Zhang JK, Hu B, Ji DS, Yu YC, Wang YS (2015) Aerosol physicochemical properties and implications for visibility during an intense haze episode during winter in Beijing. Atmos Chem Phys 15:3205–3215

Wang YQ (2014) MeteoInfo: GIS software for meteorological data visualization and analysis. Meteorol Appl 21:360–368

WHO (2005) Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide global update 2005 summary of risk assessment. http://www.who.int/mediacentre/factsheets/fs313/en/. Accessed: 10th June, 2015.

Stanovništvo (2016) OnLine First

UDK 314.48(497.11)
DOI: 10.2298/STNV151019001S
Prethodno saopštenje
Primljeno: 19.10.2015.

SEZONSKE VARIJACIJE SMRTNOSTI OD KARDIOVASKULARNIH, RESPIRATORNIH I MALIGNIH OBOLJENJA U GRADU BEOGRADU

Svetlana STANIŠIĆ STOJIĆ,[*] *Nemanja STANIŠIĆ*[*]
Andreja STOJIĆ,[*] *Vladimir DŽAMIĆ*[♦]

Cilj ovog rada je analiza sezonskih varijacija mortaliteta uzrokovanog kardiovaskularnim, respiratornim i malignim oboljenjima, kao i prikaz faktora životne sredine koji leže u osnovi ovog fenomena. Predstavljeno istraživanje se odnosi na Grad Beograd i sprovedeno je na osnovu podataka o dnevnoj smrtnosti dobijenih iz Gradskog zavoda za javno zdravlje za period od 2009. do 2014. godine, kao i podataka o godišnjoj smrtnosti dobijenih iz Republičkog zavoda za statistiku za period od 2000. do 2014. godine. Za analizu varijacija mortaliteta korišćene su Theil-Sen, smooth trend i metoda kubne spline interpolacije, dok su za ispitivanje distribucije korišćeni indeks sezonalnosti, indeks različitosti i indeks entropije. Rezultati pokazuju da je sezonalnost naročito izražena u slučaju kardiovaskularnog i respiratornog mortaliteta, sa najvišom stopom smrtnosti u februaru i martu i minimalnim vrednostima tokom letnjeg perioda. Suprotno tome, mortalitet uzrokovan malignim oboljenjima ne pokazuje značajne sezonske varijacije, a više od trećine smrtnih slučajeva se beleži među mlađim osobama, od 45 do 64 godine. Kada je u pitanju desezonalizovan trend, smrtnost od kardiovaskularnih oboljenja pokazuje stagnaciju, dok su mortalitet od malignih oboljenja i respiratorni mortalitet u umerenom odnosno značajnom porastu. Ovakav trend je uniforman u skoro svim beogradskim opštinama, a prosečne stope smrtnosti u poslednjih 15 godina su bile više u centralnim nego u perifernim zonama grada, naročito kada je u pitanju smrtnost od maligniteta. Bolje razumevanje sezonskih varijacija mortaliteta uzrokovanog hroničnim nezaraznim bolestima je neophodno kako bi se moglo preventivno delovati u cilju njegovog smanjenja, naročito onog dela koji se odnosi na kardiovaskularna i maligna oboljenja, za koji su godišnje stope među najvišim registrovanim u Evropi.

Ključne reči: *mortalitet, uzroci smrti, sezonske varijacije, Beograd.*

Uvod

Dinamika stanovništva je pod uticajem velikog broja faktora od kojih se najviše istražuje uzajamno dejstvo tri najvažnija fenomena – fertiliteta, mortaliteta i migracija, i njihov uticaj na populacioni rast, pad ili

[*] Univerzitet Singidunum, Beograd.
[♦] Institut za fiziku, Beograd.

stabilizaciju (Devedžić, 2013). Iako se Srbija po brojnim pokazateljima svrstava u zemlje u razvoju, njene demografske tendencije, kada su u pitanju očekivane promene u strukturi i broju stanovnika, su u velikoj meri podudarne onima koje se očekuju u razvijenim, zapadnim zemljama (Šuković, 2013). Kao razlog depopulacije koja se u Srbiji beleži decenijama unazad najčešće se navodi niska stopa nataliteta i horizontalna društvena pokretljivost, koja se pre svega odnosi na međunarodna migraciona kretanja mladih, na šta su uticali efekti globalizacije, tokovi međunarodnog kapitala, tehnološkog napretka, unapređenje saobraćajne strukture, razvoj telekomunikacija i transportnih sredstava i sl. (Casteles, Miller, 2008; King, 2002 u: Penev, Predojević-Despić, 2012). Međutim, činjenica je da i visoka stopa smrtnosti značajno doprinosi ovakvom stanju. Prema podacima iz 2011. godine, opšta stopa mortaliteta u Srbiji od 14,20 na 1.000 stanovnika (Marinković, 2014) je četvrta po visini u Evropi, odmah nakon vrednosti registrovanih u Bugarskoj, Belorusiji i Ukrajini za istu godinu (WHO Europe, 2015). Visoke stope smrtnosti od hroničnih, masovnih, nezaraznih bolesti u zemljama Istočne i Centralne Evrope su posledica pre svega socioekonomskih, psihosocijalnih razloga, kao i životnog stila, faktora životne sredine i odsustva medicinske nege i primarne prevencije (Müller-Nordhorn et al., 2008).

U istraživanju koje je bilo usmereno na ispitivanje uzroka mortaliteta u Srbiji, Marinković (2012) opisuje promene koje su se desile od 1950. do 2009. godine i navodi da je najveći rast relativnog učešća, od 12,9 do 61,3% u ukupnoj smrtnosti, bio vezan za oboljenja kardiovaskularnog sistema, dok je ishod infektivnih bolesti postao statistički zanemarljiv. S druge strane, relativni udeo mortaliteta uzrokovanog malignitetima se u istom periodu uvećao gotovo šest puta, zbog čega se danas svaki peti smrtni slučaj u Srbiji registruje kao posledica malignih oboljenja. Nakon inicijalnog porasta očekivanog trajanja života sa 56 na 71 godinu, koji je registrovan u periodu od 1950. do 1975, dalji rast sve do danas je bio značajno usporen porastom stope smrtnosti od kardiovaskularnih i malignih oboljenja (Marinković, 2012).

Istraživanje uticaja specifičnih faktora na smrtnost populacije datira od antičkih vremena i Hipokrata. Pišući svoje delo *Vazduh, voda i zemlja*, Hipokrat je među prvima uočio da smrtnost stanovništva zavisi i od godišnjih doba (Penev, 2014). Od 19. veka do danas, postala su brojnija naučna istraživanja čiji je predmet proučavanja uticaj faktora životne sredine, naročito sezonskih, na mortalitet i životni vek populacije. Jedan od osnivača sociologije, Emil Dirkem (Durkheim), izučavajući fenomen samoubistva i povezanost ovog ličnog čina sa društvom i društvenim uticajima, uočava još u 19. veku da su suicidi znatno ređi u zimu, a najčešći u proleće i rano leto.

DOI: 10.2298/STNV151019001S

Pitanje koje je izazivalo veliku pažnju istraživača u oblasti demografije jeste upravo da li postoji direktan kauzalitet između sezonalnog faktora i mortaliteta ili, pak, postoje određeni faktor socijalne i socioekonomske prirode koji tome doprinose. Ukoliko pretpostavimo da postoji direktan kauzalitet između sezonalnih faktora i mortaliteta, to bi nedvosmisleno značilo da u državama sa najnižom temperaturom stopa mortaliteta jeste najveća. Međutim, u svom istraživanju iz 1989. godine, Mek Ki je pokazao upravo suprotno (Mc Kee, 1989. u: Rau, 2007).

U svojoj opsežnoj naučnoj studiji, Rau ističe da je shvatanje po kome sezonalni faktor direktno dovodi do mortaliteta, krajnje simplifikovano. Analizirajući tzv. lanac uzročnosti sezonskog faktora i mortaliteta, on uočava da sezonski faktor dovodi do biomedicinske reakcije organizma (u vidu povećane koagulacije krvi, respiratornih infekcija i slično), te konsekventno, do povećanog rizika od mortaliteta (Rau, 2007).

Dodatno usložnjavanjući posmatrani lanac uzročnosti, kako bi objasnio pojavu sezonalnih paradoksa, Rau navodi postojanje različitih socijalnih i socioekonomskih faktora, koji posreduju između sezonalnog faktora, biomedicinske reakcije na ove faktore i demografske reakcije u vidu povećanog rizika od mortaliteta (Rau, 2007).

Bez obzira na aktuelnost ovog problema, u našoj zemlji nije bilo mnogo istraživanja na tu temu sve do poslednjih nekoliko godina. U studiji iz 2011. godine, analiziran je uticaj biometeoroloških faktora na stopu smrtnosti od kardiovaskularnih bolesti u Kragujevcu (Gajić et al., 2011). Takođe, u svojoj doktorskoj disertaciji, Arsenović (2014) je istraživala uticaj pojedinih biometeoroloških činilaca na stopu smrtnosti u Novom Sadu. Oba istraživanja su pokazala značajnu vezu između niskih temperatura i mortaliteta. Istraživanje koje se bavilo uticajem temperature na mortalitet u Gradu Beogradu u periodu od 1888. do 2008. godine objavljeno je 2012. godine (Đurđev et al., 2012). Autori navode da je utvrđena jaka korelacija između smrtnosti i niskih temperatura za period do Prvog svetskog rata, najverovatnije kao posledica nemogućnosti stanovništva da se prilagodi vremenskim uslovima, dok je poslednje dve decenije primetan porast mortaliteta u toploj sezoni, što je posledica dejstva ekstremno visokih temperatura.

Razumevanje sezonskih uticaja na stopu smrtnosti prouzrokovanu malignim, respiratornim i kardiovaskularnim bolestima, može da pomogne unapređenju zdravstvene kulture populacije i osvešćivanju populacije u kontekstu veće brige o zdravlju u promenljivim meteorološkim uslovima u svetlu globalnog zagrevanja i klimatskih promena. Takođe, mogu se unaprediti sociopsihološki i ekonomski aspekti društvenog života kojima bi se delovalo preventivno na druge faktore stresa iz životne sredine koji nisu ograničeni isključivo na vremenske

DOI: 10.2298/STNV151019001S

prilike a koji uzrokuju nastanak hroničnih, masovnih, nezaraznih oboljenja, kao što je zagađenje vazduha. Ključni cilj ovde prikazanog istraživanja jeste naučni opis i objašnjenje sezonalnosti mortaliteta uzrokovanog kardiovaskularnim, respiratornim i malignim bolestima u Gradu Beogradu u periodu 2009. do 2014. godine. Društveni cilj istraživanja jeste doprinos unapređivanju populacione politike u budućem periodu, na osnovu činjenica i nalaza do kojih smo došli.

Metodi

U radu su obrađeni neobjavljeni podaci o dnevnoj smrtnosti dobijeni iz Gradskog zavoda za javno zdravlje Beograd (GZJZ) za period od 2009. do 2014. godine, kao i podaci o godišnjoj smrtnosti Republičkog zavoda za statistiku (RZS), za period od 2000. do 2014. godine. Podaci se odnose na Grad Beograd i dobijeni su na lični zahtev autora.

Za grafički prikaz sezonskih varijacija mortaliteta korišćena je metoda kubne *spline* interpolacije, pri čemu je nezavisna varijabla (x) definisana kao redni broj dana u godini, a zavisna (y) kao relativni doprinos posmatranog dana ukupnoj smrtnosti pripadajuće godine izražen u procentima. Glatka kriva dobijena primenom ove metode je pogodna za vizuelnu inspekciju i uočavanje obrasca sezonske komponente.

Formalno, kubni splajn je izlomljena funkcija oblika (Pollock, 1993; McKinley, Levine, 1998):

$$S(x) = \begin{cases} S_1(x) \ za \ x_1 \leq x < x_2 \\ S_2(x) \ za \ x_2 \leq x < x_3 \\ \cdot \\ \cdot \\ \cdot \\ S_{n-1}(x) \ za \ x_{n-1} \leq x < x_r \end{cases}$$

pri čemu je s_i polinom trećeg stepena:

$$s_i(x) = a_i(x - x_i)^3 + b_i(x - x_i)^2 + c_i(x - x_i) + d_i$$

za i=1, 2, …, n-1.

Funkcija $S(x)$ interpolira sve tačke podataka, neprekidna je (polinomi se provlače kroz takozvane čvorove na kojima se spajaju podintervali interpolacije) i dva puta neprekidno diferencijabilna na opsegu vrednosti $[x_1,x_n]$.

DOI: 10.2298/STNV151019001S

Detalji u vezi sa utvrđivanjem vrednosti λ parametra splajn funkcije dati su u dokumentaciji paketa *stats* u okviru programskog jezika R (R Core Team, 2015).

Za utvrđivanje trendova stope mortaliteta, na vremenske serije desezonalizovane STL procedurom, primenjeni su *Theil-Sen* i *smooth* trend metodi paketa *openair* (Carslaw, Ropkins, 2012) u okviru programskog jezika R.

Theil-Sen metod predstavlja generalizaciju medijane u višedimenzionalnom prostoru promenljivih. Procena trenda se vrši na osnovu parametara linearnih regresija svih mogućih kombinacija *p* tačaka datog podskupa, pri čemu je rezultat definisan kao prostorna medijana koeficijenata regresije, odnosno odgovarajućih preseka. Model je robustan u odnosu na ekstremne vrednosti i daje dobar nivo poverenja nezavisno od tipa raspodele podataka.

Zbog kompleksnih veza između promenljivih, u najvećem broju primena linearna regresija predstavlja relativno grubu aproksimaciju njihove funkcionalne zavisnosti. Za analizu nelinearnih veza u ovom radu je korišćen fleksibilan *smooth* trend metod fitovanja baziran na *Generalized Additive Model* (GAM) (Wood, 2006), koji se može prikazati kao:

$$M_i = \sum_{j=1}^{n} S_j(x_{ij}) + \varepsilon_i$$

gde je M_i – *i*-ta srednja mesečna stopa mortaliteta, $s_j(x_j)$ – *smooth* funkcija *p*-te nezavisne varijable, *n* – ukupan broj nezavisnih varijabli, ε_i – *i*-ti ostatak $var(\varepsilon)=\sigma$ za koji se pretpostavlja da se pokorava normalnoj raspodeli. *Smooth* funkcija se određuje korišćenjem penalizovanog regresionog splajna kojim se tokom optimizacije fita vrši penalizacija grubosti dobijene krive (Carslaw et al., 2007).

Za analizu distribucije mortaliteta korišćeni su indeks sezonalnosti, koji predstavlja odnos mortaliteta tokom zime i leta, indeks različitosti koji pokazuje odstupanje od uniformnosti na mesečnom nivou i indeks entropije koji govori o uniformnosti distribucije mortaliteta (Rau, 2007).

Rezultati i diskusija

Statistika mortaliteta

Prema evidenciji GZJZ, u Gradu Beogradu je u periodu od 2009. do 2014. godine registrovano ukupno 113.430 smrtnih slučajeva (kategorizovanih kao A00-R99 prema Međunarodnoj statističkoj klasifikaciji bolesti i srodnih zdravstvenih problema Svetske zdravstvene organizacije, X

DOI: 10.2298/STNV151019001S

revizija), od čega je 60.407 slučajeva ili 53,25% pripisano posledicama kardiovaskularnih oboljenja (I00-I99), 4.649 slučajeva ili 4,01% je pripisano posledicama respiratornih oboljenja (J00-J98), dok je 31.191 smrtnih slučajeva ili 27,50% identifikovano kao posledica malignih oboljenja (C00-D48).

Prema podacima dobijenim od RZS, godišnja stopa smrtnosti od kardiovaskularnih oboljenja u Beogradu u periodu od 2000. do 2014. godine se kretala u rasponu od 6,35 do 6,77 na 1.000 stanovnika, i u poređenju sa stopama smrtnosti koje su zabeležene prethodnih godina na području Evrope (WHO Europe, 2015) ove vrednosti su među najvišim (tabela 1).

Kao najčešći uzrok smrti registrovana je kardiomiopatija (I42), iza čega slede srčani i moždani udar sa pratećim komplikacijama (I20-I25, I63). Prosečan godišnji broj smrtnih slučajeva registrovanih kao posledica malignih bolesti je takođe bio visok u prethodnih 15 godina, i kretao se u rasponu od 2,60 do 3,23 slučaja na 1.000 stanovnika. Najčešći uzroci smrti od malignih oboljenja su rak dojke za žene (C50), rak prostate (C61) i debelog creva (C18) za muškarce, kao i rak pluća i bronhija (C34) za oba pola. Za razliku od prethodno navedenih, godišnja stopa smrtnosti usled respiratornih oboljenja, u rasponu od 0,28 do 0,60 na 1.000 stanovnika, se može okarakterisati kao prosečna u odnosu na vrednosti koje su registrovane u drugim zemljama Evrope. Najčešći uzrok respiratornog mortaliteta u Gradu Beogradu je hronična opstruktivna bolest pluća, a stvarna stopa smrtnosti je možda i veća od zabeležene jer je kod određenog broja pacijenata koji se leče od respiratornih oboljenja smrtni ishod povezan sa poremećajem kardiovaskularnog sistema (Pope et al., 2004).

U starosnoj strukturi kardiovaskularnog i respiratornog mortaliteta udeo osoba starijih od 65 godina je veoma visok i kreće se u rasponu od 78,48 do 87,58% (tabela 1), kao što je i očekivano. Međutim, kada je u pitanju mortalitet od malignih oboljenja, više od trećine slučajeva se beleži među osobama starosti od 45 do 64 godine, što odražava zdravstveno stanje stanovnika Beograda. Na ovakav zaključak ukazuje i poređenje sa podacima iz zemalja Evrope. Tako na primer, podaci Centra za istraživanje malignih oboljenja Velike Britanije (Cancer Research UK, 2015) za period 2010. do 2012. pokazuju da se čak 78% ovih bolesti javlja kod osoba starijih od 65 godina. Na zdravstveni status ljudi u Srbiji takođe ukazuje i očekivan životni vek, koji prema podacima RZS u 2015. godini iznosi 74,3 godine što je značajno niže od 80,6 godina, koliko je očekivana dužina života u EU-28 (Eurostat, 2013).

DOI: 10.2298/STNV151019001S

Tabela 1.

Polna i starosna struktura kardiovaskularnog, respiratornog i mortaliteta od malignih bolesti za period 2000-2014.

	Godina	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Kardiovaskularni mortalitet	Ukupni mortalitet (na 1000 stanovnika)	6,77	6,47	6,76	6,73	6,56	6,76	6,50	6,49	6,61	6,61	6,57	6,46	6,47	6,35	6,44
	Muškarci	6,76	6,54	6,59	6,70	6,57	6,62	6,43	6,40	6,36	6,34	6,25	6,26	6,35	6,13	6,28
	Žene	6,78	6,41	6,91	6,76	6,54	6,90	6,57	6,58	6,83	6,85	6,86	6,65	6,58	6,55	6,59
	Učešće starosne kategorije (%)															
	0-19	0,02	0,03	0,08	0,02	0,12	0,05	0,03	0,07	0,07	0,09	0,01	0,08	0,05	0,02	0,06
	20-44	1,14	1,13	1,08	0,96	0,97	1,20	1,04	0,98	1,04	0,91	0,87	0,87	0,91	0,74	0,99
	45-64	16,59	16,13	13,95	14,06	13,17	13,25	12,52	12,25	11,85	11,41	11,90	11,60	11,67	11,95	12,03
	≥ 65	82,25	82,71	84,88	84,97	85,75	85,50	86,41	86,70	87,04	87,58	87,22	87,45	87,37	87,30	86,92
Respiratorni mortalitet	Ukupni mortalitet (na 1000 stanovnika)	0,45	0,28	0,28	0,29	0,30	0,37	0,32	0,35	0,34	0,43	0,38	0,47	0,60	0,55	0,52
	Muškarci	0,58	0,36	0,34	0,38	0,38	0,46	0,40	0,42	0,46	0,52	0,49	0,60	0,72	0,65	0,58
	Žene	0,32	0,22	0,23	0,22	0,23	0,28	0,24	0,30	0,24	0,35	0,29	0,35	0,49	0,45	0,47
	Učešće starosne kategorije (%)															
	0-19	1,15	1,35	0,89	1,30	1,46	1,19	1,95	0,87	1,45	1,29	0,79	0,64	0,70	0,44	0,69
	20-44	2,58	1,79	1,56	2,16	1,88	1,87	2,73	2,62	3,44	2,15	3,01	2,32	1,81	1,76	2,63
	45-64	16,50	18,39	15,40	15,33	12,92	16,84	16,60	17,13	14,65	15,35	16,48	18,56	15,71	15,27	17,37
	≥ 65	79,77	78,48	82,14	81,21	83,75	80,10	78,71	79,37	80,47	81,21	79,71	78,48	81,77	82,53	79,31
Mortalitet od malignih bolesti	Ukupni mortalitet (na 1000 stanovnika)	2,60	2,71	2,74	2,91	2,89	2,87	2,94	2,98	2,99	3,02	3,11	2,98	3,15	3,16	3,23
	Muškarci	2,93	3,04	3,20	3,33	3,27	3,30	3,35	3,45	3,43	3,43	3,57	3,44	3,61	3,65	3,60
	Žene	2,30	2,42	2,32	2,53	2,54	2,48	2,58	2,55	2,60	2,66	2,69	2,57	2,75	2,73	2,89
	Učešće starosne kategorije (%)															
	0-19	0,34	0,35	0,35	0,35	0,28	0,24	0,30	0,19	0,27	0,35	0,20	0,16	0,34	0,19	0,24
	20-44	4,20	3,75	3,31	3,41	3,16	3,45	3,76	2,98	3,22	2,96	3,10	3,12	2,57	2,76	2,46
	45-64	37,47	35,35	34,60	33,83	33,52	33,17	33,35	33,28	34,07	34,02	35,20	34,27	33,37	33,54	31,27
	≥ 65	57,99	60,54	61,74	62,40	63,03	63,14	62,59	63,55	62,45	62,67	61,51	62,45	63,71	63,51	66,03
	Izvor: RZS, Dodatna obrada podataka o umrlim licima, Vitalna statistika, 2015.															

DOI: 10.2298/STNV151019001S

Sezonske varijacije mortaliteta

Posmatrajući prosečan dnevni broj smrtnih događaja za ispitivani šestogodišnji period, može se zaključiti da je sezonska zavisnost naročito izražena u slučaju kardiovaskularnog i respiratornog mortaliteta, sa najvišom stopom smrtnosti u februaru i martu i minimalnim vrednostima tokom letnjeg perioda (tabela 2).

Tabela 2.
Prosečan dnevni broj umrlih po mesecima za period 2009-2014.

Mesec	Ukupno	Kardiovaskularni mortalitet	Respiratorni mortalitet	Mortalitet od malignih oboljenja
Januar	55,6	30,4	2,4	14,5
Februar	57,9	32,2	2,6	14,6
Mart	55,9	30,6	2,8	14,5
April	52,2	28,5	2,3	14,0
Maj	49,6	26,1	2,0	13,7
Juni	48,9	25,5	1,9	13,9
Juli	49,5	25,6	1,7	14,5
Avgust	47,6	23,9	1,8	14,1
Septembar	47,2	24,3	1,6	13,7
Oktobar	51,2	27,1	2,1	14,4
Novembar	52,6	28,4	2,0	14,4
Decembar	54,0	29,1	2,3	14,6

Izvor: GZJZ, Dodatna obrada podataka o umrlim licima, Vitalna statistika, 2015.

Dnevni doprinosi kardiovaskularnoj, respiratornoj i smrtnosti od maligniteta su izračunati za period od 2009. do 2014. godine i predstavljeni primenom funkcije izglačavanja (*smooth*) na grafikonu 1. Može se videti da, za razliku od kardiovaskularnog i respiratornog, mortalitet koji je posledica malignih oboljenja ne pokazuje značajne sezonske varijacije (mali raspon vrednosti na y-osi).

Dosadašnje studije sprovedene na različitim geografskim lokacijama potvrđuju postojanje sličnih sezonskih varijacija mortaliteta, a izuzetak predstavljaju nalazi iz siromašnih zemalja subsaharske Afrike, gde se uzroci mortaliteta i distribucija među starosnim grupama značajno razlikuju od onih u modernim zemljama (Egondi et al., 2012). U razvijenim zemljama, ukupna stopa smrtnosti pokazuje izrazitu sezonsku zavisnost (Diaz et al., 2013), a uzroci i mehanizmi koji leže u osnovi sezonskog obrazca su kompleksni i još nisu u potpunosti razjašnjeni. Kao najvažniji razlozi se navode akutne respiratorne infekcije i stres kardiovaskularnog sistema zbog ekstremnih visokih ili niskih temperatura, dok drugi faktori uključuju i nedostatak vitamina D zbog smanjene sunčeve svetlosti kao i sociološke i psihološke fenomene vezane za

DOI: 10.2298/STNV151019001S

novogodišnje i verske praznike (Nielsen et al., 2011). Takođe, navode se i promene nivoa zagađujućih materija u vazduhu, ali i individualni faktori koji se odnose na promene intenziteta fizičke aktivnosti i režima ishrane (Hopstock et al., 2013).

Veliki broj studija u svetu se bavio istraživanjem veze između ambijentalne temperature i mortaliteta, za koju se smatra da je ključni faktor od koga zavise sezonske varijacije smrtnosti. Obimna studija (Gasparrini et al., 2015) sprovedena u 384 grada i 13 zemalja je pokazala da je relativan rizik od izlaganja ekstremno niskim temperatura značajno veći nego rizik od smrtnosti usled izlaganja visokim temperaturama, a primećenu heterogenost u rezultatima koji se odnose na različita geografska područja autori objašnjavaju pre svega socioekonomskim, demografskim i infrastrukturnim faktorima.

Patofiziološki mehanizmi koji leže u osnovi sezonskog mortaliteta su uglavnom povezani sa kardiovaskularnim i respiratornim efektima, zbog čega su sezonske varijacije prisutne kod kardiovaskularnog i respiratornog mortaliteta, ali ne i kod mortaliteta koji je posledica malignih oboljenja (grafikon 1 i 2). Medicinske studije su pokazale da izlaganje ekstremno visokim temperaturama izaziva povećanje viskoznosti krvi koje najviše ima uticaj na starije osobe, čiji zdravstveni status i prisustvo hroničnih oboljenja ograničava adaptaciju (Breitner, 2014). Slično tome, izlaganje hladnoći dovodi do skupljanja krvnih sudova u perifernim tkivima i povećanog priliva krvi u unutrašnje organe, što ima za posledicu ubrzano izlučivanje soli i vode i povećanje viskoznosti krvi (Keatinge, 2002).

Sezonske varijacije kardiovaskularnog i respiratornog mortaliteta su veoma slične, s tim što smrtnost od kardiovaskularnih oboljenja pokazuje i dva manja porasta, krajem juna i krajem oktobra, za koje možemo pretpostaviti da potiču od naglih promena temperature. Međutim, prethodne studije koje su imale za cilj da ispitaju vezu temperature i mortaliteta uglavnom nisu uključivale ispitivanje efekta temperaturnih promena u prelaznim sezonama što bi, sudeći po ovde prikazanim rezultatima, mogla biti smernica za buduća istraživanja. Može se pretpostaviti da će ovakva istraživanja u narednom periodu biti od posebnog značaja jer se procenjuje da će porast broja smrti usled globalnog zagrevanja i ekstremno visokih temperatura nadvladati smanjenje broja smrti koje će biti registrovano zbog činjenice da su tokom hladne sezone temperature umerenije (Li et al., 2013).

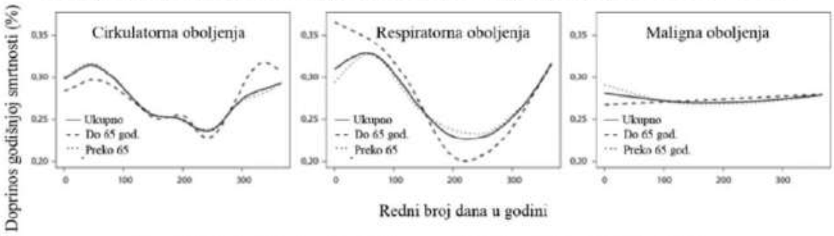
Još jedan faktor od značaja za sezonsku zavisnost mortaliteta su i virusne respiratorne infekcije, koje zajedno sa ekstremnim hladnoćama utiču na porast mortaliteta u hladnim mesecima (Mazick et al., 2012). Uzrok za njihovu učestalost su niske temperature koje dovode do rashlađivanja nazalne mukoze i suženja disajnih puteva, što smanjuje imunološki

DOI: 10.2298/STNV151019001S

odgovor. Procena broja smrtnih slučajeva koji se mogu pripisati sezonskim infektivnim oboljenjima tipa gripa se čak i u razvijenim zemljama uglavnom bazira na statističkom proračunu, a ne na rezultatima laboratorijskih analiza. Razlog je taj što je testiranje svih pacijenata sa

Grafikon 1.

Prosečni dnevni doprinosi kardiovaskularnoj, respiratornoj i smrtnosti od maligniteta, segmentirani po starosnoj kategoriji za period 2009-2014.



Izvor: GZJZ, Dodatna obrada podataka o umrlim licima, Vitalna statistika, 2015.

Grafikon 2.

Prosečni dnevni doprinosi kardiovaskularnoj, respiratornoj i smrtnosti od maligniteta, segmentirani po polu za period 2009-2014.

Izvor: GZJZ, Dodatna obrada podataka o umrlim licima, Vitalna statistika, 2015.

simptomima respiratornih oboljenja skupo, kao i to što se direktni uzročnici smrtnog ishoda (sekundarna bakterijska infekcija) najčešće ne povezuju sa virusom gripa jer nastupe onda kada se virus više ne može detektovati u krvi. Nakon istraživanja sprovedenog u SAD, Goldstein i sar. (2012) su procenili da se doprinos gripa ukupnoj stopi smrtnosti koja se registruje u hladnoj sezoni kreće u rasponu od 0,10 do 0,14 na 1.000 stanovnika.

Kada su u pitanju drugi faktori životne sredine koji utiču na sezonske varijacije mortaliteta, prethodna istraživanja su imala za cilj da ispitaju vezu između zagađenja vazduha i mortaliteta u Gradu Beogradu (Stanišić Stojić et al., 2016). Rezultati su pokazali da, od ispitivanih zagađujućih materija, sumpor dioksid i čađ, koji dominantno potiču od sagorevanja

DOI: 10.2298/STNV151019001S

lignita i mazuta u termoelektranama i industrijskim objektima, imaju najveći uticaj na kardiovaskularni i respiratorni mortalitet, naročito u zimskom periodu kada je njihova koncentracija visoka, kako zbog emisija, tako i zbog meteoroloških uslova.

Osim koncentracija zagađujućih materija, hemijski sastav suspendovanih čestica (PM_{10}) ima značajan uticaj na mortalitet, zbog čega sadašnje zakonske regulative koje se odnose isključivo na regulisanje nivoa zagađujućih materija nisu dovoljne da spreče posledice po ljudsko zdravlje (Krall et al., 2013). Pored toga što su koncentracije PM_{10} u Beogradu više od koncentracija koje se registruju u drugim evropskim metropolama (Perišić et al., 2014), poslednje studije ukazuje na to da suspendovane čestice sadrže i visoke koncentracije veoma štetnih materija, benzopirena i arsena, koje su posledica sagorevanja fosilnih goriva tokom zimskih meseci (Stojić et al., 2015a; Stojić et al., 2015b). Na osnovu navedenog može se pretpostaviti da zagađujuće materije tokom hladne sezone u velikoj meri doprinose visokim stopama smrtnosti u Gradu Beogradu.

Uticaj starosti na sezonalnost mortaliteta

Faktori životne sredine kao što su temperatura i zagađenje vazduha ne utiču jednako na sve fiziološke kategorije stanovnika. Prema Barret (2015), stare osobe, osobe sa nižim stepenom obrazovanja, kao i osobe nižeg socioekonomskog statusa koje nemaju dovoljan tehnološki i ekonomski kapacitet za prilagođavanje najviše osećaju posledice po

Tabela 3.
Sezonska distribucija mortaliteta u zavisnosti od starosti

Indeks	Mlađi od 65 godina	Stariji od 65 godina
φ 1	1,058	1,179
φ 2	0,020	0,028
φ 3	0,999	0,999

zdravlje. Tako na primer, Boulay i sar. (1999) navode da smrtnost usled hroničnih oboljenja srca i krvnih sudova u Francuskoj pokazuje izrazite sezonske varijacije sa maksimalnim vrednostima u zimskom periodu koje su identične kod oba pola i svih starosnih grupa, osim za grupu osoba starijih od 85 godina, kod kojih je vrhunac smrtnosti i hospitalizacije bio najveći u januaru, što je ranije u odnosu na ostatak populacije. Ovakva pojava se naziva *harvesting* efekat, i odnosi se na činjenicu da u uslovima ekstremne ambijentalne temperature dolazi do povećanja broja smrti u kategoriji osetljivih ljudi, što je praćeno značajnom redukcijom mortaliteta u periodu koji sledi (Ye et al., 2012). U skladu sa tim se može

DOI: 10.2298/STNV151019001S

primetiti da su sezonske varijacije kardiovaskularnog i respiratornog mortaliteta u Gradu Beogradu najizraženije kod osoba starijih od 65 godina, dok je smrtnost mlađe populacije podložna uticaju brojnih drugih faktora izuzev temperature, zbog čega je i raspodela smrtnosti za osobe mlađe od 65 godina nešto drugačija, naročito u zimskom periodu (grafikon 1). Na isti zaključak ukazuju i indeks sezonalnosti i indeks različitosti koji govore o tome da ljudi umiru više tokom zime, naročito osobe starije od 65 godina, kao i da je raspodela smrtnosti po mesecima uniformnija kod osoba mlađih od 65 godina (tabela 3).

Uticaj pola na sezonalnost mortaliteta

Podaci prikazani u tabeli 1 pokazuju da se kardiovaskularni, respiratorni i mortalitet uzrokovan malignim oboljenjima značajno razlikuju po polnoj strukturi: stopa smrtnosti od respiratornih i malignih oboljenja su više za muškarce, dok žene češće umiru od kardiovaskularnih bolesti. Sezonske varijacije kardiovaskularne smrtnosti takođe pokazuju razlike po polu, pa tako nagle promene temperature u prelaznim periodima više utiču na žene nego na muškarce (grafikon 2). Dosadašnja istraživanja su potvrdila da se predispozicije za pojavu pojedinih vrsta oboljenja razlikuju u odnosu na pol, ali očekuje se da će buduće studije ponuditi detaljnije objašnjenje za ovakve nalaze (Hecking et al., 2014).

Sadašnje pretpostavke su da registrovane razlike u smrtnosti mogu proizilaziti iz fizioloških razlika, kao i iz drugih faktora koji se ne tiču direktno bioloških funkcija. Tako, na primer, muškarci mogu biti podložniji oboljenjima koja su posledica udisanja suspendovanih čestica iz vazduha zbog većeg promera respiratornih puteva (Gehr, Heyder, 2000). Istraživanja takođe ukazuju i na to da su žene tokom života sklonije nefatalnim hroničnim oboljenjima, kao i akutnim stanjima tipa gastrointestinalnih i respiratornih infekcija. Za razliku od njih, muškarci su generalno zdraviji tokom života, ali se ova prednost gubi u kasnijim godinama kada nastupaju fatalna koronarna i maligna oboljenja, emfizem, ciroza jetre i hronična oboljenja bubrega zbog čega je i životni vek muškaraca kraći za oko 6 godina (Ross et al., 2012). Zhang i sar. (2012) objašnjavaju veću smrtnost nakon infarkta miokarda kod žena činjenicom da žene u trenutku srčanog udara pate od većeg broja hroničnih oboljenja koja ih čine podložnijim za smrtni ishod. Ahmed i sar. (2014) su takođe registrovali viši mortalitet kod žena nakon perikutanih koronarnih intervencija, što su pripisali činjenici da su žene u proseku starije kada do intervencije dođe i zbog toga podložnije komplikacijama. Marinković (2012) navodi da od bolesti srca i krvotoka u Srbiji više umiru žene jer je veći broj starih žena u populaciji. Međutim, suprotno ovim pretpostavkama, istraživanje Salam i sar. (2013) ukazuje na to da je ženski pol nezavisan prediktor mortaliteta kod pacijenata hospitalizovanih zbog

DOI: 10.2298/STNV151019001S

koronarnih simptoma, čak i nakon što je postojanje hroničnih nefatalnih oboljenja uzeto u obzir, što govori u prilog tome da postoje drugi faktori osim starosti i hroničnih oboljenja koji bi mogli biti od značaja za višu stopu kardiovaskularne smrtnosti kod žena.

Osim fizioloških razlika među polovima, treba imati u vidu da su, čak i u razvijenim zemljama, žene ograničenije kada su u pitanju socioekonomski resursi koji su značajni za zdravstveni status. U studiji koja je bazirana na višegodišnjim podacima o mortalitetu i koja obuhvatila preko 3.000 američkih okruga, Kindig i Cheng (2013) su došli do zaključka da je porast stope mortaliteta u najvećem broju slučajeva bio posledica porasta stope mortaliteta žena. Faktori koji su prepoznati kao ključni za objašnjenje stope smrtnosti su nivo obrazovanja, oblast stanovanja i sklonost duvanu, zbog čega je moguće pretpostaviti da primećena razlika između polova zapravo reflektuje razliku u statistički značajnim socioekonomskim i bihejvioralnim odrednicama.

Drugo ekstenzivno istraživanje iz 2011. godine koje je bazirano na podacima iz 30 evropskih zemalja pokazalo je da štetne navike kao što je pušenje i prekomeran unos alkohola u velikoj meri (40-60% odnosno 10-30%, respektivno) objašnjavaju razlike između polova kada su u pitanju stope smrtnosti i prosečna dužina života (McCartney et al., 2011). Ovakav nalaz, prema zaključku autora, može ukazivati na to da će sa povećanjem broja žena koje svakodnevno koriste duvan i alkohol u narednim decenijama doći do smanjenja razlike između očekivane dužine života kod muškaraca i žena, što je već primetan trend u nekim zapadnim zemljama.

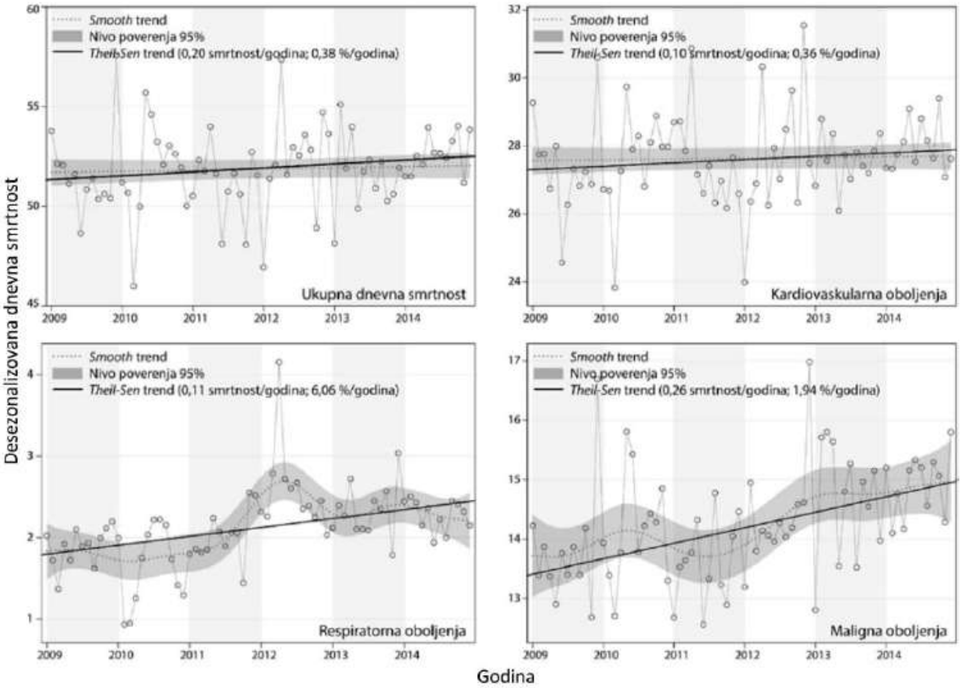
Trend mortaliteta

Na osnovu desezonalizovanog trenda tri ispitivane vrste mortaliteta za period od 2009. do 2014. godine, može se zaključiti da stopa smrtnosti od kardiovaskularnih oboljenja pokazuje zanemarljiv rast, odnosno stagnaciju (0,36% tokom posmatranog perioda), dok su mortalitet od malignih oboljenja (1,94%) i respiratorni mortalitet (6,06%) u umerenom odnosno značajnom porastu (grafikon 3).

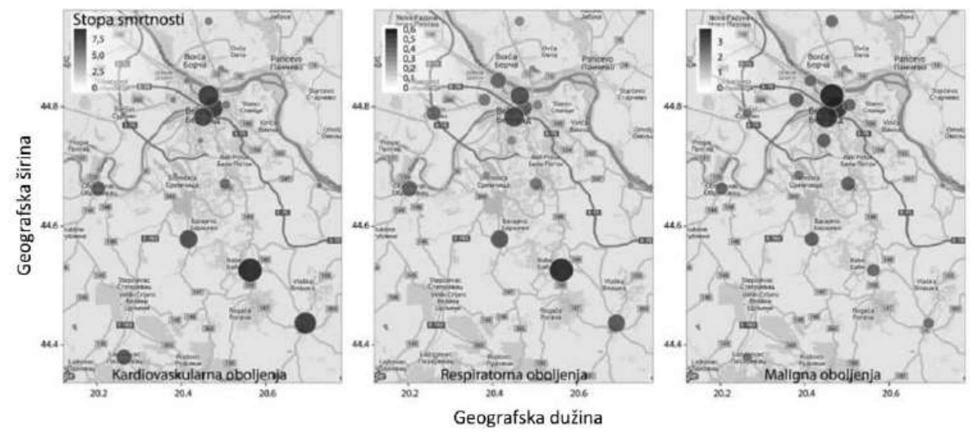
Sličan trend je registrovan u skoro svim beogradskim opštinama (tabela 3), a prosečne stope smrtnosti su više u centralnim nego u perifernim zonama grada, naročito kada je u pitanju smrtnost od maligniteta (grafikon 4). Interesantno je istaći da *smooth* trend respiratornog mortaliteta u značajnoj meri prati varijacije koncentracija suspendovanih čestica koje su registrovane od 2009. do 2014. godine i prikazane u istraživanju Perišić i sar. (2014), što može ukazivati na vezu između zagađenja vazduha i respiratornih oboljenja.

DOI: 10.2298/STNV151019001S

Grafikon 3.
Rezultati trend analize različitih tipova smrtnosti za period 2009-2014.



Grafikon 4.
Stopa smrtnosti po opštinama Grada Beograda



Izvor za grafikone 3 i 4: GZJZ, Dodatna obrada podataka o umrlim licima, Vitalna statistika, 2015.

DOI: 10.2298/STNV151019001S

Tabela 4.

Godišnji broj smrtnih slučajeva na 1.000 stanovnika u beogradskim opštinama, 2000-2014.

		2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Respiratorni mortalitet	Barajevo	0,66	0,41	0,48	0,60	0,48	0,32	0,28	0,32	0,32	0,27	0,47	0,70	0,63	0,70	0,85
	Voždovac	0,42	0,30	0,30	0,34	0,26	0,39	0,36	0,34	0,40	0,48	0,40	0,46	0,67	0,47	0,47
	Vračar	0,69	0,58	0,43	0,30	0,40	0,34	0,41	0,41	0,32	0,45	0,46	0,32	0,74	0,51	0,58
	Grocka	0,35	0,17	0,26	0,19	0,27	0,15	0,21	0,35	0,32	0,37	0,39	0,36	0,39	0,51	0,39
	Zvezdara	0,48	0,27	0,23	0,29	0,29	0,31	0,32	0,34	0,32	0,36	0,38	0,36	0,50	0,43	0,47
	Zemun	0,48	0,33	0,32	0,33	0,36	0,41	0,36	0,36	0,35	0,49	0,51	0,59	0,56	0,62	0,57
	Lazarevac	0,31	0,24	0,17	0,27	0,17	0,32	0,15	0,17	0,17	0,22	0,20	0,34	0,55	0,38	0,43
	Mladenovac	0,36	0,27	0,34	0,29	0,27	0,40	0,29	0,54	0,56	0,62	0,67	0,55	0,79	0,87	0,59
	Novi Beograd	0,37	0,24	0,30	0,28	0,30	0,42	0,29	0,42	0,33	0,43	0,32	0,55	0,62	0,57	0,55
	Obrenovac	0,55	0,38	0,38	0,38	0,38	0,49	0,29	0,29	0,45	0,57	0,47	0,48	0,59	0,58	0,65
	Palilula	0,44	0,26	0,17	0,21	0,30	0,31	0,35	0,41	0,39	0,35	0,32	0,44	0,53	0,51	0,40
	Rakovica	0,29	0,24	0,22	0,23	0,28	0,28	0,31	0,27	0,28	0,37	0,36	0,37	0,67	0,52	0,52
	Savski venac	0,58	0,42	0,50	0,36	0,58	0,68	0,58	0,44	0,35	0,52	0,35	0,43	0,80	0,89	0,56
	Sopot	0,88	0,34	0,29	0,59	0,20	0,49	0,69	0,49	0,54	1,04	0,55	0,59	0,98	0,49	0,84
	Stari grad	0,67	0,34	0,40	0,37	0,33	0,48	0,32	0,43	0,38	0,50	0,58	0,70	0,77	0,82	0,61
	Čukarica	0,38	0,18	0,21	0,25	0,23	0,34	0,26	0,23	0,25	0,40	0,25	0,45	0,52	0,46	0,55
	Surčin						0,43	0,30	0,48	0,30	0,34	0,44	0,46	0,59	0,56	0,51
Kardiovaskularni mortalitet	Barajevo	8,80	8,38	8,64	8,64	7,74	8,24	8,98	9,86	9,28	8,21	8,93	7,84	7,34	6,50	7,29
	Voždovac	7,01	6,77	7,25	7,35	6,42	6,55	6,56	6,86	6,81	6,85	7,09	6,46	6,50	6,43	6,40
	Vračar	10,30	9,25	9,30	9,19	9,64	9,29	8,80	8,48	8,43	8,61	8,17	7,16	8,52	8,62	7,17
	Grocka	5,26	5,56	5,14	5,54	5,73	6,42	5,69	6,26	6,28	6,46	5,78	5,60	5,99	5,32	5,79
	Zvezdara	6,77	6,64	6,83	6,20	6,72	6,90	6,10	6,02	6,28	5,94	5,85	5,91	5,75	5,61	5,64
	Zemun	5,63	5,67	6,47	6,42	6,39	6,24	6,21	5,93	5,97	5,76	5,72	5,86	5,87	5,66	5,92
	Lazarevac	7,96	6,32	7,31	7,19	6,86	7,56	7,18	7,44	8,48	8,20	8,86	7,37	8,12	7,88	8,51
	Mladenovac	9,99	9,44	8,57	10,00	9,51	10,21	8,53	8,39	8,57	8,83	9,26	8,80	8,42	8,40	8,12
	Novi Beograd	5,62	5,29	5,47	5,48	5,66	5,69	5,54	5,60	5,92	6,19	5,94	6,27	6,42	6,51	6,23
	Obrenovac	7,82	7,41	7,65	7,88	7,41	7,30	7,84	6,92	7,49	8,02	7,82	7,44	6,80	7,26	7,72
	Palilula	6,46	6,48	7,04	6,41	6,11	6,54	6,15	6,05	6,20	6,13	5,96	5,82	5,75	5,75	5,93
	Rakovica	5,42	5,35	5,51	5,66	5,55	5,66	6,32	5,89	5,88	6,01	5,58	6,02	6,06	6,19	6,13
	Savski venac	9,21	9,15	8,48	9,01	8,03	9,20	8,69	8,21	8,20	7,72	8,07	8,87	7,77	7,82	7,57
	Sopot	10,52	10,13	10,47	9,96	8,84	10,62	9,63	8,17	9,16	9,28	8,41	7,38	9,94	8,39	10,10
	Stari grad	10,67	8,76	9,80	10,20	9,15	8,33	8,16	7,87	8,43	7,59	8,55	8,60	9,82	7,93	8,39
	Čukarica	5,24	5,12	5,27	5,21	5,23	5,70	5,55	6,08	5,54	5,87	6,01	6,29	5,65	5,67	5,91
	Surčin						6,25	4,91	5,60	5,96	5,60	5,59	5,31	5,04	5,13	5,76
Mortalitet od malignih bolesti	Barajevo	2,84	2,82	3,03	3,50	2,85	2,96	2,75	2,78	3,20	3,13	3,34	2,88	2,84	3,21	3,85
	Voždovac	2,83	2,80	2,81	2,86	3,02	3,01	3,11	3,12	2,93	3,08	3,15	3,33	3,04	3,29	3,24
	Vračar	3,29	4,09	3,78	3,50	3,85	4,12	3,10	3,78	3,73	3,87	3,73	3,49	3,95	3,78	3,53
	Grocka	1,99	2,00	1,70	1,92	2,15	2,15	2,44	2,32	2,44	2,60	2,42	2,20	2,55	2,37	2,53
	Zvezdara	2,50	2,53	2,59	2,85	2,80	2,81	2,85	3,01	3,00	3,20	3,23	2,80	3,07	3,05	3,12
	Zemun	2,46	2,65	2,54	2,74	2,91	2,89	2,84	3,12	2,85	3,04	2,84	2,83	3,26	3,14	3,07
	Lazarevac	2,40	2,12	2,46	2,14	2,71	2,78	2,94	2,95	2,55	2,49	2,46	2,95	2,73	2,86	2,76
	Mladenovac	2,22	2,59	2,36	2,94	2,60	2,48	2,61	2,80	2,54	3,13	3,02	3,07	2,96	3,01	2,85
	Novi Beograd	2,84	2,88	2,84	3,11	3,00	2,79	3,16	2,99	3,18	3,13	3,20	3,23	3,33	3,33	3,58
	Obrenovac	2,43	2,16	2,71	2,81	2,61	2,86	2,70	3,15	2,88	3,02	3,45	2,76	3,07	3,29	3,23
	Palilula	2,49	2,76	2,70	3,01	2,85	2,71	2,70	2,83	2,96	2,85	3,25	2,96	3,07	3,12	3,12
	Rakovica	2,40	2,70	3,04	2,97	2,96	3,28	2,75	3,17	3,12	2,97	3,09	3,05	3,52	3,21	3,47
	Savski venac	3,62	3,90	3,47	4,26	3,30	3,65	3,77	2,92	3,81	3,24	3,95	3,67	4,16	3,56	4,61
	Sopot	3,07	2,89	2,55	2,40	2,85	2,95	3,06	2,62	2,82	2,98	3,03	3,15	3,89	2,72	2,77
	Stari grad	3,69	3,47	4,11	3,96	3,69	3,61	4,48	3,21	4,19	4,06	3,82	3,56	3,47	4,43	4,49
	Čukarica	2,09	2,34	2,40	2,66	2,59	2,55	2,86	2,82	2,72	2,64	2,84	2,67	2,96	3,08	3,03
	Surčin						2,11	2,32	2,65	2,89	2,79	2,86	2,68	2,56	2,44	2,43

Izvor: RZS, Dodatna obrada podataka o umrlim licima, Vitalna statistika, 2015.
Napomena: Podaci za opštinu Zemun 2000-2004. uključuju i opštinu Surčin, jer je Surčin do 2005. bio u sastavu opštine Zemun.

DOI: 10.2298/STNV151019001S

Ograničenja istraživanja

Na kraju treba skrenuti pažnju na ograničenja predstavljenog istraživanja, koja su zajednička za sve studije koje imaju za cilj ispitivanje mortaliteta, i tiču se kvaliteta podataka. S jedne strane, prednost studija koje koriste mortalitet kao pokazatelj zdravstvenog stanja populacije jeste u činjenici da je mortalitet jasan pokazatelj ishoda za razliku od podataka o broju pacijenata koji su hospitalizovani ili ambulantno lečeni, koji mogu da budu neregistrovani ili pogrešno interpretirani (Bell et al., 2011). S druge strane, eventualne nepreciznosti u utvrđivanju i izveštavanju uzroka smrti mogu smanjiti pouzdanost rezultata i zaključaka.

Zaključak

Promene broja i strukture populacije su u velikoj meri zavisne od mortaliteta, kao jednog od najvažnijih demografskih faktora. Visok mortalitet od hroničnih, masovnih, nezaraznih bolesti je učestala pojava u razvijenim zemljama Zapada, ali i u zemljama Jugoistočne Evrope u kojima socioekonomski uslovi, progresivno starenje, nivo obrazovanja i svesti, psihološki faktori i odsustvo adekvatne zdravstvene zaštite utiču na to da su multikauzalne bolesti najzastupljenije u patologiji. Prema predstavljenim podacima, svaki drugi stanovnik Srbije umre od bolesti srca i krvnih sudova, a svaki treći ili četvrti od malignih oboljenja. Iako je relativno učešće respiratornog mortaliteta u ukupnoj smrtnosti relativno nisko (4,01%), ova vrsta smrtnosti beleži najveći porast (6,06%) tokom poslednjih nekoliko godina. S druge strane, čak trećina smrtnih ishoda od malignih oboljenja spada u prevremene smrti (pre 65. godine starosti). Očekivano trajanje života, kao jedan od indikatora zdravstvenog stanja stanovnika, u Srbiji je u laganom porastu poslednjih decenija, ali ovaj porast je poslednjih godina značajno usporen porastom stope smrtnosti od kardiovaskularnih i malignih oboljenja koja su među najvišim registrovanim stopama smrtnosti u Evropi.

Sezonske varijacije mortaliteta predstavljaju fenomen sa kojim se ljudi susreću oduvek, ali je tek u poslednjih nekoliko decenija postao tema brojnih naučnih istraživanja. Relativno malo ovakvih istraživanja je do sada sprovedeno u našoj zemlji. Rezultati ovde prikazanog istraživanja ukazuju na to da su sezonske varijacije naročito izražene u slučaju kardiovaskularnog i respiratornog mortaliteta, najverovatnije zato što su patofiziološki mehanizmi, koji leže u osnovi sezonskog mortaliteta, najviše povezani sa kardiovaskularnim i respiratornim efektima. Grafički prikaz sezonskih varijacija takođe sugeriše značaj naglih promena temperature u prelaznim periodima godine, koje imaju veći uticaj na mortalitet žena nego muškaraca. Kao što je i očekivano, mortalitet starih

DOI: 10.2298/STNV151019001S

osoba pokazuje izrazite sezonske varijacije, dok mortalitet osoba mlađih od 65 godina pokazuje drugačiju distribuciju tokom godine zbog uticaja brojnih drugih faktora izuzev faktora životne sredine.

Istraživanje faktora životne sredine koji imaju dominantan uticaj na mortalitet je tema brojnih savremenih naučnih radova. Pritom, najveći izazov kod ovakvih istraživanja predstavlja procena uticaja na mortalitet svakog od faktora zasebno, jer ambijentalna temperatura, zagađenje vazduha i virusne infekcije takođe pokazuju sezonske varijacije kao i mortalitet, a u određenoj meri se radi i o međusobno zavisnim pojavama. Rezultati ovakvih istraživanja su od posebnog značaja jer obezbeđuju informacije na osnovu kojih je moguće planirati preventivne mere koje bi imale za cilj da utiču na unapređenje zdravlja stanovnika i smanjenje stope smrtnosti, naročito kada su u pitanju osetljive fiziološke kategorije ljudi.

Zahvalnica - Autori se zahvaljuju Gradskom zavodu za javno zdravlje Beograd, kao i gospođi Gordani Bjelobrk, načelnici Odseka za demografiju Republičkog zavoda za statistiku, za dodatnu obradu podataka o smrtnosti u Gradu Beogradu.

Ovaj članak je nastao kao rezultat istraživanja finansiranog od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije, u okviru projekata III43007 i III41011 interdisciplinarnih istraživanja za period 2011-2016.

DOI: 10.2298/STNV151019001S

Literatura

AHMED, A. PHAM, D., VIRANI, S., HAMZEH, I. R., JNEID, H., LAKKIS, N. & ALAM, M. (2014). Does Gender Still Influence Mortality Post Percutaneous Coronary Intervention (PCI)? A Meta-Analysis of the Impact of Gender on PCI Outcomes. *Circulation* 130 (Suppl 2): A15682-A15682.

ARSENOVIĆ, D. (2014). Uticaj temperature vazduha na sezonalnost mortaliteta u Novom Sadu (doktorska disertacija). Prirodno-matematički fakultet Univerziteta u Novom Sadu.

BARRETT, J. R. (2015). Exported Deaths and Short-Term PM_{10} Exposure: Factoring the Impact of Commuting into Mortality Estimates. *Environmental Health Perspectives* 123(1): A22.

BELL, M. L., MORGENSTERN, R. D. & HARRINGTON W. (2011). Quantifying the human health benefits of air pollution policies: Review of recent studies and new directions in accountability research. *Environmental Science & Policy* 14(4): 357-368.

BOULAY, F., BERTHIER, F., SISTERON, O., GENDREIKE, Y. & GIBELIN, P. (1999). Seasonal variation in chronic heart failure hospitalizations and mortality in France. *Circulation* 100(3): 280-286.

BREITNER, S., WOLF, K., DEVLIN, R. B., DIAZ-SANCHEZ, D., PETERS, A. & SCHNEIDER, A. (2014). Short-term effects of air temperature on mortality and effect modification by air pollution in three cities of Bavaria, Germany: a time-series analysis. *Science of the Total Environment* 485-486: 49-61.

CANCER RESEARCH UK (2015) Cancer Mortality by Age (elektronski izvor). http://www.cancerresearchuk.org/health-professional/cancer-statistics/mortality/age#heading-Zero

CARSLAW, D. C. & ROPKINS, K. (2012). Openair - An R package for air quality data analysis. *Environmental Modelling & Software* 27: 52-61.

CARSLAW, D. C., BEEVERS, S. D., & TATE, J. E. (2007). Modelling and assessing trends in traffic-related emissions using a generalised additive modelling approach. *Atmospheric Environment* 41(26): 5289-5299.

DEVEDŽIĆ, M. (2013). Raskršća demografije. *Stanovništvo* 51(2): 23-38.

DIAZ, A., GERSCHCOVICH, E. R., DÍAZ, A. A., ANTÍA, F. & GONORAZKY, S. (2013). Seasonal variation and trends in stroke hospitalizations and mortality in a South American Community Hospital. *Journal of Stroke and Cerebrovascular Diseases* 22(7): e66-e69.

ĐURĐEV, B. S., ARSENOVIĆ, D. & SAVIĆ, S. (2012). Temperature-related Mortality: Results from Belgrade in the Period 1888-2008. *Acta Geographica Slovenica* 52(2): 385-40.

EGONDI, T., KYOBUTUNGI, C., KOVATS, S., MUINDI, K., ETTARH, R. & ROCKLÖV, J. (2012). Time-series analysis of weather and mortality patterns in Nairobi's informal settlements. *Global Health Action* 5.

EUROSTAT (2013). Mortality and life expectancy statistics. Statistics Explained. Eurostat (elektronski izvor). http://ec.europa.eu/eurostat/statistics-explained/index.php/Mortality_and_life_expectancy_statistics

GAJIĆ, V., MILOJEVIĆ, D., SMAILAGIĆ, J., ĐONOVIĆ, N. & GAJIĆ, S. (2011). Biometeorološki uticaj na kardiovaskularni mortalitet. *Pons* 8(1): 3-9.

DOI: 10.2298/STNV151019001S

GASPARRINI, A., GUO, Y., HASHIZUME, M., LAVIGNE, E., ZANOBETTI, A., SCHWARTZ, J. & LEONE, M. (2015). Mortality risk attributable to high and low ambient temperature: a multicountry observational study. *The Lancet* 386(9991): 369–375.

GEHR, P. & J. HEYDER (Eds.). (2000). *Particle-lung interactions*. New York: CRC Press.

GOLDSTEIN, E., VIBOUD, C., CHARU, V. & LIPSITCH, M. (2012). Improving the estimation of influenza-related mortality over a seasonal baseline. *Epidemiology* 23(6): 829-839.

HECKING, M., BIEBER, B. A., ETHIER, J., KAUTZKY-WILLER, A., SUNDER-PLASSMANN, G., SÄEMANN, M. D. & PORT, F. K. (2014). Sex-Specific Differences in Hemodialysis Prevalence and Practices and the Male-to-Female Mortality Rate: The Dialysis Outcomes and Practice Patterns Study (DOPPS). *PLOS Medicine* 11(10): e1001750.

HOPSTOCK, L. A., BARNETT, A. G., BØNAA, K. H., MANNSVERK, J., NJØLSTAD, I. & WILSGAARD, T. (2013). Seasonal variation in cardiovascular disease risk factors in a subarctic population: The Tromsø Study 1979–2008. *Journal of Epidemiology and Community Health* 67(2): 113-118.

KEATINGE, W. R. (2002). Winter mortality and its causes. *International Journal of Circumpolar Health* 61(4): 292-305.

KINDIG, D. A. & CHENG E. R. (2013). Even as mortality fell in most US counties, female mortality nonetheless rose in 42.8 percent of counties from 1992 to 2006. *Health Affairs* 32(3): 451-458.

KRALL, J. R., ANDERSON, G. B., DOMINICI, F., BELL, M. L. & PENG, R. D. (2013). Short-term exposure to particulate matter constituents and mortality in a national study of US urban communities. *Environmental Health Perspectives* 121(10): 1148-1161.

LI, T., HORTON, R. M. & KINNEY, P. L. (2013). Projections of seasonal patterns in temperature-related deaths for Manhattan, New York. *Nature Climate Change* 3(8): 717-721.

MARINKOVIĆ, I. (2012). Uzroci smrti u Srbiji od sredine 20. veka. *Stanovništvo* 50(1): 89-106.

MARINKOVIĆ, I. (2014). Visoka smrtnost kao uzrok depopulacije u Republici Srbiji. *Demografski pregled* 51: 1-4.

MAZICK, A., GERGONNE, B., NIELSEN, J., WUILLAUME, F., VIRTANEN, M. J., FOUILLET, A. & NUNES, B. (2012). Excess mortality among the elderly in 12 European countries, February and March 2012. *Euro Surveillance* 17(14): pii=20138.

Mc CARTNEY, G., MAHMOOD, L., LEYLAND, A. H., BATTY, G. D. & HUNT, K. (2011). Contribution of smoking-related and alcohol-related deaths to the gender gap in mortality: evidence from 30 European countries. *Tobacco Control* 20(2): 166-168.

Mc KEE C. M. (1989). Deaths in Winter: Can Britain learn from Europe? *European Journal of Epidemiology* 5(2): 178–82.

McKINLEY, S. & LEVINE, M. (1998). Cubic spline interpolation. *College of the Redwoods* (elektronski izvor). http://pages.intnet.mu/cueboy/education/notes/numerical/cubicsplineinterpol.pdf

DOI: 10.2298/STNV151019001S

MÜLLER-NORDHORN, J., BINTING, S., ROLL, S. & WILLICH, S. N. (2008). An update on regional variation in cardiovascular mortality within Europe. *European heart journal* 29: 1316-1326.

NIELSEN, J., MAZICK, A., GLISMANN, S. & MØLBAK, K. (2011). Excess mortality related to seasonal influenza and extreme temperatures in Denmark, 1994-2010. *BMC Infectious Diseases* 11(1): 350-359.

PENEV, G. & PREDOJEVIĆ-DESPIĆ, J. (2012). Prostorni aspekti emigracije iz Srbije. Tri "vruće" emigracione zone. *Stanovništvo* 50(2): 35-64.

PENEV, G. (2014). Sezonalost suicida u Srbiji, 1990-2012. *Stanovništvo* 52(2): 67-89.

PERIŠIĆ, M., STOJIĆ, A., STANIŠIĆ STOJIĆ. S., ŠOŠTARIĆ, A., MIJIĆ, Z. & RAJŠIĆ, S. (2014). Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. *Air Quality, Atmosphere and Health* 1-11.

POLLOCK, D. (1993). Smoothing with cubic splines (elektronski izvor). http://www.researchgate.net/profile/D_Pollock/publication/241171192_SMOOTHING_WITH_CUBIC_SPLINES/links/0046352cfad5c46ccb000000.pdf

POPE, C. A., BURNETT, R. T., THURSTON, G. D., THUN, M. J., CALLE, E. E., KREWSKI, D. & GODLESKI, J. J. (2004). Cardiovascular mortality and long-term exposure to particulate air pollution epidemiological evidence of general pathophysiological pathways of disease. *Circulation* 109(1), 71-77.

RAU, R. (2007). *Seasonality in human mortality: a demographic approach*. Berlin: Springer

R CORE TEAM. (2015). R: A Language and Environment for Statistical Computing. Vienna, Austria: R Foundation for Statistical Computing. (elektronski izvor). http://www.r-project.org

ROSS, C. E., MASTERS, R. K. & HUMMER, R. A. (2012). Education and the gender gaps in health and mortality. *Demography* 49(4): 1157-1183.

SALAM, A., ALBINALI, H., SINGH, R., ASAAD, N., ALQAHTANI, A. & AL SUWAIDI, J. (2013). Female gender is an independent predictor of in-hospital mortality in patients hospitalized with dizziness. *Journal of the American College of Cardiology* 61(10): E81.

STANIŠIĆ STOJIĆ. S., STANIŠIĆ, N., STOJIĆ, A. & ŠOŠTARIĆ, A. (2016). Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. *Journal of Toxicology and Environmental Health, part A: Current Issues*, 79(1): 17-27.

STOJIĆ, A., STANIŠIĆ STOJIĆ, S., ŠOSTARIĆ, A., ILIĆ, L., MIJIĆ, Z. & RAJŠIĆ, S. (2015a). Characterization of VOC sources in urban area based on PTR-MS measurements and receptor modelling. *Environmental Science and Pollution Research* 17: 13137-13152.

STOJIĆ, A., STANIŠIĆ STOJIĆ, S., MIJIĆ, Z., ŠOŠTARIĆ, A. & RAJŠIĆ, S. (2015b). Spatio-temporal distribution of VOC emissions in urban area based on receptor modelling. *Atmospheric Environment* 106: 71-79.

ŠUKOVIĆ, D. (2013). Reforma penzionog sistema i problem starenja populacije. *Stanovništvo* 51(1): 91-102.

WHO EUROPE (2015). European Detailed Mortality Database. World Health Organization, Regional Office for Europe (elektronski izvor). http://data.euro.who.int/dmdb/

DOI: 10.2298/STNV151019001S

WOOD, S. (2006). *Generalized additive models: an introduction with R.* New York: CRC press.

YE, X., WOLFF, R., YU, W., VANECKOVA, P., PAN, X. & TONG, S. (2012). Ambient temperature and morbidity: a review of epidemiological evidence. *Environmental Health Perspectives* 120(1): 19-28.

ZHANG, Z., FANG, J., GILLESPIE, C., WANG, G., HONG, Y. & YOON, P. W. (2012). Age-specific gender differences in in-hospital mortality by type of acute myocardial infarction. *The American Journal of Cardiology* 109(8): 1097-1103.

Svetlana Stanišić Stojić, Nemanja Stanišić,
Andreja Stojić, Vladimir Džamić

Seasonal Mortality Variations of Cardiovascular, Respiratory and Malignant Diseases in the City of Belgrade

Summary

The main purpose of this paper is to examine seasonal variations in mortality resulting from cardiovascular diseases, respiratory diseases and cancer, as well as to provide a review of environmental factors underlying such phenomenon. The herein presented study was conducted on the territory of Belgrade based on the data on daily mortality rates obtained from the Institute of Public Health in Belgrade for the period 2009-2014, as well as the data on annual mortality rates provided by the Statistical Office of the Republic of Serbia for the period 2000-2014. The analysis of mortality variations was performed by the use of *Theil-Sen* method, *smooth trend* method and cubic *spline* interpolation, whereas desriptive tools, such as winter/summer ratio and dissimilarity index, were used to examine the seasonal pattern.

According to the Institute of Public Health, over 113430 deaths were registered in Belgrade area for the period 2009-2014, out of which 53.25% is attributed to cardiovascular diseases, 4.01% to respiratory diseases and 27.50% to cancer. The annual mortality rates caused by cardiovascular diseases and cancer on the territory of Belgrade are among the highest ranking in Europe. The leading causes of death in the observed period included: cardiomyopathy, heart attack and stroke with accompanying complications, breast cancer in women, prostate and colorectal cancer in men, lung and bronchus cancer for both genders, and chronic obstructive pulmonary disease. Cardiovascular and respiratory mortality rates are significantly higher among people aged 65 and over, whereas more than one third of deaths caused by cancer is observed among younger people aged between 45 and 64 years.

Research results show that seasonal variations were most pronounced in mortality resulting from cardiovascular and respiratory diseases, with highest mortality rates recorded in February and March and lowest during the summer season. Also, the number of deaths due to cardiovascular diseases increased twice, namely at

DOI: 10.2298/STNV151019001S

the end of June and October, which is assumed to be the result of sudden temperature changes. Nonetheless, no such seasonal variations were observed in mortality caused by cancer. Seasonal variations in mortality resulting from cardiovascular diseases also indicate gender differences, which is why sudden temperature changes in interim periods affect more women than men.

As regards deseasonalized trend, mortality caused by cardiovascular diseases stagnates, while mortality caused by cancer and mortality caused by respiratory diseases records moderate to severe increase. This is a uniform trend in almost all municipalities in Belgrade, with average mortality rates being higher in central zones than in suburbs over the last 15 years, particularly mortality caused by cancer. A slight increase in the overall mortality can also be attributed to aging of the population, which cannot be verified due to lack of available accurate data on the average age structure of Belgrade population for the observed period.

A better understanding of seasonal variations in mortality caused by chronic non-communicable diseases can contribute to improving the population health care and rising awareness of the population concerning greater health care in changeable weather conditions due to global warming and climate change. These findings can also enhance preventive action on environmental risk factors that are not limited exclusively to weather conditions, such as air pollution.

Keywords: *mortality, causes of death, seasonal variations, Belgrade*

DOI: 10.2298/STNV151019001S

DOI 10.1186/s12940-016-0164-6

Environmental Health

RESEARCH

Open Access

Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area

Svetlana Stanišić Stojić[1*], Nemanja Stanišić[2] and Andreja Stojić[3]

Abstract

Background: To propose a new method for including the cumulative mid-term effects of air pollution in the traditional Poisson regression model and compare the temperature-related mortality risk estimates, before and after including air pollution data.

Results: The analysis comprised a total of 56,920 residents aged 65 years or older who died from circulatory and respiratory diseases in Belgrade, Serbia, and daily mean PM_{10}, NO_2, SO_2 and soot concentrations obtained for the period 2009–2014. After accounting for the cumulative effects of air pollutants, the risk associated with cold temperatures was significantly lower and the overall temperature-attributable risk decreased from 8.80 to 3.00 %. Furthermore, the optimum range of temperature, within which no excess temperature-related mortality is expected to occur, was very broad, between −5 and 21 °C, which differs from the previous findings that most of the attributable deaths were associated with mild temperatures.

Conclusions: These results suggest that, in polluted areas of developing countries, most of the mortality risk, previously attributed to cold temperatures, can be explained by the mid-term effects of air pollution. The results also showed that the estimated relative importance of PM_{10} was the smallest of four examined pollutant species, and thus, including PM_{10} data only is clearly not the most effective way to control for the effects of air pollution.

Keywords: Air pollution, Temperature, Mortality, Environmental exposure, Developing countries

Background

Environmental stressors, such as extreme temperature events and air pollution, pose a significant challenge to human societies, particularly to the growing urban population worldwide [1]. While most studies investigating the adverse health effects of air pollution have adjusted for temperature as a confounder, accounting for the effects of air pollution in the studies aimed at assessing the relationship between temperature and mortality has been less common [2]. The relatively few studies considering the interactive effects of meteorological variables and air pollution on daily mortality have reported inconsistent results [3, 4]. Significant inconsistency in the effect estimates across studies is at least partly associated with the methodological differences in exposure assessment and confounder control [5]. Furthermore, the majority of studies assessed air pollution-related mortality by including lag-specific effects of pollutants, despite the fact that detrimental impact of air pollution is not limited to few days preceding adverse health outcome, particularly in highly polluted areas of developing countries.

Better understanding of the temperature-related mortality is urgently needed, when considering the upcoming atmospheric changes and projected global temperature rise of 1.8 to 4.0 °C by 2100 [6]. The relationships between temperature and mortality were reported to be linear or non-linear, with death rates increasing in either direction from an optimum value [7, 8]. However, the relative importance of cold spells and heat waves still remains an issue of scientific debate. The latest study of Gasparrini et al. [9] including more than 74 million deaths recorded in 13 countries and 384 locations showed that cold-related deaths outnumbered

* Correspondence: sstanisic@singidunum.ac.rs
[1]Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia
Full list of author information is available at the end of the article

heat-related deaths by a factor of nearly 20, and that most of the temperature-related mortality burden was attributable to milder, non-optimum weather, and not to extreme temperature events. Nevertheless, it should be emphasized that factors such as susceptibility or resilience, including air pollutants, in the most of cases have not been included in the analysis [10].

The evidence on the effects of environmental stressors in developing countries is relatively scarce because of poor environmental monitoring and a paucity of health surveillance data [11]. In this study, we compared the relative contributions from heat and cold to circulatory and respiratory mortality burden, before and after accounting for the cumulative effects of air pollution, as estimated by the method proposed herein. The study is based on data from Belgrade, Serbia, which is among the most polluted European cities [12, 13] and has recorded very high cardiovascular death rates over the last 15 years, ranging from 635 to 677 per 100,000 inhabitants [14, 15].

Methods

The mortality data were stratified into age categories, and only people aged 65 and older were included in the analysis in order to increase the statistical power. Daily data of circulatory and respiratory mortality (cause-of-death coding I00-I99 and J00-J99 according to the International Classification of Diseases 10th revision, ICD-10 code) for the period from 2009–2014 were obtained from the Institute of Public Health Belgrade. Temperature data was obtained from the Global Data Assimilation System with spatial resolution of 1° and combined over 24-h periods to provide mean values.

In order to examine the associations between environmental stressors and mortality, two separate models were specified. Namely, the first model included temperature and other factors affecting mortality, such as season and day of the week, while the second, along with the above-mentioned factors, included air pollutants: PM_{10}, NO_2, SO_2 and soot. The daily mean pollutant concentrations of PM_{10}, NO_2, SO_2 and soot were obtained from 7, 21, 22 and 16 monitoring stations, respectively, uniformly distributed throughout the city area, within the monitoring network of the Institute of Public Health Belgrade. Measurements were conducted at automatic stations using a beta-ray attenuation sampler (Thermo FH 62 I-R) for PM_{10} and referent sampling devices, Horiba APNA 360 and APSA 360 analysers, for NO_2 and SO_2, respectively. At semi-automatic measuring stations, PM_{10} concentrations were determined using a referent Sven Leckel sampler, whereas determination of NO_2 and SO_2 concentrations was performed based on ISO 6768:1998 (Modified Griess-Saltzman method) and ISO 6767:1990 (tetrachloromercurate (TCM)/pararosaniline method) standards, respectively. Soot concentrations were obtained by the use of a Pro-Ekos device based on ISO 9835:1993 standard.

The effect of temperature on mortality is shown to be both delayed in time and shifted by a so-called harvesting effect or mortality displacement – a temporal advance in deaths occurring in the frailest population, typically followed by a period of reduced mortality [6]. In order to simultaneously capture the non-linear exposure-response dependencies and determine the time period between the exposure and health outcome, we used distributed lag non-linear models (DLNM). This methodology is based on the concept of cross-basis, a bidimensional space of functions that captures simultaneously the shape of the relationship between a predictor and a dependent variable along the space of the predictor and the lag dimension of its occurrence [16]. Implementation of the DLNM modeling framework [7] is available in the statistical environment R [17]. Based on the methodology presented in Gasparrini et al. [9], we modelled the exposure-response curve using a quadratic B-spline with three internal knots placed at the 10th, 75th, and 90th percentiles of the observed temperature distribution, and the lag-response curve (with maximum lag up to 21 days) using a natural cubic B-spline with an intercept and three internal knots equally spaced on the log scale. In order to control for seasonal and long-term effects, we included a natural cubic B-spline of time with 8° of freedom per year. Finally, the model also included a categorical variable indicating the day of the week.

The quasi-Poisson regression model with no pollutants included is specified as follows:

$$E(Y_t) = \exp\{\alpha + \beta T_{t,l} + NS(time,\ df) + \lambda DOW_t\}$$

where $E(Y_t)$ is expected daily death count on day t; α is the intercept; $T_{t,l}$ is a matrix of variables obtained by the transformation of mean daily temperature, β is a vector of coefficients for $T_{t,l}$, and l is the lag day; $NS(time,df)$ is the natural cubic spline of time; and DOW_t and λ are dummy variables representing the day of the week and the corresponding vector of coefficients, respectively. Quasi-Poisson was used to compensate for overdispersion since the residual deviance was larger than the residual degrees of freedom (the dispersion parameter was 1.06). We shall refer to this model in further text as the base model.

Results and discussion

The analysis included a total of 56,920 residents aged 65 years or older who died from circulatory (93.27 %) and respiratory diseases (6.73 %). As shown in Fig. 1, mortality annual variations for the entire period exhibited a strong seasonal pattern, with peak values in the

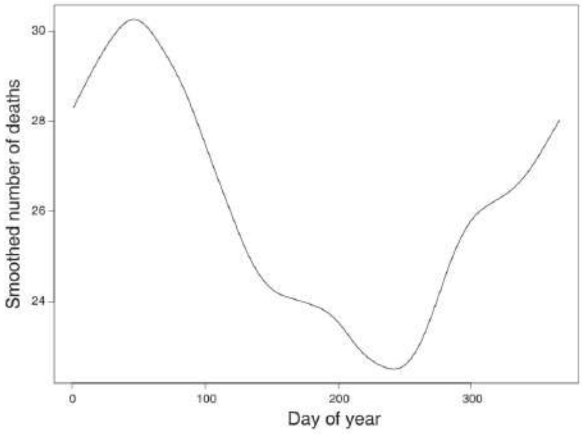


Fig. 1 Smoothed empirical mortality annual variations for the period 2009–2014. Mortality variations exhibit seasonal pattern, with peak values in the middle of February and minimum values around the start of September

middle of February and minimum values around September, 1st. Two minor increases occurred at the beginning of July and the end of October, suggesting the potential impact of sudden temperature changes on human health. The figures presenting circulatory and respiratory daily mortality segmented by age and gender, and their seasonal variations are shown in Additional files 1 and 2.

The climate in Belgrade is moderate continental with all four seasons. During the study period, mean daily temperatures were in the range from −17.4 to 30.1 °C, with the average value of 11.9 °C. The average number of days with temperatures below 0 °C was 40 per year, whereas the coldest and warmest months were January and July, with 0.4 and 22.2 °C, respectively. The average seasonal temperatures for the entire period were 12.1, 21.4, 12.7 and 1.1 °C for the spring, summer, autumn and winter, respectively.

The daily mean concentrations of PM_{10}, NO_2, SO_2 and soot for the entire period were 48.3, 32.7, 15.5 and 20.7 $\mu g\ m^{-3}$, respectively. The number of days with average PM_{10} concentrations exceeding 50 $\mu g\ m^{-3}$ was in the range from 75 to 155 per year, which is considerably higher than the Air Quality Standard margin (35 exceedances per year), whereas the mean annual NO_2 concentrations did not exceed the value of 40 $\mu g\ m^{-3}$, nor any mean daily SO_2 levels higher than the recommended limit of 135 $\mu g\ m^{-3}$ were observed.

The levels of PM_{10} and SO_2 exhibited a clear seasonal pattern, with highest concentrations observed during cold season (Additional file 3), whereas the seasonality of soot was less pronounced. Furthermore, the moving average PM_{10} and SO_2 concentrations were highly correlated, suggesting that the variations of two pollutants, particularly those long-term, were driven by the same anthropogenic and meteorological factors. Conversely, NO_2 concentrations exhibited pronounced weekly, but not seasonal variations, which can be partly attributed to the traffic-related emissions that are present throughout the year.

The lag-specific effects of temperature on mortality obtained from the base model are provided in Fig. 2. As can be seen, the heat-related mortality appears to be an acute event followed by a reduction in death rates, with maximum effects observed on the same day or lags of 1–3 days. Nevertheless, the effects of cold spells were observed to be more evenly distributed across 3–6 days of exposure with less evidence of subsequent harvesting, which complies with previous studies reporting sustained health effects of low temperatures [18].

As regards the cumulative effects of temperature over the entire lag period, the U-shaped exposure-response curve was identified as the most representative. The minimum relative risk corresponding to the optimum temperature of 21 °C is presented in Fig. 3 as a dotted line, whereas the cut-off values at the 1st and 99th percentile of the temperature distribution, which stand for extreme cold and heat, are displayed as dashed vertical lines.

According to the findings of Gasparrini et al. [9], cold temperatures were responsible for advancing a substantial fraction of deaths (7.29 %), compared to hot days (0.42 %), whereas most deaths were attributable to

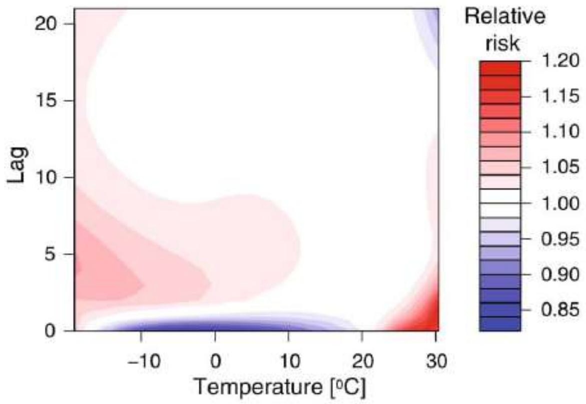


Fig. 2 Plot of the exposure-lag-response relationship between temperature and all-cause mortality, with reference at 21 °C. The effects of heat are observed on the same day or after 1–3 days, whereas the effects of cold were distributed across few days of exposure

exposure to moderate temperatures. As shown in Fig. 3, the highest relative risk was observed for a small proportion of extremely cold days, whereas the estimated effect of the days with moderate temperatures, corresponding to the smooth response, was also noticeable.

Upon estimating the effects of temperature on mortality, we proceeded to examine the effects of air pollutants. The strong positive correlations between PM_{10}, SO_2 and soot (Table 1) suggest that these species share the same origin, and thus, the effects of some pollutants may distort the observable patterns of others.

Given that the extreme cold events and increased levels of pollutants often coincide, it is necessary to understand the combined effects of these two factors on mortality. We have developed our modeling strategy relying on the following logical sequence:

1. Increased concentrations of air pollutants (at least within their normal range of concentrations) require a certain amount of time to reach their cumulative effect on mortality, the time being not less than 24 h, and thus, daily average is the level of

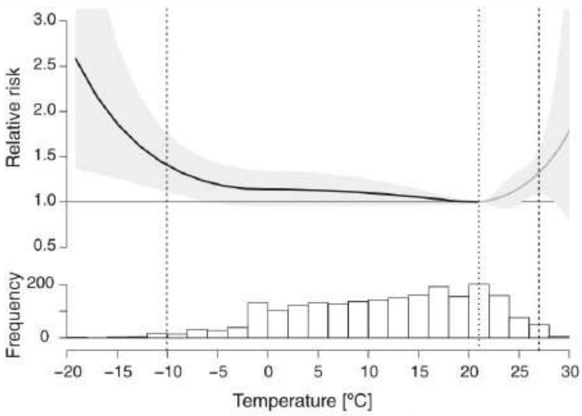


Fig. 3 Overall cumulative exposure-response curve and temperature distribution in Belgrade 2009–2014. Dotted and dashed lines represent optimum and extreme temperatures, respectively

Table 1 Pollutant correlations for the entire period, and for cold and warm season

	PM_{10}	NO_2	SO_2	Soot	PM_{10}	NO_2	SO_2	Soot
PM_{10}	1				1	0.34	0.43	0.27
NO_2	0.50	1			0.64	1	0.40	0.20
SO_2	0.67	0.36	1		0.65	0.44	1	0.23
Soot	0.66	0.44	0.56	1	0.74	0.58	0.54	1

Pollutant correlations for the entire period (left), and for cold and warm season (right, lower and upper triangular, respectively)

aggregation of the measurement data used in this and numerous other studies. This cumulative effect is expected to be more stable, and thus, statistically robust in comparison to short-term lag-specific effects (referring to lags of up to 7 days).

2. Up to the n^{th} period (day), the longer the high values of pollutants persist, the greater the cumulative effect on mortality. As the cumulative effect on mortality reaches its peak (period n), it largely depletes the pool of those susceptible in the observed population, as their death is being brought forward by a matter of a few days.
3. Owing to the aforementioned harvesting effect, the cumulative primary effect of the pollutant starts to decrease afterward, reaching its minimum value on day n1.

Based on these suppositions, two variables were used to describe the temporal distribution of the cumulative effect of each pollutant. The first variable represented the average pollutant concentrations during the specific timeframe at the end of which (day n) the primary effect of the pollutant on mortality reaches its local maximum. The second variable is defined to capture the temporal positioning of the minimum rate of mortality (day n1) attributable to the post-harvesting reduction in death rates. Accordingly, the cumulative effects of each pollutant are included as two simple moving averages (*SMA*) of its observed concentrations in 10 μg m^{-3} (*P*) over *n* consecutive days, ending on-and inclusive of-day *t*.

$$SMA(P)_{t,n} = \frac{1}{n}\sum_{i=1}^{n} P_{(t-i)+1}$$

Rather than assume any particular temporal distribution of the effect, as is typically done in the literature, we visually inspected the values of regression coefficient estimates that relate SMA concentrations of each of the four air pollutants to mortality rates within a reasonable timeframe of 60 days, seeking for "peak and trough" temporal patterns that can be attributed to the corresponding harvesting effects of the specific pollutant. The temporal pattern was expected to look as follows: the relative risk should start off at a value close to 1 and stay relatively close to 1 for short time periods (no major effect is expected within the first few days), then steadily increase to a finite value within a reasonable timeframe, and lastly, display a steady decline to a value below 1, with the decline roughly matching the timing and magnitude of the preceding increase. The duration period of the effect depends on the specific system characteristics, such as population susceptibility, pollutant concentrations and their spatio-temporal dynamics.

As certain pattern deviations were expected due to strong correlations (referring to SMA values and not daily observations), we included the pollutants in sequence iteratively, giving priority to those with stronger effects (as estimated by the assessed relative risk) and clearer temporal patterns of these effects. Figure 4 shows the procedure for determining the order of pollutant inclusion in the final model. Lags 0–60 refer to timeframes for which the relative risk was estimated by including one by one timeframe-specific SMA pollutant concentration in the model. As can be seen, once the clear harvesting effect pattern had been identified and attributed to a specific pollutant, the pollutant was added to the final model, and the estimation of the relative risk was repeated for the remaining pollutants.

As can be seen, the effects of pollutants were relatively stable between iterations due to the fact that SMA were used instead of lag values. The final model is specified as follows:

$$\begin{aligned} E(Y_t) = \exp\{ & \alpha + \beta T_{t,l} + NS(time, df) + \lambda DOW_t \\ & + \gamma_1 SMA(SO_2)_{t,19} + \gamma_2 SMA(SO_2)_{t,47}) \\ & + \gamma_3 SMA(\text{Soot})_{t,28} + \gamma_4 SMA(\text{Soot})_{t,51} \\ & + \gamma_5 SMA(NO_2)_{t,53} + \gamma_6 SMA(NO_2)_{t,21} \\ & + \gamma_7 SMA(PM_{10})_{t,3} + \gamma_8 SMA(PM_{10})_{t,10}\} \end{aligned}$$

The detailed model estimates are presented in Additional file 4, in the columns labeled "Saturated model".

The risk of excess death with short-term exposure to elevated concentrations of PM_{10} was observed, whereas for SO_2 and soot, the marked effects were found within 2–3 weeks of exposure. A 10 μg m^{-3} increase in PM_{10} concentrations is followed by a negligible increase in mortality (0.04 %), whereas a moderate increase in death rates in the range from 0.7 to 1.3 % was associated with the same increment in NO_2, SO_2 and soot concentrations. Comparable short-term health effects of exposure to PM were also reported in the extensive review of Brook et al. [19]. They concluded that the elevated $PM_{2.5}$ concentrations over 5 days lead to the increase in circulatory mortality risk by 0.4 % to 1.0 %. Thereby, it is important to mention that the health effects of $PM_{2.5}$ are more severe compared to PM_{10}, because the particles of smaller diameter penetrate deeper in the respiratory

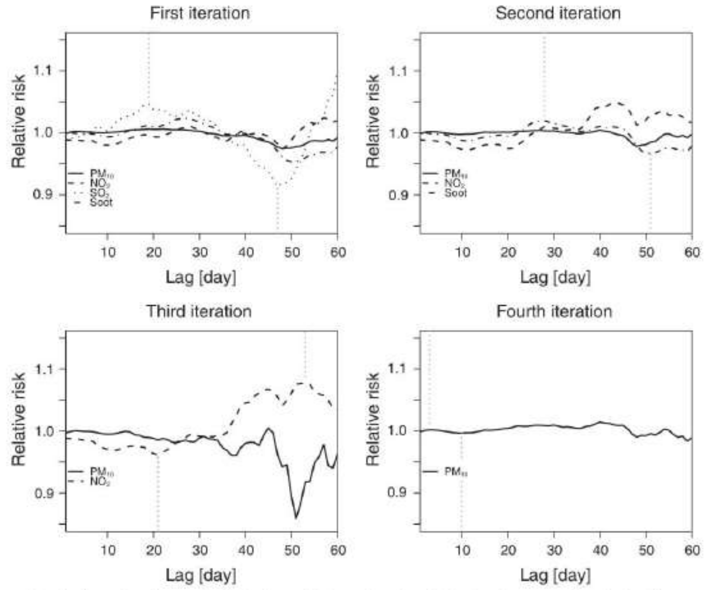


Fig. 4 The procedure for including air pollutants in the final model. The estimation of the timeframe-specific relative risk was repeated each time after exclusion of the pollutant with the most clear harvesting effect pattern. Dotted lines refer to timeframes that are associated with highest positive or negative relative risk

tract. The air pollution-related mortality estimates also comply with the findings of other extensive studies [20, 21], reporting moderate increases in mortality associated with the exposure to PM, SO_2 and NO_2. As can be seen in Fig. 4, the effect pattern was inverted in the case of NO_2, which could indicate that the exposure to high NO_2 levels reaches their maximum effect (day n) beyond the examined time period. This complies with the results of our previous study [13], aimed at investigating the association between short- and medium-term (up to 90 days) exposure to nitrogen dioxide (NO_2) and mortality within the several timeframes. As shown, the short-term exposure to NO_2 exhibited negative associations with death rates, whereas the medium-term exposure to NO_2 was associated with significant increase in mortality.

Furthermore, it could be assumed that the effects attributed to NO_2 exposure are not realistic, but rather a result of omitted variable bias, which is even more likely taking into account its considerable relative importance (Fig. 6), which was highest of all species. Likewise, Brook et al. [22] reported surprisingly strong relationship between NO_2 and non-accidental mortality across 10 cities in Canada. They assumed that NO_2 concentrations were acting as an indicator of some other variable or process, because NO_2 levels exhibit high correlations in time and space with a range of toxic traffic-related species, including volatile organic compounds and polycyclic aromatic hydrocarbons, which could also contribute to the observed effects.

In Fig. 5, the overall effects of temperature on mortality before and after accounting for air pollutant concentrations are compared.

After accounting for the effects of air pollutants, estimates of backward attributable risk of non-optimal temperature decreased from 8.80 % (5,009 people) to 3.00 % (1,706 people) (for detailed information on calculation of attributable risk see [23]). More specifically, the base model results showed that the exposure to cold temperatures was associated with significantly higher risk (7.35 %), compared to hot days (1.50 %). However, after adjusting for air pollutants, the relative risk associated with cold temperatures was lowered to 1.06 %, whereas the risk of heat-related mortality slightly increased to 1.96 %. When adopting a backward perspective, the risks are simultaneously computed for the same time t, and thus, negligible difference ($b\text{–}AF^{r_1+r_2}_{x,t} \leq b\text{–}A^{r_1}_{x,t} + b\text{–}A^{r_2}_{x,t}$) could be observed between the sum of components (1.06 % and 1.96 %) and the overall attributable risk (3.00 %) [23]. It is also worth noting that after including air pollutants in the model, the optimum temperature range was relatively broad, from −5 to 21 °C,

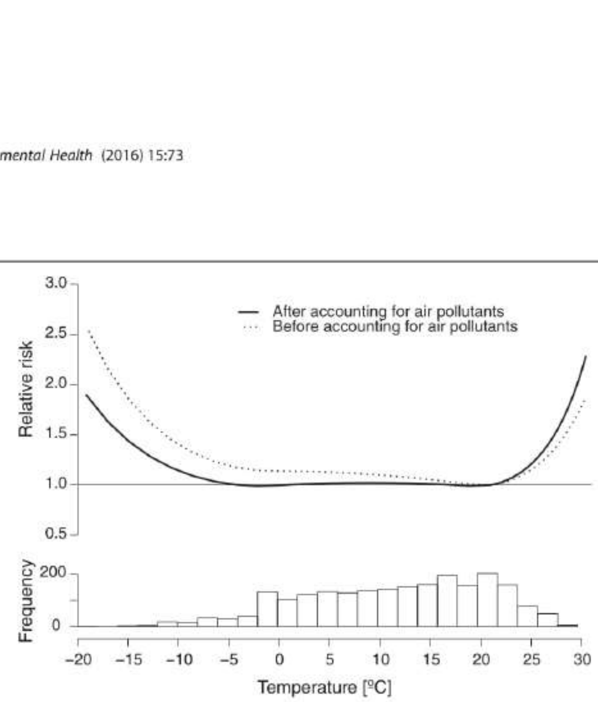


Fig. 5 Overall cumulative exposure-response curve after accounting for the effects of air pollution and temperature distribution. After adjusting for air pollution, the optimum temperature range was relatively broad

which differs from previous findings that most of related deaths were caused by moderate temperatures [9]. Correspondingly, the relative contributions of extreme temperature events have also changed (Table 2).

Anderson and Bell [24] showed that the temperature-related mortality risk was slightly lowered (approx. 0.4 % on average) after controlling for the effects of O_3 and PM_{10}. As shown in Additional file 5, the change in mortality risk after accounting for the short-term lag-effects of air pollutants was negligible. However, after accounting for the cumulative effects of air pollutants, as proposed herein, the significant change in estimated risk was observed.

As part of a supplementary analysis, and with the aim of arriving at a more parsimonious model specification, we performed optimization with respect to information criteria, and investigated whether a model with a double-threshold parameterization can be used as a reasonable approximation to the saturated model. Firstly, we examined whether some of the model terms could be left out without substantial loss to the model fit. In order to gauge the relative quality of the model in terms of the goodness-of-fit/complexity trade-off, we used a quasi-likelihood (we used the C-hat [the dispersion parameter] value obtained from the saturated model, which is 1.06) counterpart of Akaike's information criterion (QAICc), specifically its implementation available in the GLMULTI package in R [25]. An exhaustive screening, which included each of the 2,048 (2^{11}) possible models for the specified set of variables, showed that the best model, in terms of the information criteria, is the following:

$$E(Y_t) = \exp\{\alpha + \beta T_{t,l} + NS(time,\ df) + \gamma_1 SMA(SO_2)_{t,19} + \gamma_2 SMA(SO_2)_{t,47} + \gamma_3 SMA(Soot)_{t,28} + \gamma_4 SMA(Soot)_{t,51} + \gamma_5 SMA(NO_2)_{t,53} + \gamma_6 SMA(NO_2)_{t,21}\}$$

Detailed model estimates are presented in Additional file 4, "Optimal model" columns.

The screening process also enabled an insight into the estimated importance of each of the variables. The estimated importance was calculated as the sum of the relative evidence weights of all models in which the term appears. Relative evidence weights are computed as exp(ΔIC/2), where ΔIC is the difference in IC between a model and the best model, and they are normalized so that they sum up to one. They can be interpreted as probabilities for each model to be the best in the set. Given the fact that PM_{10} concentrations have the smallest estimated relative importance of all examined species (Fig. 6), including only PM_{10} in the form of a 0–1 lag variable, as performed in research [26] is clearly not

Table 2 Relative risk for the 1 and 99th percentile of the observed temperature distribution (95 % CI)

Temperature	Before accounting for the effects of air pollutants	After accounting for the effects of air pollutants
−10.0 °C	1.40 (1.12, 1.76)	1.14 (0.86, 1.51)
27.0 °C	1.32 (1.10, 1.60)	1.45 (1.20, 1.76)

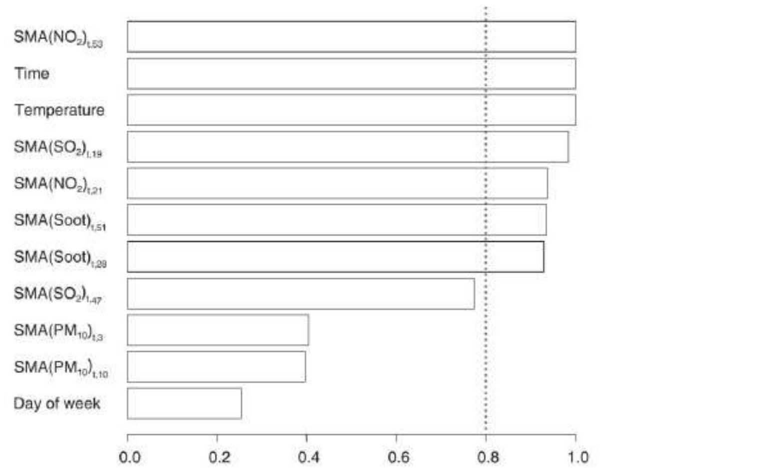


Fig. 6 Model-averaged relevance of terms. Dotted line represents threshold importance

the most effective way to control for the effects of air pollution.

Since the saturated model indicates the existence of an optimum temperature range, it is valuable to know whether a model with the double-threshold parameterization (with −5 to 21 °C being the thresholds) could be used as a simple approximation to it, without significant loss to the model fit. The analysis showed, however, that the loss in the model fit, from 0.2832 for saturated to 0.2574 for double-threshold model as measured by correlation between the predicted and the observed values (pseudo R squared), was not compensated for in terms of information criteria—QAICc increased from 12518.25 to 12553.38. Visual inspection indicated that the linear components of the double-threshold model are incapable of accurately describing the progressive nature of the effects of extreme temperatures.

In comparison to the herein proposed SMA method, DLNM framework is technically more sophisticated and more appropriate for the exploration of the particular lag-specific and exposure-level-specific pollutant effects. It is also superior when long-time series are available. However, given that DLNM framework does not employ the concept of a stable cumulative effects between pollution and mortality, but rather tries to describe the entire exposure-lag-response association, it is demanding regarding the number of parameters that need to be estimated. For instance, using DLNM for describing the effect of temperature on mortality would involve estimating a total of $5 \times 5 = 25$ parameters.[1] Furthermore, describing the effects of four air pollutants would require an additional 100 parameters on top of the 80 parameters already included in the model (25 parameters are estimated for describing the effect of temperature, 8×6 years = 48 parameters for capturing seasonal and long-term trend, 6 parameters for day of the week, and 1 overall intercept). Conversely, the herein proposed procedure requires $8 + 8 = 16$ parameters.

Furthermore, the herein proposed SMA method is the most parsimonious method that is consistent with the assumption that significant cumulative, medium-term effects of air pollutant levels on mortality exist. If this assumption is valid, which has been confirmed by previous studies, then it suffices to include only two properly selected SMA terms for each pollutant that captures the majority of their respective effects. The choice of SMA lags describes the temporal positioning of the cumulative effect's peak, while the regression estimates of the two corresponding regression coefficients describe the magnitude of the effect for each particular air pollutant. Hence, in the case of short-time series, when air pollutants are included into the research model solely to account for their effect on mortality, the SMA approach may be comparatively more efficient than DLNM.

The results of using the DLNM to model the effects of four pollutants are presented in Additional file 6. As can be seen, the observed shapes of the effects confirm the central hypothesis of our study, which is that, besides the well-evidenced short-term effects of air pollution on mortality (most visible in the case of soot), significant cumulative (perhaps even seasonal) medium-term effects of air pollutant levels on mortality (most visibly in the case of SO_2) are observed. The harvesting effect pattern is also clearly visible in both short- and medium-term effects. In Additional file 7, temperature-related mortality risk is presented, after accounting for air pollutants using SMA and DLNM.

Some general limitations of retrospective epidemiological studies aimed at health risk estimation are also applicable to this study. By analyzing the effects of air pollution and temperature, the results obtained from a number of central monitoring stations are assumed to be representative of individual exposure, although people have different activity patterns and spend a significant period of time indoors. Furthermore, certain species are selected as indicators of air pollution, although pollution refers to a complex mixture of gaseous species and particles that permanently interact and undergo physicochemical transformations [27]. However, regardless of the potential limitations, the results of retrospective epidemiological studies based on large-sample statistics remain an important source of information for designing environmental regulations [28]. The advantage of the herein proposed method is that it includes the cumulative mid-term effects of air pollution in the traditional Poisson regression model in a parsimonious way, which complies with the nature of their impact. The limitation of the proposed method is possible overfitting due to the limited number of observations, which needs to be eliminated through further studies.

Conclusions

The herein proposed method is based on the theoretical premise that there are significant cumulative mid-term effects of air pollution on mortality, which are more stable, and thus more statistically robust, than the lag-specific effects commonly included in regression models. The proposed method requires the researcher to visually identify a "peak and trough" temporal pattern for the effects of each of the pollutants, which is then included in the model using only two parameters, yielding a rather parsimonious model specification.

The presented results suggest that the inference that cold-attributable mortality currently accounts for one order of magnitude more deaths than mortality associated with heatwaves might not be globally applicable. Accounted for in an appropriate way, the effects of air pollutants explained most of the mortality previously associated with cold temperatures, and a greater temperature-attributable mortality burden was associated with the contribution of heat.

The more realistic estimates of the mortality risk associated with extreme temperature events becomes increasingly important for planning of future public health interventions and adaptation measures, with the global warming impact that is already underway. However, further research is needed to identify all environmental risk factors and clarify their complex associations, which have been largely obscured by the current approach.

Endnotes

[1]We used a quadratic B-spline with three internal knots and no intercept for the exposure-response curve: 3 df for knots + 2 df for the degree of the piecewise polynomial (quadratic) + 0 df for intercept (no intercept) = 5 df, and a natural cubic B-spline with three internal knots and an intercept for the lag-response curve: 3 df for knots + 1 df for intercept + 1 df = 5 df.

Additional files

Additional file 1: Circulatory and respiratory daily death rates segmented by age and gender. (DOCX 71 kb)

Additional file 2: Seasonal variations in circulatory and respiratory daily death rates. (DOCX 154 kb)

Additional file 3: Seasonal variations in pollutant concentrations. (DOCX 129 kb)

Additional file 4: Model estimates. (DOCX 15 kb)

Additional file 5: Temperature-related mortality risk estimates after accounting for the short-term lag-effects of air pollutants and cumulative effects of air pollutants (as proposed herein). (DOCX 158 kb)

Additional file 6: The effects of four pollutants modeled using DLNM framework. (DOCX 662 kb)

Additional file 7: Temperature-related mortality risk, after accounting for air pollutants using SMA and DLNM. (DOCX 188 kb)

Abbreviations

PM_{10}, particles smaller than 10 μm; NO_2, nitrogen dioxide; SO_2, sulfur dioxide; CI, confidence interval

Acknowledgements

The authors would like to express their deepest gratitude to the Institute of Public Health Belgrade for technical support and additional analysis of mortality rates in Belgrade.

Funding

This study was conducted as part of the projects No III43007 and No III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011–2016.

Availability of data and materials

Raw data will not be shared because the authors are not authorized for distribution of data.

Authors' contributions

SSS and AS conceived the study design. The analysis was conducted by NS. The paper was jointly written by SSS, AS and NS. All authors approved the final draft.

Competing interests

The authors declare that they have no competing interests.

Consent for publication

Not applicable.

Ethics approval and consent to participate

Not applicable.

Author details
[1]Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia. [2]Singidunum University, Danijelova 32, 11010 Belgrade, Serbia. [3]Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia.

Received: 22 February 2016 Accepted: 30 June 2016
Published online: 11 July 2016

References

1. Stieb DM, Judek S, Burnett RT. Meta-analysis of time-series studies of air pollution and mortality: effects of gases and particles and the influence of cause of death, age, and season. J Air Waste Manage Assoc. 2002;52:470–84.
2. Analitis A, Michelozzi P, D'Ippoliti D, de Donato F, Menne B, Matthies F, Atkinson RW, Iñiguez C, Basagaña X, Schneider A, Lefranc A. Effects of heat waves on mortality: effect modification and confounding by air pollutants. Epidemiology. 2014;25:15–22.
3. Pattenden S, Armstrong B, Milojevic A, Heal MR, Chalabi Z, Doherty R, Barratt B, Sari Kovats R, Wilkinson P. Ozone, heat and mortality: acute effects in 15 British conurbations. Occup Environ Med. 2010;67:699–707.
4. Burkart K, Canário P, Breitner S, Schneider A, Scherber K, Andrade H, Alcoforado MJ, Endlicher W. Interactive short-term effects of equivalent temperature and air pollution on human mortality in Berlin and Lisbon. Environ Pollut. 2013;183:54–63.
5. Hoek G, Krishnan RM, Beelen R, Peters A, Ostro B, Brunekreef B, Kaufman JD. Long-term air pollution exposure and cardio-respiratory mortality: a review. Environ Health. 2013;12:43–59.
6. Ye X, Wolff R, Yu W, Vaneckova P, Pan X, Tong S. Ambient temperature and morbidity: a review of epidemiological evidence. Environ Health Persp. 2012;120:19–28.
7. Gasparrini A. Distributed lag linear and non-linear models in R: the package dlnm. J Stat Softw. 2011;43:1–20.
8. Pinheiro SDLLD, Saldiva PHN, Schwartz J, Zanobetti A. Isolated and synergistic effe17cts of PM_{10} and average temperature on cardiovascular and respiratory mortality. Rev Saude Publ. 2014;48:881–8.
9. Gasparrini A, Guo Y, Hashizume M, Lavigne E, Zanobetti A, Schwartz J, Tobias A, Tong S, Rocklöv J, Forsberg B, Leone M, De Sario M, Bell ML, Guo Y-LL, Wu C-f, Kan H, Yi S-M, Coelho M de SZS, Saldiva PHN, Honda Y, Kim H, Armstrong B. Mortality risk attributable to high and low ambient temperature: a multicountry observational study. Lancet. 2015;386:369–75.
10. Dear K, Wang Z. Climate and health: mortality attributable to heat and cold. Lancet. 2015;386:320–2.
11. Goldberg MS, Burnett RT, Valois M-F, Flegel K, Bailar III JC, Brook J, Vincent R, Radon K. Associations between ambient air pollution and daily mortality among persons with congestive heart failure. Environ Res. 2003;91:8–20.
12. Stojić A, Stojić SS, Reljin I, Čabarkapa M, Šoštarić A, Perišić M, Mijić Z . Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. Environ Sci Pollut R. 2016;23:10722–32.
13. Stanišić Stojić S, Stanišić N, Stojić A, Šoštarić A. Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. J Toxicol Env Heal A. 2015; doi: 10.1080/15287394.2015.1101407
14. Statistical Office of the Republic of Serbia. Vital statistics - the additionally processed mortality data. 2015.
15. World Health Organization, Regional Office for Europe. Detailed Mortality Database. 2015. http://data.euro.who.int/dmdb/ Accessed 27 July 2015.
16. Gasparrini A, Armstrong B, Kenward MG. Distributed lag non-linear models. Stat Med. 2010;29:2224–34.
17. R Core Team. R. A language and environment for statistical computing. Vienna: R Foundation for Statistical Computing; 2014. http://www.r-project.org. Accessed 28 Dec 2015.
18. Breitner S, Wolf K, Devlin RB, Diaz-Sanchez D, Peters A, Schneider A. Short-term effects of air temperature on mortality and effect modification by air pollution in three cities of Bavaria, Germany: a time-series analysis. Sci Tot Environ. 2014;485:49–61.
19. Brook RD, Rajagopalan S, Pope CA, Brook JR, Bhatnagar A, Diez-Roux AV, Holguin F, Hong Y, Luepker RV, Mittleman MA, Peters A. Particulate matter air pollution and cardiovascular disease an update to the scientific statement from the American Heart Association. Circulation. 2010;121:2331–78.
20. Goldberg MS, Burnett RT, Stieb DM, Brophy JM, Daskalopoulou SS, Valois MF, Brook JR. Associations between ambient air pollution and daily mortality among elderly persons in Montreal, Quebec. Sci Tot Environ. 2013; 463:931–42.
21. Shah AS, Langrish JP, Nair H, McAllister DA, Hunter AL, Donaldson K, Newby DE, Mills NL. Global association of air pollution and heart failure: a systematic review and meta-analysis. Lancet. 2013;382:1039–48.
22. Brook JR, Burnett RT, Dann TF, Cakmak S, Goldberg MS, Fan X, Wheeler AJ. Further interpretation of the acute effect of nitrogen dioxide observed in Canadian time-series studies. J Expo Sci Environ Epidemiol. 2007;17:S36–44.
23. Gasparrini A, Leone M. Attributable risk from distributed lag models. BMC Med Res Methodol. 2014;14:55–63.
24. Anderson BG, Bell ML. Weather-related mortality: how heat, cold, and heat waves affect mortality in the United States. Epidemiology. 2009;20:205–13.
25. Calcagno V, de Mazancourt C. glmulti: an R package for easy automated model selection with (generalized) linear models. J Stat Softw. 2010;34:1–29.
26. Lin YK, Ho TJ, Wang YC. Mortality risk associated with temperature and prolonged temperature extremes in elderly populations in Taiwan. Environ Res. 2011;111:1156–63.
27. Brauer M, Amann M, Burnett RT, Cohen A, Dentener F, Ezzati M, Henderson SB, Krzyzanowski M, Martin RV, Van Dingenen R, van Donkelaar A. Exposure assessment for estimation of the global burden of disease attributable to outdoor air pollution. Environ Sci Technol. 2012;46:652–60.
28. Solomon PA, Costantini M, Grahame TJ, Gerlofs-Nijland ME, Cassee FR, Russell AG, Brook JR, Hopke PK, Hidy G, Phalen RF, Saldiva P, Sarnet SE, Balmes JR, Tager IB, Özkaynak H, Vedal S, Wierman SSG, Costa DL. Air Qual Atmos Health. 2012;5:9–62.

Chemosphere 144 (2016) 721–727

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Quantification and mechanisms of BTEX distribution between aqueous and gaseous phase in a dynamic system

A. Šoštarić [a,*], A. Stojić [b], S. Stanišić Stojić [c], I. Gržetić [d]

[a] Institute of Public Health Belgrade, Bulevar Despota Stefana 54, 11000 Belgrade, Serbia
[b] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia
[c] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia
[d] Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

HIGHLIGHTS

- On-line analytical system for studying pollutant phase distribution.
- Determination of quantitative characteristics of BTEX air–water distribution.
- Analysis of mechanisms influencing BTEX partition equilibrium.
- The significance of interfacial adsorption and van der Waals interactions.

ARTICLE INFO

Article history:
Received 2 February 2015
Received in revised form
26 June 2015
Accepted 10 September 2015
Available online xxx

Keywords:
BTEX
Distribution coefficient
Partitioning mechanisms
PTR-MS

ABSTRACT

In this study an analytical system was developed for determination of quantitative characteristics of BTEX distribution between gaseous and aqueous phase. Dynamic dilution system was coupled with Proton Transfer Reaction Mass Spectrometer (PTR-MS) to provide conditions for partitioning between the two phases resembling the interactions during rainfall. The amount of the target species retained in water were significantly higher than suggested by theoretical predictions indicating that dissolution is not the major mechanism of gaseous BTEX uptake in aqueous phase. Distribution coefficients and enrichment factors were calculated, and the possible mechanisms of partitioning were considered. As concluded, the interfacial adsorption and van der Waals interactions play significant role, whereas hydrogen-bond interactions have no major contribution to BTEX partitioning.

1. Introduction

Volatile organic compounds (VOC) are considered to be one of the key problems affecting many urban areas, given the fact that they have detrimental impact on human health and environment (Stojić et al., 2015). These species play an important role in atmospheric chemistry resulting in the formation of tropospheric ozone and increase of the atmospheric oxidizing capacity (Andrés-Hernández et al., 2013; Yin et al., 2015). Related to this, the health risk is associated with short- and long-term exposure to both VOC and their products formed through photochemical reactions, and according to the epidemiological reports, the consequences range from eye, skin, and respiratory tract irritations to serious disorders of immune system and vital organs (Lerner et al., 2014; Shekarrizfard et al., 2015). Apart from adverse effects on human health, under favorable meteorological conditions, VOC are involved in formation of secondary aerosol particles which, together with ozone (Hildebrandt et al., 2014), contribute to the global greenhouse effect and climate change (Chang et al., 2014; Bornman et al., 2015). On a global scale, VOC are omnipresent in the lower atmosphere mainly due to biogenic emissions, but in densely populated cities, dominant contributions of anthropogenic sources such as intense transportation, industrial and commercial activities, to elevated pollutant concentrations are evidenced (Pan et al., 2015).

The most abundant VOC group, commonly known as BTEX, comprises benzene and its alkyl derivates – toluene, ethylbenzene, and xylenes, which are often used as indicators of man-made pollution in urban areas (Marć et al., 2015). Besides being present in vehicle exhaust and emissions from coal and oil burning and

* Corresponding author.
E-mail address: andrej.sostaric@zdravlje.org.rs (A. Šoštarić).

http://dx.doi.org/10.1016/j.chemosphere.2015.09.042
0045-6535/© 2015 Elsevier Ltd. All rights reserved.

petrochemical plants, BTEX sources include production of plastics, resins, rubber, lubricants, adhesives, coatings, paints, detergents, drugs *etc*. However, many of their industrial applications have been limited due to the fact that International Agency for Research on Cancer (IARC, 2014) classified benzene as group 1, ethylbenzene as group 2B and toluene and xylenes as group 3 carcinogens.

The complex spatial and temporal variations of BTEX are strongly dependent on their physico-chemical properties, source characteristics, and environmental conditions (Civan et al., 2015). Processes affecting distribution of BTEX between the major environmental compartments include mixing, dilution, precipitation scavenging, wet and dry deposition, re-suspension, and photochemical reactions (Liu et al., 2015; Lebedev et al., 2015). The BTEX reactions with hydroxyl ($OH^•$) radicals, nitrate ($NO_3^•$) radicals and ozone (O_3) have been thoroughly studied, and the one with hydroxyl radicals are considered to be the most important removal process (Slominska et al., 2014; Waring and Wells, 2015). Unlike photochemical removal, phase distributions of pollutants in environmental media and wet deposition is given little attention, although it presents the way of transferring BTEX to terrestrial and aquatic systems, and has major impact on the long-range transport (Balla et al., 2014; Fernandes et al., 2014; Meckenstock et al., 2015). Various formations of atmospheric water represent an important compartment for pollutant storage and reactions (Starokozhev et al., 2009) and according to the previous studies, the BTEX concentrations in rain (Okochi et al., 2004; Mahbub et al., 2012; Mullaugh et al., 2015), fog (Valsaraj et al., 1993; Goss, 1994), dew (Okochi et al., 2005), and snow (Wania et al., 1999; Roth et al., 2004; Fries et al., 2008) are considerably higher than those predicted by the Henry's law.

The aim of this study was to empirically determine distribution coefficient (D_{OBS}) for BTEX in air–water dynamic system designed to simulate the interactions between the two phases during rainfall. The mechanisms which influence BTEX partition equilibrium and their complex environmental fate are also considered and the most feasible explanation is provided. For this purpose, dynamic dilution system (DDS) was coupled with Proton Transfer Reaction Mass Spectrometer (PTR-MS), a tool for real-time measurements of VOC with high sensitivity, fast time response, and low detection limit.

2. Methodology

2.1. Experimental setup

The experimental setup is shown in Fig. 1. Gas mixtures were generated simultaneously from VOC-free air (CH free, Messer Group GmbH) and BTEX 5 ppmV calibration referent gas (BTEX in nitrogen, Messer Group GmbH) by the use of DDS (HORIBA ASGU 370-P), containing parallel channels with mass flow controllers. The output flow of 1 L min^{-1} enabled continuous overflow of more

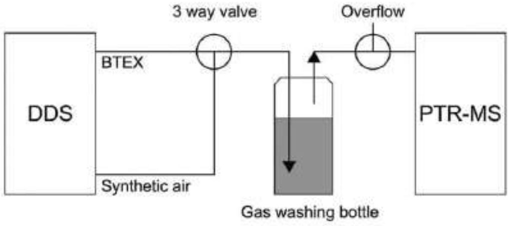


Fig. 1. Experimental setup: Dynamic Dilution System (DDS) and Proton Transfer Reaction Mass Spectrometer (PTR-MS).

than 800 mL min^{-1} at the ending aperture of the T-piece (at ambient pressure) facing the PTR-MS inlet.

The experiment included three stages. In the first stage, VOC-free air was bubbled through gas-washing bottle (GWB) filled with 18 MΩ ultrapure water (ELGA PURELAB maxima system) until any VOC content possibly present in GWB was removed. In the second, insufflation stage, the BTEX mixtures of known mixing ratios were introduced in GWB until the PTR-MS detector signal reached the plateau and the dynamic equilibrium was established. During the third, exsufflation stage, the introduction of VOC-free air induced the gradual decrease in PTR-MS signal, until BTEX were completely removed. The detection response time for all three stages with empty GWB was also determined and taken into account in further calculations. The experiment was performed with 250 and 500 mL water volumes poured in the GWBs of the same height but different diameter so that the differences in the path of the gas through the water would be minimized. The measurements were repeated 3 times per each volume/gas mixing ratio setting (constant air and water temperature of 25 °C was maintained), and the variation coefficients lower than 2% confirmed good reproducibility.

The PTR-MS used in this study is commercially available (Standard PTR-quad-MS, IONICON Analytik GmbH, Innsbruck, Austria) (Lindinger and Jordan, 1998) and only a brief description of the method will be presented here. The gas sample is introduced through a drift-tube reactor where compounds with a proton affinity higher than that of water (166.5 kcal mol^{-1}) are ionized through proton transfer reactions with H_3O^+ ions. The product ions are selected according to their mass-to-charge ratios (m/z) using a quadrupole mass spectrometer, and detected as count rates by a secondary electron multiplier. Due to this, the method is subjected to isobaric and isomeric interferences, although the results clearly indicate that certain species such as methanol, acetonitrile, acetaldehyde, benzene and toluene are free from interferences with other compounds (de Gouw et al., 2003). As PTR-MS cannot differentiate between the isobaric species, signal detected at m/z 107 refers to four compounds with the following contributions: ethylbenzene-26%, m-xylene-25.2%, p-xylene-25.3%, o-xylene-23.5%. These compounds were observed as a single specie and abbreviated as EX.

BTEX related masses and seven control parameters (m/z 21, 25, 30, 32, 37, 55, and 73) data were obtained in 1.88 s cycles (200 ms dwell time). PTR-MS was operated at 2.11 mbar, 600 V, and 60 °C drift tube conditions, producing an E_0/N ratio of 145 Td, where E_0 is electric field strength and N gas number density, providing the reaction time of 90 μs. The count rate of $H_3O^+H_2O$ was in the range from 5.3 to 7.2% of the $8.2 \cdot 10^6$ cps count rate of primary H_3O^+ ions.

Calibration of the analytical system was done by plotting average PTR-MS signal recorded at the end of the insufflation stage against gas mixing ratio levels produced by DDS. Linear fits were obtained for both tested volumes of water with the correlation coefficient (R^2) greater than 0.99.

2.2. Data processing

The obtained PTR-MS signal was subjected to baseline fitting and, depending on the stage, the time interval required for equilibrium level to be achieved is taken for insufflation (t_i), or exsufflation time (t_e). For each insufflation cycle, the quantity of target compounds retained from gaseous phase (Q_i^V (ppbV)) is calculated as the integral of the area between the obtained PTR-MS signal and equilibrium level achieved for t_i. Time required for the target compounds to be completely purged out from the aqueous phase (t_{qe}) is also determined, so that the quantity of target compounds during exsufflation stage could be calculated.

The baseline was determined using the following algorithms: an iterative algorithm using suppression of baseline by means in local windows implemented in the function baseline.fillPeaks, implementation and extension of Mark S. Friedrichs' model-free algorithm implemented in the function baseline.medianWindow (Friedrichs, 1995), and Wrapper for algorithm based on LOWESS and weighted regression baseline.rfbaseline (Ruckstuhl et al., 2001) of Baseline package (Kneen and Annegarn, 1996) of the statistical software environment R (Team, 2012). For a wide range of function parameters, the best fitting baseline for each insufflation/exsufflation cycle was determined using Mean bias error (MBE), Root Mean Square Error (RMSE), Index of Agreement (IOA) and Chi-square statistical tests. In order to quantitatively describe behavior of the investigated species, the mean value of the output of all three baseline functions was used for further calculations in order not to give preference to any of them.

3. Results and discussion

The parameters (t_i, t_e, t_{qe}, Q_i^V) calculated on the basis of statistical tests showed negligible difference between each other (Fig. 2) with the exception of those calculated on the basis of MBE which were not considered for further analysis.

As shown in Fig. 3, BTEX concentrations in aqueous phase exhibit linear dependence ($R^2 = 1$) with their gas mixing ratios which is consistent with Henry's law. Linear dependence enables us to calculate the quantity of species retained in aqueous phase for the levels of gas mixing ratios that were not subject to the experiment but are included in tested range.

The Q_i^V values were calculated for both tested volumes of water and presented in Table 1, together with their ratio. As can be seen, the ratio of BTEX uptake in 250 and 500 mL water volumes (Q_i^{500}/Q_i^{250}) amounted to 1.8 for all examined species and gas mixing ratios, excepting for lowest and highest levels of toluene, where the ratios were 1.7 and 1.9, respectively. All calculated values are lower than 2, which is the value predicted by Henry's law, and the possible reason will be addressed later in the text. The aqueous concentrations were calculated as follows: Q_i^V values for tested species were multiplied by the conversion factor (3.25 for B, 3.83 for T, and 4.41 for EX), converted to gaseous (μg m^{-3} *i.e.* ng L^{-1}) and then to aqueous concentrations (ng L^{-1} *i.e.* nM).

It has been shown that the regression coefficient of the sum of PTR-MS signals for exsufflation and insufflation phase is close to 0, which indicates that BTEX molecules are retained at the same rate at which they are eliminated.

The environmental fate of BTEX is highly dependent on the air–water equilibrium partition coefficient or Henry's law constant (K_H), defined as a ratio of partial pressure in the gas mixture (p_g) to the concentration in the aqueous solution (c_a) (refers to concentrations of less than 5–50 g L^{-1} for a compound with a molecular weight of 100 g mol^{-1}) (Staudinger and Roberts, 2001; Sarraute et al., 2004):

$$K_H = c_a / p_g \left(\text{M atm}^{-1}\right) \quad (1)$$

Basic BTEX physico-chemical properties which are relevant for the wet scavenging process are summarized in Table 2.

The D_{OBS} were calculated according to Okochi et al. (2004) as the

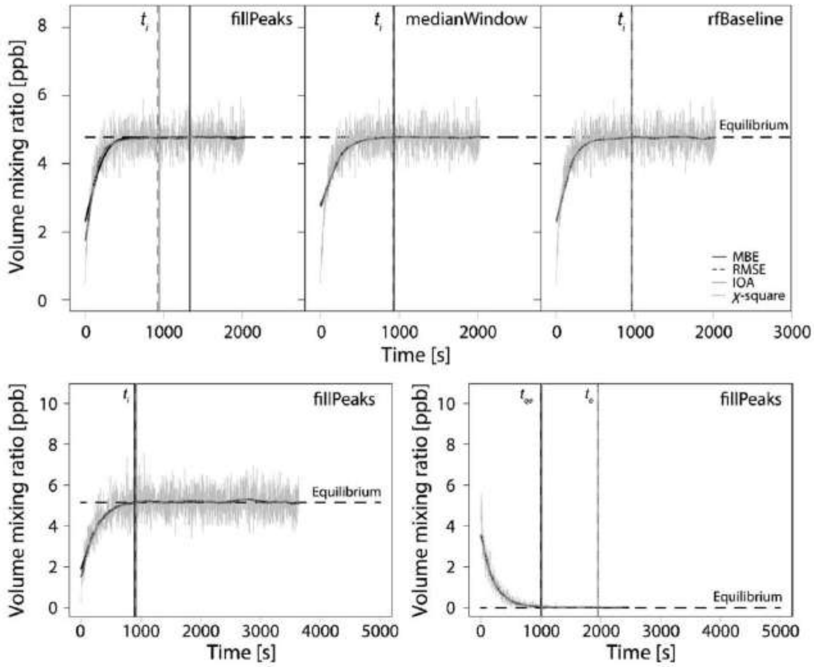


Fig. 2. Baseline functions and calculated parameters for: insufflation for 250 mL (above), and insufflation (left below) and exsufflation (right below) cycle for 500 mL water volume of 5.3 ppbV benzene gas mixing ratio.

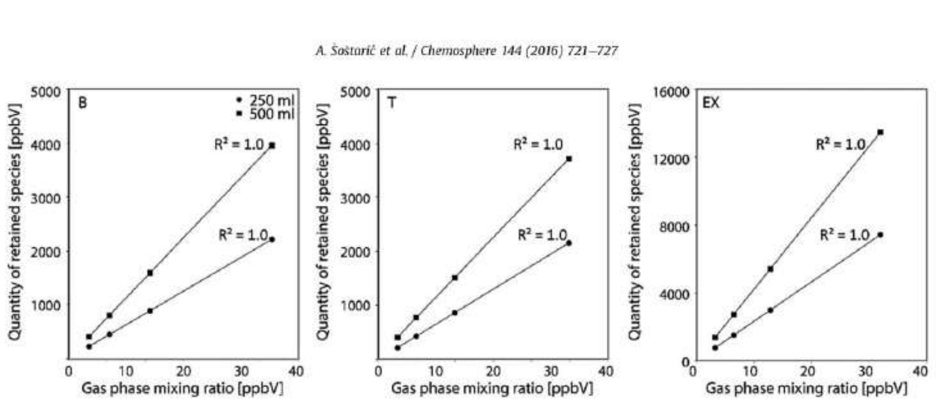


Fig. 3. Quantity of retained species as a function of gas phase mixing ratios for benzene (left), toluene (middle) and ethylbenzene and xylene isomers (right) in 250 and 500 mL.

Table 1
The quantity of uptaken species (Q_i^V) and their concentrations in water (C_i^V) depending on the gas phase mixing ratio (VMR_i) and water volume.

Compound	Level	VMR_i (ppbV)	Q_i^{250} (ppbV)	C_i^{250} (ng L^{-1})	Q_i^{500} (ppbV)	C_i^{500} (ng L^{-1})	Q_i^{500}/Q_i^{250}
B	1	5.3	230	2990	413	2685	1.8
	2	10.6	451	5863	807	5246	1.8
	3	21.2	893	11609	1595	10368	1.8
	4	53.0	2217	28821	3958	25727	1.8
T	1	5.0	215	3294	409	3133	1.9
	2	9.9	430	6588	776	5944	1.8
	3	19.9	861	13191	1510	11567	1.8
	4	49.7	2154	32999	3713	28442	1.7
EX	1	16.0	764	13477	1383	12198	1.8
	2	32.0	1504	26531	2726	24043	1.8
	3	63.9	2986	52673	5413	47743	1.8
	4	159.8	7430	131065	13473	118832	1.8

ratio between aqueous concentrations C_i^V (nM) and gas phase mixing ratios VMR_i (ppbV), and the obtained results, together with the enrichment factor (E) calculated as the ratio of D_{OBS} and K_H (Okochi et al., 2004) are presented in Table 3. For all three investigated species and two tested volumes the following values were calculated for gas mixing ratios of 5, 10, 20 and 50 ppbV: Q_i^V, C_i^V, D_{OBS}, E and the BTEX uptake per 1 L (Q_i^N). Such a calculation was performed so that the behavior under experimental conditions could be comparable for all investigated species at the same gas mixing ratios.

Average values of E (B: 32.0; T: 38.0; EX: 42.6, Table 3) were significantly higher than 1 for all examined species, indicating that their aqueous concentrations are higher than predicted by Henry's law (Table 2). The higher E values might result from the fact that, unlike previous studies designed to use aqueous solutions of organic species (Karl et al., 2003; von Hartungen et al., 2004; Aprea et al., 2007), we introduced BTEX gaseous mixture in water until the equilibrium was established. As can be seen, less soluble species have higher E values (Table 2:W; Table 3:E), which is consistent with the findings of Starokozhev et al. (2009) who examined removal efficiency of organic compounds in snow, with conclusion that efficiency values of some species, including m/p-xylene and o-xylene, were independent from their water solubility and volatility.

In the available literature the following factors for enhanced uptake of VOCs in atmospheric water were considered: surface-active agents induced dissolution into rainwater, influence of the temperature on the K_H, formation of hydrogen bond between VOCs and atmospheric water, and air–water interfacial adsorption.

According to several studies (Dewulf et al., 1995; Feigenbrugela et al., 2004; Allou et al., 2011), K_H of VOCs is highly dependent on several factors such as: temperature, pH, compound hydration, complexity of mixtures, suspended solids, presence of surfactants, and the concentrations of different constituents present in the water such as dissolved salts, organic material and acids. For

Table 2
Physico-chemical properties of BTEX: MW – molecular weight, WS – water solubility at 25 °C, K_H – Henry's law constant at 25 °C (Dewulf et al., 1995), K_{ow} – octanol–water partition coefficient (Soil screening guidance, US EPA), IP-ionization potential (Ionization Potential for Common Industrial Gases), and A_{vdW} – total van der Waals surface area.

Compound	MW (g mol^{-1})	WS (mg L^{-1})	log Kow	KH (M atm^{-1})	IP (eV)	AvdW[b] (Å 2)
Benzene	78	1750	2.13	0.21	9.24	88
Toluene	92	526	2.75	0.18	8.82	104
Ethylbenzene	106	169	3.14	0.15	8.76	116
m-Xylene	106	161	3.20	0.25	8.56	122
p-Xylene	106	185	3.17	0.17	8.46	120
o-Xylene	106	178	3.13	0.16	8.56	119
EX[a]	106	173	3.16	0.18	8.59	119

[a] Values which are presented for the EX are obtained by averaging data for particular compounds that are represented by m/z 107.
[b] Values are available on: http://asd.molfield.org/.

Table 3
The results of air–water partition: the quantity of BTEX retained from gaseous phase (Q_i^V), the quantity uptaken per L (Q_i^N), aqueous concentration (C_i^V), distribution coefficient (D_{OBS}), and enrichment factor (E).

V (mL)	VMR_i (ppbV)	Q_i^V (ppbV)			Q_i^N (ppbV)			C_i^V (ng L^{-1})			C_i^V (nM)			D_{OBS}			E		
		B	T	EX	B	T	EX	B	T	EX	B	T	EX	B	T	EX	B	T	EX
250	5	218	216	254	871	864	1015	2831	3307	4476	36	36	42	7.3	7.2	8.4	34.6	39.9	46.9
	10	426	433	486	1704	1731	1942	5539	6629	8565	71	72	81	7.1	7.2	8.1	33.8	40.0	44.9
	20	843	866	949	3370	3465	3797	10954	13271	16743	140	144	158	7.0	7.2	7.9	33.4	40.1	43.9
	50	2092	2167	2340	8369	8668	9360	27199	33197	41277	349	361	389	7.0	7.2	7.8	33.2	40.1	43.3
500	5	391	411	458	782	822	916	2540	3147	4039	33	34	38	6.5	6.8	7.6	31.0	38.0	42.3
	10	762	780	878	1525	1560	1757	4956	5976	7747	64	65	73	6.4	6.5	7.3	30.3	36.1	40.6
	20	1506	1519	1719	3011	3038	3438	9786	11635	15163	125	126	143	6.3	6.3	7.2	29.9	35.1	39.7
	50	3735	3735	4242	7470	7470	8483	24278	28610	37411	311	311	353	6.2	6.2	7.1	29.6	34.6	39.2
												Average		6.7	6.8	7.7	32.0	38.0	42.6

instance, in natural environment, the partitioning between gaseous and aqueous phase is complicated due to the presence of suspended compounds, chloride, ammonia, and oil in atmospheric water observed as a result of anthropogenic pollutant emissions and the application of a snow-melting agent (Xue et al., 2015). However, the impact of temperature and concentrations of salts and other constituents in water could not be of relevance for enrichment achieved in our experiment, since it was performed at constant temperature of 25 °C using ultra-pure water.

Several studies were focused on VOC distribution between ambient air and rain. Okochi et al. (2004) reported that the VOC dissolution in rainwater according to the effective K_H induced by surfactants present in droplets could contribute to the enrichment since the rainwater in urban location was probably more affected by organic aerosols that allowed for enhanced dissolution of hydrophobic BTEX (Mullaugh et al., 2015). They also emphasized the relationship between the temperature and K_H and consequently the influence of the temperature on the E value. As stated in the study of Staudinger and Roberts (2001) K_H increases by a factor of 1.6 for every 10 °C increase over the ambient range. Sato et al. (2006) reported rainwater VOC concentrations to be higher than the values predicted by Henry's law, due to supersaturation. Field and laboratory experiments in their work suggested that dissolved organic compounds such as humic-like substances originating from ambient air could increase the saturation of rainwater with ambient VOC by reducing the surface tension of droplets.

Valsaraj et al. (1993) examined the enrichment of hydrophobic organic compounds in fog droplets with respect to several factors, and reported that the air–water interfacial area available for adsorption is of utmost significance in explaining the process. In a similar studies, Goss (1994, 2004) discussed the enrichment by surface adsorption but they also took into account formation of hydrogen bond between VOC and atmospheric water, with the conclusion that the adsorption processes which significantly contribute to air/water partitioning are often neglected due to limited understanding of molecular interactions and lack of quantitative data. Roth et al. (2004) encountered hydrogen bonding as a mechanism involved in interactions between VOC and snow crystals. In further text we will discuss the influence of hydrogen bonding and surface adsorption on the E values.

In the formation of hydrogen bond with water molecules BTEX act as a hydrogen-bond acceptors. As Furutaka and Ikawa (2002) explained, the ability of the BTEX to be the hydrogen-bond acceptors is related to their electron release tendency which is represented by the ionization potential (*IP*). Since BTEX *IP* is sorted in the following order: B > T > EX, and negatively correlated with E values (Fig. 4a), it can be assumed that the enhanced uptake of investigated species from gaseous to aqueous phase is not primarily associated with hydrogen bonding.

According to Goss (1994) adsorption on the air–water interface is strong enough to explain the enrichment of organic compounds in fog droplets, whereas Valsaraj et al. (1993) showed that hydrophobicity of the compound plays an important role in determining the degree of enrichment. Furthermore, octanol–water partition coefficient (K_{ow}) as the indicator of the hydrophobicity, is also related with E, and the high correlation between E and $logK_{ow}$ indicates that the mechanism other than dissolution has substantial influence on the enrichment process (Fig. 4b). In compliance with this, Okochi et al. (2004) in their study which focused on the rainwater concentrations of chlorinated hydrocarbons and

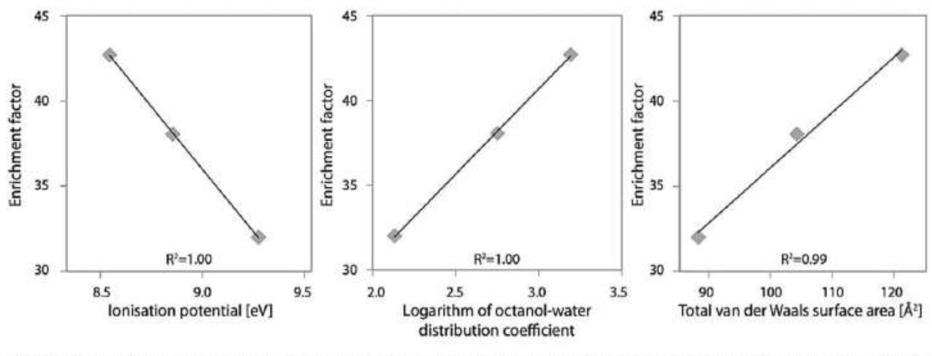


Fig. 4. Correlation between enrichment factor and ionization potential (left), logarithm of octanol–water distribution coefficient (middle), and total van der Waals surface area (right).

monocyclic aromatic hydrocarbons also reported that the enrichment factors for both investigated groups tend to increase with the rise of the K_{ow} value.

According to Roth et al. (2004) the interfacial adsorption is associated with van der Waals interactions while Kelly et al. (2004) predicted adsorption coefficients at air–water interfaces by using total van der Waals surface area (A_{vdW}) of the solute only. Fig. 4c represents the correlation between A_{vdW} and E for the target species. High correlation between E and A_{vdW} indicates that van der Waals interactions are probably the major phenomenon leading to the interfacial adsorption and enhanced BTEX uptake in water. Furthermore, Valsaraj et al. (1993) reported that specific adsorption area plays a significant role in adsorption which explained why raindrops, with smaller specific area, are one to two orders of magnitude less enriched in hydrophobic compounds compared to fog droplets.

Our results showed that the average E values for all tested species (Table 3) were higher for the tests performed with the 250 mL water volume. The length of both GWB was the same, but due to a smaller diameter of 250 mL GWB, the dispersion of gas bubbles was more intense, as was the collisions frequency between gas bubbles and water molecules leading to increased interaction surface between the two phases and consequently to a larger enrichment.

The contribution of dissolution described by the Henry's law implies strong linear correlation between quantities of retained species in aqueous phase and gas mixing ratios of BTEX ($R^2 = 0.99$). Nevertheless, mechanisms other than dissolution are also shown to contribute to the linearity of the relationship.

4. Conclusions

Partitioning of organic contaminants between the gaseous and aqueous phase significantly affects the concentrations, transport, transformations and variability of the investigated pollutants, and therefore the studies aimed at investigating BTEX partition equilibrium provide a solid basis for understanding their environmental fate. Nevertheless, the previously published findings related to the contribution of various atmospheric water formations in removing organic pollutants from the atmosphere are scarce. In this study, BTEX distribution coefficients between gaseous and aqueous phase in dynamic system were quantitatively determined, and the presented results could serve for clarification of phenomena being observed in real-world samples, particularly because in natural environment the partitioning between gaseous and aqueous phase is complicated mainly due to the presence of suspended compounds and thus, previous studies reported contradictory results. Detailed investigation of the partitioning process can be conducted by modifying the parameters related to temperature, pH, and other relevant factors.

Because the distribution coefficients significantly exceeded the value predicted by Henry's law, with the calculated enrichment factors showing variations in the range from 32.0 to 42.6, possible mechanisms of uptake other than dissolution, such as formation of hydrogen bonds between VOCs and atmospheric water and air—water interfacial adsorption were considered and discussed. The negative correlation of IP and E showed that hydrogen bonding between aqueous phase and BTEX is not relevant in terms of explaining the mechanisms of partitioning between gaseous and aqueous phase, whereas positive correlation between calculated enrichment factor and parameters characterizing interfacial adsorption indicated that adsorption is the mechanism which has major impact on BTEX partitioning.

The herein presented method can be applied for determination of the efficiency of wet deposition, as the important VOC removal mechanism. Thereby, the analysis of different water samples would be useful, particularly considering the fact that various formations of atmospheric water, including rain, fog, dew and snow are complex mixtures characterized by different pH and different content of salts, organic material and acids. The advantage is low limit of detection because variation of sample volume and flow of the purge/calibration gas ensures that any reasonable amount of pollutant can be detected, provided that there is sufficient amount of sample. Furthermore, no sample preparation is needed and the method can be applied for investigation of many other pollutant species.

Acknowledgments

This paper was realized as part of projects No 176006 and No III43007, which were financed by the Ministry of Education, Science and Technological Development of the Republic of for the period 2011–15, and was supported by the Institute of Public Health of Belgrade, Serbia.

References

Allou, L., El Maimouni, L., Le Calvé, S., 2011. Henry's law constant measurements for formaldehyde and benzaldehyde as a function of temperature and water composition. Atmos. Environ. 45, 2991–2998.
Andrés-Hernández, M.D., Kartal, D., Crowley, J.N., Sinha, V., Regelin, E., Martínez-Harder, M., Nenakhov, V., Williams, J., Harder, H., Bozem, H., Song, W., Thieser, J., Tang, M.J., Hosaynali Beigi, Z., Burrows, J.P., 2013. Diel peroxy radicals in a semi-industrial coastal area: nighttime formation of free radicals. Atmos. Chem. Phys. 13, 5731–5749.
Aprea, E., Biasioli, F., Märk, T.D., Gasperi, F., 2007. PTR-MS study of esters in water and water/ethanol solutions: fragmentation patterns and partition coefficients. Int. J. Mass Spectrom. 262, 114–121.
Balla, D., Papageorgiou, A., Voutsa, D., 2014. Carbonyl compounds and dissolved organic carbon in rainwater of an urban atmosphere. Environ. Sci. Pollut. Res. 21, 12062–12073.
Bornman, J.F., Barnes, P.W., Robinson, S.A., Ballare, C.L., Flint, S.D., Caldwell, M.M., 2015. Solar ultraviolet radiation and ozone depletion-driven climate change: effects on terrestrial ecosystems. Photochem. Photobiol. Sci. 14, 88–107.
Chang, H.H., Hao, H., Sarnat, S.E., 2014. A statistical modeling framework for projecting future ambient ozone and its health impact due to climate change. Atmos. Environ. 89, 290–297.
Civan, M.Y., Elbir, T., Seyfioglu, R., Kuntasal, Ö.O., Bayram, A., Doğan, G., Yurdakul, S., Andiç, Ö., Müezzinoğlu, A., Sofuoglu, S.C., Pekey, H., Pekey, B., Bozlaker, A., Odabasi, M., Tuncel, G., 2015. Spatial and temporal variations in atmospheric VOCs, NO_2, SO_2, and O_3 concentrations at a heavily industrialized region in Western Turkey, and assessment of the carcinogenic risk levels of benzene. Atmos. Environ. 103, 102–113.
de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., Fall, R., 2003. Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry. Int. J. Mass Spectrom. 223–224, 365–382.
Dewulf, J., Drijvers, D., van Langenhove, H., 1995. Measurement of Henry's law constant as function of temperature and salinity for the low temperature range. Atmos. Environ. 29, 323–331.
Feigenbrugela, V., Le Calvé, S., Mirabela, P., Louis, F., 2004. Henry's law constant measurements for phenol, o-, m-, and p-cresol as a function of temperature. Atmos. Environ. 38, 5577–5588.
Fernandes, A.N., Gouveia, C.D., Grassi, M.T., da Silva Crespo, J., Giovanela, M., 2014. Determination of monoaromatic hydrocarbons (BTEX) in surface waters from a Brazilian subtropical hydrographic basin. Bull. Environ. Contam. Toxicol. 92, 455–459.
Friedrichs, M.S., 1995. A model-free algorithm for the removal of baseline artifacts. J. Biomol. NMR 5, 147–153.
Fries, E., Sieg, K., Püttmann, W., Jaeschke, W., Winterhalter, R., Williams, J., Moortgat, G.K., 2008. Benzene, alkylated benzenes, chlorinated hydrocarbons and monoterpenes in snow/ice at Jungfraujoch (46.6 N, 8.0 E) during CLACE 4 and 5. Sci. Total Environ. 391, 269–277.
Furutaka, S., Ikawa, S.I., 2002. π-hydrogen bonding between water and aromatic hydrocarbons at high temperatures and pressures. J. Chem. Phys. 117, 751–755.
Goss, K.U., 1994. Predicting the enrichment of organic compounds in fog caused by adsorption on the water surface. Atmos. Environ. 28, 3513–3517.
Goss, K.U., 2004. The air/surface adsorption equilibrium of organic compounds under ambient conditions. Crit. Rev. Environ. Sci. Technol. 34, 339–389.
Hildebrandt Ruiz, L., Paciga, A.L., Cerully, K., Nenes, A., Donahue, N.M., Pandis, S.N., 2014. Aging of secondary organic aerosol from small aromatic VOCs: changes in chemical composition, mass yield, volatility and hygroscopicity. Atmos. Chem. Phys. Discuss. 14, 31441–31481.
International Agency for Research on Cancer (IARC – a division of WHO), 2014. IARC

monographs on the evaluation of carcinogenic risks to humans. In: Agents Classified by the IARC Monographs, Volumes 1–111. Available: http://monographs.iarc.fr/ENG/Classification/.
Ionization Potential for Common Industrial Gases, Available at: http://www.indsci.com/docs/manuals/VX500_IP.pdf
Karl, T., Yeretzian, C., Jordan, A., Lindinger, W., 2003. Dynamic measurements of partition coefficients using proton-transfer-reaction mass spectrometry (PTR–MS). Int. J. Mass Spectrom. 223, 383–395.
Kelly, C.P., Cramer, C.J., Truhlar, D.G., 2004. Predicting adsorption coefficients at air–water interfaces using universal solvation and surface area models. J. Phys. Chem. 108, 12882–12897.
Kneen, M.A., Annegarn, H.J., 1996. Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 109–110, 209–213.
Lebedev, A.T., Mazur, D.M., Polyakova, O.V., Hänninen, O., 2015. Snow samples as markers of air pollution in mass spectrometry analysis. In: Environmental Indicators. Springer, Netherlands, pp. 515–541.
Lerner, J.E.C., Kohajda, T., Aguilar, M.E., Massolo, L.A., Sánchez, E.Y., Porta, A.A., Opitz, P., Wichmann, G., Herbarth, O., Mueller, A., 2014. Improvement of health risk factors after reduction of VOC concentrations in industrial and urban areas. Environ. Sci. Pollut. Res. 21, 9676–9688.
Lindinger, W., Jordan, A., 1998. Proton-transfer-reaction mass spectrometry (PTR–MS): on-line monitoring of volatile organic compounds at pptv levels. Chem. Soc. Rev. 27, 347–375.
Liu, Y., Yuan, B., Li, X., Shao, M., Lu, S., Li, Y., Chang, C.-C., Wang, Z., Hu, W., Huang, X., He, L., Zeng, L., Hu, M., Zhu, T., 2015. Impact of pollution controls in Beijing on atmospheric oxygenated volatile organic compounds (OVOCs) during the 2008 Olympic Games: observation and modeling implications. Atmos. Chem. Phys. 15, 3045–3062.
Mahbub, P., Goonetilleke, A., Ayoko, G.A., 2012. Prediction of the wash-off of traffic related semi-and non-volatile organic compounds from urban roads under climate change influenced rainfall characteristics. J. Hazard. Mater. 213, 83–92.
Marć, M., Bielawska, M., Wardencki, W., Namieśnik, J., Zabiegała, B., 2015. The influence of meteorological conditions and anthropogenic activities on the seasonal fluctuations of BTEX in the urban air of the Hanseatic city of Gdansk, Poland. Environ. Sci. Pollut. Res. 1–15.
Meckenstock, R.U., Elsner, M., Griebler, C., Lueders, T., Stumpp, C., Dejonghe, W., Huang, W.E., Schmidt, S.I., Smolders, E., Sorensen, S.R., Springael, D., Van Breukelen, B.M., 2015. Biodegradation: updating the concepts of control for microbial clean-up in contaminated aquifers. Environ. Sci. Technol. 49, 7073–7081.
Mullaugh, K.M., Hamilton, J.M., Avery, G.B., Felix, J.D., Mead, R.N., Willey, J.D., Kieber, R.J., 2015. Temporal and spatial variability of trace volatile organic compounds in rainwater. Chemosphere 134, 203–209.
Okochi, H., Kataniwa, M., Sugimoto, D., Igawa, M., 2005. Enhanced dissolution of volatile organic compounds into urban dew water collected in Yokohama, Japan. Atmos. Environ. 39, 6027–6036.
Okochi, H., Sugimoto, D., Igawa, M., 2004. The enhanced dissolution of some chlorinated hydrocarbons and monocyclic aromatic hydrocarbons in rainwater collected in Yokohama, Japan. Atmos. Environ. 38, 4403–4414.
Pan, X., Kanaya, Y., Tanimoto, H., Inomata, S., Wang, Z., Kudo, S., Uno, I., 2015. Examining the major contributors of ozone pollution in a rural area of the Yangtze River Delta region during harvest season. Atmos. Chem. Phys. 15, 6101–6111.
Roth, C.M., Goss, K.U., Schwarzenbach, R.P., 2004. Sorption of diverse organic vapors to snow. Environ. Sci. Technol. 38, 4078–4084.
Ruckstuhl, A., Jacobson, M., Field, R., Dodd, J., 2001. Baseline subtraction using robust local regression estimation. J. Quant. Spectrosc. Radiat. Transf. 68, 179–193.
Sarraute, S., Delepine, H., Costa Gomes, M.F., Majer, V., 2004. Aqueous solubility, Henry's law constants and air/water partition coefficients of n-octane and two halogenated octanes. Chemosphere 57, 1543–1551.
Sato, E., Kiyoshi Matsumoto, K., Okochi, H., Igawa, M., 2006. Scavenging effect of precipitation on volatile organic compounds in ambient atmosphere. Bull. Chem. Soc. Jpn. 79, 1231–1233.
Shekarrizfard, M., Valois, M.F., Goldberg, M.S., Crouse, D., Ross, N., Parent, M.E., Yasmin, S., Hatzopoulou, M., 2015. Investigating the role of transportation models in epidemiologic studies of traffic related air pollution and health effects. Environ. Res. 140, 282–291.
Słomińska, M., Konieczka, P., Namieśnik, J., 2014. The fate of BTEX compounds in ambient air. Crit. Rev. Environ. Sci. Technol. 44, 455–472.
Soil screening guidance, US EPA, Available at: http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf
Starokozhev, E., Fries, E., Cycura, A., Püttmann, W., 2009. Distribution of VOCs between air and snow at the Jungfraujoch high alpine research station, Switzerland, during CLACE 5 (winter 2006). Atmos. Chem. Phys. 9, 3197–3207.
Staudinger, J., Roberts, P.V., 2001. A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. Chemosphere 44, 561–576.
Stojić, A., Stojić, S.S., Šoštarić, A., Ilić, L., Mijić, Z., Rajšić, S., 2015. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ. Sci. Pollut. Res. 1–16.
Team, R.C., 2012. R: a Language and Environment for Statistical Computing.
Valsaraj, K.T., Thoma, G.J., Reible, D.D., Thibodeaux, L.J., 1993. On the enrichment of hydrophobic organic compounds in fog droplets. Atmos. Environ. 27, 203–210.
von Hartungen, E., Wisthaler, A., Mikoviny, T., Jaksch, D., Boscaini, E., Dunphy, P.J., Märk, T.D., 2004. Proton-transfer-reaction mass spectrometry (PTR-MS) of carboxylic acids: determination of Henry's law constants and axillary odour investigations. Int. J. Mass Spectrom. 239, 243–248.
Wania, F., Mackay, D., Hoff, J.T., 1999. The importance of snow scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbon vapors. Environ. Sci. Technol. 33, 195–197.
Waring, M.S., Wells, J.R., 2015. Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: magnitudes and impacts of oxidant sources. Atmos. Environ. 106, 382–391.
Xue, B.X., Wei, L., Li, C.Y., Li, T.Y., 2015. A study of the distribution and composition of pollutants in snow collected from streets and a treatment system for recycling snow in winter cities. Desalin. Water Treat. 54, 1470–1478.
Yin, S., Zheng, J., Lu, Q., Yuan, Z., Huang, Z., Zhong, L., Lin, H., 2015. A refined 2010-based VOC emission inventory and its improvement on modeling regional ozone in the Pearl River Delta Region, China. Sci. Total Environ. 514, 426–438.

Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lesa20

Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area

Marija N. Todorovic[a], Mirjana D. Perisic[a], Maja M. Kuzmanoski[a], Andreja M. Stojic[a], Andrej I. Sostarić[b], Zoran R. Mijic[a] & Slavica F. Rajsic[a]

[a] Institute of Physics Belgrade, University of Belgrade, Belgrade, Serbia

[b] Institute of Public Health Belgrade, Belgrade, Serbia

Published online: 07 Aug 2015.

Journal of Environmental Science and Health, Part A (2015) 0, 1–9

ISSN: 1093-4529 (Print); 1532-4117 (Online)
DOI: 10.1080/10934529.2015.1059110

Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area

MARIJA N. TODOROVIĆ[1], MIRJANA D. PERIŠIĆ[1], MAJA M. KUZMANOSKI[1], ANDREJA M. STOJIĆ[1], ANDREJ I. SOSTARIĆ[2], ZORAN R. MIJIĆ[1] and SLAVICA F. RAJŠIĆ[1]

[1]*Institute of Physics Belgrade, University of Belgrade, Belgrade, Serbia*
[2]*Institute of Public Health Belgrade, Belgrade, Serbia*

The aim of this study was to assess PM_{10} pollution level and estimate required source emission reduction in Belgrade area, the second largest urban center in the Balkans. Daily mass concentrations and trace metal content (As, Cd, Cr, Mn, Ni, Pb) of PM_{10} were evaluated for three air quality monitoring sites of different types: urban-traffic (Slavija), suburban (Lazarevac) and rural (Grabovac) under the industrial influence, during the period of 2012–13. Noncompliance with current Air Quality Standards (AQS) was noticeable: annual means were higher than AQS at Slavija and Lazarevac, and daily frequency threshold was exceeded at all three locations. Annual means of As at Lazarevac were about four times higher than the target concentration, which could be attributed to the proximity of coal-fired power plants, and dust resuspension from coal basin and nearby ash landfills. Additionally, levels of Ni and Cr were significantly higher than in other European cities. Carcinogenic health risk of inhabitants' exposure to trace metals was assessed as well. Cumulative cancer risk exceeded the upper limit of acceptable US EPA range at two sites, with Cr and As as the major contributors. To estimate source emission reduction, required to meet AQS, lognormal, Weibull and Pearson 5 probability distribution, functions (PDF) were used to fit daily PM_{10} concentrations. Based on the rollback equation and best fitting PDF, estimated reduction was within the range of 28–98%. Finally, the required reduction obtained using two-parameter exponential distribution suggested that risks associated to accidental releases of pollutants should be of greater concern.

Keywords: PM_{10}, health risk, PDF, source reduction, trace metals.

Introduction

Air pollution is one of the dominant factors influencing quality of the environment in urban and industrial areas. The impact of ambient particulate matter (PM) is one of the major concerns because of its adverse effects on human health. Relationship between the exposure to PM_{10} (aerodynamic diameter less than 10 μm) and acute and chronic health effects have been demonstrated by previous epidemiological studies.[1,2] Their ability to penetrate deep into the lungs increases the risk of acute respiratory infections, lung cancer and chronic respiratory and cardiovascular diseases. This is partially related to the presence of PM_{10}-bound trace metals. Trace metals in the atmosphere are mainly emitted in particulate form and, due to their persistency, can be widely dispersed in the environment. Most of them are toxic and, according to US EPA IRIS,[3] Cd, Cr, Ni, Pb and As have been classified as known and possible human carcinogens. To regulate concentration levels, based on health impact criteria, EU commission established annual PM_{10} limit value of 40 $\mu g\ m^{-3}$ and a criterion that daily limit value of 50 $\mu g\ m^{-3}$ is not to be exceeded more than 35 times in a calendar year.[4] Target (Ni, As and Cd) and limit (Pb) values for concentrations of PM_{10}-bound metals were set as well.[5]

Each region, due to its specificity, requires different mitigation measures to meet the Air Quality Standards (AQS). The municipality of Belgrade is a commercial center of the Republic of Serbia and, as an important road and industry intersection, requires special attention. Previous studies conducted to estimate the influence of PM_{10} on air quality of this area have mostly been focused on highly urbanized part of Belgrade.[6–10] Recently developed air quality network allows determination of pollution levels in a much broader area, which can be helpful to identify potential emission sources and develop air pollution control strategy.

Information about the frequency distribution of PM_{10} mass concentrations is useful in developing air pollution control strategy. Since PM_{10} concentrations can be regarded as generally random variables affected by emission, meteorological conditions and topography, they can be subjected to statistical processing to determine the

Address correspondence to Marija N. Todorović, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, Zemun 11080, Serbia; E-mail: marija.todorovic@ipb.ac.rs
Received March 27, 2015.

appropriate frequency distribution. Different types of probability distribution functions (PDF) have been used for that purpose including lognormal, Pearson 5, Weibull and gamma.[11–13]

Concentrations of a pollutant, which originates from a single emission source and is subjected to successive mixing and dilution, can be well described by lognormal distribution.[14] When air pollution is significantly under the influence of intensities and positions of emission sources, combined with background level and dispersion processes, measured concentrations follow the Pearson 5 distribution.[10] Finally, pollutant concentrations that are largely affected by meteorological processes obey the Weibull distribution.[15] When known, specific PDF of PM_{10} concentrations allows prediction of the number of exceedance days and required source emission reduction in order to comply with the current AQS.[12]

Sometimes the tail of the PDF diverges in the high concentration region and can cause inaccuracies in further calculations. In these cases, for more precise estimate of exceedances, their recurrence interval (return period), and the required emission reduction, two-parameter exponential distribution derived from extreme value theory can be applied.[7]

In this study, we present preliminary statistical analysis of mass concentrations and trace metal content of PM_{10} obtained from monitoring sites of three different types in Belgrade area during 2012 and 2013. Additionally, we report rough estimates of carcinogenic health risk which is related to the exposure of inhabitants to PM_{10}-bound trace metals. Lognormal, Pearson 5 and Weibull PDF were applied to fit PM_{10} mass concentrations, and the best fitted PDF was used to estimate reduction of PM_{10} source emissions necessary to meet the EU AQS at each site. Fitting of PM_{10} concentrations in the high concentration regions (over 75th percentile) by two-parameter exponential function was used to predict the return period of exceedances of US EPA AQS critical value[16] (150 $\mu g\ m^{-3}$) and to estimate the required emission reduction.

Methodology

Data used in this study were obtained by a certified laboratory at the Institute of Public Health of Belgrade.[17] Samples were collected during 2012 and 2013 at three different types of air quality monitoring sites in Belgrade area - Slavija, Lazarevac and Grabovac (Fig. 1). Daily mass concentrations as well as trace metal content (As, Cd, Cr, Mn, Ni and Pb) of PM_{10} were analyzed according to EN 12341:1998[18] and EN 14902:2005[19] standards, respectively. Unpaired two-sided t-tests for comparisons of annual means of PM_{10} and trace metal concentrations were employed on the logarithmically transformed data at significance level of $P < 0.05$. The inter-site relationships of PM_{10} and concentrations of metals were assessed by estimating Pearson's correlation coefficients. Tests were performed using StatSoft version 8.0 for Windows.

Fig. 1. Location of sampling sites and CFPP in Belgrade area.

Study area

Belgrade area is recognized as the second largest urban center in the Balkan Peninsula. With about 1.6 million citizens it comprises 22.5% of the population and 3.6% territory of the Republic of Serbia. To describe the influence of different PM_{10} sources in this area, data were obtained from three types of monitoring sites. Slavija is an urban-traffic station, located in the very center of Belgrade, and is taken into consideration as a representative of highly urbanized area. Lazarevac is a suburban sampling site placed in the namesake city about 50 km southeast from Belgrade in the middle of Kolubara lignite basin, the biggest coal basin in Serbia (covers an area of almost 600 km^2 and 70% of total coal production in Serbia).

Most of the lignite produced in the basin (90%) is used for electricity generation in the Coal Fired Power Plants (CFPP) Nikola Tesla A and B in Obrenovac, and Kolubara in Veliki Crljeni. These CFPP and their ash landfills have been recognized as a significant stationary sources of PM emission in Belgrade area, and moreover, as potential transboundary impactors.[20] To estimate their local influence, data were obtained from Grabovac monitoring site, located in a rural area about 10 km south from the CFPP and about 5 km southeast from one of their ash landfills (Fig. 1).

Health risk assessment

To estimate the carcinogenic health risk associated with exposure to analyzed PM_{10}-bound trace metals, the US EPA health risk assessment model was used.[21,22]

Chronic daily intake (CDI) describes the exposure to a chemical and is calculated as follows:

$$CDI = \frac{C \cdot IR \cdot EF \cdot ED}{BW \cdot AT} \qquad (1)$$

where C represents concentration of the chemical in the air, IR is the average inhalation rate of an adult (2×10^4 L day^{-1}); EF is exposure frequency (it is presumed that a person is exposed to the contaminated air for 350 days per year), ED is exposure duration and describes how long a person is exposed to the contaminated air over the course of their lifetime (30 years), BW is average body weight of an adult (70 kg) and AT is period over which the exposure is averaged (70 years). The capacities of chemical in air to cause adverse health effects, toxicity parameters, are given as slope factor (SF).

Carcinogenic health risk due to exposure to PM_{10}-bound trace metals was assessed by calculating the incremental lifetime cancer risk (ILCR) value:

$$\mathrm{ILCR} = \mathrm{CDI} \times \mathrm{SF} \times 10^{-6} \tag{2}$$

which represents an incremental probability of an individual developing cancer over lifetime as a result of exposure to these metals through inhalation. The ILCR level of 10^{-6} is typically the baseline level of risk that is acceptable while 10^{-4} presents the upper limit of the range of acceptability.[23]

Toxicity parameters used in Equations 1 and 2 in this study were calculated from Unit Risk and Reference Concentration values obtained from Risk Assessment Information System (RAIS)[24] and Integrated Risk Information System (IRIS)[3] chemical toxicity databases, and all calculations were done with assumption that the bioavailability of trace metals was 100%.[25]

Assessment of source emission reduction

In this study, lognormal, Weibull and Pearson 5 probability distributions were used to fit the PM_{10} mass concentrations from each sampling site (Eqs. 3–5).

$$f_l(x) = \frac{1}{x\sigma'\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\ln x - \mu'}{\sigma'}\right)^2} \tag{3}$$

$$f_W(x) = \frac{\alpha x^{\alpha-1}}{\beta^{\alpha}} e^{-\left(\frac{x}{\beta}\right)^{\alpha}} \tag{4}$$

$$f_{P5}(x) = \frac{1}{\beta\Gamma(\alpha)} \frac{e^{-\frac{\beta}{x}}}{\left(\frac{x}{\beta}\right)^{\alpha+1}} \tag{5}$$

where α and $\sigma' = \sqrt{ln(1 + (\frac{\sigma}{\mu})^2)}$ are shape factors, β and $\mu' = ln\left(\frac{\mu^2}{\sqrt{\sigma^2+\mu^2}}\right)$ are scale factors for the corresponding functions, x is pollutant concentration, μ is mean value, σ^2 is variance and $\Gamma(\alpha)$ is the Gamma function.[7]

The distributions' parameters were estimated using maximum likelihood estimation while Kolmogorov-Smirnoff (K-S) and Anderson-Darling (A-D) statistical tests were used to evaluate the goodness of fit. Also, the fitted distributions were ranked according to the Schwartz Information Criterion (SIC), Akaike Information Criterion (AIC) and Hannan–Quinn Information Criterion (HQIC), which are superior in terms of goodness of fit ranking.[10]

The best fitting PDF for each site was used to assess the required source emission reduction in order to meet the AQS. This is done by employing a rollback equation:

$$R = \frac{E\{C\} - E\{C\}_s}{E\{C\} - C_b} \tag{6}$$

where $E\{C\}$ present the mean concentration of the actual distribution, $E\{C\}_s$ the expected average concentration of a fitted distribution where probability to exceed 50 $\mu g\, m^{-3}$ equals 0.09589 (35/365), while C_b presents the background concentration.[26]

Usually, the rollback equation is applied with assumption that the background concentrations in examined area are equal to zero, which causes lower estimates of required emission reduction. To assess the local background level in this study, trajectory sector analysis (TSA) was applied. A two-step procedure was used for differentiation between locally emitted and transported PM_{10}. First, the dominant local contribution was excluded from the time series, providing a baseline, using a frequency differentiated nonlinear digital filtering algorithm implemented in the function baseline.rollingBall ($w_m = 3$, $w_s = 2$) of the Baseline package[27] of the statistical software environment R[28] (Fig. 2).

Then, trajectory sector analysis (TSA) was applied to the derived baseline for determination of the local background and regional transport contributions, as described in Stojić et al.[29] Air-mass back trajectories were computed using the HYSPLIT model.[30] Daily 96-h back trajectories, starting from the sampling site at 0, 6, 12, 18 UTC each day, were evaluated for six different heights (350, 500, 750, 1000, 1500 and 2000 m) for each measurement site. Each trajectory reaching the ground level was excluded from the analysis (25.1%).

Occasionally, the tail of the PDF can diverge in the high concentration region. In these cases, for more precise analyses, a two-parameter exponential distribution can be applied. A two-parameter exponential distribution represents cumulative frequency distribution (F_L) of high concentrations over a specific percentile:

$$F_L = 1 - e^{-y_n}, \; y_n = b_m(x_n - \phi) \tag{7}$$

where y_n, b_m and ϕ present the variate and parameters, respectively and x_n is the chosen concentration exceeding a specific percentile.

The return period $R_p(x_c)$ is defined as the number of averaging observations between exceedances of the given

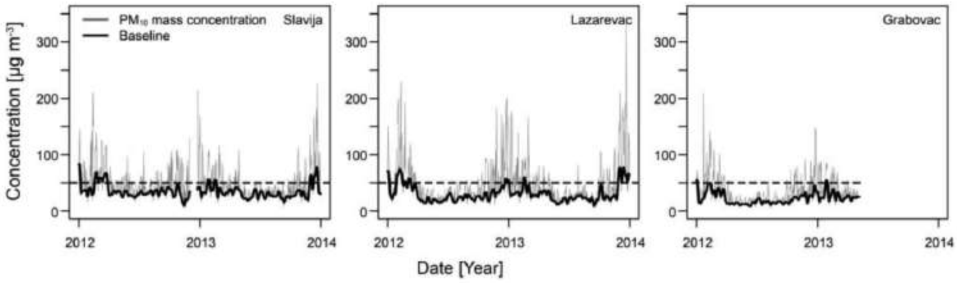


Fig. 2. PM_{10} time series and derived baseline at three sampling sites. Dashed line shows the current AQS (50 µg m^{-3}).

critical concentration x_c and can be calculated as follows:

$$R_p(x_c) = \frac{1}{(1-f)(1-F_L(x_c))} \quad (8)$$

where f is the chosen specific percentile.[12] According to Lu[12] the prediction of a critical concentration return period can also be used to estimate the required source emission reduction.

Results and discussion

Table 1 shows the basic statistical parameters of daily PM_{10} mass concentrations, number of samples exceeding the daily AQS and their average concentrations at three measurement sites in the Belgrade area. At the Grabovac sampling site data were incomplete during the 2013 and thus excluded from some of the further analyses.

The frequency of daily exceedances of PM_{10} mass concentrations was significantly above the stated AQS limit at all stations. The highest concentrations and most exceedance days were observed during the colder part of the year (Fig. 2), which could be possibly attributed to the traffic density and combustion of fossil fuels during the heating season. Additionally, the lack of vertical transport and dilution of pollutants due to low planetary boundary layer and low wind speed could as well enhance PM_{10} accumulation during the cold seasons.[31]

The annual mean values exceeded AQS limit value at Slavija and Lazarevac during both years. A previous source apportionment study[9] based on PM_{10} and its chemical constituents collected at the centrally located urban monitoring sites in Belgrade showed that the major contributors to PM_{10} concentrations were fossil fuel combustion and traffic exhaust. Thus, we assume that high PM_{10} level at Slavija was probably caused by these sources. High annual means and pollution episodes of very high concentrations at Lazarevac could be attributed to the proximity of the coal mine and the CFPP Kolubara. The annual means were lower at Lazarevac in comparison to Slavija (two-sided t-test, $P < 0.05$) in 2012, while the t-test indicated that the difference between the mean PM_{10} concentrations in 2013 was not significant ($P = 0.053$). Grabovac, a rural location, was characterized with annual mean below the AQS limit in 2012, but also with episodic increases of PM_{10} concentrations which were possibly the result of ash drift from the nearby landfill and the proximity of CFPP Nikola Tesla.

In Table 2[32–37] we present the average concentrations of PM_{10}-bound metals (Ni, As, Cd, Mn, Cr and Pb) at the three monitoring sites in Belgrade area and some European urban monitoring sites.

Levels of Ni, Cr and As at all locations were significantly higher than those in other European cities (particularly noticeable for Cr), while Mn, Cd and Pb concentrations were comparable, but still generally higher. Elevated atmospheric concentrations of these elements

Table 1. Basic statistics for PM_{10} mass concentrations [mg m^{-3}], number of samples exceeding the daily AQS and their average concentrations.

							Exceedances(Conc > 50 µg m^{-3})	
Monitoring site	*Year*	*N*	*Mean*	*Min*	*Max*	*Std. Dev.*	*N*	*Mean*
Slavija	2012	321	53.51	7.43	213.59	29.85	127	81.20
	2013	353	45.88	7.24	226.51	28.02	97	80.29
Lazarevac	2012	341	47.48	9.42	228.99	38.05	96	94.08
	2013	354	46.73	7.99	341.21	39.54	94	96.78
Grabovac	2012	336	33.46	5.80	209.24	25.41	60	76.85

Table 2. Comparison of the trace element concentrations [μg m^{-3}] with results obtained in other European urban sites. CI represents 95% confidence interval.

Monitoring site	Study period	*Cr* Mean (±CI)	*Mn* Mean (±CI)	*Ni* Mean (±CI)	*As* Mean (±CI)	*Cd* Mean (±CI)	*Pb* Mean (±CI)
Slavija	2012	19.15 (±1.22)	21.00 (±2.29)	11.18 (±1.59)	4.87 (±0.96)	0.25 (±0.07)	18.18 (±2.61)
	2013	28.65 (±5.00)	18.96 (±1.96)	16.15 (±2.72)	6.54 (±1.57)	0.73 (±0.43)	20.73 (±2.99)
Lazarevac	2012	16.68 (±1.07)	10.61 (±1.36)	5.27 (±0.80)	23.15 (±7.14)	0.27 (±0.07)	14.50 (±2.53)
	2013	25.10 (±1.85)	11.22 (±1.49)	6.73 (±0.82)	29.45 (±9.4)	0.45 (±0.09)	16.65 (±3.91)
Grabovac	2012	7.33 (±0.58)	3.25 (±0.28)	2.55 (±0.31)	4.00 (±1.26)	0.14 (±0.04)	5.62 (±0.71)
Budapest[32]	2004–2007	6.89	26.80	2.70	—	1.15	30.40
Flanders[33]	2006–2007	3.50	8.90	3.60	3.80	—	21.00
Edinburgh[34]	1999–2000	1.60	2.90	3.40	0.37	0.34	14.00
Stockholm[35]	2003–2004	6.10	15.60	2.90	1.04	0.12	7.20
Iturrama[36]	2009	2.81	6.88	2.21	0.21	0.04	3.33
Plaza de la Cruz[36]	2009	2.33	7.07	0.98	0.13	0.12	4.33
Bern[37]	2008–2009	4.90	12.20	2.20	0.52	0.11	6.20
Zurich[37]	2008–2009	2.00	5.60	1.00	0.52	0.12	5.20

were previously reported in Serbia[8,38] and partially explained by geological nature of Ni and Cr. Nickel is additionally emitted from vehicle exhaust as main additive in fuels,[39] and its elevated concentrations in this area could also be caused by prevalent use of old vehicles with high fuel consumption. This assumption was corroborated by about two time higher Ni concentrations at Slavija (two-sided *t*-test, $P < 0.05$), compared to the other two locations. Note that, although high, concentrations of Ni did not exceed the prescribed target value (20 ng m^{-3}).

Annual mean of As at Slavija exceeded the target value (6 ng m^{-3}) in 2013, while at Lazarevac it was about four times higher than the target value for both years of considered period. Arsenic is characteristic for coal combustion[40] and its high concentrations at Lazarevac and Grabovac were possibly caused by the proximity of CPPF, and the dust resuspension from coal basin and ash landfill.

High correlation of As and PM_{10} concentrations at Lazarevac and Grabovac (0.87 and 0.72, respectively) also indicated that the major source of emitted particles in this area could be associated with fossil fuel combustion. Since there is sufficient evidence that inorganic arsenic compounds are lung carcinogens in humans[3] these threshold transgressions require special attention and continuous monitoring which could help in making potential abatement strategies. Our future studies will be focused on source apportionment analyses, needed for better understanding of main sources that contribute to the PM_{10} and its chemical constituents at Lazarevac and Grabovac.

Average annual concentrations of Cd and Pb, although high, did not exceed the specified target (Cd) and limit (Pb) values. Levels of Pb and Mn were higher at Slavija than at Lazarevac and Grabovac (two-sided *t*-test, $P <$ 0.05), which could be attributed to the influence of traffic emissions, road dust resuspension and some local production at Slavija as identified by Mijic et al.[9]

Health risk assessment

The two-year average concentrations of PM_{10}-bound trace metals at the studied locations were used to estimate the health (cancer) risk associated with adults' exposure to them through inhalation (Table 3). Cumulative cancer risks, determined as a sum of individual ILCR, were 1.31 $\times 10^{-4}$, 1.51×10^{-4} and 6.09×10^{-5} at Slavija, Lazarevac and Grabovac, respectively. Note that the upper limit of

Table 3. Values of slope factor (SF [mg^{-1} kg day]), chronic daily intake (CDI [ng kg^{-1} day^{-1}]) and calculated incremental lifetime cancer risk (ILCR) for analyzed PM_{10}-bound trace metals.

Monitoring site	*Metal*	*SF*	$CDI_{canc.}$	*ILCR*
Slavija	Pb	4.20×10^{-2}	2.29	9.60×10^{-8}
	Cd	6.30×10^{0}	0.06	3.69×10^{-7}
	Ni	1.68×10^{0}	1.6	2.70×10^{-6}
	Cr	4.20×10^{1}	2.81	1.18×10^{-4}
	Mn	—	—	—
	As	15.05×10^{0}	0.67	1.01×10^{-5}
	Sum			1.31×10^{-4}
Lazarevac	Pb	4.20×10^{-2}	1.82	7.68×10^{-8}
	Cd	6.30×10^{0}	0.04	2.69×10^{-7}
	Ni	1.68×10^{0}	0.7	1.18×10^{-6}
	Cr	4.20×10^{1}	2.45	1.03×10^{-4}
	Mn	—	—	—
	As	15.05×10^{0}	3.09	4.65×10^{-5}
	Sum			1.51×10^{-4}
Grabovac	Pb	4.20×10^{-2}	0.87	3.64×10^{-8}
	Cd	6.30×10^{0}	0.02	1.20×10^{-7}
	Ni	1.68×10^{0}	0.38	6.44×10^{-7}
	Cr	4.20×10^{1}	1.17	4.91×10^{-5}
	Mn	—	—	—
	As	15.05×10^{0}	0.73	1.10×10^{-5}
	Sum			6.09×10^{-5}

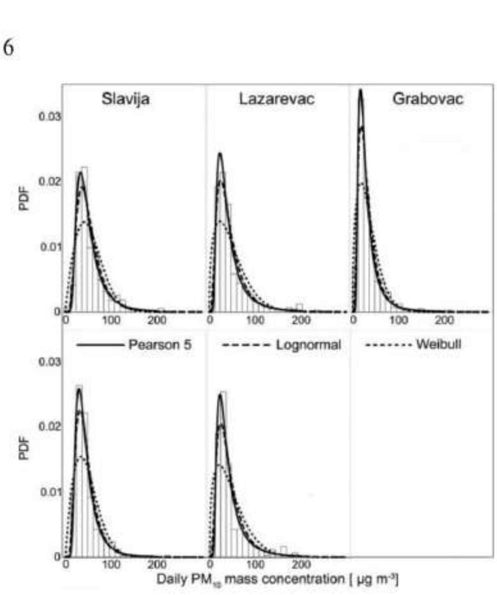


Fig. 3. Fit of daily PM_{10} concentrations with lognormal, Weibull and Pearson 5 distributions at Slavija, Lazarevac and Grabovac in 2012 (upper panel) and 2013 (lower panel).

the acceptable ILCR range of values was exceeded at Slavija and Lazarevac. These values imply that the emission reduction measures are required at Slavija and Lazarevac area.

Chromium was the major contributor to the obtained cumulative cancer risks –90%, 68% and 80% at Slavija, Lazarevac and Grabovac, respectively. Hexavalent Cr is a human pulmonary carcinogen, while trivalent Cr is considered as much less toxic and their ratio mostly depends on type of emission source of this element. Origin of Cr is considered as mainly anthropogenic (industrial processes, fuel combustion, etc.), thus suggesting the need for substantial reduction in emissions of this metal, but its potential geological origin in this area indicates the need for additional speciation to give more precise results. Contribution of As to the estimated cancer risk at Lazarevac was very high (31%) in comparison to Grabovac (18%) and Slavija (8%), suggesting the impact of coal mine and thermal power plant emissions to the obtained health risk.

Assessment of source emission reduction

Mass concentrations of PM_{10} measured at Slavija, Lazarevac and Grabovac were fitted with lognormal, Weibull and Pearson 5 theoretical distributions for each year of the analyzed period (Fig. 3). These PDF were already successfully used to assess some statistical properties of PM_{10} mass concentrations in highly urbanized Belgrade area.[7] In this study, besides urban traffic location, PDF were applied to the data obtained from another two types of monitoring sites (suburban and rural under the industrial influence). Note that the data from Grabovac for 2013 were excluded from analyses, because they were available only for the first part of the year.

The estimated distribution parameters and results of K-S, A-D test and information criteria for different fitted distributions are shown in Table 4. At all three locations, the Pearson 5 distribution was found to be the most appropriate for representing daily PM_{10} concentrations during 2012 and 2013. It gave a good prediction of the values in the middle (K–S value up to 0.05) and the tails (A–D value

Table 4. Estimated parameters for lognormal (L), Pearson 5 (P5) and Weibull (W) distributions applied on PM_{10} mass concentrations.

					Mean	*Std. Dev.*	*Goodness of fit*					*Number of exc.*	
Station	*Year*	*PDF*	α/μ	β/σ	*[μg m⁻³]*	*[μg m⁻³]*	*K-S*	*A-D*	*SIC*	*AIC*	*HQIC*	*Calc.*	*Obs.*
Slavija	2012	L	3.85	0.50	53.31	28.38	0.07	1.61	2949	2942	2945	145	
		P5	4.18	173.90	54.62	36.96	0.05	1.00	2961	2954	2957	135	127
		W	1.93	60.67	53.81	29.03	0.11	8.02	3019	3011	3014	162	
	2013	L	3.69	0.50	45.33	28.74	0.09	3.00	3123	3116	3119	116	
		P5	4.55	162.73	45.87	23.9	0.05	1.07	3111	3103	3106	107	97
		W	1.80	51.99	46.23	26.57	0.14	13.3	3239	3231	3234	139	
Lazarevac	2012	L	3.63	0.64	46.43	33.00	0.08	2.61	3152	3145	3148	113	
		P5	2.91	91.89	48.09	50.39	0.04	0.44	3132	3124	3127	102	96
		W	1.44	52.94	48.06	33.92	0.14	11.26	3253	3245	3248	136	
	2013	L	3.61	0.65	45.52	32.96	0.09	3.61	3265	3257	3260	113	
		P5	2.84	86.77	47.26	51.68	0.05	0.96	3243	3235	3238	102	94
		W	1.39	51.88	47.32	34.43	0.15	13.13	3376	3368	3371	137	
Grabovac	2012	L	3.30	0.63	32.97	22.84	0.06	1.55	2868	2860	2863	55	
		P5	2.95	66.86	34.28	35.15	0.03	0.34	2857	2849	2852	54	60
		W	1.50	37.47	33.82	22.96	0.10	7.87	2955	2947	2950	72	

up to 1.0) of the empirical distributions.[15] Information criteria also assessed Pearson 5 distribution as the best fit for the considered period.

Concerning the Pearson 5 distribution, the parameter β is related to the source emission strength, meaning that the pollution is more severe if this factor is larger.[12] The estimated β values implied that the PM_{10} pollution was more significant at Slavija and Lazarevac. As already mentioned, the heavy traffic flow rate, as well as stationary local emissions which could be attributed to local heating units during the winter, probably caused the high PM_{10} pollution at Slavija monitoring site. Lazarevac was probably affected by the closeness of the coal mines and the thermal power plant. PM_{10} pollution was the lowest at Grabovac during 2012, which may be due to the rural location of the measuring site, but also due to the improvements in technology of maintaining nearby coal ash landfill.

Assuming unchanged spatial distribution of emission sources, meteorological conditions and nonreactive species, PM_{10} source emission reduction required to meet AQS can be estimated on the basis of a rollback equation and Pearson 5 PDF. The required emission reduction range was calculated with the values of local background determined by TSA (maximum reduction) and regional natural background concentration of 10 $\mu g\ m^{-3}$ (minimal reduction) based on results presented by Viana et al.[41] TSA derived local background concentrations were 35.7 and 31.4 $\mu g\ m^{-3}$ at Slavija, and 20.4 and 24.0 $\mu g\ m^{-3}$ at Lazarevac for 2012 and 2013, respectively, and 26.1 at Grabovac for 2012.

Slavija is characteristic due to the closeness to constant particle emission from traffic included in forming of the background levels at this location. To exclude its contribution and get more reliable estimate of emission reduction, the calculated background level was reduced by 21% (contribution of traffic emissions in Belgrade estimated by Mijic et al.[9]). The estimated maximum required emission reductions were 97 and 78% for 2012 and 2013 (Fig. 4), while the minimal reductions were 46 and 36.5%. This indicated that the levels of PM_{10} may meet the AQS only by applying a multiyear abatement emission strategy.

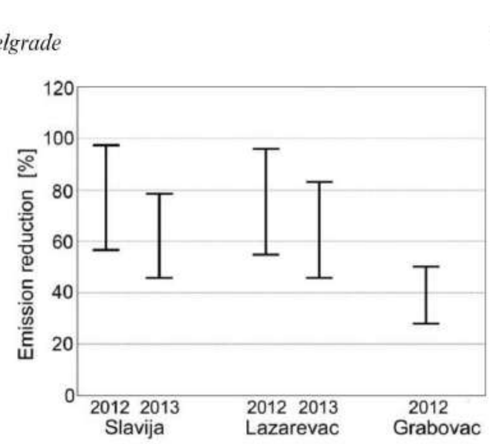


Fig. 4. Estimated ranges (min-max) of required source emission reduction [%].

At Lazarevac and Grabovac, the required source emission reduction was high as well (up to 96%). Results of TSA showed that the contribution of the long-range transport to the obtained PM_{10} concentrations at all sampling sites was not significant (2–10%), thus indicating that the abatement strategy should be focused on reducing emission from local sources, such as traffic and individual heating unites at Slavija, and possibly on technological improvement of industrial facilities in proximity to Lazarevac and Grabovac.

To predict the return period of the critical PM_{10} concentration (150 $\mu g\ m^{-3}$) exceedances, a two-parameter exponential distribution was applied. Figure 5 shows the fitted theoretical lines of the variate (Y_n) and PM_{10} concentrations over the 75th percentile (x_n) at the sampling sites. The coefficients of determination, with values $R^2 = 0.995$, $R^2 = 0.988$ and $R^2 = 0.978$ indicate that theoretical distribution successfully fits the observed high concentration range at all sampling sites. The observed and estimated number of days when critical value was exceeded, as well as predicted return periods, are presented in Table 5. In comparison to Slavija, return period of exceedance days at Lazarevac was twice as high. This may be attributed to

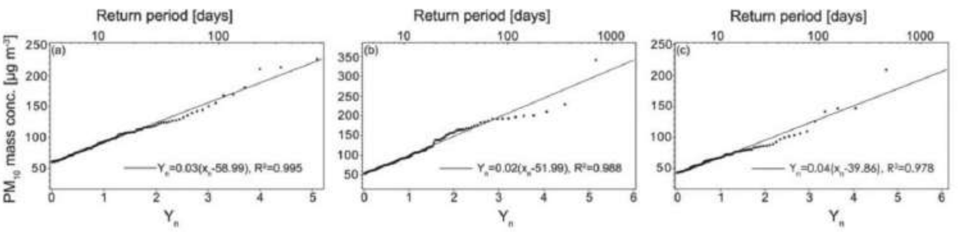


Fig. 5. Fit of variate y_n and PM_{10} concentration over a 75th percentile obtained by two-parameter distribution function at Slavija (a), Lazarevac (b) and Grabovac (c).

Table 5. Observed and estimated number of exceeded daily concentrations, predicted return period (RP) and estimated source emission reduction by two-parameter exponential distribution.

	Number of exceedance [days]			
	Observed	*Estimated*	*RP [days]*	*R [%]*
Slavija	8	11	67	24
Lazarevac	27	24	31	44
Grabovac	1	2	212	9

accidental releases of PM_{10}, caused by combination of strong nearby emission sources and meteorological conditions.

Source emission reduction was derived using the predicted return period of prescribed critical concentration. The calculated values are presented in Table 5. The US EPA AQS critical PM_{10} concentration was set to monitor and control the accidental releases of PM_{10} and the estimated source emission reduction, even in this case, ranged from 9% (Grabovac) up to 44% (Lazarevac). The obtained results suggest the need for mitigation measures to comply with air quality standards as well as to reduce potential impact to the health of inhabitants in Belgrade area.

In such an effort, a further study that would focus on resolving the contribution of emission sources to PM_{10} level in wider area of Belgrade is needed. Due to the fact that particulate matter and its bound metals can be widely dispersed in atmosphere, suggested abetment measures would not influence just the air quality in this area, but also in a much wider region.

Conclusion

In this study, statistical characteristics of mass concentrations and trace metal (Mn, Cr, Ni, Cd, As and Pb) content of PM_{10} collected at three different monitoring sites (urban-traffic, and suburban and rural under the industrial influence) in Belgrade area during 2012 and 2013 were presented. In comparison with EU AQS, the results showed that the annual limit of PM_{10} mass concentrations was exceeded at two, and daily frequency value at all three locations. Concentrations of As exceeded the target value at Lazarevac four times during both years of considered period, while at Slavija target value was exceeded during the 2013. Levels of Cr, Mn and Ni were found to be significantly higher than in other European cities as well. Cumulative cancer risks of inhabitants' exposure to trace metals exceeded the upper value of the US EPA acceptability range at Slavija and Lazarevac with Cr and As as the major contributors.

At all three locations, the Pearson 5 distribution was found to be the most appropriate for representing measured PM_{10} mass concentrations. The estimated source emission reductions, with values up to 97%, indicated that it might be difficult to meet the AQS at the present moment. The required reductions obtained using two-parameter exponential distribution (up to 44%) suggested that risks associated to accidental releases of pollutants, which result in acute exposure to high concentrations with potential impacts on human health, should be considered as well. The results of TSA showed that the long-range transport contribution to the obtained PM_{10} concentrations at all sampling sites was not significant (2–10%). This indicates that the abatement strategy should be focused on reducing emission from local sources, such as traffic and individual heating unites at Slavija, and possibly on technological improvement of industrial facilities in proximity to Lazarevac and Grabovac. The contribution of the mentioned emission sources remains to be investigated in future studies.

Acknowledgments

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

Funding

This article was realized as part of project No. III43007 financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011–15.

References

[1] De Kok, T.; Driece, H.; Hogervorst, J.; Briede, J. Toxicological assessment of ambient and traffic-related particulate matter: a review of recent studies. Mutat. Res. **2006**, *613*(2–3), 103–122.
[2] Kelly, J.; Fussell, C. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. **2012**, *60*, 504–526.
[3] US Environmental Protection Agency. Integrated Risk Information System (IRIS). Office of Research and Development: Washington, DC, 2013. Available at http://www.epa.gov/iris (accessed Jul 2014).
[4] Directive 2004/107/EC of the European parliament and of the council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Off. J. Eur. Union *23*, 1–16.
[5] Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air and cleaner air for Europe. Off. J. Eur. Union, *155*, 1–44.
[6] Rajsic, S.; Mijic, Z.; Tasic, M.; Radenkovic, M.; Joksic, J. Evaluation of the levels and sources of trace elements in urban particulate matter. Environ. Chem. Lett. **2008**, *6*(2), 95–100.

[7] Mijic, Z.; Tasic, M.; Rajsic, S.; Novakovic, V. The statistical character of PM_{10} in Belgrade. Atmos. Res. **2009**, *92*(4), 420–426.
[8] Mijic, Z.; Stojic, A.; Perisic, M.; Rajsic, S.; Tasic, M.; Radenkovic, M.; Joksic, J. Seasonal variability and source apportionment of metals in the atmospheric deposition in Belgrade. Atmos. Environ. **2010**, *44*(30), 3630–3637.
[9] Mijic, Z.; Stojic, A.; Perisic, M.; Rajsic, S.; Tasic, M. Receptor modelling studies for the characterization of PM10 pollution sources in Belgrade. Chem. Ind. Chem. Eng. Q. **2012**, *18*(4), 623–634.
[10] Perisic, M.; Stojic, A.; Stanisic Stojic, S.; Sostaric, A.; Mijic, Z.; Rajsic, S. Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Qual. Atmos. Heal. **2014**, 1–11. doi: 10.1007/s11869-014-0292-5
[11] Lu, H. The statistical characters of PM10 concentration in Taiwan area. Atmos. Environ. **2002**, *36*(3), 491–502.
[12] Lu, H. Estimating the emission source reduction of PM10 in central Taiwan. Chemosphere **2004**, *54*(7), 805–814.
[13] Morel, B.; Yeh, S.; Cifuentes, L. Statistical distributions for air pollution applied to the study of the particulate problem in Santiago. Atmos. Environ. **1999**, *33*(16), 2575–2585.
[14] Ott, P. The composting of farmyard manure with mineral additives and under forced aeration, and the utilization of FYM and FYM compost in crop production. PhD dissertation, 1990, Universitätdes Landes, Hessen.
[15] Aleksandropoulou, V.; Eleftheriadis, K.; Diapouli, E.; Torseth, K.; Lazaridis, M. Assessing PM_{10} source reduction in urban agglomerations for air quality compliance. J. Environ. Monit. **2012**, *14*(1), 266–278.
[16] US Environmental Protection Agency. The National Ambient Air Quality Standards for Particle Pollution. US EPA: Washington, DC, 2012.
[17] IPHB. Institute of Public Health of Belgrade. Available at www.zdravlje.org.rs (in Serbian) (accessed Jul 2014).
[18] EN 12341:1998, Air quality - Determination of the PM_{10} fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods.
[19] EN 14902:2005, Ambient air quality - Standard method for the measurement of the Pb, Cd, As and Ni in the PM_{10} fraction of suspended particulate matter.
[20] EEA 2007. Europe's environment. The fourth assessment. Resource document. European Environmental Agency, Office for Official Publications of the European Communities, Luxemburg 2007. Available at http://ftp.eea.europa.eu/www/eea-data/Belgrade_EN_all_chapters_incl_cover.pdf (accessed Aug 2014).
[21] US Environmental Protection Agency. Risk Assessment Guidance for Superfund Volume I, Human Health Evaluation Manual (Part A). Interim final. Office of Emergency and Remedial Response. USEPA: Washington, DC, 1989.
[22] US Environmental Protection Agency. Risk Assessment Guidance for Superfund (RAGS), Vol. 1. Human Health Evaluation Manual Supplemental Guidance: Standard Default Exposure Factors. OSWER Directive 9285.6-03. Office of Emergency and Remedial Response. USEPA: Washington, DC, 1991.
[23] US Environmental Protection Agency. Guidelines for Carcinogen Risk Assessment. Risk Assessment Forum. USEPA: Washington, DC, 2005. Available at http://www.epa.gov/raf/publications/pdfs/cancer_guidelines_final_3-25-05.pdf. (accessed July 2014).
[24] RAIS. Risk Assessment Information System. Oak Ridge National Laboratory. 2013 Available at http://rais.ornl.gov (accessed July 2014).
[25] Diaz, R.; Dominguez, E. Health risk by inhalation of PM2.5 in the metropolitan zone of the City of Mexico. Ecotoxicol. Environ. Saf. **2009**, *72*(3), 866–871.
[26] Georgopoulos, P.; Seinfeld, J. Statistical distributions of air pollutant concentrations. Environ. Sci. Technol. **1982**, *16*(7), 401–416.
[27] Kneen, M.; Annegarn, H. Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. Nucl. Instru. Meth. Phys. Res. Sect. B Beam Interact. Mater. Atoms **1996**, *109*(1–2), 209–213.
[28] Team, R.C. R: A language and environment for statistical computing. 2012 Available at http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf (accessed Apr 2014).
[29] Stojić, A.; Stojić, S.S.; Mijić, Z.; Šoštarić, A.; Rajšić, S. Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos. Environ. **2015**, *106*, 71–79.
[30] Draxler, R.; Rolph, G. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY, 2014. Available at http://ready.arl.noaa.gov/HYSPLIT.php. (accessed July 2014).
[31] Engler, C.; Birmili, W.; Spindler, G.; Wiedensohler, A. Analysis of exceedances in the daily PM_{10} mass concentration (50 $\mu g\ m^{-3}$) at a roadside station in Leipzig, Germany. Atmos. Chem. Phys. Discuss. **2012**, *12*(4), 10107–10123.
[32] Muránszky, G.; Óvári, M.; Virág, I.; Csiba, P.; Dobai, R.; Záray, G. Chemical characterization of PM10 fractions of urban aerosol. Microchem. J. **2011**, *98*(1), 1–10.
[33] Vercauteren, J.; Matheeussen, C.; Wauters, E.; Roekens, E.; Van Grieken, R.; Krata, A.; Makarovska, Y.; Maenhaut, W.; Chi, X.; Geypen, B. An extensive look at the local differences in chemical composition of PM_{10} in Flanders, Belgium. Atmos. Environ. **2011**, *45*(1), 108–116.
[34] Heal, M.; Hibbs, L.; Agius, R.; Beverland, I. Total and water soluble trace metal content of urban background PM_{10}, $PM_{2.5}$ and Black Smoke in Edinburgh. UK. Atmos. Environ. **2005**, *39*(8), 1417–1430.
[35] Johansson, C.; Norman, M.; Burman, L. Road traffic emission factors for heavy metals. Atmos. Environ. **2009**, *43*(31), 4681–4688.
[36] Aldabe, J.; Elustondo, D.; Santamaría, C.; Lasheras, E.; Pandolfi, M.; Alastuey, A.; Querol, X.; Santamaría, J. Chemical characterisation and source apportionment of $PM_{2.5}$ and PM_{10} at rural, urban and traffic sites in Navarra (North of Spain). Atmos. Res. **2011**, *102*(1–2), 191–205.
[37] Gianini, M.; Gehrig, R.; Fischer, A.; Ulrich, A.; Wichser, A.; Hueglin, C. Chemical composition of PM_{10} in Switzerland: An analysis for 2008/2009 and changes since 1998/1999. Atmos. Environ. **2012**, *54*, 97–106.
[38] Environmental Quality in Belgrade. Kvalitet životne sredine grada Beograda u 2011. Available at http://www.zdravlje.org.rs/publikacije/Zivotna-sredina-bgd-2011-II%20korektura.pdf, pp. 145. (in Serbian, accessed Aug 2014).
[39] US Environmental Protection Agency. Technical Support Document: Control of Emissions of Hazardous Air Pollutants from Motor Vehicles and Motor Vehicle Fuels. Office of Transportation and Air Quality: Washington, DC, 2000. Available at http://www.epa.gov/otaq/regs/toxics/r00023.pdf (accessed Aug 2014).
[40] Pacyna, E.G.; Pacyna, J.M.; Fudala, J.; Strzelecka-Jastrzab, E.; Hlawiczka, S.; Panasiuk, D.; Friedrich, R. Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmos. Environ. **2007**, *41*(38), 8557–8566.
[41] Viana, M.; Pey, J.; Querol, X.; Alastuey, A.; de Leeuw, F.; Lükewille, A. Natural sources of atmospheric aerosols influencing air quality across Europe. Sci. Total Environ. **2014**, *472*, 825–833.

Journal of Toxicology and Environmental Health, Part A
Current Issues

ISSN: 1528-7394 (Print) 1087-2620 (Online) Journal homepage: http://www.tandfonline.com/loi/uteh20

Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia

Svetlana Stanišić Stojić, Nemanja Stanišić, Andreja Stojić & Andrej Šoštarić

http://dx.doi.org/10.1080/15287394.2015.1101407

Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia

Svetlana Stanišić Stojić[a], Nemanja Stanišić[b], Andreja Stojić[c], and Andrej Šoštarić[c]

[a]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia; [b]Singidunum University, Belgrade, Serbia; [c]Institute of Physics Belgrade, University of Belgrade, Belgrade, Serbia; [c]Institute of Public Health Belgrade, Belgrade, Serbia

ABSTRACT

The aim of this study was to investigate the association between short- and long-term exposure to particulate matter (PM_{10}), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and soot and mortality attributed to circulatory and respiratory diseases in Belgrade area (Serbia). The analyzed data set comprised results of regular pollutant monitoring and corresponding administrative records on frequency of daily mortality in the period 2009–2014. Nonlinear exposure–response dependencies and delayed effects of temperature were examined by means of distributed lag nonlinear models. The air pollutant loadings and circulatory system-related death rates in Belgrade area are among the highest in Europe. Data demonstrated that excess risk of death with short-term exposure to elevated concentrations of PM_{10}, SO_2, and soot was not significant, whereas marked effect size estimates for exposure over 90 d preceding mortality were found. The influence of chronic exposure was shown to be greater for respiratory than circulatory system-related mortality. When stratified by age and gender, higher risk was noted for male individuals below the age of 65 years.

ARTICLE HISTORY
Received 24 August 2015
Accepted 25 September 2015

Over the last several decades, levels of respirable particulate matter (PM) and inorganic gaseous pollutants, such as nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), have been globally recognized as a serious issue with a wide range of adverse health effects (Beckerman et al., 2012; Chiu et al., 2013; Costa et al., 2014; Chang et al., 2015). Despite the fact that the overall impact of outdoor exposure is estimated to be relatively small, public health burden is growing in urban areas (Barrett, 2015), with 9 out of 10 individuals being exposed to pollutant levels exceeding the recommended limits (Costa et al., 2014; World Health Organization [WHO], 2014). The overwhelming evidence corroborates that reduction in air pollutant concentrations may lead to increasing overall life expectancy (Barrett, 2015), although there is still little evidence of a threshold at which no mortality risk and adverse health outcomes would be expected (Buekers et al., 2011). The current legislative guidelines, including the National Ambient Air Quality Standards (U.S. Environmental Protection Agency [EPA]) and Air Quality Framework Directive (European Union [EU]), primarily rely on data from retrospective epidemiological studies that analyze large-sample statistics. Regardless of the potential limitations mentioned in the literature, these results have served as a basis for designing abatement strategies, thus enhancing air quality and life expectancy, despite growth of population and industrial progress (Solomon et al., 2012).

The aims of this study were to investigate the association between air pollution and mortality, and to test the hypothesis that the cardiovascular and respiratory mortality observed effects are related to exposure to PM_{10} (particles with diameter less than 10 μm), NO_2, SO_2, and soot. The study is based on multiple-year measurements and administrative records in the Belgrade, Serbia, area. Former Yugoslavian countries represent a European region with little information on the levels of atmospheric pollution and related health outcomes (Bartoš et al., 2009). A serious problem of air pollution in Serbia emerged partly due to a weak framework of environmental policy and

CONTACT Svetlana Stanišić Stojić sstanisic@singidunum.ac.rs Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia.

partially as a result of outdated technology and equipment in all economic sectors. Technological obsolescence of the energy-generating system, low energy efficiency, and increased reliance on sulfur-containing lignite and fuel oil, not only for industrial activities but also for residential heating, place a significant burden on the environment. The annual mean PM_{10} concentration of 38.2 μg/m^3 in 2008 was considerably below the mean in the last decade in Serbia (Perišić et al., 2014), but still higher than levels measured in other European cities for the same year: Brussels (28 μg/m^3), Zagreb (34 μg/m^3), Prague (27 μg/m^3), Dusseldorf (29 μg/m^3), Frankfurt (27 μg/m^3), Budapest (29 μg/m^3), Rome (35 μg/m^3), Amsterdam (24 μg/m^3), Madrid (26 μg/m^3), and Geneva (22 μg/m^3) (WHO, 2008–2013). With respect to mortality rate, cardiovascular diseases were the leading cause of death in Belgrade over the last 15 years with frequencies of 635 to 677 per 100,000 inhabitants (Statistical Office of the Republic of Serbia, 2015), which were among the highest values in the European Union (EU) region ("Detailed Mortality Database," World Health Organization 2010, in World Health Organization, Regional Office for Europe, n.d.).

Belgrade, the capital of Serbia, is positioned at the confluence of two international waterways, and as such represents an important regional traffic hub that bridges the roads of Eastern and Western Europe. Several industrial emission sources, comprising the petrochemical facility, nitric plant, oil refinery, and glass industry, are located in the suburban area of Belgrade 7 to 13 km in the north/northeast direction. Further, surface lignite exploitation and thermal plants that produce more than 50% of electricity for the Serbian market are located in the municipalities of Belgrade, ranging from 25 to 40 km in the south/southwest direction. There are approximately 200,000 households that obtain heat through a district heating system comprising 14 plants located throughout the city of Belgrade, where gas, fuel oil, and locally produced lignite are burned. In addition, an equal number of households use local fireboxes that burn solid and liquid fuels with high sulfur content and unknown content of other elements. Besides these factors, increasing traffic congestion and a significant share of old and poorly maintained vehicles contribute to this issue. With respect to automobiles, the ownership rate in Serbia rose from 200 passenger cars per 1000 subjects in 2000 to 344 cars per 1000 subjects in 2011 (Stojić et al., 2015); thus, vehicle traffic is one of the major sources of urban pollution.

Methods

The mortality rates were divided into the following age groups: ≤65 years, >65 years, and unknown. The group of unknown age was excluded from the cause-specific analysis because the average daily mortality was low. Daily time-series data of total mortality and mortality attributed to circulatory and respiratory system diseases (I00–I99 and J00–J99, respectively, according to the International Statistical Classification of Diseases [ICD-10] code) for the 2009–2014 period were obtained from the Institute of Public Health Belgrade. The daily mean concentrations of PM_{10}, NO_2, SO_2, and soot were obtained from 7, 21, 22, and 16 monitoring stations, respectively, uniformly distributed within the monitoring network of the Institute of Public Health Belgrade throughout the city area. Measurements were performed at the automatic stations by means of a beta-ray attenuation sampler (Thermo FH 62 I-R) for PM_{10} and referent sampling devices, Horiba APNA 360 and APSA 360 analyzers, for NO_2 and SO_2, respectively. A referent Sven Leckel sampler for PM_{10} was utilized at semiautomatic measuring stations, whereas for determination of NO_2 and SO_2 concentrations, this was performed based on ISO 6768:1998 (modified Griess–Saltzman method) and ISO 6767:1990 (tetrachloromercurate [TCM]/pararosaniline method) standards, respectively. Soot concentrations were obtained by the use of a Pro-Ekos device based on the ISO 9835:1993 standard. Meteorological data obtained from the Global Data Assimilation System with spatial resolution of 1 degree were combined over 24-h periods to provide a mean, median, maximum, minimum, and range for temperature, relative humidity, and atmospheric pressure.

In order to determine the influence of air pollutants on mortality frequency, it was necessary to control for effects of other confounding factors affecting results, such as season, temperature, and day of the week (Tsai et al., 2014). The influence of temperature is shown to be both delayed in time and shifted by the so-called "harvesting effect," a temporal advance in deaths that may have occurred later in time in the absence of exposure to heat or cold, which is typically followed by a period of reduced mortality (Ye et al., 2012). In order to simultaneously capture the nonlinear exposure-response dependencies and delayed effects of temperature, distributed lag nonlinear models (DLNMs) were utilized. This methodology is based upon the definition of a "cross-basis," a bidimensional space of functions that simultaneously describes the shape of the relationship along both the space of the predictor and the lag dimension of its occurrence (Gasparrini et al., 2012). The implementation of the DLNM framework is available in the statistical environment R (Gasparrini 2011). Based upon the methodology presented by Gasparrini et al. (2015), the exposure-response curve was modeled with a quadratic B-spline with three internal knots placed at the 10th, 75th, and 90th percentiles of the observed local temperature distribution and the lag-response curve (maximum lag up to 21 d) with a natural cubic B-spline with an intercept and three internal knots placed at equally spaced values in the log scale. In order to control for seasonal and chronic effects, a natural cubic B-spline of time with 8 degrees of freedom per year was included. Finally, the model also included an indicator of day of the week.

The "base model" (quasi-Poisson regression with no pollutants) is specified as follows:

$$E(Y_t) = \exp\{\alpha + \beta T_{t,l} + NS(time, df) + \lambda DOW_t\}$$

where Y_t is a daily death count on day t; α is the intercept; $T_{t,l}$ is a matrix of variables obtained by temperature transformation; β is a vector of coefficients for $T_{t,l}$; l is lag day; $NS(time, df)$ is the natural cubic spline of time; and DOW_t and λ are dummy variables representing day of the week and corresponding vector of coefficients, respectively.

The effects of the four examined air pollutants (PM_{10}, SO_2, NO_2, and soot) on mortality rate were assumed to be linear and examined by means of inclusion of variables representing their concentration levels (intervals of 10 $\mu g/m^3$) in the aforementioned base model. For each pollutant, a separate model was specified for each of the 5 following time frames: lag0, lag1, moving average of 3 d, moving average of 30 d, and moving average of 90 d. Separate models were further specified for circulatory and respiratory system-related deaths, as well as for gender and age categories within the circulatory category, the size of which allowed us to do so. In order to examine the combined effect of air pollutants, a multipollutant model was specified for each of the five time frames.

Results and discussion

The annual mean PM_{10} concentrations in Belgrade area were in the range from 39.74 to 62.32 $\mu g/m^3$, whereas 24-h average PM_{10} concentration for the entire period amounted to 48.31 $\mu g/m^3$. The registered exceedances of the proposed air quality guideline value of 50 $\mu g/m^3$ ranged from 75 to 154 d per year, corresponding to a range from 20.5 to 42.2% of total number of days. The PM_{10} exceedances were mostly registered in urban streets with severe traffic congestion. The daily mean concentrations of NO_2, SO_2, and soot were 15.52, 32.68, and 20.71 $\mu g/m^3$ for the entire period, respectively. The observed PM_{10}, SO_2, and soot levels exhibited clear seasonal pattern with highest values registered during the cold season (particularly SO_2) due to fuel burning for heating operations, as well as low planetary boundary-layer height, low wind speed, and stable atmospheric conditions that favor pollutant accumulation (Figure 1). Conversely, NO_2 concentrations did not exhibit a marked seasonal dependence, while average concentrations for warm (April through October) and cold season are almost identical, indicating that NO_2 did not originate from heating. An increase in NO_2 concentrations has been observed since 2011, probably as the result of greater volume of traffic, and thus, hourly concentrations were found to exceed target values occasionally throughout the year, particularly in congested streets operating at their upper capacity.

The daily mortality rate in Belgrade area for the observed period included 113,615 deaths, out of which 60,505 (53.2%) and 4,657 (4.1%) were

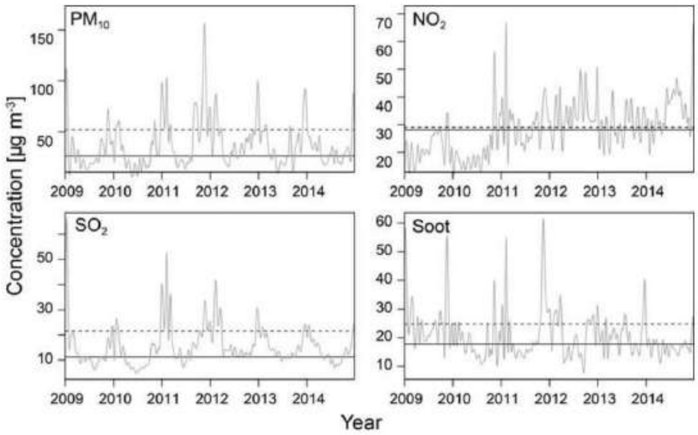


Figure 1. Seasonal patterns in pollutant concentrations. The mean values are indicated by solid and dashed lines for warm (April through October) and cold seasons, respectively.

related to circulatory and respiratory diseases, respectively. The leading specific causes of death were cardiomyopathy (I42), followed by myocardial and cerebral infarction with subsequent complications (I20–I25, I63). Further, respiratory-related mortality was mainly attributed to chronic obstructive pulmonary disease (COPD), accounting for almost 50% of cases, while these values might be higher when taking into account that COPD patients are prone to death due to pneumonia or cardiovascular disease (Pope et al., 2004). When compared to the EU mortality statistics ("Detailed Mortality Database," World Health Organization 2010, in World Health Organization, Regional Office for Europe, n.d.), the death rates associated with cardiovascular diseases in Belgrade area would be ranked high, immediately following the highest crude death rates (deaths per 100,000 inhabitants) registered in Bulgaria (987.4 deaths/1000,000), Romania (729.5), Latvia (727.1), Lithuania (762.8), and Hungary (658.2). With respect to respiratory system-related mortality, the United Kingdom, Denmark, and Portugal recorded the highest death rates of 122.2, 105.1, and 111.5 per 100,000 inhabitants, respectively, whereas the mean annual death rate from Belgrade area of 40 per 100,000 inhabitants is comparable to values of 54.0, 62.5, and 44.3 per 100,000 inhabitants detected in neighboring countries, Bulgaria, Hungary, and Croatia, respectively.

The observed daily mortality frequency was fitted to values in the base model, and corresponding data are presented in Figure 2. The graph illustrates that the base model captured the existing temporal variations in mortality (namely, long-term trend, seasonal, and day-of-the-week specific variations), yielding residuals centered around zero, with no apparent systematic pattern.

The estimated percent changes in mortality rate due to a 10-μg/m^3 increase in pollutant concentrations are summarized in Table 1. As can be seen, excess risk of death due to short-term exposure to elevated concentrations of PM_{10}, SO_2 and soot was estimated to be relatively small, not exceeding 1%. In contrast, a significant impact of long-term variations in pollutant concentrations was found, with severalfold higher and significant effect size estimates for exposure over 90 d preceding the death. Hoek et al. (2013) concluded that the existing epidemiologic studies provide relatively scarce evidence on the association between chronic PM_{10} exposure and mortality, whereas influence of chronic exposure to other pollutants is better documented. Thus, wider confidence intervals and larger variability of the estimated effects are often reported for mortality associated with respiratory diseases, due to the limited number of

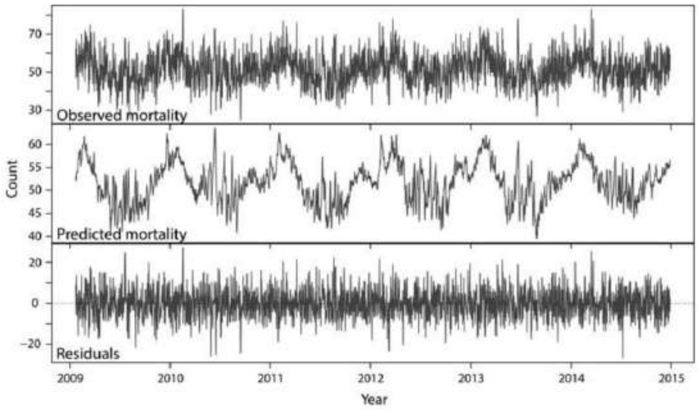


Figure 2. The observed daily counts of total mortality, fitted values from the base model, and corresponding residuals.

observations. When comparing to the previous findings, our results are consistent with several studies showing that adverse health effects associated with air pollution persisted to a month and/or longer after exposure, consequently outweighing the short-term effects during 0–3 d lag periods (Zanobetti et al., 2003; Heinrich et al., 2012; Beverland et al., 2012). The correlation between long-term exposure to air pollutants and respiratory-related disease mortality was shown to be greater than for the cardiovascular system, which is in agreement with previous observations (Carey et al., 2013; Tsai and Yang, 2014).

The impact of a 90-d exposure was also pronounced when stratifying by age groups, with higher risk estimated for the population below the age of 65 years, which may be attributed partly to the fact that these individuals are more physically active and spend more time outdoors. However, these results are not in compliance with the majority of daily time-series studies conducted in the United States and EU, reporting that elderly subjects are more susceptible to air pollutant effects (Ostro et al., 2006; Perez et al., 2015). According to Pope et al. (2006), age alone is a confounding factor for susceptibility only in the case of preexisting health issues. Data showed that only participants who were previously diagnosed with obstructive atherosclerosis during coronary angiography suffered from ischemic events shortly after exposure to air pollutants. The greater susceptibility of individuals below the age of 65 years in our study may also be related to low education and socioeconomic status in developing countries as important contributing factors for pollution-related mortality, including poor nutrition, less access to health care, and higher psychosocial stress than would normally be expected in a younger population (O'Neill et al., 2005). Research results on Serbian population adverse health effects in 2013, encompassing 6,500 households, highlighted smoking as one of the most important risk factors, with about 30% of daily smokers among the adults older than 20 years (Ministry of Health of the Republic of Serbia, Belgrade, 2013). In addition, the same investigation revealed that 47.5% of the adult population in the Republic of Serbia in 2013 was diagnosed with hypertension or potential hypertension (systolic blood pressure ≥ 140 mm Hg, and/or diastolic pressure ≥ 90 mm Hg, or consumption of antihypertensive agents). The overall measure of population health, known as average life expectancy, was estimated at 74.3 years in Belgrade area, reaching 73.6 years for men and 78.5 years for women (Statistical Office of the Republic of Serbia, 2015). These values are below the average life expectancy of 80.6 years recorded in the EU-28 ("Mortality and Life Expectancy Statistics," 2013).

In the case of NO_2, the results indicate that the greatest effects of exposure might also be expected within the time frame of weeks to months.

Table 1. The Individual Effects: The Estimated Percentage Changes in Mortality due to a 10-µg m^{-3} Increase in Pollutant Concentrations.

Pollutant	Period	Total	CS-RM	CS-RM ≤ 65	CS-RM > 65	CS-RM male	CS-RM female	RS-RM
PM_{10}	Lag 0	0.02%	0.03%	0.10%	0.01%	0.10%	0.00%	−1.00%*
		(−0.20%, 0.30%)	(−0.30%, 0.40%)	(−1.00%, 1.00%)	(−0.30%, 0.40%)	(−0.40%, 1.00%)	(−0.50%, 0.40%)	(−2.00%, 0.20%)
	Lag 1	−0.03%	0.10%	0.10%	0.10%	0.05%	0.20%	−1.00%*
		(−0.30%, 0.20%)	(−0.20%, 0.50%)	(−1.00%, 1.00%)	(−0.20%, 0.50%)	(−0.40%, 1.00%)	(−0.20%, 1.00%)	(−2.00%, 0.10%)
	MA 3	0.30%*	0.40%*	1.00%	0.30%	1.00%***	0.02%	0.10%
		(−0.03%, 1.00%)	(−0.03%, 1.00%)	(−0.30%, 2.00%)	(−0.10%, 1.00%)	(0.20%, 1.00%)	(−1.00%, 1.00%)	(−1.00%, 2.00%)
	MA 30	0.50%	0.50%	1.00%	0.40%	0.10%	1.00%	−0.02%
		(−0.40%, 1.00%)	(−1.00%, 2.00%)	(−2.00%, 5.01%)	(−1.00%, 2.00%)	(−2.00%, 2.00%)	(−1.00%, 3.00%)	(−3.99%, 4.01%)
	MA 90	6.02%***	4.01%*	6.02%	4.01%	5.01%	4.01%	9.04%
		(2.00%, 9.04%)	(−1.00%, 9.04%)	(−7.97%, 19.18%)	(−1.00%, 9.04%)	(−2.00%, 12.07%)	(−3.00%, 10.05%)	(−7.97%, 25.32%)
NO_2	Lag 0	−0.30%	−1.00%	1.00%	−1.00%*	−0.40%	−1.00%	−3.99%**
		(−1.00%, 0.40%)	(−2.00%, 0.30%)	(−2.00%, 3.00%)	(−2.00%, 0.20%)	(−2.00%, 1.00%)	(−2.00%, 0.50%)	(−6.98%, −1.00%)
	Lag 1	−0.02%	−0.30%	1.00%	−1.00%	−1.00%	0.10%	−3.00%*
		(−1.00%, 1.00%)	(−1.00%, 1.00%)	(−1.00%, 3.00%)	(−1.00%, 0.40%)	(−2.00%, 0.40%)	(−1.00%, 1.00%)	(−5.98%, 0.04%)
	MA 3	0.10%	−1.00%	1.00%	−1.00%	1.00%	−1.00%*	−3.99%*
		(−1.00%, 1.00%)	(−2.00%, 1.00%)	(−2.00%, 4.01%)	(−2.00%, 0.50%)	(−1.00%, 2.00%)	(−3.00%, 0.10%)	(−7.97%, 0.30%)
	MA 30	0.20%	1.00%	1.00%	1.00%	−1.00%	2.00%	−3.99%
		(−3.00%, 3.00%)	(−3.00%, 5.01%)	(−8.96%, 12.07%)	(−3.00%, 5.01%)	(−6.98%, 5.01%)	(−3.00%, 8.03%)	(−16.86%, 10.05%)
	MA 90	10.05%*	3.00%	15.11%	2.00%	13.08%	−5.98%	5.01%
		(−1.00%, 21.22%)	(−11.93%, 19.18%)	(−25.66%, 57.60%)	(−14.89%, 18.16%)	(−8.96%, 35.62%)	(−26.64%, 15.11%)	(−47.82%, 60.78%)
SO_2	Lag 0	0.50%	0.30%	4.01%**	−0.30%	2.00%	−1.00%	−4.99%
		(−1.00%, 2.00%)	(−1.00%, 2.00%)	(0.05%, 9.04%)	(−2.00%, 1.00%)	(−1.00%, 4.01%)	(−3.00%, 1.00%)	(−9.95%, 1.00%)
	Lag 1	0.40%	1.00%	2.00%	0.30%	−1.00%	2.00%	−4.99%
		(−1.00%, 2.00%)	(−1.00%, 2.00%)	(−3.00%, 6.02%)	(−1.00%, 2.00%)	(−3.00%, 1.00%)	(−0.40%, 4.01%)	(−9.95%, 1.00%)
	MA 3	1.00%	1.00%	5.01%	−0.02%	3.00%**	−2.00%	−4.99%
		(−0.40%, 3.00%)	(−2.00%, 3.00%)	(−1.00%, 11.06%)	(−2.00%, 2.00%)	(0.10%, 7.02%)	(−4.99%, 1.00%)	(−12.92%, 3.00%)
	MA 30	1.00%	3.00%	2.00%	4.01%	1.00%	5.01%	0.10%
		(−3.99%, 6.02%)	(−3.00%, 10.05%)	(−15.87%, 20.20%)	(−3.00%, 10.05%)	(−7.97%, 11.06%)	(−3.99%, 14.10%)	(−22.74%, 23.27%)
	MA 90	16.13%*	6.02%	19.18%	5.01%	20.20%	−3.99%	47.07%
		(−2.00%, 34.58%)	(−17.84%, 31.49%)	(−47.82%, 91.99%)	(−21.76%, 31.49%)	(−15.87%, 57.60%)	(−37.29%, 29.42%)	(−40.17%, 142.25%)
Soot	Lag 0	0.10%	0.20%	2.00%	−0.04%	0.20%	0.20%	−3.00%*
		(−1.00%, 1.00%)	(−1.00%, 1.00%)	(−1.00%, 4.01%)	(−1.00%, 1.00%)	(−1.00%, 2.00%)	(−1.00%, 2.00%)	(−6.98%, 0.20%)
	Lag 1	0.10%	1.00%	2.00%	0.40%	0.20%	1.00%	−3.00%
		(−1.00%, 1.00%)	(−0.40%, 2.00%)	(−0.40%, 5.01%)	(−1.00%, 1.00%)	(−1.00%, 2.00%)	(−0.40%, 2.00%)	(−5.98%, 1.00%)
	MA 3	1.00%	1.00%	3.00%*	0.20%	2.00%*	−0.40%	−2.00%
		(−0.30%, 1.00%)	(−1.00%, 2.00%)	(−0.30%, 6.02%)	(−1.00%, 1.00%)	(−0.10%, 3.00%)	(−2.00%, 1.00%)	(−5.98%, 2.00%)
	MA 30	2.00%	2.00%	6.02%	1.00%	1.00%	3.00%	6.02%
		(−1.00%, 4.01%)	(−1.00%, 6.02%)	(−3.00%, 15.11%)	(−2.00%, 5.01%)	(−3.99%, 6.02%)	(−2.00%, 8.03%)	(−5.98%, 19.18%)
	MA 90	16.13%***	18.16%**	37.69%*	15.11%*	27.37%**	11.06%	19.18%
		(5.01%, 26.34%)	(3.00%, 33.55%)	(−2.00%, 80.04%)	(−0.40%, 31.49%)	(6.02%, 50.22%)	(−8.96%, 31.49%)	(−31.49%, 73.58%)

Note. CS-RM, circulatory system-related mortality, RS-RM, respiratory system-related mortality. Significance: $*p < .1$; $**p < .05$; $***p < .01$.

However, exposure of up to 3 d preceding death was negatively associated with all causes of mortality, particularly respiratory system related. Bearing in mind that the link between NO_2 exposure and mortality was already demonstrated in a number of epidemiological studies (Faustini et al., 2014), the observed negative correlation may be attributed to a "harvesting" effect in the frailest individuals that occurs with a time lag that requires further investigation. The other possibility is that the observed inverse NO_2 effect pattern might be a result of omitted variable bias. Such a possibility is supported by Brook et al. (2007), claiming that an unrealistically strong relationship between NO_2 exposure and mortality is driven by the fact that NO_2 exhibits high correlations in time and space with a range of traffic-related and photochemically formed toxic pollutants, which is why it appears as an indicator of some other variable or process. When considering individual effects, the strongest associations were noted between all-cause mortality and chronic exposure to SO_2 and soot, with the latter being significant.

The combined effects of all pollutants are presented in Figure 3. As noted, a 10-μg/m^3 short-term rise in SO_2 and soot concentrations was followed by an increase of 1% in number of daily deaths, whereas greater effects of exposure over the period of 3 d preceding death were only observed for respiratory outcomes. Similarly, the influence of cumulative exposure over the last 90 d were predominantly related to soot with elevated concentrations of SO_2 correlated with a significant rise in number of deaths attributed to respiratory diseases. These findings are consistent with previous studies demonstrating beneficial health effects from reducing SO_2 emissions in terms of respiratory mortality and hospital admissions

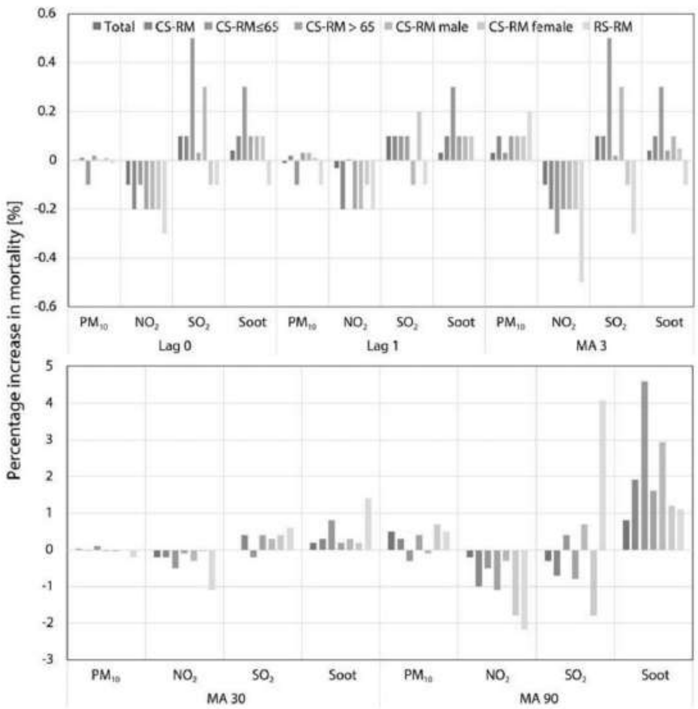


Figure 3. The combined effects of pollutants: the estimated percentage changes in mortality due to a 10-μg/m^3 increase in pollutant concentrations. Lag0, pollutant concentrations on the date death occurred; Lag1, pollutant concentrations on the day before death; MA3, MA30, and MA90, average pollutant concentrations over the period of 3, 30, and 90 d preceding death, respectively.

(Chen et al., 2012; Dockery et al., 2013). The observed long-term effects of soot were particularly pronounced and significant for circulatory system-related mortality. As regards PM_{10}, the chronic effects were followed by a significant elevation in total and cardiovascular outcomes (5 and 3%, respectively).

The differences in pollutant nature and origin affect the role in health risk. For instance, inorganic gaseous oxides are not homogeneously spatially distributed in urban environments as PM (Beelen et al., 2014). Further, locally specific conditions, such as low energy efficiency and burning of sulfur-containing coal and fuel oil in Belgrade area, in particular contribute to observations of reported SO_2 and PM_{10} concentrations being higher than in other studies conducted in the United States or Europe. Soot refers to a carbon-rich material formed by incomplete combustion of fossil fuels and biomass, and its association with all-cause mortality was particularly notable (Petzold et al., 2013). Studies demonstrated that soot particles comprise a significant health risk due to the presence of bound polycyclic aromatic hydrocarbons (PAH), compounds that trigger formation of reactive oxygen species (ROS), which further leads to inflammation and cellular damage (Ghio et al., 2012; Shiraiwa et al., 2012; Muala et al., 2013).

Regarding the more susceptible gender, conflicting findings are found, and drawing definite conclusions based upon between-study comparisons is complicated by the fact that studies differ with regard to many factors (Hoek et al., 2013; LaKind et al., 2015). Findings demonstrated that the male population appears to be more susceptible to ambient air pollution, which needs to be considered with caution due to the lack of data on lifestyle factors, particularly smoking. The observed relationship may be associated with smaller diameter of proximal airways and lower respiratory minute volume in females, which result in a major portion of PM_{10} being deposited in the upper respiratory region and efficiently removed by mucociliary clearance (Gehr and Heyder, 2000).

Our study, just like other retrospective epidemiological studies, has certain limitations that are worth mentioning and that might affect the estimated health risk in a way that is difficult to predict. The evaluation of adverse health effects might be biased by confounding factors that often remain unrecognized. One of the most evident uncertainties is related to the fact that individual monitoring is cost prohibitive, and data obtained from a limited number of monitoring stations do not reflect individual exposure (Barrett, 2015). Further, Ghio et al. (2012) suggested that PM_{10} mass concentration is not the only aspect that needs to be considered when evaluating the adverse health effects of exposure, since physical features and chemical composition are also implicated in particles' relative toxicity. At present, it is still not clear which elements or compounds pose the greatest risk (Gray et al., 2015). Retrospective studies are also limited by the lack of adjustment for potential confounding factors, such as smoking, alcohol use, age or body mass index (BMI), and presence of preexisting circulatory diseases or associated clinical conditions, including hypertension, diabetes, mellitus, hypercholesterolemia, use of antihypertensive drugs, lipid-lowering agents, and antidiabetic compounds (Gibbson et al., 2013; Sui et al., 2013). Finally, it needs to be emphasized that mortality rate attributed to pollutant exposure should not be simply interpreted as the only preventable fraction, as removing one risk factor in multicausal diseases may give rise to the relative importance of other relevant causes (Künzli et al., 2000).

Conclusions

The results of our study indicate that adverse health effects are associated with exposure to high levels of air pollutants. The findings suggest that adverse health effects are not solely observed in a short period of time, but remain persistent chronically upon exposure. Until recently, significant heterogeneity was observed in the estimates of the effects of pollution on mortality, which highlights the magnitude and complexity of the problem. Therefore, further studies are required to expand existing knowledge and provide more comprehensive information on how diverse populations respond to air pollutants. The locally specific factors affecting the association between pollutant exposure and mortality include PM_{10}

chemical composition, existing pollutant emission sources, population characteristics, and socioeconomic factors. In the present study, it is also necessary to take into consideration the fact that the reported levels of air pollutants in the study area, namely, SO_2 and PM_{10}, exceed those observed in other European cities.

Funding

This study was conducted as part of projects III43007 and III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011–2015.

References

Barrett, J. R. 2015. "Exported" deaths and short-term PM_{10} exposure: Factoring the impact of commuting into mortality estimates. *Environ. Health Perspect.* 123: A22.

Bartoš, T., Čupr, P., Klánová, J., and Holoubek, I. 2009. Which compounds contribute most to elevated airborne exposure and corresponding health risks in the Western Balkans? *Environ. Int.* 35: 1066–1071.

Beckerman, B. S., Jerrett, M., Finkelstein, M., Kanaroglou, P., Brook, J. R., Arain, M. A., Sears, M. R., Stieb, D., Balmes J., and Chapman, K. 2012. The association between chronic exposure to traffic-related air pollution and ischemic heart disease. *J. Toxicol. Environ. Health A* 75: 402–411.

Beelen, R., Raaschou-Nielsen, O., Stafoggia, M., Andersen, Z. J., Weinmayr, G., Hoffmann, B., Wolf, K., Samoli, E., Fisher, P., Nieuwenhuijsen, M., Vineis, P., Xun, W. W., Katsouyanni, K., Dimakopolou, K., Oudin, A., Forsberg, B., Modig, L., Havulinna, A. S., Lanki, T., Turunen, Oftedal, B., Nystad, W., Nafstad, P., De Faire, U., Pedersen, N. L., Östenson, C-G., Fratiglioni, L., Penell, J., Korek, M., Pershagen, G., Eriksen, K. T., Overvad, K., Ellermann, T., Eeftens, M., Peeters, P. H., Meliefste, K., Wang, M., Bueno-de-Mesquita, B., Sugiri, D., Krämer, U., Heinrich, J., De Hoogh, K., Key, T., Peters, A., Hampel, R., Concin, H., Nagel, G., Ineichen, A., Schaffner, E., Probst-Hensch, N., Künzli, N., Schindler, C., Schikowski, T., Adam, M., Phuleria, H., Vilier, A., Clavel-Chapelon, F., Declercq, C., Grioni, S., Krogh, V., Tsai, M-Y., Ricceri, F., Sacerdote, C., Galassi, C., Migliore, E., Ranzi, A., Cesaroni, G., Badaloni, C., Forastiere, F., Tamayo, I., Amiano, P., Dorronsoro, M., Katsoulis, M., Trichopoulou, A., Brunekreef, B., and Hoek., G. 2014. Effects of long-term exposure to air pollution on natural-cause mortality: An analysis of 22 European cohorts within the multicentre ESCAPE project. *Lancet* 383: 785–795.

Beverland, I. J., Cohen, G. R., Heal, M. R., Carder, M., Yap, C., Robertson, C., Hart, C. L., and Agius, R. M. 2012. A comparison of short-term and long-term air pollution exposure associations with mortality in two cohorts in Scotland. *Environ. Health Perspect.* 120: 1280–1285.

Brook, J. R., Burnett, R. T., Dann, T. F., Cakmak, S., Goldberg, M. S., Fan, X., and Wheeler, A. J. 2007. Further interpretation of the acute effect of nitrogen dioxide observed in Canadian time-series studies. *J. Expos. Sci. Environ. Epidemiol.* 17: S36–S44.

Buekers, J., Stassen, K., Panis, L. I., Hendrickx, K., and Torfs, R. 2011. Ten years of research and policy on particulate matter air pollution in hot spot Flanders. *Environ. Sci. Policy* 14: 347–355.

Carey, I. M., Atkinson, R. W., Kent, A. J., van Staa, T., Cook, D. G., and Anderson, H. R. 2013. Mortality associations with long-term exposure to outdoor air pollution in a national English cohort. *Am. J. Respir. Crit. Care Med.* 187: 1226–1233.

Chang, C. C., Chiu, H. F., and Yang, C. Y. 2015. Fine particulate air pollution and outpatient department visits for headache in Taipei, Taiwan. *J. Toxicol. Environ. Health A* 78: 267–277.

Chen, R., Huang, W., Wong, C. M., Wang, Z., Thach, T. Q., Chen, B., and Kan, H., on behalf of the CAPES Collaborative Group. 2012. Short-term exposure to sulfur dioxide and daily mortality in 17 Chinese cities: The China Air Pollution and Health Effects Study (CAPES). *Environ Res.* 118: 101–106.

Chiu, H. F., Tsai, S. S., Weng, H. H., and Yang, C. Y. 2013. Short-term effects of fine particulate air pollution on emergency room visits for cardiac arrhythmias: A case-crossover study in Taipei. *J. Toxicol. Environ. Health A* 76: 614–623.

Costa, S., Ferreira, J., Silveira, C., Costa, C., Lopes, D., Relvas, H., Borrego, C., Roebeling, P., Miranda, A. I., and Paulo Teixeira, J. 2014. Integrating health on air quality assessment—Review report on health risks of two major European outdoor air pollutants: PM and NO_2. *J. Toxicol. Environ. Health B* 17: 307–340.

Dockery, D. W., Rich, D. Q., Goodman, P. G., Clancy, L., Ohman-Strickland, P., George, P., and Kotlov, T. 2013. Effect of air pollution control on mortality and hospital admissions in Ireland. *Research Report (Health Effects Institute)* 176: 3–109.

Faustini, A., Rapp, R., and Forastiere, F. 2014. Nitrogen dioxide and mortality: Review and meta-analysis of long-term studies. *Eur. Respir. J.* 44: 744–753.

Gasparrini, A. 2011. Distributed lag linear and non-linear models in R: The package dlnm. *J. Stat. Software* 43: 1.

Gasparrini, A., Armstrong, B., and Kenward., M. G. 2012. Multivariate meta-analysis for non-linear and other multi-parameter associations. *Stat. Med.* 31: 3821–3839.

Gasparrini, A., Guo, Y., Hashizume, M., Lavigne, E., Zanobetti, A., Schwartz, J., Tobias, A., Tong, S., Rocklöv, J., Forsberg, B., Leone, M., De Sario, M., Bell, M. L., Guo, Y-L. L., Wu, C-F., Kan, H., Yi, S-M., Coelho, M. de S. Z. S., Saldiva, P. H. N., Honda, Y., Kim, H., and Armstrong, B. 2015. Mortality risk attributable to high and low ambient temperature: A multicountry observational study. *Lancet* 386: 369–375.

Gehr, P., and Heyder, J., eds. 2000. *Particle–lung interactions*. Boca Raton, FL: CRC Press.

Ghio, A. J., Carraway, M. S., and Madden, M. C. 2012. Composition of air pollution particles and oxidative stress in cells, tissues, and living systems. *J. Toxicol. Environ. Health B* 15: 1–21.

Gibbons, G. H., Harold, J. G., Jessup, M., Robertson, R. M., and Oetgen, W. J. 2013. The next steps in developing clinical practice guidelines for prevention. *Circulation* 128: 1716–1717.

Gray, D. L., Wallace, L. A., Brinkman, M. C., Buehler, S. S., and La Londe, C. 2015. Respiratory and cardiovascular effects of metals in ambient particulate matter: A critical review. *Rev. Environ. Contam.* 234: 135–203.

Heinrich, J., Thiering, E., Rzehak, P., Krämer, U., Hochadel, M., Rauchfuss, K. M., Gehring, U., and Wichmann, H. E. 2012. Long-term exposure to NO_2 and PM_{10} and all-cause and cause-specific mortality in a prospective cohort of women. *Occup. Environ. Med.* 70: 179–186.

Hoek, G., Krishnan, R. M., Beelen, R., Peters, A., Ostro, B., Brunekreef, B., and Kaufman, J. D. 2013. Long-term air pollution exposure and cardio-respiratory mortality: A review. *Environ. Health* 12: 43.

Künzli, N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O., Filliger, P., Herry, M., Horak, F. Jr, Puybonnieux-Texier, V., Quenel, P., Schneider, J., Seethaler, R., Vergnaud, J.-C., and Sommer, H. 2000. Public-health impact of outdoor and traffic-related air pollution: A European assessment. *Lancet* 356: 795–801.

LaKind, J. S., Goodman, M., Makris, S. L., and Mattison, D. R. 2015. Improving concordance in environmental epidemiology: A three-part proposal. *J. Toxicol. Environ. Health B* 18: 105–120.

Ministry of Health of the Republic of Serbia, Belgrade. 2013. Results of the National Health Survey of the Republic of Serbia. http://www.batut.org.rs/index.php?content=1129 (accessed July 23, 2015).

Mortality and life expectancy statistics. 2013. Eurostat, Statistics explained. http://ec.europa.eu/eurostat/statistics-explained/index.php/Mortality_and_life_expectancy_statistics (accessed July 15, 2015).

Muala, A., Nicklasson, H., Boman, C., Nyström, R., Swietlicki, E., Bosson-Damewood, J., Blomberg, A., Sandström, T., and Löndahl, J. 2013. Respiratory tract deposition of inhaled wood smoke particle in healthy volunteers and patients with chronic obstructive pulmonary disease. *Eur. Respir. J.* 42(suppl. 57): P3630.

O'Neill, M. S., Hajat, S., Zanobetti, A., Ramirez-Aguilar, M., and Schwartz, J. 2005. Impact of control for air pollution and respiratory epidemics on the estimated associations of temperature and daily mortality. *Int. J. Biometeorol.* 50: 121–129.

Ostro, B., Broadwin, R., Green, S., Feng, W. Y., and Lipsett, M. 2006. Fine particulate air pollution and mortality in nine California counties: Results from CALFINE. *Environ. Health Perspect.* 114: 29–33.

Perez, L., Grize, L., Infanger, D., Künzli, N., Sommer, H., Alt, G. M., and Schindler, C. 2015. Associations of daily levels of PM_{10} and NO_2 with emergency hospital admissions and mortality in Switzerland: Trends and missed prevention potential over the last decade. *Environ. Res.* 140: 554–561.

Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z., and Rajšić, S. 2014. Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. *Air Qual. Atmos. Health* 1–11. doi:10.1007/s11869-014-0292-5

Petzold, A., Ogren, J. A., Fiebig, M., Laj, P., Li, S-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A., and Zhang, X.-Y. 2013. Recommendations for reporting" black carbon" measurements. *Atmos. Chem. Phys.* 13: 8365–8379.

Pope, C. A. III, and Dockery, D. W. 2006. Health effects of fine particulate air pollution: Lines that connect. *J. Air Waste Manage. Assoc.* 56: 709–742.

Pope, C. A., Burnett, R. T., Thurston, G. D., Thun, M. J., Calle, E. E., Krewski, D., and Godleski, J. J. 2004. Cardiovascular mortality and long-term exposure to particulate air pollution epidemiological evidence of general pathophysiological pathways of disease. *Circulation* 109: 71–77.

Shiraiwa, M., Selzle, K., and Pöschl, U. 2012. Hazardous components and health effects of atmospheric aerosol particles: Reactive oxygen species, soot, polycyclic aromatic compounds and allergenic proteins. *Free Radical Res.* 46: 927–939.

Solomon, P. A., Costantini, M., Grahame, T. J., Gerlofs-Nijland, M. E., Cassee, F. R., Russell, A. G., Brook, J. R., Hopke, P. K., Hidy, G., Phalen, R. F., Saldiva, P., Sarnat, S. E., Balmes, J. R., Tager, I. B., Özkaynak, H., Vedal, S., Wierman, S. S. G., and Costa, D. L. 2012. Air pollution and health: Bridging the gap from sources to health outcomes: Conference summary. *Air Qual. Atmos. Health* 5: 9–62.

Statistical Office of the Republic of Serbia. 2015. The additionally processed mortality data. Vital statistics.

Stojić, A., Stanišić Stojić, S., Mijić, Z., Šoštarić, A., and Rajšić, S. 2015. Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. *Atmos. Environ.* 106: 71–79.

Sui, X., Li, H., Zhang, J., Chen, L., Zhu, L., and Blair, S. N. 2013. Percentage of deaths attributable to poor cardiovascular health lifestyle factors: Findings from the Aerobics Center Longitudinal Study. *Epidemiol. Res. Int.* 2013: 437465.

Tsai, S. S., and Yang, C. Y. 2014. Fine particulate air pollution and hospital admissions for pneumonia in a subtropical city: Taipei, Taiwan. *J. Toxicol. Environ. Health A* 77: 192–201.

Tsai, S. S., Chen, C. C., and Yang, C. Y. 2014. Short-term effect of fine particulate air pollution on daily mortality: A case-crossover study in a tropical city, Kaohsiung, Taiwan. *J. Toxicol. Environ. Health A* 77: 467–477.

World Health Organization. 2008–2013, Database: Outdoor air pollution in cities. http://www.who.int/phe/health_topics/outdoorair/databases/en (accessed June 25, 2015).

WHO. 2014. Ambient (outdoor) air quality and health. Fact sheet No. 313. Geneva, Switzerland: World Health Organization.

World Health Organization, Regional Office for Europe. n.d. Detailed mortality database. [27/07/2015] http://data.euro.who.int/dmdb (accessed July 27, 2015).

Ye, X., Wolff, R., Yu, W., Vaneckova, P., Pan, X., and Tong, S. 2012. Ambient temperature and morbidity: A review of epidemiological evidence. *Environ. Health Perspect.* 120: 19–28.

Zanobetti, A., Schwartz, J., Samoli, E., Gryparis, A., Touloumi, G., Peacock, J., Anderson, R. H., Le Tertre, A., Bobros, J., Celko, M., Goren, A., Forsberg, B., Michelozzi, P., Rabczenko, D., Hoyos, S. P., Wichmann, H. E., and Katsouyanni, K. 2003. The temporal pattern of respiratory and heart disease mortality in response to air pollution. *Environ. Health Perspect.* 111: 1188.

Air Qual Atmos Health
DOI 10.1007/s11869-016-0411-6

Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation

Mirjana Perišić[1] · Slavica Rajšić[1] · Andrej Šoštarić[2] · Zoran Mijić[1] · Andreja Stojić[1]

Received: 21 January 2016 / Accepted: 19 May 2016

Abstract The aim of this study was to identify levels of population health risk caused by the inhalation of PM_{10}-bound species in an urban area. A combination of multiple location measurements, several analytical tools, and cancer and non-cancer health risk assessment was used to evaluate influences of proximate anthropogenic activities and air pollution transport. The concentrations of PM_{10}, six trace metals (As, Cd, Cr, Mn, Ni and Pb) and benzo[*a*]pyrene were measured at 15 air quality monitoring stations during the period 2011–2015 in a wide area of Belgrade (Serbia). Significant population health risk was estimated as a result of exposure to particulate air pollution. The concentrations of PM_{10}, As, Ni and benzo[*a*]-pyrene exceeded the EU Directive limit and target values. Of all the analysed species, Cr was the major contributor to carcinogenic health risk. Besides strong local sources related to traffic and industry, the influence of transported pollution is estimated in the range 8.95–36.07 %, with potentially the most important sources being located in East and West Europe.

Keywords Health risk · PM_{10} · Trace metals · Transport

Electronic supplementary material The online version of this article (doi:10.1007/s11869-016-0411-6) contains supplementary material, which is available to authorized users.

✉ Mirjana Perišić
mirjana.perisic@ipb.ac.rs

1 Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

2 Institute of Public Health Belgrade, Bulevar Despota Stefana 54, 11000 Belgrade, Serbia

Published online: 31 May 2016

Introduction

Particulate matter with an aerodynamic diameter of less than 10 μm (PM_{10}) has been recognised as a threat to public health on a global scale (WHO 2013; Fuzzi et al. 2015). Epidemiological studies suggest a strong exposure–response correlation between ambient concentrations and short- (hospital admission and premature mortality) and long-term (lung cancer and cardiovascular and immunological diseases) health effects (Valavanidis et al. 2008; Anderson et al. 2012; Stanišić Stojić et al. 2015). Of the entire population, children represent the most sensitive group due to their rapid growth and development of the lungs and immune systems (Mathew et al. 2015; Zhanghua et al. 2015). The composition of PM_{10} varies greatly and depends on many factors, but in urban areas, transition metals, ions (sulphate and nitrate) and organic compounds represent the major components. Numerous studies have indicated that some of the PM-bound species induce very harmful health effects (An et al. 2013; Pandeya et al. 2013; Szabó et al. 2015), noting that the inhalation of chromium-containing aerosols is one of the major concerns (Langard and Costa 2014; Laulicht et al. 2014). This element is emitted to the environment during various natural and anthropogenic activities in mainly two oxidation states: trivalent and hexavalent, where Cr(VI) is considered as more toxic due to its high solubility and mobility. It is a well-reported occupational carcinogen associated with lung, nasal and sinus cancers (Mishra and Bharagava 2016). Likewise, the International Agency for Research on Cancer (IARC 1990) recognised that almost all nickel compounds have been classified as human carcinogens. Based on epidemiological studies, following inhalation exposure, the respiratory system is the primary target of nickel toxicity (Schaumloffel 2012). Several reports from the United States Environmental Protection Agency (USEPA 2011a, 2015) have considered cancer risks caused by the inhalation of nickel compounds emitted by large oil combustion and petroleum refining sources. Arsenic compounds threaten the gastrointestinal tract, circulatory system, liver, kidney and skin (EA 2008; Pushan et al. 2007), whilst benzo[*a*]pyrene (BaP), a well-known polycyclic aromatic hydrocarbon, may cause respiratory tract irritation, damage of the reproductive system and different types of cancer (Kim 2013). BaP is emitted from the incomplete combustion of various fuels, and according to AQE (2015), the main sources of this compound are domestic heating, coal burning and road traffic. Compounds with cadmium are primarily toxic to the kidneys and also cause bone demineralisation, but in polluted industrial areas, excessive exposure to airborne Cd may impair lung function and increase the risk of lung cancer (Bernard 2008). Cadmium is a component of petrol and diesel fuel, and alloyed with copper, it is used in the production of car radiators and car paints (ANPI 2015). In an urban environment, cadmium-laden ultrafine dust occurs in close proximity to busy roads as a result of vehicles, road surface wear and vehicular fuel emissions (Murphy and Hutchinson 2015). Also, an important source of cadmium compounds are coal combustion processes, whether heating in houses or electricity production in industrial areas (Flagan and Seinfeld 2012). Manganese is released to the environment from anthropogenic (industry, fossil fuel combustion and traffic) and natural emission sources (volcanic eruptions and erosion of manganese-containing soils). Evidence for the neurotoxic effects of environmental manganese on children is increasing and includes associations with cognition, memory, behaviour and motor function (WHO 2004). Some epidemiological studies have also examined manganese–lead interaction in early childhood, a period of potentially heightened susceptibility to neurotoxins (Henn et al. 2012). On the other hand, besides anaemia and reproductive problems, exposure to higher lead concentrations can severely damage the brain and kidneys in adults or children and ultimately cause death. The USEPA (2006) classified lead and inorganic lead compounds as 'probable human carcinogens'.

Like most metropolitan areas, Belgrade (Serbia) has significant air pollution problems, mainly as a result of high population density (the average is 3241 people/km^2: AQP 2015) and the accumulation of major economic activities in the region (Rajšić et al. 2008; Mijić et al. 2012; Stojić et al. 2015a). SE Belgrade, about 30 km from the city centre, is home to several industrial facilities, including the largest thermal power plants, Nikola Tesla A and B, and Kolubara A, and the largest lignite coal basins in Serbia. The production capacity of these plants is greater than 50 % of the electricity used in Serbia and, with the coal basin, represents important sources of air pollution in the Belgrade suburban area. Coal mine and combustion processes are characterised by the emission and resuspension of large amounts of particulate dust, which, in the case of the exploitation of lignite, contain a significant portion of arsenic compounds (Jamshed et al. 2015). In the suburban parts of Belgrade, arsenic and BaP are the products of incomplete combustion of fossil and solid fuels, despite the removal of a large number of individual heating units and the transition to a distant heating system in recent years (Perišić et al. 2015). In the municipality of Rakovica, 10 km away from the centre, a large foundry for metal casting production is located, representing the main source of air pollution, especially for heavy metals, in this area.

Generally, the use of outdated technologies in all production sectors, rise in the number of vehicles and the transport of pollutants from neighbouring industrial countries have led to a severe degradation of air quality in the last two decades in Belgrade (Stojić et al. 2016). According to the Environmental Quality Report (EQR 2014), for the period 2000–2013, the number of days with the average PM_{10} concentrations higher than the daily limit values of 50 $\mu g\ m^{-3}$ proposed by EU Directive 2008/50/EC was in the range of 21–345 (at different locations). Because human health represents the main concern in the regulation of urban air quality, the important question is to what extent people are actually exposed to the observed pollution levels.

This study presents analysis of the 5-year data (2011–2015) of PM_{10} and PM_{10}-bound trace metals (As, Cd, Cr, Mn, Ni and Pb) and BaP concentrations in the greater Belgrade area from 15 representative monitoring stations of different types. The measured concentrations and toxicity information were used to characterise the distribution of cumulative cancer and non-cancer health risks, in accordance with the USEPA health risk assessment model (USEPA 2005, 2013) and the California Environmental Protection Agency (CalEPA) Air Toxics Hot Spots Program (CalEPA 2003, 2008). The CalEPA model was used to consider the exposure of the population in different age stages. In recent years, the World Health Organization (WHO) reports have emphasised that transport of particulate matter (PM) contributes significantly to exposure and to health effects (WHO 2006). In order to identify the impact of potential remote emission sources to air pollution in the Belgrade area, advanced trajectory ensemble models (TEMs) were applied based on PM_{10} and trace metal data.

Materials and methods

Sampling sites

With 22.5 % of the country's population, Belgrade represents the largest urban area in the Republic of Serbia and, with 1.6 million citizens, the second largest urban centre in the Balkans. It is located at the confluence of two international waterways and represents an important regional traffic core of connections between Eastern and Western Europe. In this study, data of ambient daily PM_{10} concentrations and corresponding species were obtained from 15 monitoring stations of the Air Pollution Monitoring Network supervised by the Institute of Public Health of Belgrade (IPHB). The measurements were conducted at 11 urban, 2 suburban industrial and 2 rural industrial stations (Fig. 1 and Electronic supplementary material (ESM) Table S-1). Urban stations are mainly located in the city centre, in densely populated zones with heavy and slow traffic. All common forms of public transportation—buses, trolleybuses and trams—are in use, and the route of the international highway E75 passes through the city. The total number of vehicles in the city consists of approximately 40,000 passenger vehicles, 1000 diesel-fuelled city buses, 400 heavy-duty trucks, 108 trams and 76 trolleys per day (Vuković et al. 2015). ESM Fig. S-1 represents the traffic scenario in Belgrade with the main routes and traffic areas. The suburban industrial area is under the influence of intensive industrial activities—the largest coal basin in Serbia, Kolubara, and three large thermal power plants (Nikola

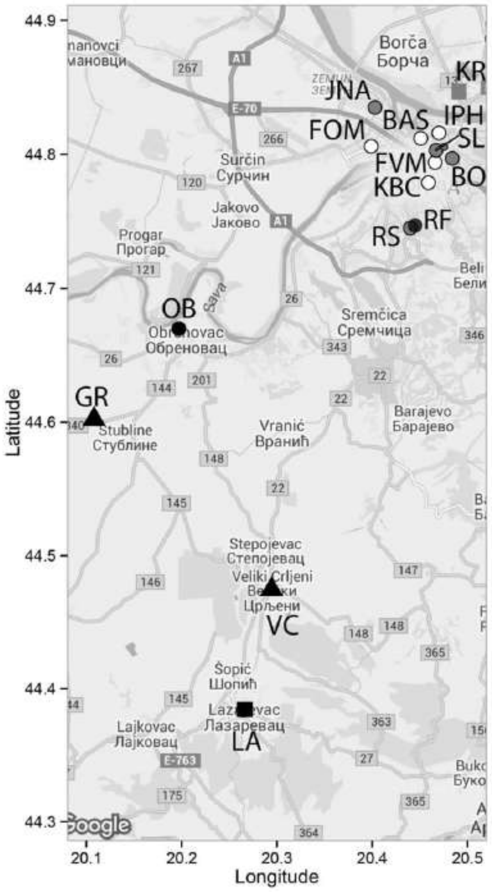


Fig. 1 Sampling site locations in the Belgrade city metropolitan area: urban (*circles*); suburban industrial (*squares*); rural industrial locations (*triangles*); locations exposed to traffic (*white*); traffic and heating (*grey*); and locations near industrial sources (*black*)

Tesla A, TENT A; Nikola Tesla B, TENT B; and Kolubara A)—located about 30 km S–SW from the city centre (ESM Fig. S-2). Rural industrial sites, VC and GR, are located near the coal basin, as well as ash disposal in the electricity production area (Fig. 1). In order to illustrate the primary land use in Belgrade, in ESM Fig. S3, the main industrial areas, agricultural lands, residential areas and urban cores are presented.

Sampling and analysis

The analysed dataset includes PM_{10} mass concentrations, obtained by means of reference Sven Leckel samplers, and daily concentrations of trace metals (As, Cd, Cr, Mn, Ni and Pb) and BaP determined by the use of reference methods: gas chromatography mass spectrometry (Agilent GC 6890 MSD 5975) and inductively coupled plasma mass spectrometry (Agilent 7500) according to standards EN 12341[1] and EN 14902[2], respectively. Values below the method detection limits were replaced by 1/2DL. Details of the measurement methodology, as well as the accuracy and precision of the detection methods, are presented in ESM Table S-1.

Statistical analysis

Basic statistical and trend analyses of measured species were performed by the use of the 'openair' package (Carslaw and Ropkins 2012). The Theil–Sen method within the package Median Based Linear Models ('mblm') was used for trend analysis of the measured concentrations. Deseasonalised time series were obtained using the function SmoothTrend implemented in the 'openair' package. The relative importance of each measured variable to the prediction of PM_{10} mass concentrations, which enabled a better insight into PM_{10} sources, was determined by the use of the 'randomForest' package (Liaw and Wiener 2002). An appropriate number of trees was determined to assure out-of-bag error convergence (i.e. an unbiased internal error estimate of the prediction error) in order to stabilise the error and avoid overfitting. In order to evaluate the temporal distribution and seasonal pattern of the measured variables, the non-parametric probability density function (PDF) was performed with the 'ggplot2' package (Wickham and Chang 2015). The procedure assumes dispersion of the mass of the empirical distribution function over a regular grid and then uses the fast Fourier transform to convolve this approximation with a discretised version of the kernel. Subsequently, a linear approximation is applied to evaluate the density at the specified points. All of the aforementioned packages were implemented in the statistical software environment R (Team RC 2012).

[1] Determination of the PM_{10} fraction of suspended particulate matter—reference method and field test procedure to demonstrate reference equivalence of measurement methods.

[2] Standard method for the measurement of Pb, Cd, As and Ni in the PM_{10} fraction of suspended particulate matter.

Health risk assessment

Trace metal and BaP concentrations were used to characterise the distribution of cumulative cancer and non-cancer health risks in accordance with the USEPA (USEPA 2013) and CalEPA health risk assessment models (CalEPA 2003, 2008). All necessary health risk assessment model calculations are obtainable in the ESM. A detailed description of the USEPA and CalEPA models, and the general principles of model uncertainty, may be found elsewhere (Slezakova et al. 2011; Morello-Frosch et al. 2000; USEPA 2005; CalEPA 1996). Additional toxicity information and the parameters used for calculation in this study were obtained from the USEPA Integrated Risk Information System, Risk Assessment Information System and CalEPA chemical toxicity databases. According to USEPA, the incremental lifetime cancer risk (ILCR), or cancer risk (CR), determined by the CalEPA model represents an incremental probability of an individual developing cancer over their lifetime as a result of exposure to a carcinogenic compound. The cumulative cancer risk (CCR) posed to a receptor is the sum of the total risks from each individual exposure pathway (e.g. oral, dermal, inhalation, etc.) and/or might result from exposure to emissions from multiple species. Here, the CCR represents the sum of the ILCR (or CR) values obtained from exposure through inhalation to each of the five trace metals (As, Cd, Cr, Ni and Pb) and BaP. The acceptable baseline risk level is below 10^{-6}, whilst 10^{-4} is the upper limit of the range of acceptability. The CalEPA model was used in order to emphasise the increased sensitivity to carcinogens during early-in-life exposure and thus considers in detail different features: dose of air inhalation, age sensitivity factor, fraction of time spent at home and exposure duration for six age groups of the population (third trimester of pregnancy, $0<2$, $2<9$, $2<16$, $16<30$ and $30<70$ years). CR values were calculated and expressed for each age group and then summed to estimate the total cancer risk for the population aged 9, 30 and 70 years. Cumulative CR was obtained as the sum of the individual chemical total cancer risks for a 70-year exposure period and corresponds to the cumulative ILCR value obtained by the USEPA. All calculations were performed with the assumption that the bioavailability of trace metals and BaP in PM_{10} was 100 % (Diaz and Dominguez 2009).

Potential non-cancer effects of some chemicals were represented in terms of hazard quotient (HQ), which, for a single substance, is the ratio of the potential exposure to a substance (measured concentrations) and the level at which no adverse effects are expected (reference dose). An estimated HQ value above 1 indicates that, in this case, the concentration exceeds the threshold level and should be of public health concern (USEPA 2011b). When exposure involves more than one chemical and/or multiple exposure pathways, the sum of the individual HQs is represented as the hazard index (HI).

Transport analysis

The regional and long-range transport analyses of PM_{10}, As, Cr, Ni and Pb were performed by the use of 72-h air mass back trajectories and several models. The sampling site SL, located in the middle of the city centre at one of the largest squares and traffic junctions in Belgrade, and also with the highest number of concentration data, was chosen as a representative receptor site to investigate the influence of transport. The trajectories were dynamically calculated at half of the planetary boundary layer (PBL) height above the receptor site since the vertical profiles of pollutant concentrations remained relatively constant around that altitude (Stull 1988). Four trajectories, at 00, 06, 12 and 18 UTC, were calculated for each day using the HYSPLIT model (Draxler and Rolph 2014) and the 'opentraj' package (Opentraj 2015). The PBL height included in GDAS1 (GDAS 2015) was calculated for the receptor site using the MeteoInfo software (Wang 2014). Each trajectory that reached the ground level was excluded from the analysis (about 16 %). To differentiate between the loadings of transported and background pollution to the observed mass concentrations, a pronounced local contribution was excluded from the time series by the use of a frequency-differentiated nonlinear digital filtering algorithm implemented in the function baseline RollingBall (wm = 2, ws = 2) of the 'baseline' package (Kneen and Annegarn 1996) of the statistical software R, thus providing a baseline. Subsequently, trajectory sector analysis (TSA) was applied to the derived baseline in order to obtain the mean background levels and time series of transported pollution according to Stojić et al. (2015b, c). Furthermore, estimation of the potential non-local emission sources and their impacts on the observed concentrations of PM_{10} and constituents was performed using advanced TEMs including a potential source contribution function (PSCF), concentration weighted trajectory (CWT), residence time weighted concentration (RTWC) and the simplified quantitative transport bias analysis (sQTBA), all implemented in MetCor statistical software (MetCor v.1.0, revision 30; Rastogi 2013; Sofowote et al. 2015). All TEMs involve counting the frequency of back trajectory segment endpoints in grid cells that make up the geographical domain of interest for the receptor site. The main difference between the models is the method of incorporation of the measured concentrations within the trajectory endpoint frequency in each grid cell. PSCF shows the percentage frequency of trajectory segment endpoints above a concentration threshold relative to the total trajectory segment endpoints in each grid cell. In CWT, every concentration is used as a weighting factor for the residence times of all trajectories in each grid cell and then is divided by the cumulative residence time from all trajectories. RTWC applies a similar concept; however, the concentrations are equally divided along each trajectory initially and then the logarithm of the redistributed concentrations is used as a weighting factor. The model sQTBA uses Gaussian distributions to calculate the natural transport potential function of a substance based on the distance and time interval away from the receptor (Watson et al. 2008). Visualisation of the TEM outputs and health risk results used the 'raster' and 'rasterVis' (Hijmans et al. 2015) packages from the statistical software R.

Results and discussion

Statistical analysis

The basic statistical parameters and average annual concentrations of PM_{10}, PM_{10}-bound trace metals and BaP are presented in ESM Tables S-2a and S-2b, respectively. The annual average PM_{10} concentrations were 32.49–80.62 μg m^{-3}, with the lowest values in the inhabited parts of suburban and rural areas and the highest concentrations observed at the sites affected by industrial pollution and intensive traffic. The seasonal variability of the concentrations (ESM Fig. S-1a–o) could be the consequence of specific meteorological conditions (Rost et al. 2009) and the intensification of anthropogenic pollution sources during the colder part of the year. A bimodal type of PDF characterises winter, indicating the existence of more than one dominant source, especially in areas where individual heating installations are in use. Trend analysis (ESM Fig. S-2a, b) generally showed a temporal decrease of the PM_{10} concentration in the Belgrade area. At two sampling sites of different type (VC affected by industrial pollution and FVM close to highway E75), PM_{10} reduction was noticeable (about 11 % or 7 μg m^{-3} for the entire period). A significant increase of the concentration level of 4.5 % (1.4 μg m^{-3}) for the entire period was observed at sampling site KBC.

The average concentrations of PM_{10}-bound Mn, Ni, Cd and Pb were generally lower compared to other European cities, whilst the concentrations of As and Cr were higher (EEA 2015; Murillo et al. 2013; Querol et al. 2009). Arsenic concentrations were above the lower assessment threshold (2.4 ng m^{-3}: EU 2004) at almost all stations. The target value (6 ng m^{-3}) was exceeded at sampling sites LA and VC during every year of the analysed period, with the maximum annual averages for 2013 as 29.4 and 16.5 ng m^{-3}, respectively. The shape of the PDF of As (Fig. 2 and ESM Fig. S-1a–n) and its strong seasonal dependency suggest the existence of more intensive emission sources during the heating season, particularly in densely inhabited areas.

Areas affected by lignite coal mining and combustion processes are characterised by high values of As in ambient air, as previously evidenced by Todorović et al. (2015). This metal in coal occurs in the form of both organic and inorganic compounds and can be totally volatilised during combustion (WHO 2001). Thus, coal burning might be one of the most important emission sources of arsenic during winter in this region. The decreasing trend over the years in urban areas could be induced by the implementation of remote heating systems in the city itself, but increasing trends are still present in rural industrial parts.

The chromium concentrations averaged for the considered period were 7.05–24.65 ng m^{-3}, with the highest values at traffic-exposed locations. Trend analysis indicated a significant increase at all sampling sites (ESM Fig. S-2a–h), with a growth rate of up to 9.26 ng m^{-3} (260 %) for the entire period at sampling site LA. The growth trend of chromium concentrations, in contrast to the descending PM_{10} trend, indicates a change in the composition of PM_{10} during the examined period. Unlike the other species, Cr showed higher concentrations mostly during the warm part of the year (ESM Fig. S-1a–o). In spring, the observed values of Cr were more concentrated in the middle of the distribution than in the tails (bell-shaped PDF curve), assuming a considerably strong homogeneous distribution of Cr in PM_{10}, which was much less affected by significant human activities. This result can also be inferred as a consequence of the fairly convincing crustal emissions (Pongpiachan and Iijima 2016). The absence of rainfall during summer caused increased resuspension of dust, which may contain chromium compounds, whilst the multimodal probability distribution of Cr concentration indicates the existence of more sources of different types and intensities.

At four sampling sites affected by traffic pollution (BAS, FVM, KBC and JNA), the observed Ni concentrations exceeded the limit value of 20 ng m^{-3} (ESM Table S-2b). High Ni concentrations characterise each mode of transportation due to the high level of Ni in diesel, petrol and fuel additives and also may be released through the engine exhaust due to wear and tear of the engine (Menzie et al. 2009). Close to highway E75, an increase of Ni concentration was observed at the rate of 2.66 ng m^{-3} (15 %) for the entire period, but the most important growth trend was noted at two sampling sites away from the city centre (KR and RS). At these sites, located in residential areas, the average Ni concentrations for the analysed period were 7.11 and 9.04 ng m^{-3}, respectively, but the increasing trends of 62 and 72 % for the entire period may be an indicator of reinforcing the existing or forming additional sources of nickel in this area. At urban locations BAS and JNA, analyses showed decreasing trends, which resulted in a decrease of Ni concentrations below the limit value in 2015.

The PDF for Mn during each season indicated the contribution of dissimilar emission sources and higher concentrations during the spring and summer. The highest Mn concentrations were observed in the proximity of the central bus station (BAS, 68.22 ng m^{-3}) and near the foundry complex (RF, 65.19 ng m^{-3}), where the increasing trend during recent years was very high (293 %). Concerning anthropogenic activities, almost 80 % of the industrial emissions of manganese are attributable to iron and steel production facilities, whilst power plant and coke oven emissions contribute about 20 %

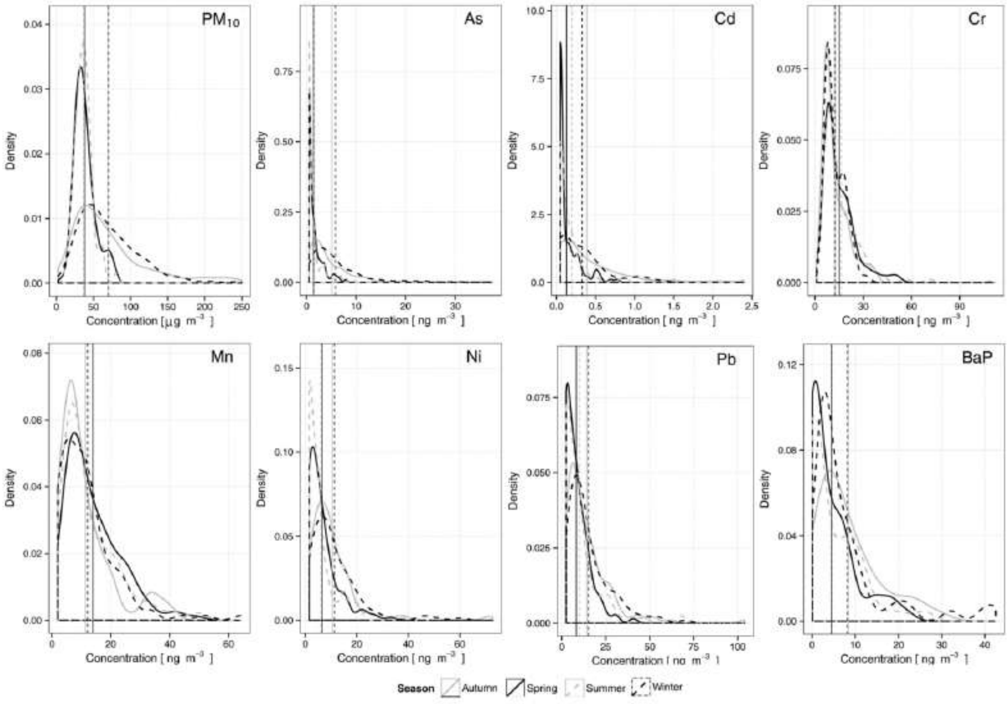


Fig. 2 Probability distribution of PM_{10}, As, Cd and Cr (*above*) and Mn, Ni, Pb and BaP (*below*) concentrations measured at sampling site SL

(ATSDR 2012). Also, close to the foundry (RF), the average Pb concentrations were the highest in the examined area (89.41 ng m^{-3}), with a positive growth rate of 9 %. At the other sites, Pb levels were significantly lower, much below the limit values (500 ng m^{-3}), because lead usage as a gasoline additive was prohibited in 2011. According to the PDF, the high Cd levels characterised winter, suggesting the impacts of fossil fuel burning and increased traffic intensity during this colder part of the year.

Due to exceeding the limit value (1 ng m^{-3}, Directive 2004/107/EC) at all sampling sites, BaP remains one of the main concerns in the area. According to the results of the random forest model (ESM Table S-3), BaP was also the most important measured variable predicting PM_{10} mass concentrations at almost all sampling sites, followed by As at some urban locations. The highest annual average BaP concentration (56.84 ng m^{-3} in 2015) with an increasing trend of 42 % was observed in the area near to the coal mine and thermal power plant (LA). At the other locations, the annual average concentrations were in the range 0.75–12.39 ng m^{-3}, with a significant decreasing trend in the city centre as a result of transferring to the remote heating system. The PDF of BaP shows a very strong seasonal variability, with distribution shifting to higher concentration levels and more than ten times higher mean concentrations through the colder part of the year.

Health risk assessment

The results of the health risk assessment, CCR and HI values calculated according the USEPA and CalEPA models in the wide Belgrade area and urban part of the city, are presented in Fig. 3 and ESM Tables S-4a and S-4b.

Based on the average As concentrations for the whole analysed period, the ILCR values were higher than 10^{-5} in the surroundings of the industrial complexes. Toxic non-cancer health effects were significant too, with an HQ index value of 1.23 (ESM Tables S-4a and S-4b). The oxidation state of chromium in the compounds, present in ambient air, determines the toxicity of these compounds. Hexavalent chromium (Cr(VI)), mainly originating from anthropogenic sources, is the only form that is considered as highly carcinogenic. There is no information provided regarding the chromium oxidation state, and in this case, it is usual to generate 'default' speciation profiles. Mancuso (1997), forming the basis for the estimation of cancer potency for Cr compounds, suggests that

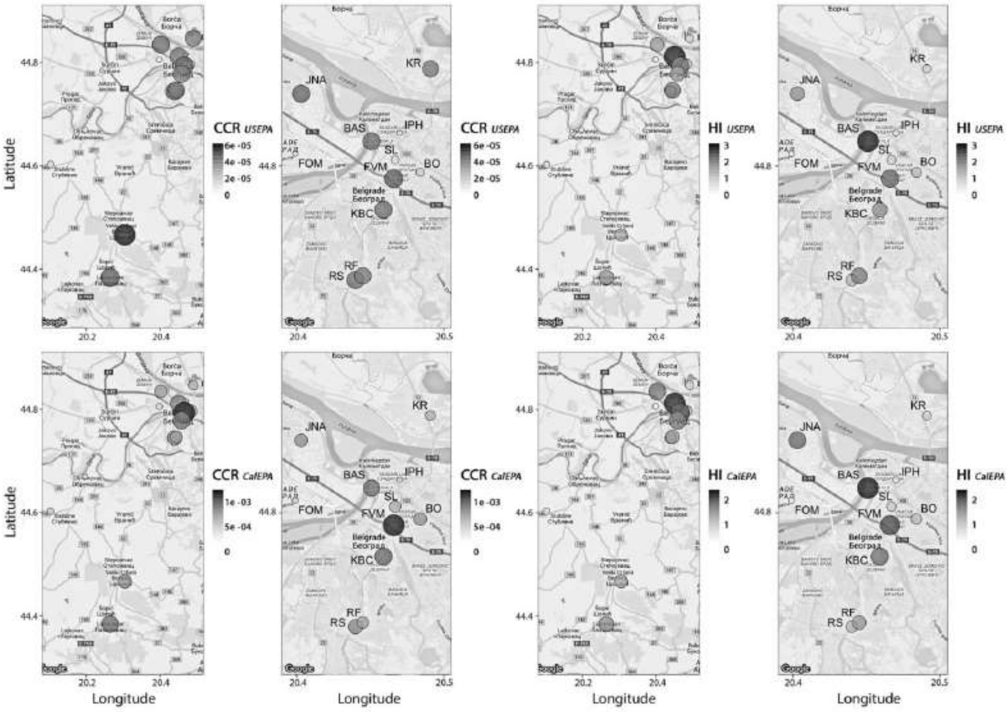


Fig. 3 Cumulative cancer health risk (*CCR*) and hazard index (*HI*) according to the USEPA (*above*) and CalEPA (*below*) models for the Belgrade area and urban city centre

in an urban area, one-seventh of the total chromium concentrations is hexavalent (Cr(VI)). According to this proposal, only one-seventh of the measured Cr concentrations was used for the calculation of ILCR/CR values. Additionally, CalEPA, as a health protective assumption, recommends a high value of cancer potency factor for Cr(VI), which causes higher CR values compared to ILCR. ILCR was in the range from 4.97×10^{-6} to 1.74×10^{-5} at the sampling site located near the road, whilst CR values were above the acceptable risk level for each age group in the wide Belgrade area (ESM Tables S-4a and S-4b). Bearing in mind the increasing trend of concentrations in the examined area, the cancer health risk will exceed the acceptable level according to both models in the next 2 years. The ILCR and CR for Ni, Cd and Pb compounds were in the acceptable range, with the highest values in the urban area. Even with the highest concentrations observed during the winter months, the risk was acceptable both for the population of children and adults. For Mn and Ni compounds, the estimated non-cancer effects were significant, with the highest HQ values (above 1) at traffic-exposed sampling sites. In the industrial areas, the ILCR value for BaP was 1.19×10^{-5}, whilst according to the CalEPA model, CR was above the acceptable level (8.98×10^{-4}), with the highest estimated risk for the most sensitive age groups ($0 < 2$ and $2 < 16$ years old). Regarding the seasonal average concentrations of BaP, the cancer health risk calculated for spring and summer, the seasons with the lowest concentrations, was within the acceptable level.

Based on the concentrations of five trace metals (As, Cd, Cr, Ni and Pb) and BaP, the CCR approached the acceptable level (10^{-6}) according to the USEPA, whilst regarding the CalEPA model, the values were higher than 10^{-4}. The highest CCR values were noted not only in urban areas in the city centre but also in the suburban industrial area near to the coal mine (Fig. 3). Chromium and arsenic with different shares were major contributors to CCR. Portions of Cr compounds were higher in the urban city centre with intensive traffic, whilst As was dominant in industrial areas (70 %). The portion of BaP in CCR was about 10 % at all sampling sites, whilst Pb had the largest influence (3 %) in the vicinity of the foundry (RF). Ni and Cd had no significant contribution to the obtained CCR.

The toxic non-cancer impact on human health of the five trace metals (As, Cd, Cr, Mn and Ni) at traffic-exposed locations can be represented in the following order HQNi > HQCr > HQAs > HQMn > HQCd, whilst at the places with industrial facilities, the largest contribution arises from arsenic compounds. HI values were higher than 1 at ten sampling sites, suggesting significant toxic effects (ESM Tables S-4a and S-4b).

Transport analysis

Besides strong and dominant proximate sources, the concentrations of some compounds may be noticeably influenced by transported pollution from remote sources. The PDF of PM_{10} and some of the analysed trace metals indicates the contribution of more than one source during each season (ESM Fig. S-1a–o). According to the TSA, at sampling site SL, Cd and As mainly originated from local sources, whilst the highest background levels were observed for Mn and Cr (Table 1). Consequently, the shares of transported pollution amounted from 8.95 % in Mn to 36.07 % in As concentrations. Also, very high background levels were observed for PM_{10} (55 %), whilst about 16 % of concentrations were transported to this area during the analysis period. Bearing in mind the amount of transported pollution (>10 %), TEMs were applied in order to resolve potential distant sources of PM_{10}, As, Cr, Ni and Pb. Cd was excluded from this analysis due to low concentrations, whilst BaP was not considered because of an insufficient number of data.

The results of TEM applied on PM_{10} concentrations showed that the area was influenced by strong regional sources located in the E and S–SW (PSCF) and distant sources in the E–NE regions (CWT, RTWC and sQTBA; Fig. 4). Regarding the As compounds, the results of the PSCF and CWT models indicate the influence of polluted air masses from the W, E and SE areas, whilst RTWC specified potentially the most important sources being located in Germany, Poland, Croatia and Ukraine. Both PSCF and CWT suggest a potential origin of chromium compounds in Eastern European countries and the area surrounding the Black Sea. RTWC highlights strong sources in West Europe and also in eastern areas, whilst sQTBA estimates the largest importance of regional and proximate sources. Ni compounds may be transported from the E and SW regions, with the exception of the sQTBA model, which suggests very distant sources in North Europe. In the case of Pb compounds, the source areas identified by PSCF and CWT are located in neighbouring countries; model RTWC emphasised strong sources in Denmark, Poland, Romania and Bulgaria, whilst sQTBA indicated the dominant influence of nearby sources (ESM Fig. S-3a–d).

Conclusion

The levels of ambient PM_{10} and PM_{10}-bound metals (As, Cd, Cr, Mn, Ni and Pb) and BaP concentrations, and the potential adverse inhalation health outcomes, were observed in a large urban area. Different analytical methods, including basic statistical, probability density function, random forest and trend analysis, were complemented by the USEPA and CalEPA models of health risk assessment and an improved transport analysis based on trajectory sector analyses and trajectory ensemble models. The highest average PM_{10} concentrations were obtained at the places affected by industrial pollution and intensive traffic. Arsenic, chromium and BaP had the largest impact on the air quality and population cancer health risk. With the highest values for CCR, areas affected by coal mining and combustion processes could represent the most endangered zones. Within these locations, even with the lowest As concentrations, during summer, the ILCR values remained over 10^{-5}. The average BaP concentrations in the surroundings of industrial activities have to be reduced more than tenfold in order to approach the acceptable range of cancer health risk. Toxic, non-cancer health risks were highest for As, Ni and Cr compounds. The maximum hazard indices were estimated for urban locations, indicating the threat of traffic pollution. Along with pronounced local contribution, the results of the trajectory sector analyses estimated the contributions of potential remote emission sources of different species in the range of 8.95–36.07 %. Transport pathways associated

Table 1 Contribution of transport, background and local production to the measured concentrations of PM_{10}, As, Cd, Mn, Ni and Pb at sampling site SL during the period 2011–2015

	PM_{10} ($\mu g\ m^{-3}$)	As ($ng\ m^{-3}$)	Cd ($ng\ m^{-3}$)	Cr ($ng\ m^{-3}$)	Mn ($ng\ m^{-3}$)	Ni ($ng\ m^{-3}$)	Pb ($ng\ m^{-3}$)
Mean	54.02	3.48	0.26	14.06	12.46	8.52	12.04
Transported	8.71	1.25	0.05	2.28	1.11	1.72	2.26
Transported (%)	16.12	36.07	20.62	16.24	8.95	20.16	18.77
Background	30.05	0.52	0.06	8.66	7.11	3.18	4.40
Background (%)	55.61	14.89	22.84	61.61	57.04	37.28	36.52
Local production	15.27	1.70	0.15	3.11	4.24	3.63	5.39
Local production (%)	28.26	49.04	56.54	22.15	34.01	42.56	44.71

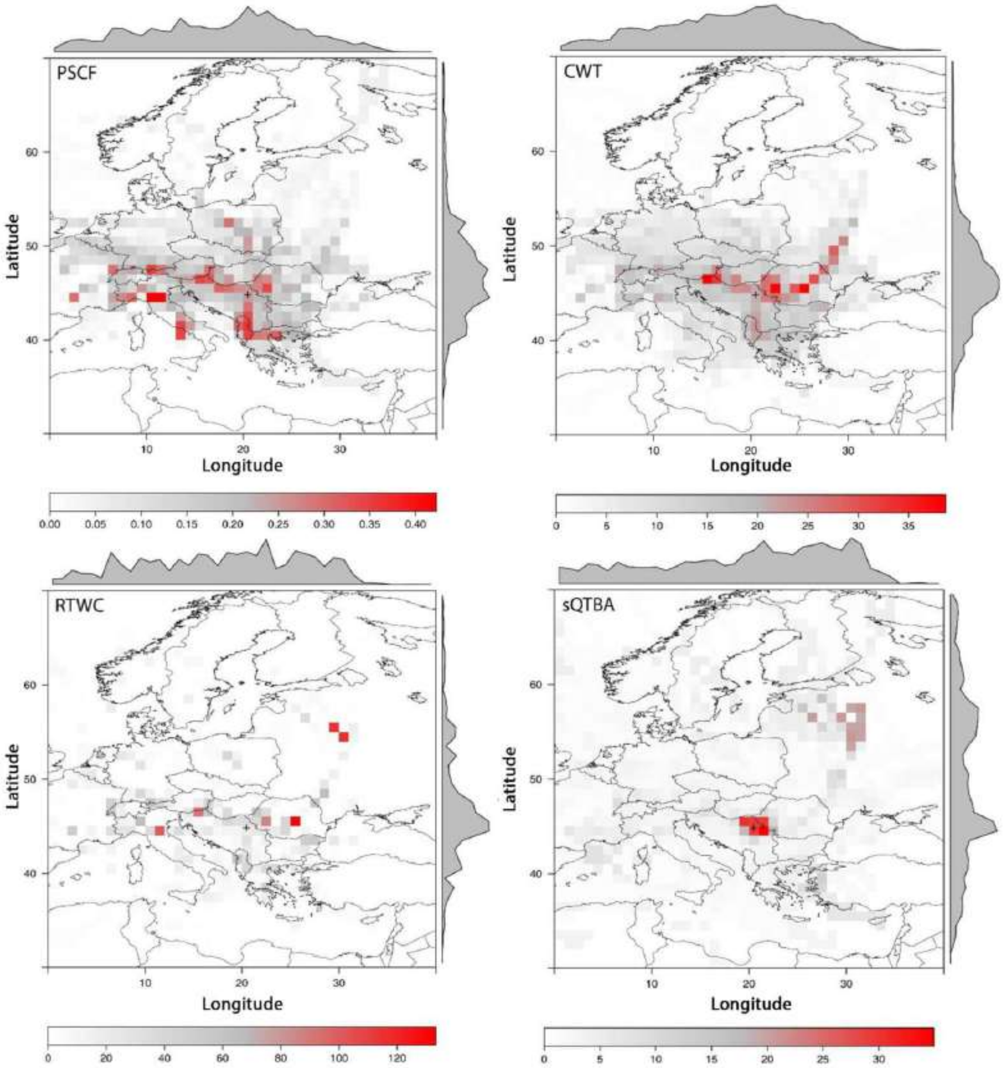


Fig. 4 Potential sources of PM_{10} resolved using the PSCF (probability), CWT, TRCW and sQTBA (in micrograms per cubic metre) models at sampling site SL during the period 2011–2015

mainly with eastern air masses appeared to have a significant impact on the air quality of the Belgrade area. In the forthcoming period, control of biomass burning, due to a transfer to the distant heating system in the city centre, and implementations of new technologies in the industrial sector might be principal objectives in mitigating the air quality and population health risk in the study area. Furthermore, since the long-range transport significantly contributes to PM_{10} and some trace metal concentrations, global action must accompany local and national efforts to reduce pollution emissions and their effects on human health.

Acknowledgments This study was performed as part of projects no. III43007 and no. III41011, which were founded by the Ministry of Education, Science and Technological Development of the Republic of

Serbia within the framework of integrated and interdisciplinary research for the period 2011–2016. The authors gratefully acknowledge Mr. Ankit Rastogi and the MetCor Project Team.

References

An X, Hou Q, Li N, Zhai S (2013) Assessment of human exposure level to PM_{10} in China. Atmos Environ 70:376–386

Anderson J, Thundiyil JG, Stolbach A (2012) Clearing the air: a review of the effects of particulate matter air pollution on human health. J Med Toxicol 8:166–175. doi:10.1007/s13181-011-0203-1

ANPI (2015) Australian Government Department of the Environment National Pollutant Inventory. Cadmium and compounds. http://www.npi.gov.au/resource/cadmium-and-compounds. Accessed 3 January 2016

AQE (2015) Air qualiti in Europe - 2015 report. European environment agency, publications office of the European Union, Luxembourg

AQP (2015) Air quality plan in agglomerations Belgrade. http://www.beograd.rs/download.php/documents/PlankvalitetavazduhaEkologija.pdf (in Serbian). Accessed 3 January 2016

ATSDR (2012) Agency for Toxic Substances and Disease Registry. Toxicological Profile for Manganese. http://www.atsdr.cdc.gov/toxprofiles/tp151-c6.pdf Accessed in 3rd January 2016

Bernard A (2008) Cadmium & its adverse effects on human health. Indian J Med Res 128:557–564

CalEPA (1996) Risk Assessment Advisory Committee. A review of the California Environmental Protection Agency's risk assessment practices, policies, and guidelines. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. http://oehha.ca.gov/risk/raac/AppA_GnoB.pdf. Accessed 3 January 2016

CalEPA (2003) Air Toxic Hot Spots Program guidance manual for preparation of health risk assessment. Office of Environmental Health Hazard Assessment (OEHHA), California Environmental Protection Agency. http://oehha.ca.gov/

CalEPA (2008) Air Toxics Hot Spots risk assessment guidelines, technical support document for the derivation of noncancer reference exposure levels. Office of Environmental Health Hazard Assessment (OEHHA), California Environmental Protection Agency. http://oehha.ca.gov/Assessed. Accessed 3 January 2016

Carslaw DC, Ropkins K (2012) Openair—an R package for air quality data analysis. Environ Model Softw 27:52–61. doi:10.1016/j.envsoft.2011.09.008

Diaz RV, Dominguez ER (2009) Health risk by inhalation of $PM_{2.5}$ in the metropolitan zone of the City of Mexico. Ecotox Environ Safe 72: 866–871

Draxler RR, Rolph GD (2014) HYSPLIT (HYbrid single-particle Lagrangian integrated trajectory) model. Access via NOAA ARL READY website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring

EA (2008) A review of toxicity of arsenic in air. Science Report - SC020104/SR4, Bristol, UK

EEA (2015) Report no 5/2015. Air quality in Europe—2015 report. European Environment Agency, Copenhagen

EQR (2014) http://www.beograd.rs/download.php/documents/Plan.pdf (in Serbian). Accessed 3 January 2016

EU (2004) Directive of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Directive 2004/107/EC

Flagan R, Seinfeld J (2012) Fundamentals of air pollution engineering. Dover Publication, Mineola

Fuzzi S, Baltensperger U, Carslaw K, Decesari S, Deniervan der Gon H, Facchini MC et al. (2015) Particulate matter, air quality and climate: lessons learned and future needs. Atmos Chem Phys 15:8217–8299

GDAS (2015) Global Data Assimilation System. https://www.ready.noaa.gov/gdas1.php. Accessed 3 January 2016

Henn BC, Schnaas L, Ettinger AS et al (2012) Associations of early childhood manganese and lead coexposure with neurodevelopment. Environ Health Perspect 120(1):126–131

Hijmans RJ, van Etten J, Cheng J, Mattiuzzi M, Sumner M, Greenberg JA et al. (2015) Package 'raster', R package

IARC (International Agency for Research on Cancer) (1990) Monograph on the evaluation of carcinogenic risks to humans, vol. 49. Lyons, France, pp 318–411

IPHB (Institute of Public Health of Belgrade). Available at www.zdravlje.org.rs (in Serbian). Accessed in 2015

Jamshed A, Tasneem GK, Jameel AB, Hassan IA, Mariam SA, Naeem U, Sadaf SA, Saima S (2015) Monitoring of arsenic fate with proximate parameters and elemental composition of coal from Thar coalfield, Pakistan. J Geochem Explor 159:227–233

Kim KH (2013) A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ Int 60:71–80

Kneen MA, Annegarn HJ (1996) Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. Nucl Instr Meth B 109:209–213

Langard S, Costa M (2014) Chromium. In: Nordberg G (ed) Handbook on the toxicology of metals, 4th edn. Elsevier, London

Laulicht F, Brocato J, Ke Q, Costa M (2014) Carcinogenicity of metals. In: Nordberg G (ed) Handbook on the toxicology of metals, 4th edn. Elsevier, London

Liaw A, Wiener M (2002) Classification and regression by random Forest. R News 2(3):18–22

Mancuso TF (1997) Chromium as an industrial carcinogen: part 1. Am J Ind Med 31:129–139

Mathew J, Goyal R, Taneja KK, Arora N (2015) Air pollution and respiratory health of school children in industrial, commercial and residential areas of Delhi. Air Qual Atmos Health 8:421–427

Menzie CA, Ziccardi LM, Lowney YW, Fairbrother A, Shock SS, Tsuji JS, Hamai D, Proctor D, Henry E, Su SH, Kierski MW, McArdle ME, Yost LJ (2009) Importance of considering the framework principles in risk assessment for metals 1. Environ Sci Tech 43(22): 8478–8482

Mijić Z, Stojic A, Perisic M, Rajsic S, Tasic M (2012) Receptor modeling studies for the characterization of PM_{10} pollution sources in Belgrade. Chem Ind Chem Eng Q 18(4):623–634

Morello-Frosch RA, Woodruff TJ, Axelrad DA, Caldwell JC (2000) Air toxics and health risks in California: the public health implications of outdoor concentrations. Risk Anal 20(2):273–292

Murillo JH, Roman SR, Marin JFR, Ramos AC, Jimenez SB, Gonzalez SB, Baumgardner DG (2013) Chemical characterization and source apportionment of PM_{10} and $PM_{2.5}$ in the metropolitan area of Costa Rica, Central America. Atmos Pollut Res 4:181–190

Murphy D, Hutchinson D (2015) Cadmium, road dust and rheumatoid arthritis: an alternative hypothesis to general air pollution. J Inflamm 12:58–70

Opentraj (2015) https://cran.r-project.org/web/packages/opentraj/opentraj.pdf. Accessed in 2015

Pandeya P, Patelb DK, Khana AH, Barmana SC, Murthyb RC, Kisku GC (2013) Temporal distribution of fine particulates ($PM_{2.5}$, PM_{10}), potentially toxic metals, PAHs and metal-bound carcinogenic risk in the population of Lucknow City, India. J Environ Sci Health A 48(7):730–745. doi:10.1080/10934529.2013.744613

Perišić M, Stojić A, Stojić SS, Šoštarić A, Mijić Z, Rajšić S (2015) Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Qual Atmos Health 8(4):379–389

Pongpiachan S, Iijima A (2016) Assessment of selected metals in the ambient air PM10 in urban sites of Bangkok (Thailand). Environ Sci Poll Res 23(3):2948–2961

Pushan S, Vladimir S, Chris S, Peter FN (2007) Speciation of arsenic and selenium in coal combustion products. Energy Fuel 21:506–512

Querol X, Alastuey A, Pey J et al (2009) Variability in regional background aerosols within the Mediterranean. Atmos Chem Phys 9: 4575–4591

Rajšić S, Mijić Z, Tasić M, Radenković M, Joksić J (2008) Evaluation of the levels and sources of trace elements in urban particulate matter. Environ Chem Lett 6:95–100

Rastogi AK (2013) http://code.google.com/p/metcor/. Accessed 3 January 2016

Rost J, Holst T, Sahn E, Klingner M, Anke K, Ahrens D, Mayer H (2009) Variability of PM_{10} concentrations dependent on meteorological conditions. Int J Environ Pollut 36(1):3–18

Mishra S, Bharagava RN (2016) Toxic and genotoxic effects of hexavalent chromium in environment and its bioremediation strategies. J Environ Sci Health C 34:1–32. doi:10.1080/10590501.2015.1096883

Schaumloffel D (2012) Nickel species: analysis and toxic effects. J Trace Elem Med Biol 26:1–6. doi:10.1016/j.jtemb.2012.01.002

Slezakova K, Castro D, Begonha A, Delerue-Matos C, da Conceição Alvim-Ferraz M, Morais S, do Carmo Pereira M (2011) Air pollution from traffic emissions in Oporto, Portugal: health and environmental implications. Microchem J 99(1):51–59

Sofowote U, Su Y, Dabek-Zlotorzynska E, Rastogi A, Brook J, Hopke F (2015) Sources and temporal variations of constrained PMF factors obtained from multiple-year receptor modeling of ambient $PM_{2.5}$ data from five speciation sites in Ontario, Canada. Atmos Environ 108:140–150

Stanišić Stojić S, Stanišić N, Stojić A, Šoštarić A (2015) Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. J Toxicol Environ Health A 23:1–11. doi:10.1080/15287394.2015.1101407

Stojić A, Stojić SS, Mijić Z, Ilić L, Tomašević M, Todorović M, Perišić M (2015a) Comprehensive analysis of VOC emission sources in Belgrade urban area. In: Cohen A (ed) Urban and built environments: sustainable development, health implications and challenges. Nova Science, New York, ISBN: 978-1-63483-067-6

Stojić A, Stojić SS, Šoštarić A, Ilić L, Mijić Z, Rajšić S (2015b) Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ Sci Pollut Res 22(19):13137–13152

Stojić A, Stojić SS, Mijić Z, Šoštarić A, Rajšić S (2015c) Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos Environ 106:71–79

Stojić A, Stojić SS, Reljin I, Čabarkapa M, Šoštarić A, Perišić M, Mijić Z (2016) Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. Environ Sci Pollut Res 1–11. doi:10.1007/s11356-016-6266-4

Stull RB (1988) An introduction to boundary layer meteorology. Springer, London

Szabó J, Nagy AS, Erdős J (2015) Ambient concentrations of PM_{10}, PM_{10}-bound polycyclic aromatic hydrocarbons and heavy metals in an urban site of Győr, Hungary. Air Qual Atmos Health 8(2): 229–241

Team RC (2012) R: a language and environment for statistical computing. http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf. Accessed 3 January 2016

Todorović M, Perišić M, Kuzmanoski M, Stojić A, Šoštarić A, Mijić Z, Rajšić S (2015) Assessment of PM_{10} pollution level and required source emission reduction in Belgrade area. J Environ Sci Health A 50(13):1351–1359. doi:10.1080/10934529.2015.1059110

USEPA (2005) Chapter 8—Interpreting uncertainty for human health risk assessment. In: Human Health Risk Assessment Protocol. US EPA Region Multimedia Planning and Permitting Division, Office of Solid Waste Center for Combustion Science and Engineering. https://www.weblakes.com/products/iraph/resources/hhrap/chp_8.pdf. Accessed 3 January 2016

USEPA (2006) Air quality criteria for lead, final report. EPA/600/R-05/144aF-bF, 2006, U.S. Environmental Protection Agency, Washington, DC. http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=158823#Download. Accessed 3 January 2016

USEPA (2011a) Methods to develop inhalation cancer risk estimates for chromium and nickel compounds. US EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711

USEPA (2011b) Exposure factors handbook. Office of Research and Development, Washington, DC

USEPA (2013) Integrated Risk Information System (IRIS). United States Environmental Protection Agency. http://www.epa.gov/iris. Accessed 3 January 2016

USEPA (2015) Residual risk assessment for the petroleum refining source sector. EPA's Office of Air Quality Planning and Standards Office of Air and Radiation. https://www3.epa.gov/airtoxics/petrefine/604_RTR_Assessment091715withAppendices.pdf. Accessed 3 January 2016

Valavanidis A, Konstantinos F, Thomais V (2008) Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. J Environ Sci Health C 26:339–362

Vuković G, Aničić Urošević M, Goryainova Z, Pergal M, Škrivanj S, Samson R, Popović A (2015) Active moss biomonitoring for extensive screening of urban air pollution: magnetic and chemical analyses. Sci Total Environ 521:200–210

Wang YQ (2014) MeteoInfo: GIS software for meteorological data visualization and analysis. Meteorol Appl 21(2):360–368

Watson JG, Chen LWA, Chow JC, Doraiswamy P, Lowenthal DH (2008) Source apportionment: findings from the U.S. Supersites Program. J Air Waste Manag 58:265–288. doi:10.3155/1047-3289.58.2.265

WHO (2001) Arsenic and arsenic compounds. "Environmental health criteria, vol. 224". World Health Organization, Geneva

WHO (2004) Concise International Chemical Assessment Document 63. Manganese and its compounds: environmental aspects. World Health Organization, Geneva

WHO (2006) Health risk of particulate matter from long-range transboundary air pollution. Regional Office for Europe, World Health Organization, Copenhagen

WHO (2013) Health risks of air pollution in Europe—HRAPIE project. Regional Office for Europe, World Health Organization, Copenhagen

Wickham H, Chang W (2015) Ggplot2: an implementation of the grammar of graphics, version 1.0. 1

Zhanghua C, Muhammad TS, Sandrah PE, Carrie VB, Frank DG (2015) Chronic effects of air pollution on respiratory health in Southern California children: findings from the Southern California Children's Health Study. J Thorac Dis 7(1):1–11

Int. J. Environ. Sci. Technol.
DOI 10.1007/s13762-016-1208-8

ORIGINAL PAPER

Forecasting hourly particulate matter concentrations based on the advanced multivariate methods

M. Perišić[1] · D. Maletić[1] · S. S. Stojić[2] · S. Rajšić[1] · A. Stojić[1]

Received: 22 April 2016 / Revised: 11 July 2016 / Accepted: 19 November 2016

Abstract In this study, several multivariate methods were used for forecasting hourly PM_{10} concentrations at four locations based on SO_2 and meteorological data from the previous period. According to the results, boosted decision trees and multi-layer perceptrons yielded the best predictions. The forecasting performances were similar for all examined locations, despite the additional PM_{10} spatio-temporal analysis showed that the sites were affected by different emission sources, topographic and microclimatic conditions. The best prediction of PM_{10} concentrations was obtained for industrial sites, probably due to the simplicity and regularity of dominant pollutant emissions on a daily basis. Conversely, somewhat weaker forecast accuracy was achieved at urban canyon avenue, which can be attributed to the specific urban morphology and most diverse emission sources. In conclusion to this, the integration of advanced multivariate methods in air quality forecasting systems could enhance accuracy and provide the basis for efficient decision-making in environmental regulatory management.

Editorial responsibility: An-Lei Wei.

Electronic supplementary material The online version of this article (doi:10.1007/s13762-016-1208-8) contains supplementary material, which is available to authorized users.

✉ M. Perišić
mirjana.perisic@ipb.ac.rs

[1] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

[2] Singidunum University, Danijelova 32, 11010 Belgrade, Serbia

Published online: 03 December 2016

Keywords Air quality · Environmental pollution · Regulatory management · Supervised learning algorithms

Introduction

Over the last century, changes in emission sources, methane concentrations and climate have affected atmospheric composition and led to the significant increase in the levels of particulate matter (PM) and gaseous pollutants, particularly in developing countries (Fang et al. 2013). According to recent estimates, about 3.5 million cardiopulmonary deaths annually and globally can be attributed to exposure to anthropogenic $PM_{2.5}$, and the projections are that this number could double by 2050 (Lelieveld et al. 2015). In addition to stringent abatement measures, the accurate and reliable prediction of air pollutant episodes and establishment of an early public warning system is of vital importance for the increase in life expectancy and reduction of health care expenditures.

Despite the fact that significant progress has been made through integration of different scientific approaches, modeling of air pollution data remains a challenge, due to complexity and non-linear nature of atmospheric phenomena and processes (Pai et al. 2013). The variety of techniques and tools described in the literature for air quality forecasting covers simple empirical approaches, statistical approaches including artificial neural networks and fuzzy logic methods, and physically-based approaches including deterministic methods and ensemble and probabilistic methods (Zhang et al. 2012). The deterministic approach mostly refers to meteorological and chemical transport models, such as sophisticated Community Air Quality Modelling System (CMAQ) for prediction of air quality index at locations with no real-time measurements.

The chemical transport models were first used in Germany for air quality forecasting purposes, and soon many other developed countries became aware of the benefits of such implementation and launched the centralized air quality forecasting systems based on different tools, from simple empirical to online-coupled meteorology and chemistry models. While deterministic models don't require a large quantity of observational data, they do demand sufficient knowledge and understanding of pollutant emission sources, transport and atmospheric reactions and transformations under the planetary boundary layer (Feng et al. 2015). Since crucial knowledge in this area is often limited and some processes are too complex to be presented within a model, deterministic models are computationally expensive and time-consuming for routine predictions and often employ approximations and simplifications that lead to strong biases and inaccuracy, thus making the forecasts useless for timely management of critical situations (Cobourn 2010; Russo and Soares 2014).

Over the last decade, the parametric or non-parametric statistical approaches have been proposed as a more economical alternative for discovering the underlying site-specific dependencies between pollutant concentrations and potential predictors (Feng et al. 2015). The most commonly examined were artificial neural networks, based on artificial neurons or nodes capable of learning relationships between the routinely-measured pollutant data and selected predictors through embedded functions and data from the previous period (Fernando et al. 2012). Unlike deterministic models, artificial neural networks provide more accurate air quality forecasts, whereas their major disadvantages are associated with "black box" nature and poor generalization performance (Moustris et al. 2013). Furthermore, both statistical and deterministic approaches show satisfactory or good performance in forecasting concentrations closer to average values, whereas the prediction of extreme pollution events is more challenging.

As summarized by Zhang et al. (2012), the integration of advanced statistical methods in future air quality forecasting systems could considerably reduce forecasting biases and further enhance accuracy. In our previous study, MVA methods were successfully applied for forecasting the contributions of industry and vehicle exhaust to volatile organic compound (VOC) levels in the urban area, with smallest relative forecast error of only 6% (Stojić et al. 2015a). In this study, we compared the performance of twelve advanced multivariate (MVA) methods for PM_{10} forecasting relying on meteorological data and SO_2 concentrations. The analysis was based on a multi-year dataset collected at four different locations, affected by traffic or industry emissions. The herein employed MVA classification and regression methods belong to the supervised learning algorithms designed within Toolkit for Multivariate Analysis (TMVA; Hoecker et al. 2007) within the ROOT framework (Brun and Rademakers 1997), for extracting the maximum available information from the extensive data in high-energy physics.

Materials and methods

The analyzed dataset comprising 5-year (2011–2015) hourly concentrations of PM_{10}, SO_2 and meteorological data (atmospheric pressure, temperature, humidity, wind speed and direction), was obtained from the automatic monitoring stations within the Institute of Public Health network, at four different sites (Fig. 1, Supplementary Material). In the urban area, mostly affected by vehicle-exhaust emissions, measurements were conducted at the Institute of Public Health and New Belgrade, the sites characterized as being urban canyon avenue (UCA) and urban boulevard (UB), respectively, due to their topographic configuration. In the area influenced by emissions from fossil fuel burning for industry and heating operations, the data were collected in Obrenovac and Grabovac, the sites corresponding to urban industry (UI) and rural industry (RI), respectively. The measurements at industrial sites were incomplete due to severe floods that affected the area in 2014. The concentrations of PM_{10} and SO_2 were measured by means of referent beta-ray attenuation (Thermo FH 62-IR) sampler and referent sampling device Horiba APSA 360, respectively. The meteorological data were obtained by using Lufft WS500-UMB Smart Weather Sensor. The accuracy and precision of detection methods are provided in Stojic et al. (2016).

The analyses of daily, weekly, seasonal and annual dynamics, trend (Pretty 2015) and periodicity were performed by means of Openair (Carslaw and Ropkins 2012) and Lomb (Ruf 1999) packages within the Statistical Software Environment R (Team 2012). The relationships between pollutant concentrations and wind characteristics were investigated by the use of bivariate polar plot and bivariate cluster analyses within the Openair package. The contribution of local emission sources, background and transport to the observed PM_{10} pollution was analyzed using the 72-h air mass back trajectories and trajectory sector analysis (TSA) as described in Stojić et al. (2016).

The following MVA methods were used for PM_{10} forecasting: Boosted decision trees (BDT, BDTG, BDTMitFisher), Artificial Neural Network Multilayer

Perceptron (MLP), MLP with Bayesian Extension (MLPBNN), Support Vector Machine (SVM), k-nearest neighbor (KNN), Linear Discriminant (LD), Boosted Fisher Discriminant (BoostedFisher), Multidimensional Probability Density Estimator Range Search Method (PDERS), Predictive Learning via Rule Ensembles (RuleFit) and Function Discriminant Analysis (FDA). All methods were used for both classification and regression. The five-year dataset was divided into two equal subsets, each consisting of PM_{10} concentrations and input data (meteorological and SO_2). One subset was used for method trainings, either to differentiate between high and low importance indicators for PM_{10} concentrations (classification), or to determine an approximation of the underlying functional behavior defining PM_{10} concentrations (regression). The other subset was utilized for method performance testing.

Results and discussion

Previous studies aimed at investigating the origin and spatio-temporal distribution of different pollutant species converge on the conclusion that poor air quality presents an important health risk factor in Belgrade area (Perišic et al. 2015; Stojić et al. 2015b). In the previous years, the mean annual PM_{10} concentrations in Belgrade area were in the range from 39.74 to 62.32 μg m^3, whereas the exceedances of the proposed air quality guideline value of 50 μg m^3 were registered during 20.5–42.2% of total number of days (Stanišić Stojić et al. 2016).

Specifics of measurement sites

In order to examine the MVA forecasting performances, PM_{10} observational data from four measurement sites affected by different emission sources were collected and analyzed (Fig. 1, Supplementary Material). The two locations defined as urban were affected by traffic emissions throughout the year. However, specific microclimatic conditions associated with contrasting urban morphology between UCA and UB plays an important role in spatial distribution of particles. The presence of tall buildings along both sides of the canyon avenue induces a complex wind flow that does not enhance the pollutant dispersion due to terrain configuration, but it facilitates suspension, particularly fine PM fraction (Vardoulakis et al. 2003). Furthermore, frequent congestions in the canyon avenue compared to free flowing traffic in the wide boulevard contributed to higher PM_{10} concentrations at UCA throughout the year, with the exception of winter season, when the air quality at UB was additionally affected by fuel burning from the neighboring heating plant.

The herein presented industrial locations were affected either by fuel burning emissions only (RI), or by emissions from both industrial activities and vehicle exhaust (UI). Within the range of 15–20 km in NW/N and SE/S direction around the two industrial sites, the strong emission sources including three thermal power plants, four open-pit mines of high-sulfur lignite and several coal ash disposal sites are located.

As can be seen, the highest mean PM_{10} concentration for the entire period was registered at UI (Table 1, Supplementary Material), which was partly driven by extreme pollutant loadings in 2012 (Fig. 2, Supplementary Material). It should be noted that the PM_{10} variations at two industrial locations exhibited similar pattern, only with less significant deviations at rural site, which points to the prevalence of the same emission sources.

Daily mean PM_{10} exceedances (>50 μg m^{-3}) were commonly observed, whereas the episodes of extreme pollutant levels were registered only at UI (Fig. 3, Supplementary Material). The winter PM_{10} concentrations were considerably higher at all examined locations, which can be partly attributed to heating operations, but also to lower planetary boundary layer (PBL) height in winter season. Unsurprisingly, the lowest PM_{10} levels for the entire period were observed at rural site, particularly during spring and summer season, with the values of 29.15 and 32.09 μg m^{-3} being registered, respectively. Conversely, the highest concentrations in warm season were measured at UCA, the only site predominately affected by traffic. The differences between the summer and winter concentrations were relatively small at UCA and RI, whereas the inter-seasonal variations at two other sites exposed to the emissions from two strong sources were almost two times higher.

In Fig. 4, Supplementary Material, daily, weekly and seasonal PM_{10} variations are displayed. Accordingly, the lowest concentrations were registered in May and June, probably due to intense precipitations. The particle resuspension processes and atmospheric photochemical reactions in dry summer months starting from July, led to the rising pollutant levels, particularly at industrial sites in the vicinity of ash disposals. The accumulation of particles during working days was followed by a significant decrease at the weekend at two locations dominated by vehicle exhaust emissions, whereas the weekday/weekend difference was not observed at UI and RI sites. As regards diurnal PM_{10} variations, the same pattern was detected at all locations: daytime levels tended to be low with the exception of morning and afternoon rush hours, whereas the pronounced increase in nighttime concentrations could be attributed to stable atmospheric conditions and shallow PBL.

According to bivariate and cluster analysis, the average contributions of the surrounding emission sources were dominant at all locations (Fig. 1), particularly at UCA (59.5 μg m^{-3}), due to limited pollutant dispersion, and UI (73.1 μg m^{-3}), which has been directly exposed to emissions from the thermal plant which produces more than 50% of electricity for the Serbian market. The UCA is located in the central city area and thus, the polluted air masses were observed to come from all directions, whereas at UB, the impact of heating plant emissions from S and intersections with intensive traffic coming from E can be noted. In the case of industrial locations, local sources appeared to be particularly significant during the heating season, whereas in spring and summer, both UI and RI were affected by emissions from ash disposals and lignite mining sites in NW/N and SE/S. The dynamics of cluster contributions on a daily, weekly and seasonal basis are shown in Fig. 5, Supplementary Material. As can be seen, local emissions, corresponding to cluster 4 at industrial sites, exhibited extremely regular daily variations, which suggests the prominent role of anthropogenic sources. The rush hour peaks were noticeable only in the variations of locally-emitted PM_{10} concentrations at UCA (cluster 4), since the site has been dominated by traffic emissions.

The analysis was also performed to determine the impact of local emissions, transported pollution and background on the air quality at examined locations. According to TSA results, the estimated share of background was highest at rural site (48%), whereas the contribution of local production was the most significant factor (43%) for PM_{10} concentrations at UI, as previously shown by bivariate and cluster analysis.

Upon the presented analysis, we have reached the conclusion that the selected locations are substantially different in terms of air quality and factors closely associated with it, including micro-climatic conditions, topographic features and proximity of strong sources. This was considered a prerequisite for examining the dependency between the efficiency of MVA methods for air quality forecasting and site characteristics.

Classification MVA methods

As previously mentioned, the 5-year dataset, including PM_{10} and SO_2 concentrations, and meteorological data, was divided into two subsets equal in size, used for training and testing of MVA methods, respectively. In order to account for seasonal, *i.e.* weekday/weekend variations, two new variables were introduced for classification purposes: Yearreal is a quotient of the ordinal number of a day and total number of days per year, while Weekreal represents

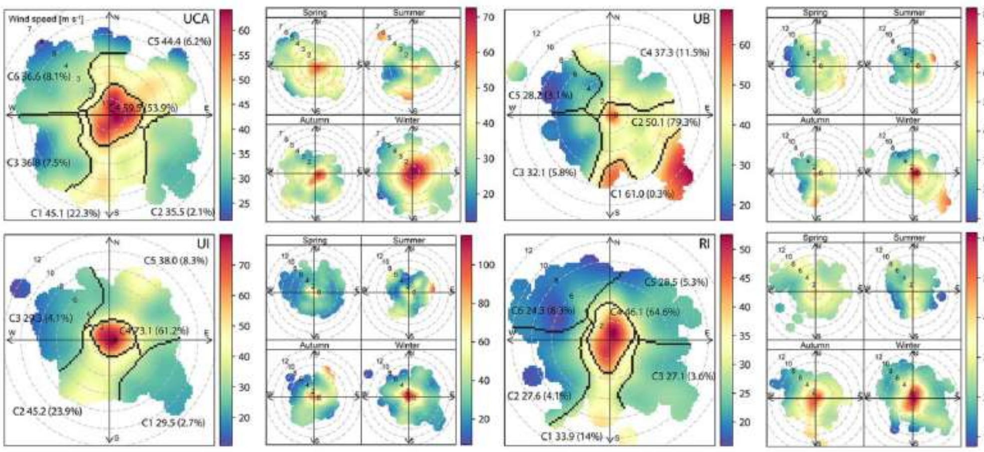


Fig. 1 The relationship between PM_{10} concentrations and wind characteristics: bivariate cluster plot [frequency (%) and average contributions (μg m^{-3})] for the entire period (*left*) and seasonal variations (μg m^{-3}) (*right*)

the quotient of the ordinal number of a day and number 7. Correlation and mutual information of input variables and the observed PM_{10} mass concentrations for all sampling sites are presented in Table 1.

For the purposes of classification, the PM_{10} levels above 50 μg m^{-3} are considered to require the increased level of caution, whereas those exceeding 100 μg m^{-3} are considered extremely high—alarm triggering values, both of which are chosen as arbitrary limits. The estimation of classification method performances by using the Receiver Operating Characteristic (ROC) curve is presented in Fig. 2. The highest separation between background and predicted PM_{10} concentrations was observed when PM_{10} classifier value of 100 μg m^{-3} was taken into account (Fig. 3), whereas somewhat poorer results were obtained for 50 μg m^{-3}, which suggests that including additional meteorological or pollutant variables as input data might further enhance classification performance.

Table 1 Correlation (C) and mutual information (MI) of input variables (P, pressure; T, temperature; Rh, relative humidity; ws, wind speed; Yearreal, day of year; Weekreal, day of week) and measured PM_{10} concentrations at all sampling sites

Variable	UCA		UB		UI		RI	
	C	MI	C	MI	C	MI	C	MI
P	0.18	1.31	0.26	0.97	0.20	1.49	0.29	1.26
T	0.21	1.40	0.30	1.21	0.28	1.69	0.22	1.39
Rh	0.24	1.47	0.24	1.29	0.22	1.86	0.19	1.60
ws	0.29	1.39	0.25	0.82	0.26	1.57	0.32	1.18
SO_2	0.25	1.63	0.09	1.39	0.20	1.87	0.32	1.59
Yearreal	0.04	1.49	0.05	1.31	0.09	1.86	0.12	1.53
Weekreal	0.02	0.12	0.03	0.11	0.02	0.18	0.02	0.14

The comparison of the results by evaluating signal and background efficiencies revealed that certain MVA methods are capable of classifying the PM_{10} levels which are considered to require a high degree of caution (Table 2, left). The results showed that BDTG and MLP exhibit the best results for all examined locations. Signal and background separation was most efficiently performed for RI and UB, and to a somewhat lower extent for UCA.

Regression MVA methods

Regression MVA methods were applied to interpret the relationships between pollutant concentrations and the examined input data. Similar to classification methods, BDTG and MLP exhibited the most satisfying performances with absolute and relative errors presented in Table 2, right. The MVA method performance was best for PM_{10} loadings at industrial sites, around 25%, while the forecast quality could be clearly seen at RI location, Fig. 4. It can be assumed that more accurate air quality forecasts can be

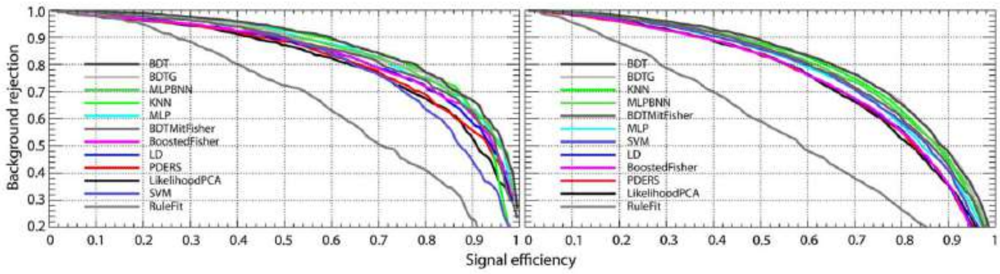


Fig. 2 ROC curves for MVA classification methods with PM_{10} classifier value of 100 μg m^{-3} (*left*) and 50 μg m^{-3} (*right*) for all sampling sites

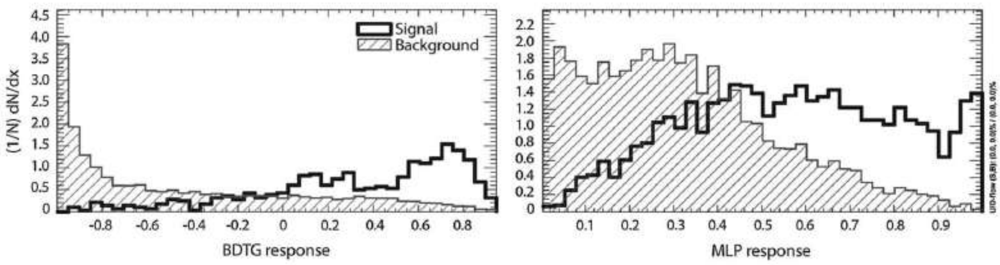


Fig. 3 MVA classification method response for PM_{10} classifier value of 100 μg m^{-3} (*left*) and 50 μg m^{-3} (*right*) for UCA site

Table 2 The comparison of best performing methods for ROC, separation and significance values for all measurement sites (left) and absolute (µg m^{-3}) and relative (%) errors of the best performing regression methods (right)

Sampling site	Method	Classification			Regression	
		ROC	Separation	Significance	Absolute error	Relative error
UCA	BDTG	0.806	0.282	0.883	17.2	29.6
	MLP	0.772	0.226	0.755	21.8	37.5
UB	BDTG	0.868	0.408	1.12	13.9	26.8
	MLP	0.841	0.352	1.015	17.4	33.5
UI	BDTG	0.855	0.379	1.059	15.6	24.6
	MLP	0.826	0.323	0.956	24.0	37.9
RI	BDTG	0.867	0.412	1.172	10.6	25.2
	MLP	0.837	0.345	0.962	15.1	36.0

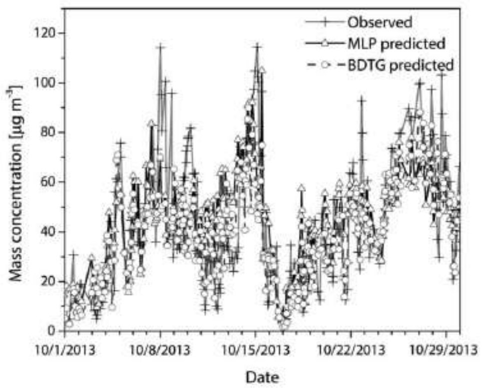


Fig. 4 The comparison of time series of the observed and best performing MVA-predicted PM_{10} concentrations (µg m^{-3}) at RI site

achieved at the locations such as RI, which are affected by less significant number of emission sources. Furthermore, the simplicity and regularity of dominant pollutant emissions on a daily, weekly and seasonal basis, as registered at UI location, as well as minor deviations from the commonly observed pollutant loadings, which is particularly evident for air quality forecasting at rural site, are probably the additional factors associated with forecast accuracy.

Conversely, the weakest MVA method performance was derived for PM_{10} concentrations at UCA, probably because the urban morphology of the canyon avenue represents the additional factor modifying the pollutant levels in a less predictable manner. Furthermore, the emission sources in the central city zone are diverse and primarily refer to traffic congestions and intense atmospheric reactions that take place in stagnant conditions of the canyon street. Moreover, they also relate to local fireboxes in residential area where lignite is burned

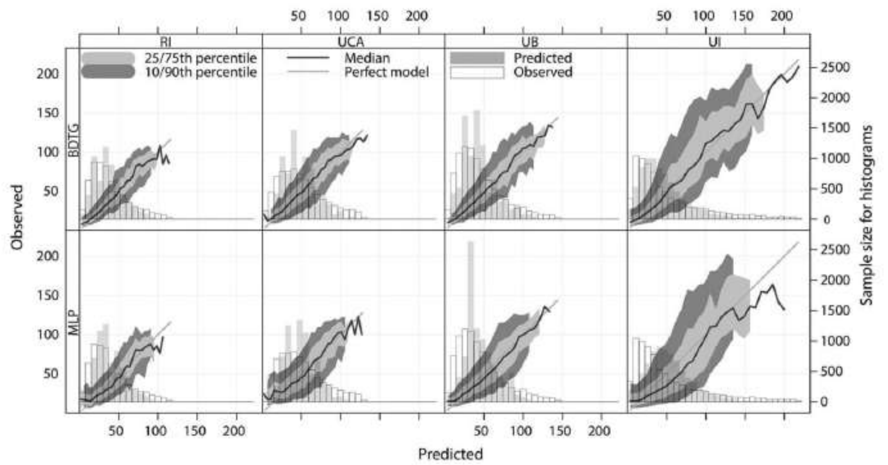


Fig. 5 The comparison of the observed and best performing MVA-predicted PM_{10} mass concentrations (µg m^{-3})

during autumn and winter season and local manufactures that are associated with pollutant emissions highly variable in time and intensity.

As can be seen in Fig. 5, the PM_{10} time series evaluated by means of MVA regression methods correlated very well with the observed concentrations at all sampling sites. Mutual information obtained for BDTG-predicted and the observed PM_{10} mass concentrations were 0.71, 0.7. 0.65 and 0.64 for RI, UB, UCA and UI, respectively. This suggests that significant input variables were used for the forecasting process. In addition, it could be noted that their distributions are relatively well.

Although the other MVA methods employed in the present study generated similar results when being used for classification, they generated the significant PM_{10} forecast errors when being used for regression, at least based on the observed input variables. The herein presented errors are mostly in compliance with the findings of our previous study, aimed at forecasting the contributions from traffic and industry to the observed VOC concentrations in the urban area, which suggests that both PM and VOC, as important air quality indicators, can be predicted using the MVA methods.

Conclusion

In this study, the performances of MVA methods for forecasting PM_{10} concentrations and prediction of related health-damaging events were evaluated on the basis of datasets from traffic- and industry-affected locations with substantial differences in air quality, which has also been verified through additional analyses. The results of both classification and regression methods were rather promising, particularly considering the fact that the presented forecast accuracy referred to hourly concentrations. The quality of the prediction might be partly dependent on microclimatic conditions, topographic characteristics, presence of strong emission sources and other site characteristics, as well as on the input data. All that implies that the selection of additional or different variables could enhance the method forecasting performances. The importance of accurate air quality forecasts as part of the management system is reflected in the potential applications, including health alerts for susceptible categories, operational planning, as well as amendment of pollutant time-series and reduction of regular monitoring expenditures.

Acknowledgements This study was carried out as part of the Project No. III43007, III41011 and OI171002, financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011–2016.

References

Brun R, Rademakers F (1997) ROOT—an object oriented data analysis framework. Nucl Instrum Methods A 389:81–86

Carslaw DC, Ropkins K (2012) Openair-an R package for air quality data analysis. Environ Model Softw 27:52–61

Cobourn WG (2010) An enhanced $PM_{2.5}$ air quality forecast model based on nonlinear regression and back-trajectory concentrations. Atmos Environ 44:3015–3023

Fang Y, Mauzerall DL, Liu J, Fiore AM, Horowitz LW (2013) Impacts of 21st century climate change on global air pollution-related premature mortality. Clim Change 121:239–253

Feng X, Li Q, Zhu Y, Hou J, Jin L, Wang J (2015) Artificial neural networks forecasting of $PM_{2.5}$ pollution using air mass trajectory based geographic model and wavelet transformation. Atmos Environ 107:118–128

Fernando HJS, Mammarella MC, Grandoni G, Fedele P, Di Marco R, Dimitrova R, Hyde P (2012) Forecasting PM_{10} in metropolitan areas: efficacy of neural networks. Environ Pollut 163:62–67

Hoecker A, Speckmayer P, Stelzer J, Therhaag J, Von Toerne E, Voss H, Backes M, Carli T, Cohen O, Christov A, Dannheim D, Danilowski K, Henrot-Versille S, Jachowski M, Kraszewski K, Krasznahorkay A, Kruk M, Mahalalel Y, Ospanov R, Prudent X, Robert A, Schouten D, Tegenfeldt F, Voigt A, Voss K, Wolter M, Zemla A (2007) TMVA users guide—toolkit for multivariate data analysis, PoSACAT 040. http://arxiv.org/abs/physics/0703039. Accessed 14 June 2015

Lelieveld J, Evans JS, Fnais M, Giannadaki D, Pozzer A (2015) The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature 525:367–371

Moustris KP, Larissi IK, Nastos PT, Koukouletsos KV, Paliatsos AG (2013) Development and application of artificial neural network modeling in forecasting PM_{10} levels in a Mediterranean city. Water Air Soil Pollut 224:1–11

Pai TY, Hanaki K, Chiou RJ (2013) Forecasting hourly roadside particulate matter in Taipei County of Taiwan based on first-order and one-variable grey model. CLEAN Soil Air Water 41:737–742

Perišić M, Stojić A, Stojić SS, Šoštarić A, Mijić Z, Rajšić S (2015) Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Qual Atmos Health 8:379–389

Pretty R (2015) TheilSen {openair} tests for trends using Theil–Sen estimates. http://www.inside-r.org/packages/cran/openair/docs/TheilSen. Accessed 12 Dec 2015

Ruf T (1999) The Lomb-Scargle periodogram in biological rhythm research: analysis of incomplete and unequally spaced time-series. Biol Rhythm Res 30:178–201

Russo A, Soares AO (2014) Hybrid model for urban air pollution forecasting: a stochastic spatio-temporal approach. Math Geosci 46:75–93

Stanišić Stojić S, Stanišić N, Stojić A, Šoštarić A (2016) Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. J Toxicol Environ Health A 79:17–27

Stojić A, Maletić D, Stojić SS, Mijić Z, Šoštarić A (2015a) Forecasting of VOC emissions from traffic and industry using classification and regression multivariate methods. Sci Total Environ 521:19–26

Stojić A, Stojić SS, Mijić Z, Šoštarić A, Rajšić S (2015b) Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos Environ 106:71–79

Stojić A, Stanišić Stojić S, Reljin I, Čabarkapa M, Šoštarić A, Perišić M, Mijić Z (2016) Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long term measurements. Environ Sci Pollut Res. doi:10.1007/s11356-016-6266-4

Team RC (2012) R: a language and environment for statistical computing. http://cran.case.edu/web/packages/dplR/vignettes/timeseries-dplR.pdf. Accessed 10 June 2015

Vardoulakis S, Fisher BE, Pericleous K, Gonzalez-Flesca N (2003) Modelling air quality in street canyons: a review. Atmos Environ 37:155–182

Zhang Y, Bocquet M, Mallet V, Seigneur C, Baklanov A (2012) Real-time air quality forecasting, part I: history, techniques, and current status. Atmos Environ 60:632–655

Публикације категорије М30

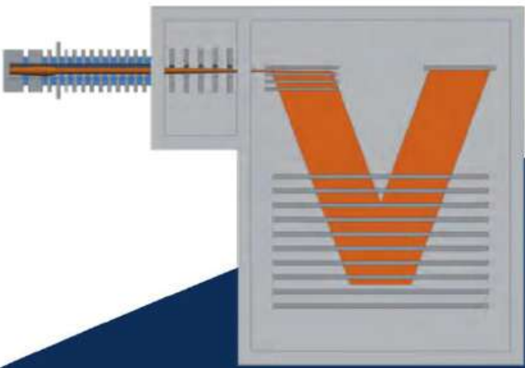
Публикације после избора у претходно звање

CONFERENCE SERIES

Armin Hansel, Jürgen Dunkl

Contributions

8th International Conference on
Proton Transfer Reaction
Mass Spectrometry and its Applications



innsbruck university press

CONFERENCE SERIES

innsbruck university press

universität
innsbruck

Armin Hansel
Jürgen Dunkl
Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

Local Organizing Committee:

Armin Hansel, Jürgen Dunkl, Sandra Naschberger
Institute for Ion Physics and Applied Physics, University of Innsbruck, Austria

Thomas Karl – Session Chair of Applications in Environmental Science
Institute of Atmospheric and Cryospheric Sciences, University of Innsbruck, Austria

Franco Biasioli – Session Chair of Applications in Food Science
Fondazione Edmund Mach di San Michele all'Adige, Italy

Jonathan Beauchamp – Session Chair of Applications in Health Science
Fraunhofer-Institut für Verfahrenstechnik und Verpackung IVV, Freising, Germany

Jens Herbig – Session Chair of Applications in the Industry
Ionicon Analytik Ges.m.b.H., Innsbruck, Austria

Universität Innsbruck
1st edition

www.uibk.ac.at/iup
ISBN 978-3-903187-46-7

8th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications

Contributions

Editors:
Armin Hansel
Jürgen Dunkl

Institut für Ionenphysik und Angewandte Physik
der Leopold-Franzens-Universität Innsbruck
Technikerstr. 25
A-6020 Innsbruck, Austria

Innsbruck, Austria
4th February – 8th February, 2019

Contents

Applications in Food Science

Instruments & Technology and Future Trends

Applications in the Industry

Contributed Papers (Posters)

Explainable machine learning prediction of VOC in an university building microenvironment

Andreja Stojić[1], Gordana Vuković[1], Svetlana Stanišić[2], Vladimir Udovičić[1], Nenad Stanić[2] and Andrej Šoštarić[3]

[1] *Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Pregrevica 118, 11000 Belgrade, Serbia, andreja@ipb.ac.rs*

[2] *Singidunum University, Danijelova 32, 11000 Belgrade, Serbia*

[3] *Institute of Public Health Belgrade, Despota Stefana 54, 11000 Belgrade, Serbia*

Abstract

In this study we applied a novel SHapley Additive exPlanations feature attribution framework to examine the relevance of meteorological parameters and identify key factors that govern indoor and outdoor isoprene concentrations obtained by PTR-MS measurements in an university environment. According to the results, ambient temperature appeared to be far the most important predictor of isoprene levels, followed by relative humidity and air pressure.

Introduction

Spatial evolution of isoprene concentrations in different environments depends on biogenic and anthropogenic emission sources and ambient conditions. Even the past environmental conditions experienced by the leaves, the soil moisture stress, and the age of leaves, have shown to affect isoprene fluxes (Müller et al., 2008). Once emitted in the air, isoprene fate is also dependent on meteorological conditions – it is dispersed under the influence of wind, subjected to photochemical reactions being predominantly enhanced by solar radiation (Cheng et al., 2018), or it acts as a precursor in the reactions of secondary organic aerosol formation under low relative humidity conditions (Zhang et al., 2011). In this study, we used the SHapley Additive exPlanations (SHAP) framework to obtain a more detailed insight into the meteorological factors that govern isoprene concentrations in indoor and outdoor environment.

Experimental Methods

Isoprene concentrations were measured in real time using proton transfer reaction mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria) in the period from March to July 2016. The measurement site was located at Singidunum University, Belgrade, Serbia (44°78' N, 20°48' E). Drift tube parameters included: pressure, ranging from 2.04 to 2.14 mbar; temperature 60^0C; E/N parameter, 145 Td providing reaction time of 90 µs. The count rate of $H_3O^+H_2O$ was 3 to 8% of the $9.2 \cdot 10^6$ counts s^{-1} count rate of primary H_3O^+ ions.

Regression analysis by means of eXtreme Gradient Boosting (XGBoost Python Package) was implemented for estimating the relationships between isoprene indoor/outdoor concentrations and meteorological parameters, including outdoor temperature, pressure, relative humidity and wind speed and direction, as well as the indoor temperature, pressure and relative humidity.

Accurate interpretation a model's prediction supports deeper understanding of the process being modeled. The SHAP method (Lundberg and Lee, 2017), based on unification and additive attribution algorithms, offers uniquely consistent, locally accurate attribution values attributing to each feature the change in the expected model prediction when conditioning on that feature.

Results and Discussion

The SHAP analysis (Stojić et al., 2019) was successfully applied to reveal in which respect the ambient conditions affected indoor and outdoor concentrations of isoprene as confirmed by the XGBoost predicted/observed relative errors of 18% and 25%, and the correlation coefficients of 0.88 and 0.91, respectively. The SHAP summary plot and the magnitude of mean SHAP values, as a measure of feature importance (Figure 1), suggest that ambient temperature appeared to be far the most important predictor of isoprene outdoor levels, followed by relative humidity and pressure, whereas the impact of wind speed and direction could be considered negligible.

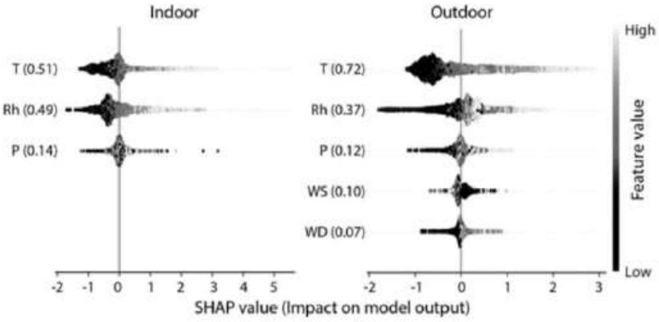


Figure 1: SHAP summary plot and mean SHAP value magnitude (values in brackets).

The dot density, in which each dot represents a particular measurement, show that lower temperatures were the most common in the dataset. However, a smooth increase in the model's output and long-tailed distribution reaching to the right suggest that increased temperature and its extreme values could significantly affect outdoor isoprene distribution. Similar results were registered for indoor isoprene (Figure 1). Furthermore, the SHAP analysis allowed for distinguishing between main (Figure 2) and interaction effects (Figure 3, right) of the most influential predictors of indoor and outdoor isoprene levels.

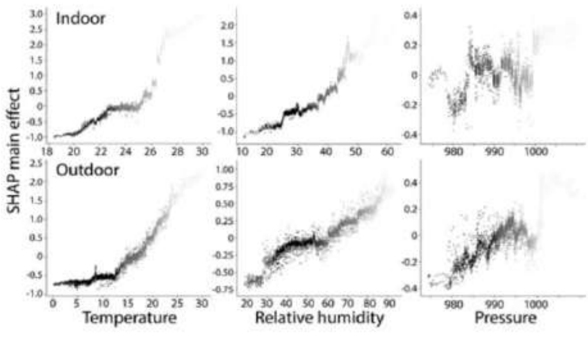


Figure 2: SHAP main effects.

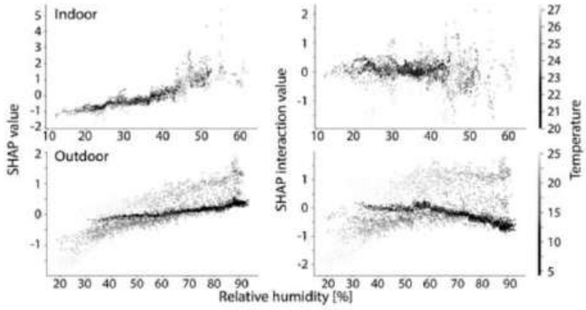


Figure 3: SHAP dependence (left) and interaction plots (right).

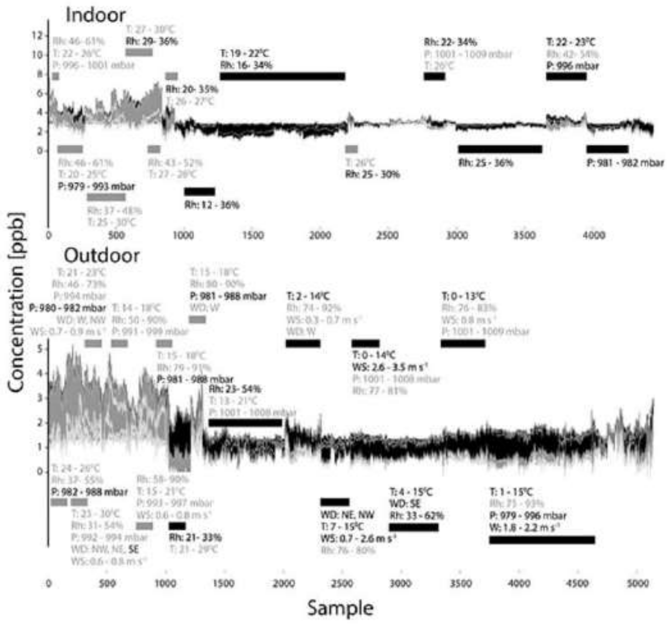


Figure 4: SHAP supervised clustering (contributors which push the model output from the base value `higher/lower are presented in grey/black`*).*

As showed by SHAP dependence plot (Figure 3, left), relative humidity has a stronger influence on isoprene concentrations in indoor than outdoor environment. Additionally, the same Figure reveals that higher indoor air temperatures were accompanied by increased relative humidity. For outdoor, the opposite tendency was observed, but with lower SHAP values and related impact on the model's output. Interactions among temperature and relative humidity caused most of the variance in the isoprene concentrations, as can be seen in Figure 3 (right). Supervised SHAP clustering classified indoor and outdoor isoprene level of pollutants into several subgroups, annotated by features which define them (Figure 4). As can be noted, the relationships between indoor/outdoor isoprene concentrations and ambient conditions were particularly evident for the temperatures above 15°C and relative humidity exceeding 40%.

As can be concluded, our knowledge of isoprene/volatile organic compound behavior and environmental fate could benefit from further investigation of interrelationships between major air pollutants and meteorological features.

Acknowledgments

This paper was realized as part of projects No III43007 and No III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-19.

References

[1] J.F., Müller, T., Stavrakou, S., Wallens, I.D., Smedt, M.V., Roozendael, M.J., Potosnak, J., Rinne, B., Munger, A. Goldstein, and A.B., Guenther, Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model, Atmospheric Chemistry and Physics, 8(5), 1329-1341, (2008).

[2] X. Cheng, H. Li, Y. Zhang, Y. Li, W. Zhang, X. Wang, F. Bi, H. Zhang, J. Gao, F. Chai, X. Lun, Y. Chen, J. Gao, J. Lv, Atmospheric isoprene and monoterpenes in a typical urban area of Beijing: Pollution characterization, chemical reactivity and source identification, Journal of Environmental Sciences, 71, 150–167, (2018).

[3] H. Zhang, JD. Surratt, YH. Lin, J. Bapat, RM. Kamens, Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions, Atmospheric Chemistry and Physics, 11, 6411–6424, (2011).

[4] S.M. Lundberg, and S.I. Lee, A unified approach to interpreting model predictions. In Advances in Neural Information Processing Systems, pp. 4765-4774, (2017).

[5] XGBoost Python Package, Available at: https://github.com/dmlc/xgboost/tree/master/python-package

[6] A. Stojić, N. Stanić, G. Vuković, S. Stanišić, M. Perišić, A. Šoštarić, L. Lazić, Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition, Science of The Total Environment, 653, 140–147, (2019).

Multifractality of isoprene temporal dynamics in outdoor and indoor university environment

Andreja Stojić[1], Gordana Vuković[1], Svetlana Stanišić[2], Vojin Ćućuz[3], Dragomir Trifunović[3], Vladimir Udovičić[1] and Andrej Šoštarić[4]

[1] *Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Pregrevica 118, 11000 Belgrade, Serbia, andreja@ipb.ac.rs*

[2] *Singidunum University, Danijelova 32, 11000 Belgrade, Serbia*

[3] *School of Electrical Engineering, University of Belgrade, 73 Bulevar kralja Aleksandra, 11000 Belgrade, Serbia*

[4] *Institute of Public Health Belgrade, Despota Stefana 54, 11000 Belgrade, Serbia*

Abstract

In this study the multiscale multifractal method was used with the aim to capture the fractal behaviour of indoor and outdoor isoprene time series obtained by PTR-MS measurements in an university environment (Belgrade, Serbia), as well as to investigate to what extent variations in isoprene levels can be considered random or persistent. As shown, isoprene time series exhibited persistency, slightly affected by the concentrations occurring randomly only at the level of small fluctuations and small scales within the time frame of 20 hours. The results herein presented contribute to better understanding of isoprene temporal evolution and provide theoretical background for enhanced forecasting of volatile organic compound concentrations in general.

Introduction

A number of literature sources have demonstrated that the behavior of heterogeneous and dynamic environmental systems or nonlinear processes, such as temporal and spatial evolution of isoprene, can be described by multifractal formalism. In this study we used multiscale multifractal method (MMA) for capturing the fractal behavior of isoprene outdoor and indoor concentration time series in an university environment and to investigate to what extent variations in isoprene levels can be considered random or persistent.

Experimental Methods

Isoprene concentrations were measured in real time using proton transfer reaction mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria) in the period from March to July 2016. The measurement site was located at Singidunum University, Belgrade, Serbia (44°78' N, 20°48' E). Drift tube parameters included: pressure, ranging from 2.04 to 2.14 mbar; temperature, 60 0C; voltage, 600 V; E/N parameter, 145 Td providing reaction time of 90 μs. The count rate of H3O+H2O was 3 to 8% of the 9.2·106 counts s−1 count rate of primary H3O+ ions. The measurements were performed continuously, except for brief interruptions for background level determination (10 min, 4 times per day) and calibration (5 times for the entire period).

Data Analysis

MMA is a generalization of the standard multifractal detrended fluctuation analysis (MF-DFA) (Stojić et al, 2016), which adds the dependence on scale, providing a broader analysis of the fluctuation properties, as well as more general and stable results (Stojić et al, 2017, Gierałtowski et al, 2012). For imputing missing data we employed *missForest,* a random forest based non-parametric algorithm available in R package and capable to deal with high dimensions, complex interactions and nonlinear data structure. The algorithm uses bootstrap aggregation of multiple regression trees and continues repeating the imputation procedure until a pre-defined stopping criterion is met, *i.e.* until the difference between the newly imputed data matrix and the previous one increases for the first time with respect to both variable types.

Results and Discussion

The complete indoor and outdoor isoprene time series obtained by missing value imputations are presented in Figure 1. The correlation between indoor and outdoor pollutant concentrations was 0.74. The *missForest* algorithm performed well, with predicted/observed out-of-bag normalized root mean squared error (NRMSE) of 0.009/0.011, and 0.078/0.083; and imputation out-of-bag NRMSE of 0.009 and 0.075, for indoor and outdoor isoprene concentrations, respectively.

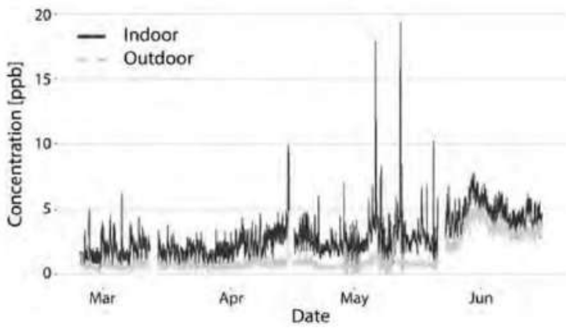


Figure 1: Isoprene indoor/outdoor time series.

The density of Miss Forest predicted and observed isoprene concentrations are in good agreement (Figure 2). Both indoor and outdoor isoprene concentrations fluctuated randomly over time (Hurst exponent, H=0.7–1.35), and their variation patterns were characterized by long-range correlated and persistent structure (Figure 3). Furthermore, the investigation of randomized isoprene time-series (Figure 4) revealed that the multifractality of the compound's indoor and outdoor concentration originates from both nonlinear correlations and a fat-tailed probability distribution.

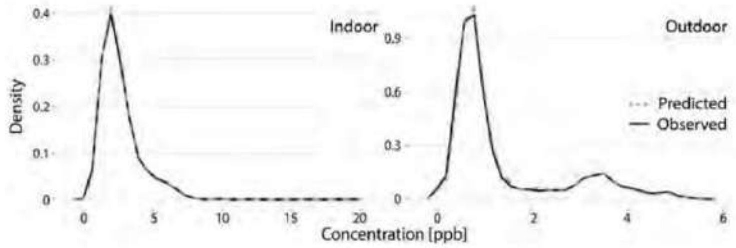


Figure 2: The density of predicted and observed isoprene concentrations.

As indicated by the minima and maxima of Hurst exponent and multifractal parameter (Figure 3), the indoor isoprene time-series were more influenced by small fluctuations compared to outdoor isoprene time-series, which mainly approached the most recognized fractal phenomena with long memory known as "pink noise". The variations could be explored with respect to different emission sources of isoprene that dominate over indoor and outdoor environment. Current knowledge suggests that three main sources of outdoor isoprene refer to vehicle emissions, evaporative emissions from petroleum products and plant emissions, although at temperatures exceeding 25°C dominant part of outdoor isoprene might be assigned to biogenic sources (Bari et al., 2015). On the other hand, the indoor isoprene levels are mostly affected by adhesives, coatings and the occupant's breath (Huang et al., 2016). In addition, non negligible factors are distinguishing features of interior spaces and occasional contributions of outdoor air through air-conditioning and building openings.

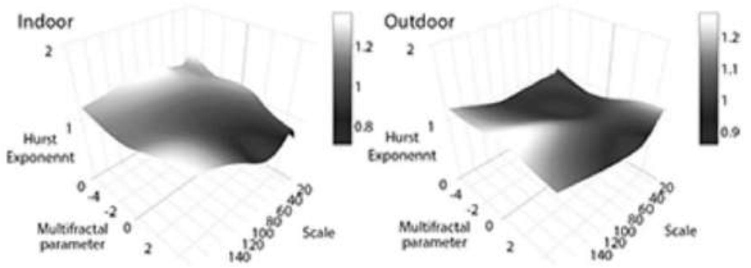


Figure 3: Isoprene indoor/outdoor time series Hurst surfaces.

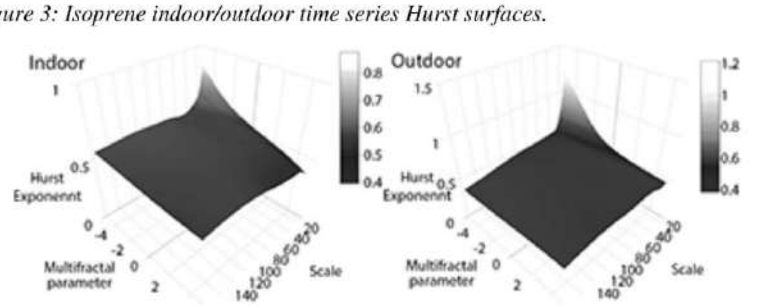


Figure 4: Isoprene randomized indoor/outdoor time series Hurst surfaces.

Indoor and outdoor isoprene time-series could be considered statistically different as indicated by the values of generalized distance Hurst coefficient (Figure 5) which highly exceeded the threshold value (0.065). The differences are primarily caused by strong fluctuations in both domains (negative and positive) of the multifractality parameter's interval at temporal scales between 60 and 160.

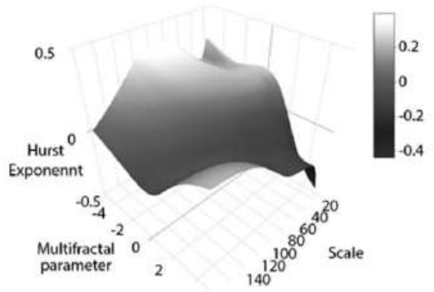


Figure 5: The difference between isoprene indoor and outdoor time series Hurst surfaces

Acknowledgments

This paper was realized as part of projects No III43007 and No III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-19.

References

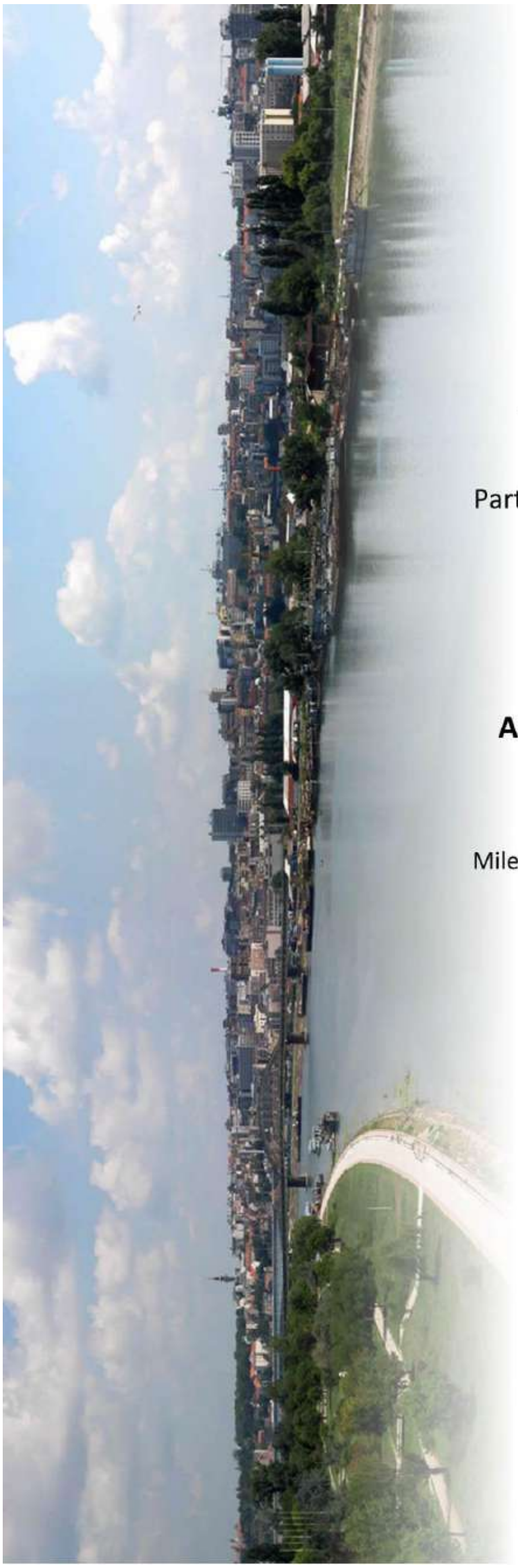
[1] J. Gierałtowski, J. Żebrowski, and R. Baranowski, Multiscale multifractal analysis of heart rate variability recordings with a large number of occurrences of arrhythmia, Physical Review E 85(2), 021915, (2012).

[2] A. Stojić, S.S. Stojić, I. Reljin, M. Čabarkapa, A. Šoštarić, M. Perišić, and Z. Mijić, Comprehensive analysis of PM10 in Belgrade urban area on the basis of long-term measurements. Environmental Science and Pollution Research, 23(11), 10722-10732, (2016).

[3] A. Stojić, S. Stanišić Stojić, M. Perišić, and Z. Mijić, Multiscale multifractal analysis of nonlinearity in particulate matter time series. 6th International WeBIOPATR Workshop & Conference Particulate Matter: Research and Management, September 6-8, Belgrade, Serbia, pp. 1-4, (2017).

[4] Md. A. Bari, W. B. Kindzierski, A. J. Wheeler, M.-É. Héroux, L. A. Wallace, Source apportionment of indoor and outdoor volatile organic compounds at homes in Edmonton, Canada, Building and Environment 90, 114–124, (2015).

[5] Z. Huang, Y. Zhang, Q. Yan, Z. Zhang, X. Wang, Real-time monitoring of respiratory absorption factors of volatile organic compounds in ambient air by proton transfer reaction time-of-flight mass spectrometry, Journal of Hazardous Materials 320, 547–555, (2016).



WeBIOPATR 2019

The Seventh International WEBIOPATR
Workshop & Conference
Particulate Matter: Research and Management

Abstracts of Keynote Invited Lectures and Contributed Papers

Milena Jovašević-Stojanović and Alena Bartoňová, Eds

Public Health Institute of Belgrade

Belgrade 2019

ABSTRACTS OF KEYNOTE INVITED LECTURES AND CONTRIBUTED PAPERS

The Seventh International WeBIOPATR Workshop & Conference

Particulate Matter: Research and Management

WeBIOPATR 2019

1st to 3rd October, 2019

Belgrade, Serbia

Editors

Milena Jovašević-Stojanović

Alena Bartoňová

Publisher

Public Health Institute of Belgrade

Prof. Dr Dušanka Matijević, Director

Boulevar Despota Stefana 54a

Serbia, 11000 Belgrade

Printed by

Printing office of the Public Health Institute of Belgrade

Number of copies

150

ISBN 978-86-83069-56-9

www.zdravlje.org.rs

SCIENTIFIC COMMITTEE

Aleksandar Jovović, Serbia
Alena Bartoňová, Norway
Antonije Onjia, Serbia
David Broday, Israel
Dikaia Saraga, Greece
Griša Močnik, Slovenia
Ivan Gržetić, Serbia
María Cruz Minguillón, Spain
Milena Jovašević-Stojanović, Serbia
Radim J. Šrám, Czech Republic
Renata Kovačević, Serbia
Selahattin Incecik, Turkey
Slobodan Ničković, Serbia
Simone Barreira Morais, Portugal
Zoran Mijić, Serbia
Zoran Ristovski, Australia
Zorana Jovanović-Andersen, Denmark

ORGANIZING COMMITTEE

Aleksandra Stanković, Serbia
Alena Bartoňová, Norway
Andrej Šoštarić, Serbia
Anka Cvetković, Serbia
Biljana Filipović, Serbia
Branislava Matić, Serbia
Dejan Lekić, Serbia
Dragan Alavantić, Serbia
Ivan Lazović, Serbia
Jasmina Jović-Stošić, Serbia
Maja Jovanović (Secretary), Serbia
Marija Živković (Secretary), Serbia
Milena Jovašević-Stojanović, Serbia
Miloš Davidović, Serbia
Mira Aničić Urošević, Serbia
Mirjana Perišić, Serbia
Nenad Živković, Serbia
Tihomir Popović, Serbia
Vesna Slepčević, Serbia
Viša Tasić, Serbia

CONFERENCE TOPICS

1. **Atmospheric Particulate Matter - Physical and Chemical Properties**
    i. Sources and formation of particulate matter
    ii. Particulate matter composition and levels outdoors and indoors
    iii. Environmental modeling
    iv. Nanoparticles in the environment
2. **Particulate Matter and Health**
    i. Exposure to particulate matter
    ii. Health aspects of atmospheric particulate matter
    iii. Full chain approach
3. **Particulate Matter and Regulatory Issues**
    i. Issues related to monitoring of particulate matter
    ii. Legislative aspects
    iii. Abatement strategies

Organizers

Vinča Institute of Nuclear Sciences, Serbia
Public Health Institute of Belgrade, Serbia
NILU Norwegian Institute for Air Research, Norway

The Seventh WeBIOPATR Workshop and Conference,
Particulate Matter: Research and Management, WEBIOPATR 2019
is supported by:
Ministry of Education, Science and Technological Development of Republic of Serbia

PREFACE

The International Workshop and Conference, Particulate Matter: Research and Management – WeBIOPATR is a biennial event held in Serbia since 2007. The conference addresses air quality in general and particulate matter specifically. Atmospheric particulate matter arises both from primary emissions and from secondary formation in the atmosphere. It is one of the least well understood local and regional air pollutants, has complex implications for climate change, and is perhaps the pollutant with the highest health relevance. It also poses many challenges to monitoring.

By WeBIOPATR, we aim to link the research communities with relevance to particulate matter with the practitioners of air quality management on all administrative levels, in order to facilitate professional dialogue and uptake of newest research into practice. The workshops usually draw an audience of about 70, and attract media attention in Serbia. It enjoys support of the responsible authorities: Ministry of Education, Science and Technological Development, Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency whose sponsorship is indispensable and gratefully acknowledged. We enjoy also support of international bodies such as the WHO.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007, associated with a project funded by the Research Council of Norway. The 2nd workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. WeBIOPATR2011 was held in Beograd 14.-17. 11. 2011 and for the first time, included a dedicated student workshop. WeBIOPATR2013 was held in Beograd 2.-4. 10. 2013. It covered the traditional PM research and management issues, discussions on how to encourage citizens to contribute to environmental governance, and how to develop participatory sensing methods. WeBIOPATR2015 was held in Beograd 14.-16.10. 2015. Own sessions were devoted to sensor technologies for air quality monitoring, utilizing information and input from the EU FP7 funded project CITI-SENSE (http://co.citi- sense.eu) and the EU COST action EuNetAir (www.eunetair.it). WeBIOPATR2017, the 6th conference, was held in Beograd 6.-8.9. 2017, with a wider than before Western Balkan participation.

WeBIOPATR2019 will be held 1.-3 -10-2019 in the Mechanical Faculty, University of Belgrade. It has attracted a record 58 contributions, and is bringing together scientists from 12 countries, documenting that the issues of atmospheric pollution, with their wide implications for climate change, human health and ecosystem services, are no less important today.

We are grateful to our unrelenting national and international partners for their support for this event.

Welcome to Beograd, and have a stimulating and productive time!

Milena Jovašević-Stojanović and Alena Bartoňová

TABLE OF CONTENTS

4.2. PARSING ENVIRONMENTAL FACTORS WHICH SHAPE PARTICULATE MATTER POLLUTION USING EXPLAINABLE ARTIFICIAL INTELLIGENCE

A. Stojić (1), M. Perišić (1), G. Jovanović (1), S. Stanišić (2), N. Stanić (2), T. Milićević (1)
(1) Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Serbia
(2) Singidunum University, Serbia
andreja.stojic@ipb.ac.rs

The unpredicted rate and the diversity of modern world development lead to unprecedented changes in the environment which require deep understanding of their nature and measures that might be undertaken to prevent further environment deteoritation. To tackle the root causes which shape air pollution, understanding the fundamental mechanisms of nature must rely on highly sophisticated machine learning algorithms and the interpretation frameworks aimed at delivering explainable predictive analytis (Stojić et al. 2018). In this paper, we utilize the statistical analysis of SHapley Additive exPlanation (SHAP) values to reveal the environmental conditions which shape PM_{10} pollution in an urban area (Belgrade, Serbia).

To examine the evolution of PM levels in the context of the urban environment, eXtreme Gradient Boosting regression analysis (XGBoost) was performed to obtain dependency between PM_{10} and criteria air pollutants (NO_x, NO, NO_2, SO_2, CO), volatile aromatics (benzene, toluene, ethylbenzene and xylene), meteorological factors (visibility, ceil height, wind speed and direction, relative humidity, dew point, atmospheric pressure, temperature and 25 1-degree-Global Data Assimilation System surface parameters), as well as temporal and seasonal variations (trend, day length, daylight, weekday, weekend, sunrise angle, month and season). All the measured concentrations and parameters were obtained from the automatic monitoring network of the Institute of Public Health Belgrade, Serbia. XGBoost is a supervised ensemble learning method which implements iterative combining of ensembles of weak prediction models into a single strong learner (Stojić et al. 2019). The dataset was divided into stratified training (80%) and validation (20%) sets. Hyperparameter tuning was implemented using an advanced grid search and stratified cross-validation replicated ten times. Moreover, to test the stability of the obtained model, 100 times replicated bootstrap procedure was performed.

Subsequently, SHAP framework was applied on the obtained regression function to deliver model explanations. The framework is based on unification of additive attribution algorithms, individualized for each prediction, offering uniquely consistent and locally accurate attribution values. It overcomes the drawback of other methods inconsistency, suppressing the possibility of underestimating the importance of a feature with a certain attribution value. Finally, fuzzy clustering of SHAP attributions was performed to obtain clusters of environmental factors (forces) which govern PM evolution in complex urban environment.

Six clusters of forces were identified, all dominated by CO, but with the ambivalent impact on PM levels. Namely, the clusters which represent the ambient in which the highest PM_{10} concentrations occur, are related to the highest concentrations of CO and benzene. On the contrary, essentially different interrelations between these compounds can be attributed to a lower concentration range of PM, suggesting different emission sources regime and different atmospheric chemistry. Also, visibility appears to be extracted as the most important variable, which clearly depicts fundamentally different atmospheric conditions regarding PM occurrence in different environmental clusters.

Acknowledgments

This study was performed as a part of projects no. III43007 and no. III41011, which were funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the framework of integrated and interdisciplinary research for the period 2011–2019.

REFERENCES

Stojić, A., Stanić, N., Vuković, G., Stanišić, S., Perišić, M., Šoštarić, A. and Lazić, L. 2019. Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition. Science of The Total Environment, 653, 140–147.

Stojić, A., Vuković, G., Perišić, M., Stanišić, S. and Šoštarić, A. 2018. Urban air pollution: an insight into its complex aspects. In: A Closer Look at Urban Areas, Nova Science Publishers, NY, USA.

10.3. RECEPTOR ORIENTED MODELING OF URBAN PARTICULATE AIR POLLUTION: SOURCE CHARACTERIZATION AND SPATIAL DISTRIBUTION

M. Perišić (1), A. Stojić (1), S. Stanišić (2), G. Jovanović (1)

(1) Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Serbia

(2) Singidunum University, Serbia

mirjana.perisic@ipb.ac.rs

Urban atmosphere is a complex system, in which air pollutants' levels are not only driven by the features of emission sources and variations of meteorological conditions, but also by the pollutant interactions and area-specific factors which have an impact on atmospheric chemistry. Nowadays, the application of advanced analytical methods is required to gain reliable information for better understanding of underlying factors which shape the air pollution phenomena in the urban environment. In this paper, we used the methodology based on receptor oriented modeling (Stojić and Stojić 2017) to investigate the spatial distribution of pollutants, their concentrations and potential emission sources in the urban core of the City of Belgrade, Serbia.

The database used in this study included the concentrations of suspended particulates matter (PM_{10}), inorganic and organic gaseous pollutants (NO_X, SO_2, CO, benzene and toluene), measured during the period of two years at the monitoring site Institute of Public Health Belgrade (Serbia). The chosen station, within the Air Quality Monitoring Network of Belgrade, is located in a densely populated part of the city, near intensive traffic activities, exposed to emission of local fireboxes and central district heating, as well as under the influence of various industrial emissions. Based on the pollutant concentrations and meteorological parameters (wind speed and wind direction), measured at the sampling site, the developed receptor-oriented model provides a detailed information on pollutants' concentrations and their mutual correlations in a wide area, not covered by the regulatory monitoring network.

The obtained interactive maps contain the results of the correlation analysis, as well as the relations between the concentrations of benzene and toluene, and measured air pollutants (PM_{10}, NOx, CO, and SO_2). The highest correlations of benzene and PM_{10} ($r = 0.8$) were observed along the large traffic routes, in Brankova Street and Bulevar Kralja Aleksandra Street, as well as in the northwestern part of the city center, suggesting that the intensive traffic represents the common source of gaseous and particulate pollution (Stojić et al. 2018). Furthermore, high correlations ($r > 0.7$) between benzene and combustion gases (NOx, CO, SO_2) in the western region reflect the influence of distant sources associated with the thermal power plants Nikola Tesla in Obrenovac, while relatively low correlations between benzene and combustion gases in the northern and eastern part of the city indicate that benzene in this area possibly originates from industrial-petrochemical emissions near Pančevo (Stojić et al. 2015). Also, high correlations ($r > 0.7$) between toluene and NOx, which are indicators of fossil fuel combustion from traffic and heating, suggest the shared origin of these compounds in all the parts of the city included in the analysis, except for the old city core and Kalemegdan (north-west), where the toluene is probably present due to the enhanced retention of aged air in streets of urban-canyon type.

Acknowledgments

This study was performed as a part of projects no. III43007 and no. III41011, which were funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the framework of integrated and interdisciplinary research for the period 2011–2019. Also, this paper presents a part of the results of the project realized with the support of the Green Fund of the The Ministry of Environmental Protection of the Republic of Serbia.

REFERENCES

Stojić, A., Stojić, S. S., Šoštarić, A., Ilić, L., Mijić, Z. and Rajšić, S. 2015. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling, Environmental Science and Pollution Research, 22(17), 13137–13152.

Stojić, A., Stojić and S. S. 2017. The innovative concept of three-dimensional hybrid receptor modeling. Atmospheric Environment, 164, 216–223.

Stojić, A., Vuković, G., Perišić, M., Stanišić, S. and Šoštarić, A. 2018. Urban air pollution: an insight into its complex aspects. In: A Closer Look at Urban Areas, Nova Science Publishers, NY, USA.

11.6. EXPLAINABLE RELATIONS OF PARTICULATE MATTER AND ENVIRONMENTAL FACTORS IN AN URBAN AREA

G. Jovanović (1), A. Stojić (1), M. Perišić (1), S. Stanišić (2), N. Stanić (2) and T. Milićević (1)
(1) Institute of Physics Belgrade, National Institute of the Republic of Serbia, University of Belgrade, Serbia
(2) Singidunum University, Serbia
gordana.vukovic@ipb.ac.rs

In this study we focused on examining the dependencies between particulate matter (PM), and other air pollutants and atmospheric conditions in an urban environment. Briefly, eXtreme Gradient Boosting regression (XGBoost) was performed to obtain the relations between concentrations of PM_{10} and volatile organic compounds, inorganic gaseous pollutants, measured and modeled meteorological parameters, as well as parameters representing temporal and seasonal variations (Stojić et al. 2018). The relations were further analyzed by the use of Shapley Additive exPlanation (SHAP) summary and dependence distributions. The details about the methods applied are given elsewhere (Stojić et al. 2019).

The results indicate that, although CO individually achieves the highest impact on PM_{10} levels, meteorological conditions play the major role in shaping its environmental fate in an urban environment. Among other polluting species, the relation with benzene can be considered to be substantial, while the impact of other compounds found in the urban atmosphere, such as inorganic gaseous pollutants or other aromatics, can be considered to be significantly lower. The influence of CO is different, depending on the CO concentration range. The concentrations below 1 mg m^{-3} are associated with lower PM; in the CO concentration range between 1 and 1.5 mg m^{-3} the influence on PM levels can be considered negligible, while an increase in CO above 1.5 mg m^{-3} is accompanied by an increase of PM_{10}. This impact is largely determined by seasonality, indicating a strong influence of emission source, particularly the combustion of fossil fuels for heating purposes. However, it can be noticed that, even during the colder part of a year, low CO concentrations, being always followed by low concentrations of NO_x, SO_2 and volatile aromatics, stay related with lower PM levels. High-level CO concentration range is associated with complex interactions with other environmental factors, which need to be further addressed.

Low ceil height, even when being registered along with low visibility, does not have to be unambiguously associated with increased levels of PM. However, it can be seen that low cloudiness generally leads to a decrease in PM concentrations, which cannot be attributed to an increase in humidity or wet deposition, because with the highest relative humidity (Rh) values, the contribution of low cloudiness to an increase in PM can be extremely high. On the other hand, several of the most extreme PM events, associated with the highest impact on PM concentration, occurred with good visibility and max ceil height. Low visibility conditions, on their own, lead to an increase in PM levels. The lowest impact was observed for the highest concentrations of CO and benzene, and the lowest concentrations of other aromatics during the colder part of a year, and thus can be attributed to the the activation of the combustion emission sources emitting a lower share of PM. The ambient conditions which correspond to lower Rh (lower than 60%) and higher visibility contribute to the decrease in PM concentrations. Only with humidity above 80% and reduced visibility, an increase in PM concentrations up to about 10 μg m^{-3} was evident. The highest positive impact of relative humidity cannot be associated with high low and medium cloudiness, while the situation is indeterminate as for high cloudiness. At the end of the analyzed period, there was a noticeable change in the impact of the temporal trend on PM levels. The results clearly identify the suppression of the combustion sources which, in addition to CO emission, contain PM. This event was followed by the appearance of a pronounced combustion source which, besides CO, emits a large amount of particulatte pollution.

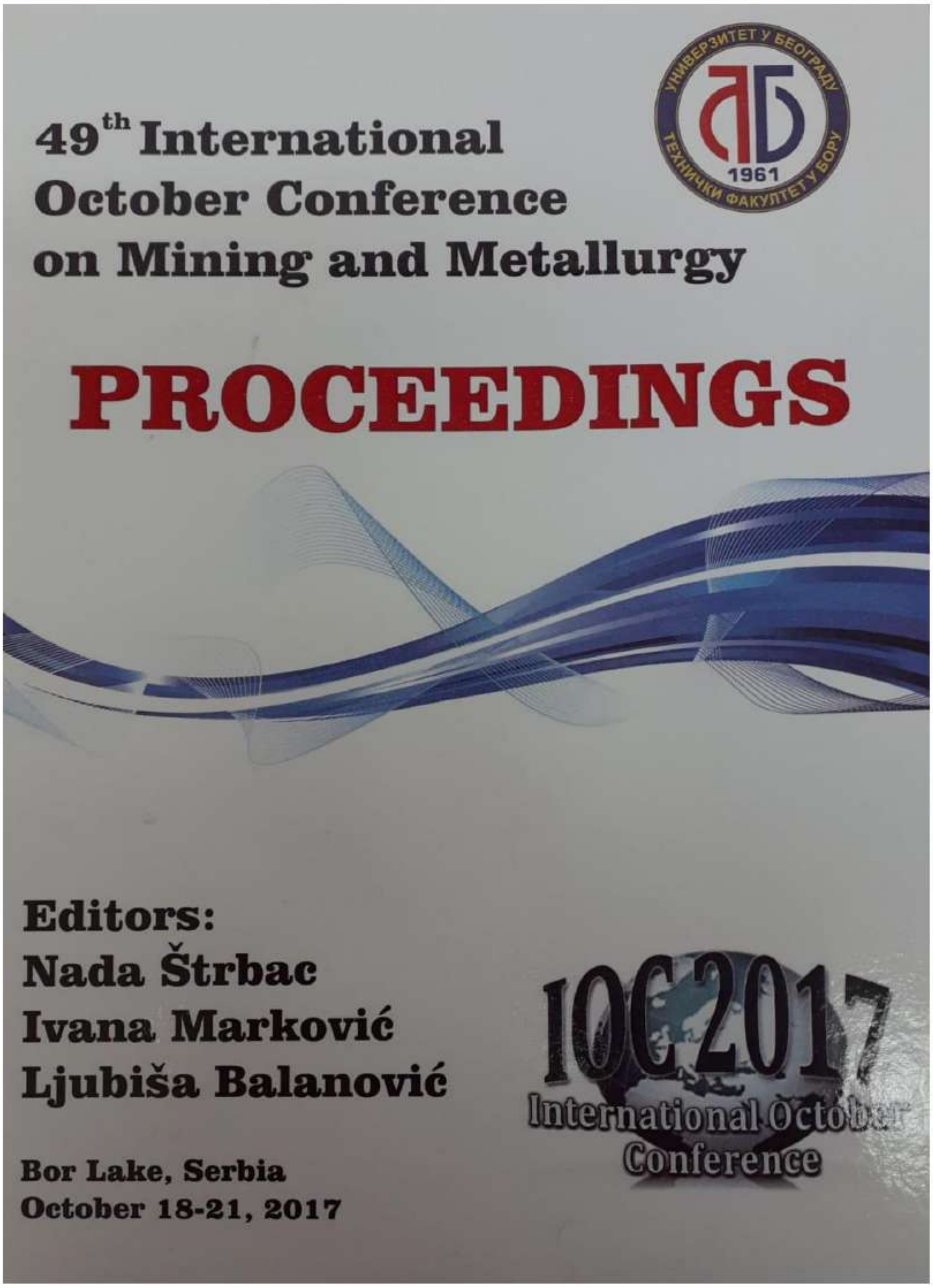
ACKNOWLEDGMENTS

This study was performed as a part of projects no. III43007 and no. III41011, which were funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the framework of integrated and interdisciplinary research for the period 2011–2019.

REFERENCES

Stojić, A., Stanić, N., Vuković, G., Stanišić, S., Perišić, M., Šoštarić, A. and Lazić, L. 2019. Explainable extreme gradient boosting tree-based prediction of toluene, ethylbenzene and xylene wet deposition. Science of The Total Environment, 653, 140–147.

Stojić, A., Vuković, G., Perišić, M., Stanišić, S. and Šoštarić, A. 2018. Urban air pollution: an insight into its complex aspects. In: A Closer Look at Urban Areas, Nova Science Publishers, NY, USA.



УНИВЕРЗИТЕТ У БЕОГРАДУ
ТЕХНИЧКИ ФАКУЛТЕТ У БОРУ
1961
49th International
October Conference
on Mining and Metallurgy
PROCEEDINGS
Editors:
Nada Štrbac
Ivana Marković
Ljubiša Balanović
IOC2017
International October
Conference
Bor Lake, Serbia
October 18-21, 2017

PROCEEDINGS,
49th INTERNATIONAL OCTOBER CONFERNCE
on Mining and Metallurgy

Editors:
Prof. dr Nada Štrbac
Doc. dr Ivana Marković
Doc. dr Ljubiša Balanović
University of Belgrade, Technical Faculty in Bor

Technical Editor:
M. Sc. Uroš Stamenković
University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor
For the publisher: Dean Prof. dr Nada Štrbac
Circulation: 200 copies

Printed by "Happy trend DOO", Zaječar, 2017

ISBN 978-86-6305-066-2

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

622(082)
669(082)

INTERNATIONAL October Conference on Mining and Metallurgy (49 ; 2017 ; Bor Lake)
Proceedings / 49th International October Conference on Mining and Metallurgy - IOC 2017,
Bor Lake, Serbia, October 18-21, 2017;
[organized by] University of Belgrade, Technical Faculty Bor and Mining and Metallurgy Institute Bor;
editors Nada Štrbac, Ivana Marković, Ljubiša Balanović. - Bor : University of Belgrade, Technical Faculty,
2017 (Zaječar : Happy trend). - XXIII, 664 str. : ilustr. ; 25 cm

Tiraž 200. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-066-2

a) Рударство - Зборници b) Металургија - Зборници

COBISS.SR-ID 246349324

Bor Lake, Serbia, October 18-21, 2017

Conference is financially supported by
The Ministry of Education, Science and
Technological Development of the
Republic of Serbia

SCIENTIFIC COMMITTEE

ORGANIZING COMMITTEE

PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the 49th International October Conference on Mining and Metallurgy (IOC 2017) held at Bor Lake, Serbia, 18 – 21 October 2017.

The IOC 2017 has been organized by the University of Belgrade, Technical Faculty in Bor, in cooperation with Mining and Metallurgy Institute Bor. It is devoted to presenting recent research results and advances in the fields of geology, mining, metallurgy, materials science, technology, environmental protection, and related engineering topics. The primary goal of IOC is to bring together academics, researchers, and industry engineers to exchange their experiences, expertise and ideas, and also to consider possibilities for collaborative research.

This year's conference is dedicated to the memory of Professor Dragana Zivkovic who was one of our most loyal and active Committee members. The 4th International Student Conference on Technical Sciences (ISC 2017) will take place within the frame of IOC 2017. ISC provides a unique opportunity for the students from both the country and the region to promote scientific research and discuss future directions of research with the experts and specialists.

These proceedings include 153 papers from authors coming from universities, research institutes and industries in 30 countries: Austria, Bosnia and Herzegovina, Bulgaria, China, Croatia, Czech Republic, France, Germany, Hungary, India, Iran, Italy, Japan, Jordan, Kazakhstan, Libya, Macedonia, México, Montenegro, Norway, Poland, Romania, Russia, Slovakia, Slovenia, South Africa, Spain, Turkey, USA and Serbia.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged. The support of the sponsors and their willingness and ability to cooperate has been of great importance for the success of IOC 2017. The Organizing Committee would like to extend their appreciation and gratitude to all the sponsors and friends of the Conference for their donations and support.

We would like to thank all the authors who have contributed to these proceedings, and also to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to IOC 2017. Sincere thanks to all the people who have contributed to the successful organization of IOC 2017.

We look forward to welcoming you to the 50th International October Conference on Mining and Metallurgy (IOC 2018), which will be held in October 2018.

On behalf of the 49th IOC Organizing Committee,

Assistant Professor Ivana Marković, PhD

TABLE OF CONTENTS

Plenary Lectures

Section Lectures

Conference Papers

AIR MASS TRANSPORT OVER BALKANS REGION IDENTIFIED BY ATMOSPHERIC MODELING AND AEROSOL LIDAR TECHNIQUE

Zoran Mijić, Mirjana Perišić, Luka Ilić, Andreja Stojić, Maja Kuzmanoski
Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

Abstract
This study combines atmospheric modeling with lidar measurements in order to assess the origin of aerosols traveling over Balkan region, having an impact on regional radiative budget and air quality. Particulate matter potential source regions and transport pathways were investigated using hybrid receptor modeling and mass concentrations measured in Belgrade, Serbia. In addition, the case study evidencing transport of Saharan dust particles simulated by the DREAM model was presented. The capability of the lidar technique to derive range-resolved vertical profiles of aerosol optical parameters was used to analyze the aerosol layers altitude and temporal evolution.

***Keywords**: atmospheric modeling, transport, PM*

1. INTRODUCTION

Suspended particulate matter (PM) in the atmosphere, commonly known as aerosol, plays an important role in the climate system. Besides significant effect on climate change, air quality and human health, aerosols affect long-range transport and deposition of toxics and nutrients. The complexity of aerosol processes in the atmosphere leads to large uncertainties in understanding of their role in many of the major environmental issues [1]. The direct (scattering and absorbing incoming solar radiation) and indirect aerosol effects (as they act as a cloud condensation nuclei) make the two largest contributions to the total uncertainty of radiative forcing. Regarding the impact of aerosols on air quality, the same processes that govern the global distribution, control the aerosol properties on regional and local scales. While *in situ* measurements are most adequate for air quality monitoring at the ground level, the assessment of impact of remote sources and transformation processes requires aerosol vertical distribution observations. Key parameters to be observed for this purpose are the presence, altitude and extent of elevated aerosol layers, the height of the planetary boundary layer (PBL), aerosol type, and mass concentration. Since long-range transport occurs at elevated layers, surface-based measurements of aerosol properties, such as chemical composition and size distribution are not sufficient. For global coverage including all relevant parameters, an integrated approach including ground-level and airborne in-situ measurements, ground-based remote sensing, and space-borne observations in combination with advanced modeling is necessary. Large observational networks such as the European Aerosol Research Lidar Network (EARLINET) [2], provide the long-term measurement series needed to build an aerosol vertical profile climatology at the continental scale. The capability of the lidar system (Light Detection And Ranging) to derive range-resolved aerosol vertical profiles with high spatial and temporal resolution is used to identify layers altitude and temporal evolution of intrusions. Using altitudes as inputs in air mass back-trajectories tracing method identification of aerosol sources at large distances from the measurement point, if their contribution is important, can be conducted. In this study hybrid receptor models for identification of potential source regions of PM affecting air quality in Belgrade are presented together with a case study evidencing transport of Saharan dust particles.

2. METHODOLOGY

Lidar technique is an active remote sensing method based on laser emission of the short-duration light pulses to the atmosphere and the analysis of the return signal. The intensity of the light backscattered by atmospheric molecules and particles is measured versus time – through the telescope receiver, collimating optics, a bandpass filter for daylight suppression – by an appropriate detector. For vertical profiling and remote sensing of atmospheric aerosol layers, Raman lidar at the Institute of Physics Belgrade (44.860 N, 20.390 E) has been used. It is bi-axial system with combined elastic and Raman detection designed to perform continuous measurements of aerosols in the PBL layer and the lower free troposphere. It is based on the third harmonic frequency of a compact, pulsed Nd:YAG laser, emitting pulses of 65 mJ output energy at 355 nm with a 20 Hz repetition rate. The optical receiver is a Cassegrain reflecting telescope with a primary mirror of 250 mm diameter and a focal length of 1250 mm. Photomultiplier tubes are used to detect elastic backscatter lidar signal at 355 nm and Raman signal at 387 nm. The detectors are operated both in the analog and photon-counting mode with lidar profiles averaging time of the order of 1 min and the spatial raw resolution of the detected signals of 7.5 m. Lidar measurements can be used in synergy with numerical models in order to validate and compare information about aerosols. In this paper DREAM (Dust Regional Atmospheric Model) model, designed to simulate and/or forecast the atmospheric cycle of mineral dust aerosol [3], is used to analyze dust transport. To estimate potential PM remote emission sources and their impact at the receptor site, concentration weighted trajectory (CWT) hybrid receptor model [4] was applied to the data set comprised of hourly PM_{10} mass concentrations obtained from Belgrade suburban location "Ovča" during the period 2012-14, and 72-h air masses back-trajectories, calculated according to Perišić et al. [5]. Furthermore, to obtain the vertical profile of PM, concentration weighted boundary layer (CWBL) hybrid receptor model [6], which uses a two-dimensional grid and a planetary boundary layer height, or any altitude in general, as a frame of reference, was used. Although the model can be applied for analyzing the pollutant concentration vertical distribution along the transport pathway, in this paper we present its usage for the receptor site solely.

3. RESULTS AND DISCUSSION

According to the CWT analysis, the most prominent PM_{10} sources were located in neighboring countries and in the areas NW, E and S of Belgrade. Significant impact of Central and Eastern European sources was registered during the autumn season (Figure 1–left panel).

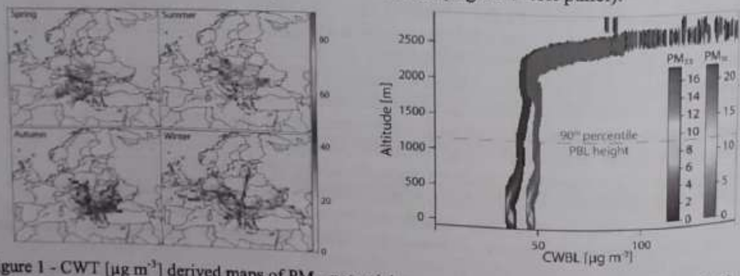


Figure 1 - CWT [µg m^{-3}] derived maps of PM_{10} potential sources in Europe – seasonal variations (left), and CWBL derived PM altitude distribution above the receptor site (right) – color scales indicate the number of events

Very similar, almost constant PM altitude distribution over the receptor site was observed for both coarse and fine particles (Figure 1–right panel), and the most common PBL heights (within 90th percentile). However, given the number of events (colored scale), it can be seen that concentrations exhibit decreasing trend to the height of about 400 m because the species emitted or generated near the ground level are mostly trapped and concentrated within the PBL, whereas free atmosphere concentrations remain low. Large CWBL values at higher altitudes correspond to rare PBL fluctuations which are not statistically significant, so the model results cannot be taken into consideration.

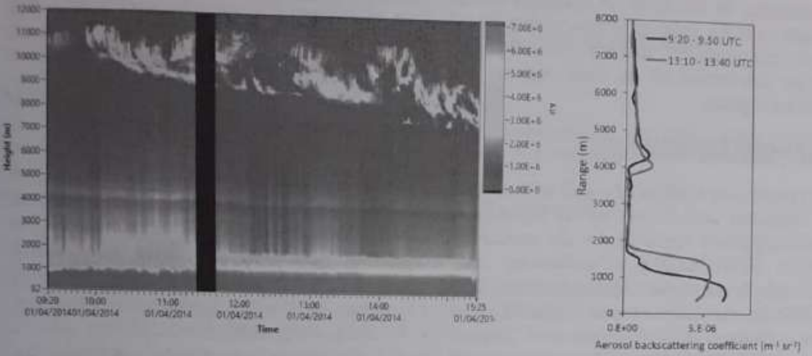


Figure 2 – Lidar range corrected signal (left) and backscatter coefficient at 355 nm (right) in Belgrade

Another aspect of aerosol climatology over Balkans region is related to the intrusions of Saharan dust which usually occurs during spring and summer periods. Such a case study evidencing transport of Saharan dust on 1st April 2014 is presented. From the RCS lidar time series (Figure 2), but also from the calculated backscatter coefficients profiles, the direct presence of an aerosol layer around 4-5 km altitude over Belgrade can been seen. This event was also successfully forecasted by DREAM model (Figure 3-left panel).

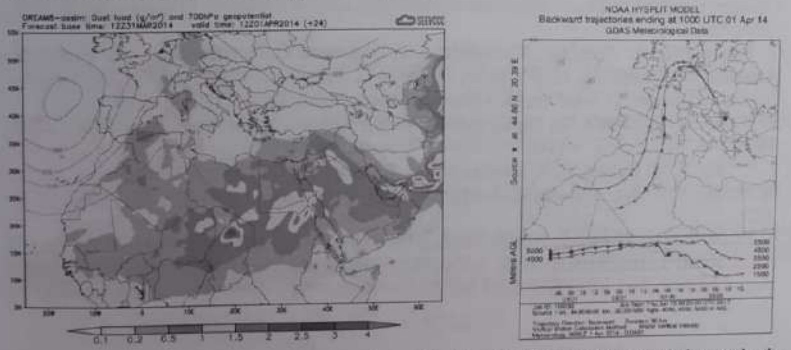


Figure 3 – Dust load over South Europe, estimated by the DREAM model (left) and air mass back-trajectories ending over Belgrade on 1st April, 2014 (righ)

Since the aerosols serve as a valuable tracer of air motion, using lidar observed altitudes of aerosol layer as inputs in the HYSPLIT [7] back-trajectory tracing method the source of aerosols was confirmed. As shown in Figure 3 (right panel) air masses reaching Belgrade traveled over

South Europe (Mediterranean Sea, Spain) and West Europe being influenced by continental pollution too.

4. CONCLUSION

The main advantage of lidar – real time observation of aerosol layering is that it can be used for air mass origin and path identification. Furthermore, in combination with statistical and numerical modeling, this technique can provide important information about aerosol type and distribution. In this paper we presented a case analysis of aerosol transport process affecting air quality over the Balkans region evidencing transport of Saharan dust particles over Serbia. Air mass back-trajectory analysis combined with hybrid receptor modeling were used to assess spatial distribution of the main regional sources for aerosols affecting air quality over the Balkans regions.

ACKNOWLEDGEMENTS

This paper was realized as a part of the projects III43007 and III41011 financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2017. The publication was supported by the project GEO-CRADLE (Coordinating and integRating state-of-the-art Earth Observation Activities in the regions of North Africa, Middle East, and Balkans and Developing Links with GEO related initiatives towards GEOSS), Grant Agreement No. 690133, funded under European Union Horizon 2020 Programme - Topic: SC5-18b-2015, Integrating North African, Middle East and Balkan Earth Observation capacities in GEOSS. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

REFERENCES

[1] T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, P. M. Midgley, IPCC: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.

[2] G. Pappalardo, A. Amodeo, A. Apituley, A. Comeron, V. Freudenthaler, H. Linné, A. Ansmann, J. Bösenberg, G. D'Amico, I. Mattis, L. Mona, U. Wandinger, V. Amiridis, L. Alados Arboledas, D. Nicolae, M. Wiegner, Atmos. Meas. Tech. 7 (2014) 2389.

[3] S. Nickovic, G. Kallos, A. Papadopoulos, O. Kakaliagou, J. Geophys. Res. 106 (2001) 1813.

[4] Y. K. Hsu, T. M. Holsen, P. K. Hopke, Atmos. Environ. 37(4) (2003) 545-562.

[5] M. Perišić, S. Rajšić, A. Šoštarić, Z. Mijić, A. Stojić, Air Qual Atmos Health 10 (2017) 93-103.

[6] A. Stojić, S. Stanišić Stojić., Atmos. Environ. 164 (2017) 216-223.

[7] A. F. Stein, R. R. Draxler, G. D. Rolph, B. J. B. Stunder, M. D. Cohen, F. Ngan, Bull. Amer. Meteor. Soc. 96 (2015) 2059-2077.


ISBN 978-86-6305-066-2

WeBIOPATR2017

Particulate Matter: Research and Management

Proceedings from the
6th WeBIOPATR
Workshop & Conference
Belgrade, Serbia
6.-8.9.2017

Milena Jovašević-Stojanović
and Alena Bartoňová, eds.

Belgrade 2019

The 6th WeBIOPATR Workshop and Conference,
Particulate Matter: Research and Management,
WEBIOPATR2017 is organized by:

Vinča Institute of Nuclear Sciences, Serbia
Public Health Institute of Belgrade, Serbia
NILU Norwegian Institute for Air Research, Norway

The 6th WeBIOPATR Workshop and Conference,
Particulate Matter: Research and Management,
WeBIOPATR2017 is supported by:

Ministry of Education, Science and Technological Development of

Republic of Serbia

PROCEEDINGS

The Sixth International WeBIOPATR Workshop & Conference
Particulate Matter: Research and Management
WeBIOPATR2017

6 - 8 September 2017
Belgrade, Serbia

Editors
Milena Jovašević-Stojanović
Alena Bartoňová

Publisher
Vinča Institute of Nuclear Sciences
Dr Zlatko Rakočević, Director
P.O. Box 522
11001 Belgrade, Serbia

Printed by
Vinča Institute of Nuclear Sciences

Number of copies
150

ISBN: 978-86-7306-152-8

Vinča Institute of Nuclear Sciences
www.vin.bg.ac.rs

SCIENTIFIC COMMITTEE

Dr Alena Bartoňová, Norway

Dr Bojan Radak, Serbia

Prof. Dr David Broday, Israel

Dr Med Elizabeta Paunović, Germany

Dr Maria Cruiz Min, Spain

Dr Milena Jovašević-Stojanović, Serbia

Prof. Dr Nenad Živković, Serbia

Prof. Dr Radim Šrám, Czech Republic

Dr Renata Kovačević, Serbia

Dr Slobodan Nićković, Serbia

Prof. Dr Simone Barreira Morais, Portugal

Zoran Mijić, Serbia

Prof. Dr Zoran Ristovski, Australia

Dr Zorana Jovanović-Andersen, Denmark

ORGANIZING COMMITTEE

Vinča Institute of Nuclear Sciences, Belgrade: Serbia
Dr Dragan Alavantić, Serbia
MS Ivan Lazović, Serbia
MS Maja Jovanović, Serbia (Secretary)
Dr Milena Jovašević-Stojanović (Co-chair)
Dr Miloš Davidović, Serbia (Secretary)
Dr Snežana Pašalić, Serbia

NILU - Norwegian Institute for Air Research, Kjeller
Dr Alena Bartoňová, Norway (Co-chair)

Public Health Institute of Belgrade, Belgrade
Dr Anka Cvetković, Serbia
MS Andrej Šoštarić, Serbia
Vesna Slapčević, Serbia

Ministry of Environmental Protection of RS
Ms Biljana Filipović, Serbia

Serbian Environmental Protection Agency
Mr Dejan Lekić, Serbia
Mr Tihomir Popović, Serbia

National Institute of Public Health "Dr Milan Jovanović-Batut", Belgrade
Dr Med Branislava Matić, Serbia

Military Medical Academy, Belgrade
Prof. Dr Jasmina Jović-Stošić, Serbia

Institute of Physics, Belgrade
Dr Mira Aničić Urošević, Serbia

Faculty of Occupational Protection, University of Niš
Prof. Dr Nenad Živković, Serbia

Medical Faculty, University of Niš
Prof. Dr Aleksandra Stanković, Serbia

Institute of Metallurgy and Mining, Bor
Dr Viša Tasić, Serbia

Mechanical Faculty, University of Belgrade
Prof. Dr Aleksandar Jovović, Serbia

CONFERENCE TOPICS

ATMOSPHERIC PARTICULATE MATTER - PHYSICAL AND CHEMICAL PROPERTIES	• *sources and formation of particulate matter* • *particulate matter composition and levels outdoors and indoors* • *environmental modeling* • *nanoparticles in the environment*
PARTICULATE MATTER AND HEALTH	• *exposure to particulate matter* • *health aspects of atmospheric particulate matter* • *full chain approach*
PARTICULATE MATTER AND REGULATORY ISSUES	• *issues related to monitoring of particulate matter* • *legislative aspects* • *abatement strategies*

PREFACE

The International Workshop and Conference, Particulate Matter: Research and Management – WeBIOPATR is a biennial event held in Serbia since 2007. The conference addresses air quality in general and particulate matter specifically. Atmospheric particulate matter arises both from primary emissions and from secondary formation in the atmosphere. It is one of the least well-understood local and regional air pollutants, has complex implications for climate change, and is perhaps the pollutant with the highest health relevance. It also poses many challenges to monitoring.

By WeBIOPATR, we aim to link the research communities with relevance to particulate matter with the practitioners of air quality management on all administrative levels, in order to facilitate professional dialogue and uptake of newest research into practice. The workshops usually draw an audience of about 70, and attract media attention in Serbia. It enjoys support of the responsible authorities, Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency whose sponsorship is indispensable and gratefully acknowledged. We enjoy also support of international bodies such as the WHO.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007, associated with a project funded by the Research Council of Norway. The 2nd workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. WeBIOPATR2011 was held in Beograd 14.-17. 11. 2011 and for the first time, included a dedicated student workshop. WeBIOPATR2013 was held in Beograd 2.-4. 10. 2013. It covered the traditional PM research and management issues, discussions on how to encourage citizens to contribute to environmental governance, and how to develop participatory sensing methods. WeBIOPATR2015 was held in Beograd 14.-16.10. 2015. Own sessions were devoted to sensor technologies for air quality monitoring, utilizing information and input from the EU FP7 funded project CITI-SENSE (http://co.citi-sense.eu) and the EU COST action EuNetAir (www.eunetair.it).

We have now the pleasure to present to you the proceedings of the 6th conference held in Beograd 6.-8.9. 2017. We are excited to have contributions from old friends and new acquaintances, and we are especially pleased with a wider than before Western Balkan participation. The contributions were reviewed. The language editing was performed by Dr Simon Smith, PhD, to whom we would like to extend out sincere thanks. Technical manuscript preparation was graciously done by Dr Milos Davidovic, PhD, to whom we are very grateful.

We are hoping that you, the reader, will extend your support to WeBIOPATR also in the future. The issues of atmospheric pollution, with their wide implications for climate change, human health and ecosystem services, are no less important today than before. Addressing them requires a strong scientific community and commitment of all societal actors. Your contribution will make a difference.

Milena Jovašević-Stojanović and Alena Bartoňová

CONTENTS

5.4. RELATIVE IMPORTANCE OF GASEOUS POLLUTANTS AND AEROSOL CONSTITUENTS FOR IDENTIFICATION OF PM_{10} SOURCES OF VARIABILITY

M. Perišić (1), G. Vuković (1), Z. Mijić (1), A. Šoštarić (2) and A. Stojić (1)
(1) Institute of Physics, University of Belgrade, Pregrevica 118, Serbia
(2) Institute of Public Health of Belgrade, Boulevard of Despot Stefan 54a, Belgrade, Serbia
mirjana.perisic@ipb.ac.rs

ABSTRACT

This study combines advanced statistical methods including time series decomposition, source apportionment and supervised learning algorithms, to identify the main sources of particulate matter (PM_{10}) variability in an urban area within Belgrade. The analyses indicated that the season, (i.e., meteorological conditions) strongly influenced daily and annual PM_{10} variations particularly during the colder part of the year. A guided regularized random forest model estimated that As, Cd, BaP, CO, and benzene have the highest relative importance for the prediction of PM_{10}. Polar plot source apportionment revealed common sources of pollution at specific directions. Specifically, emissions of PM_{10}, CO and benzene could be attributed to heating and gasification processes, while processes in oil refineries and chemical industries produced PM_{10} and toluene.

INTRODUCTION

Due to adverse effects on human health and the increased risk of morbidity and mortality, particulate matter (PM) is one of the most studied atmospheric pollutants, and perhaps, the most pressing issue in worldwide air quality regulation (Fuzzi et al, 2015, Stanišić Stojić et al, 2016). Even though significant progress has been made through the integration of different scientific approaches, modelling of air pollution data remains a challenge due to the complexity and non-linear nature of atmospheric phenomena and processes (Pai et al, 2013). During the last decade, poor air quality in Belgrade, with many PM_{10} limit value exceedances (Directive 2008/50/EC), has been identified as an important environmental risk factor (Perišić et al, 2015, 2017). Identification of factors affecting PM_{10} concentration variability could provide better insight into the aerosol spatiotemporal distribution and source composition, revealing their dominant sources in an urban area (Stojić et al, 2016).

Apart from the commonly used methods for data analysis, this study adopts the advanced statistical classifier, guided regularized random forest (GRRF), widely applied in many fields for feature selection. Moreover, the study demonstrates the possibilities of source apportionment analysis, which combines correlation and regression statistics with the bivariate polar plot analysis, to offer considerably more insight into air pollution sources.

METHODOLOGY

The analysed dataset, comprised of daily PM_{10} and its constituent concentrations (As, Cd, Cr, Mn, Ni, Pb, BaP, Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}), and hourly PM_{10} and gaseous pollutant concentrations (CO, SO_2, NO, NO_2, NO_x, benzene, toluene, o- and m, p xylene) have been obtained from an Institute of Public Health regular monitoring station located within an urban area in Belgrade (Longitude 20.470, Latitude 44.817) from 2011 - 2016. The time series of PM_{10} concentrations was resolved into the additive components of the multi-year and seasonal trends, as well as the remainders using the Loess smoothing decomposition model (LSD) (Li et al, 2014). Daily, weekly and seasonal periodicity was analyzed by the use of Lomb-Scargle periodogram (*Lomb* package within the statistical software environment *R*) (Ruf, 1999; Team, 2014). Bivariate polar plot analysis was used for identification of the main PM_{10} emission sources (Carslaw and Ropkins, 2012), while the advanced bivariate polar plots, coupled with pair-wise statistics, were applied to distinguish specific sources and to gain information about pollutant relationships. The model includes a weighted Pearson correlation, linear regression slope and Gaussian kernel to locally weight the statistical calculations on a wind speed-direction surface together with variable-scaling (Grange et al, 2016). Feature selection was implemented using a GRRF ensemble learning method (Deng and Runger, 2013). GRRF can select compact feature subsets revealing higher order variable interactions, thus moderating the problem of dimensionality and avoiding the effort to analyze irrelevant or redundant features.

RESULTS AND DISCUSSION

Annual concentrations of PM_{10} and BaP exceeded prescribed limit values of 50 $\mu g\ m^{-3}$ and 1 ng m^{-3}, respectively (Directive 2000/69/EC, Directive 2008/50/EC) every year of the period examined. The most abundant aerosol constituents were Cr, Pb and Mn (Figure 1), while SO_4^{2-} and NO_3^- were the ions with the highest concentrations.

In an urban area, the dominance of sulfate and nitrate ions is related to fossil fuel burning and traffic exhaust emission of SO_2 and NO_x, which, in the presence of water, transform into these ions. In addition, NH_4^+ and Ca^{2+} cations are usually presented as neutralizing agents for SO_4^{2-} and NO_3^- in heterogeneous atmospheric chemical reactions.

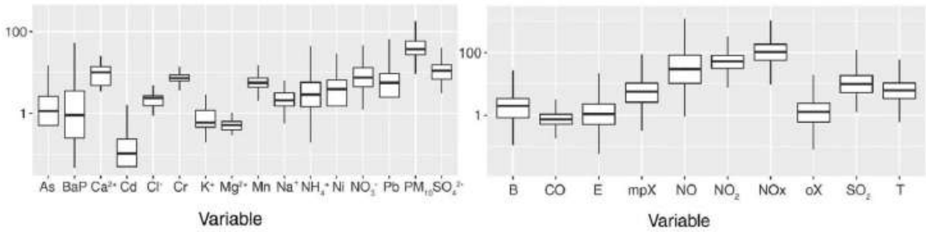


Figure 1. *PM_{10} concentration [μg m^{-3}], its chemical constituent (ions and BaP [μg m^{-3}], metals [ng m^{-3}]) (left) and gaseous pollutant [μg m^{-3}] (right) whisker plots*

Spectral analysis (Figure 2, left) reveals the highest normalized power values are attributed to the periods of 12 and 24 h, 7 days, and 1 and 3 months. This implies that meteorological conditions and anthropogenic emissions are strongly affected by aerosol daily and seasonal variations, and weekly periodicity, respectively (Bigi, 2016).

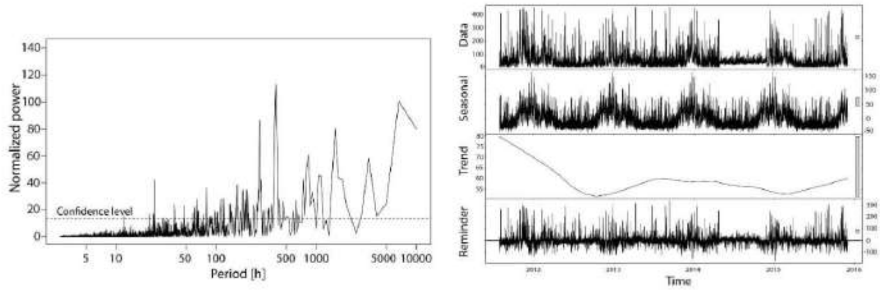


Figure 2. *PM_{10} Lomb-Scargle periodogram (left) and PM_{10} time series decomposition [μg m^{-3}] (right)*

Decomposed PM_{10} time series indicates a decreasing multi-year trend and significant impact of the seasonal component. Large variance of the remainder component possibly occurs as a result of short-term air pollution episodes (Figure 2, right). The conventional bivariate polar plot approach reveals the pronounced influence of both local and remote sources on PM_{10} variability (Figure 3).

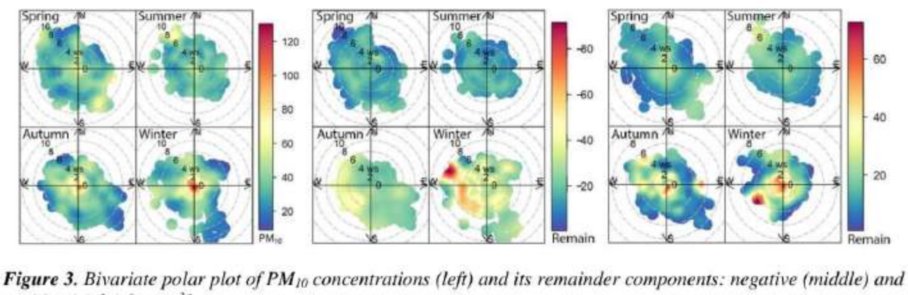


Figure 3. *Bivariate polar plot of PM_{10} concentrations (left) and its remainder components: negative (middle) and positive (right) [μg m^{-3}]*

Bivariate polar plot analysis of the remainder component, separately applied on positive and negative values, confirms that the episodes of the highest variations mainly occur during the colder part of the year. Positive variations related to SW and negative related to NW winds with speeds greater than 6 m s^{-1}.

The highest Pearson's correlation coefficients were obtained between concentrations of PM_{10} and its constituents (BaP (0.83), As (0.81), Cd (0.79) and Pb (0.66)), as well as for the gaseous pollutants: CO (0.56), benzene (0.46), NO (0.35), and NO_x (0.35). Similarly, the GRRF estimated the highest relative importance of As, Cd, BaP, CO and benzene for the prediction of PM_{10}, indicating that the environmental burden is mainly associated with fossil fuel combustion, particularly pronounced during the colder part of the year. An inconsistency between the correlation and GRRF analysis was observed for toluene. This compound had a higher importance for PM_{10} prediction than NO_x, but its correlation coefficient was among the lowest (0.25).

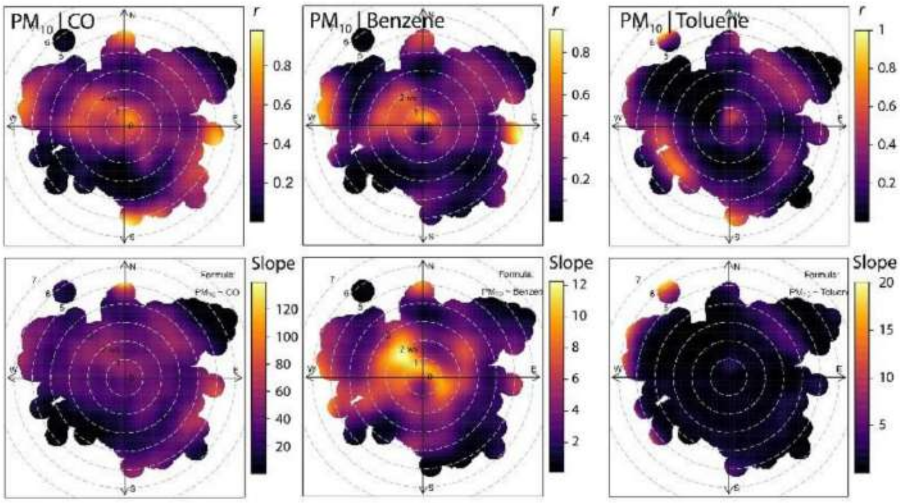


Figure 4. *Bivariate polar source apportionment*

Even though Pearson's coefficients did not indicate a significant correlation between PM_{10} and gaseous pollutants ($r < 0.6$), the bivariate polar source apportionment (Figure 4) showed that during episodes of north-westerly winds, concentrations of PM_{10} and benzene and CO were more correlated ($r \approx 0.7$) probably because of several common sources in the vicinity of the sampling site. Source composition obtained from slope diagrams reveals a 1:0.1 and 1:12 contribution of PM_{10}, CO and benzene, respectively. This could be associated with various biomass combustion processes (traffic activities, heating plants and individual heating units) (Yokelson et al, 2007). Besides the vicinity of the sampling site, particulate matter and toluene shared prominent sources located in the SW, S, NE and SE directions ($r > 0.8$, wind speed > 4 m s-1). Unlike southern and western sources, characterized by PM_{10} to toluene ratio of 1:1 which could be related to mineral oil and gas refineries, the source located on the north-east is characterized by the ratio of 1:6 indicating influences from the chemical industry, and chemical installations for production, on an industrial scale, of basic organic chemicals including aromatic hydrocarbons (European Commission, 2006).

CONCLUSIONS

Due to the pronounced nonlinearity and complexity of atmospheric processes in the troposphere of an urban environment, the application of multivariate and nonlinear methods is required to gain reliable information for a better understanding of the underlying factors which determine the air pollution phenomena. Methods such as feature selection based on advanced supervised learning algorithms, advanced source apportionment techniques and time series decomposition and detailed component analysis, are capable of providing this information, particularly for characterization of variable pollution sources. Summarizing this study, it has been shown that locally emitted and transported pollution, as well as meteorological factors, have the highest impact on urban air quality.

ACKNOWLEDGMENTS

This paper was completed as part of the project titled "Studying climate change and its influence on the environment: impacts, adaptation and mitigation" (III43007) financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2017. The publication was supported by the project GEO-CRADLE (Coordinating and integRating state-of-the-art Earth Observation Activities in the regions of North Africa, Middle East, and Balkans and Developing Links with GEO related initiatives towards GEOSS), Grant Agreement No. 690133, funded under European Union Horizon 2020 Programme - Topic: SC5-18b-2015, Integrating North African, Middle East and Balkan Earth Observation capacities in GEOSS.

REFERENCES

1. Bigi, A. and Ghermandi, G. 2016. Trends and variability of atmospheric $PM_{2.5}$ and $PM_{10-2.5}$ concentration in the Po Valley, Italy. Atmospheric Chemistry and Physics 16, 15777-15788.
2. Carslaw, D.C., Ropkins, K. 2012. Openair - an R package for air quality data analysis. Environmental Modelling and Software 27-28, 52-61.
3. Deng, H. and Runger, G. 2013. Gene selection with guided regularized random forest. Pattern Recognition 46, 3483-3489.
4. Directive 2000/69/EC of the European Parliament and of the council of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air. Official Journal of the European Communities L313, 12-21 (13/12/2000).
5. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of the European Union L152/3, 6-15 (11/06/2008).Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier Van Der Gon, H., Facchini, M.C., Fowler, D., Koren, I., Langford, B., Lohmann, U. and Nemitz, E. 2015. Particulate matter, air quality and climate: lessons learned and future needs. Atmospheric Chemistry and Physics 15, 8217-8299.
6. European Commission, 2006. Guidance Document for the implementation of the European Pollutant Release and Transfer Register (E-PRTR).
7. Grange S.K., Lewis A. and Carslaw D. 2016. Source apportionment advances using polar plots of bivariate correlation and regression statistics. Atmospheric Environment 145, 128-134.
8. Li, L., Qian, J., Ou, C. Q., Zhou, Y. X., Guo, C. and Guo, Y. 2014. Spatial and temporal analysis of Air Pollution Index and its timescale-dependent relationship with meteorological factors in Guangzhou, China, 2001-2011. Environmental Pollution 190, 75-81.
9. Ruf, T. 1999. The Lomb-Scargle periodogram in biological rhythm research: analysis of incomplete and unequally spaced time-series. Biological Rhythm Research 30, 178-201.
10. Pai, T.Y., Hanaki, K., Chiou, R.J. 2013. Forecasting hourly roadside particulate matter in Taipei County of Taiwan based on firstorder and one-variable grey model. CLEAN Soil Air Water 41, 737-742.
11. Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z. and Stojić, A. 2017. Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation. Air Quality, Atmosphere and Health 10, 93-103.
12. Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z., and Rajšić, S. (2015). Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. *Air Quality, Atmosphere & Health*, *8*(4), 379-389.
13. Stanišić Stojić, S., Stanišić, N., Stojić, A., and Šoštarić, A. 2016a. Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia, Journal of Toxicology and Environmental Health, Part A 79, 17-27.
14. Stojić, A., Stojić, S. S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M. and Mijić, Z. 2016. Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements. Environmental Science and Pollution Research 23, 10722-10732.
15. R Core Team, 2014. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org/.
16. Yokelson, R. J., Urbanski, S. P., Atlas, E. L., et. al, 2007. Emissions from forest fires near Mexico City. Atmospheric Chemistry and Physics 7, 5569-5584.

6.1. MULTISCALE MULTIFRACTAL ANALYSIS OF NONLINEARITY IN PARTICULATE MATTER TIME SERIES

A. Stojić (1), S. Stanišić Stojić (2), M. Perišić (1), Z. Mijić (1)

(1) Institute of Physics, University of Belgrade, Belgrade, Serbia, (2) Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

andreja.stojic@ipb.ac.rs

ABSTRACT

In this study the multiscale multifractal method was used with aim of capturing the fractal behaviour of the particulate matter time series obtained from an urban area in Belgrade, Serbia, as well as investigating their persistence properties and heterogeneity features. As shown, the $PM_{2.5}$ time series exhibited persistency, slightly affected by the concentrations occurring randomly only at the level of small fluctuations and small scales. Compared to $PM_{2.5}$, PM_{10} concentrations were shown to display more stochastic behaviour with more frequent random fluctuations being observed at small scales. The results herein presented contribute to the current understanding of the structural complexity of the temporal evolution of particulate matter and provide a theoretical background for enhanced air pollution modelling.

INTRODUCTION

Comprehensive analyses, conducted over the past few years, of air pollutant emission sources, their subsequent distribution and relationship to mortality caused by circulatory, respiratory and malignant diseases suggest that the exposure to particulate matter (PM) has detrimental effects on human health in the Belgrade area (Stanišić Stojić et al, 2016a, 2016b). Besides the fact that PM levels in Serbia are higher than in most European cities, with a significant number of air quality standard exceedances, our studies have shown that suspended particles also contain high concentrations of carcinogenic contaminants, such as arsenic and benzo(a)pyrene (Stojić et al, 2015a, 2015b, 2016, Perišić et al, 2015, 2017).

Diverse methods have been implemented to provide relevant information for efficient air quality management, including deterministic models, statistical analysis, neural networks, fuzzy models, geographic information system, remote sensing and trend analysis (Yu et al, 2011). Multifractality is one of the inherent properties that can be recognized in physical, chemical, biological, social and other systems, that are described as very complex at different spatial and temporal scale levels (Glushkov et al, 2014). The atmosphere is a complex system that exhibits nonlinear behavior involving both deterministic and stochastic components (Lorenz and Haman, 1996). In previous studies, the multifractal approach has been applied to analyse average ozone concentrations (Kocak et al, 2000), nonlinearity in NO_2 and CO time series (Kumar et al, 2008) and the daily air pollution index (Sivakumar et al, 2007). The aim was to provide information essential to better understand the behaviour of pollution and to forecast the temporal evolution of the species (Dong et al, 2017). The multifractal method was used herein to reveal PM fluctuation properties, *i.e.* to investigate to what extent, and on which time scale, changes in $PM_{2.5}$ and PM_{10} concentration levels can be considered random or persistent.

METHODOLOGY

In this study, multiscale multifractal analysis (MMA) was used to investigate the presence of fractal behaviour in the complex time series of $PM_{2.5}$ and PM_{10} concentrations. Data was obtained during a period of almost three years (2012-2014) of regular pollutant monitoring in Belgrade (suburban site Ovča, Longitude 20.528, Latitude 44.884, Serbia) provided by the Institute of Public Health Belgrade. MMA is a generalization of the standard multifractal detrended fluctuation analysis (MF-DFA), which adds the dependence on scale, providing a broader analysis of the fluctuation properties, as well as, more general and stable results (Gierałtowski et al, 2012).

RESULTS AND DISCUSSION

Measured PM concentrations are presented in Figure 1. According to the results, multiscale multifractal derived Hurst surfaces confirmed the non-linear behavior of PM time series (Figure 2).

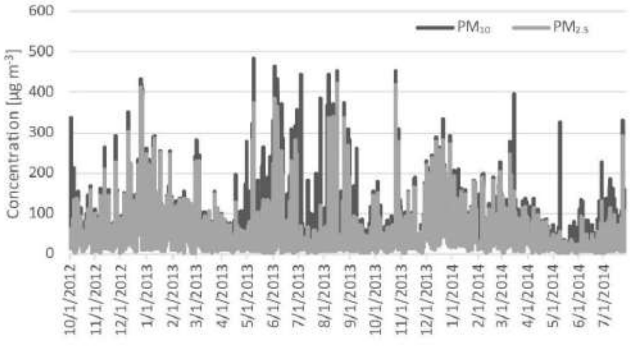


***Figure 1**. Measured $PM_{2.5}$ and PM_{10} concentrations.*

For most of the scale and multifractal parameter values, the local Hurst exponent remains in the interval between 1 and 1.5 indicating persistency of the $PM_{2.5}$ time series, while slightly affected by the concentrations occurring randomly. Such random concentration values occur only at the level of small fluctuations for scales below 44, which corresponds to a period of about 2 days. At this scale, there emerges a clear crossover resulting from the different correlation properties. Given that the sampling site was not directly exposed to intense PM bursts, the occurrence of concentrations in narrow bands (Hurst exponent equals 2) was not recorded. The PM_{10} Hurst surface reveals similar features, except that in the area of small variance and scales below 90, its growth to a maximum of approximately 1.9 is steeper, almost reaching black noise area values of local Hurst exponent. Compared to $PM_{2.5}$, the PM_{10} Hurst structure around its maximum corresponds to visibly more pronounced peaks in the time series (Figure 1). However, unlike $PM_{2.5}$, the PM_{10} Hurst surface shows no crossover.

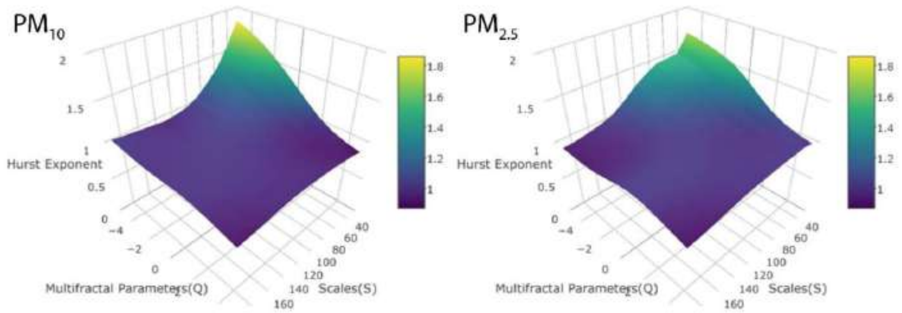


***Figure 2**. MMA derived particulate matter Hurst surfaces.*

In addition, the generalized distance coefficient (0.069) between Hurst surfaces of PM fractions is higher than the threshold value (0.065) and implies that the $PM_{2.5}$ and PM_{10} time series must be considered statistically different. The difference is particularly pronounced in the area of small fluctuations and medium scales (Figure 3).

Furthermore, it is shown that the source of multifractality, examined by PM time series randomization, originates from both nonlinear correlations and a fat-tailed probability distribution (Figure 4).

The findings of Lalwani (2016) and Liu et al. (2015) confirmed the existence of multifractality in the PM time series and found that daily pollutant concentrations exhibited high persistence in a period of approximately one year. As argued, the persistence in the air pollutant concentrations over longer period of time may be governed by the impact of background levels, seasonal trend or intrinsic evolution of the system.

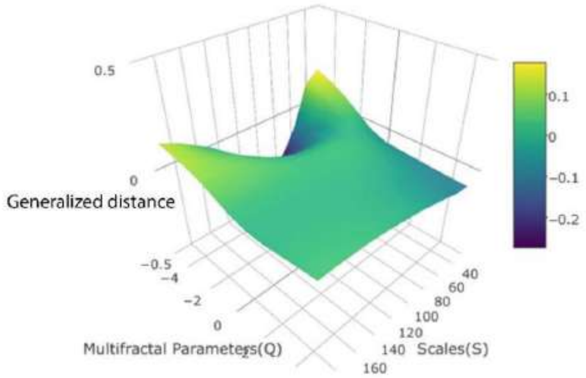


***Figure 3**. Generalized $PM_{10}/PM_{2.5}$ Hurst surface distance.*

The difference in the behavior of the $PM_{2.5}$ and PM_{10} time series was proven by Xue et al. (2015), who employed a multifractal analysis to explore temporal fluctuations and self-similarities within the PM time series and to understand their behaviour associated with diffusion, spreading and coagulation processes. Using the multifractal detrended fluctuation analysis method, the researchers registered the pronounced multifractality and long-term persistence of the $PM_{2.5}$ time-series, whereas the PM_{10} time series were shown to have stochastic behaviour.

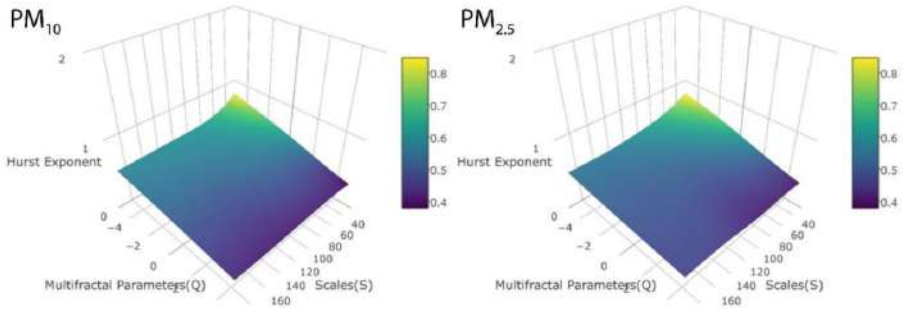


***Figure 4**. MMA derived Hurst surfaces for randomized PM time series.*

CONCLUSIONS

In this study, the multifractal approach was used to analyse the temporal dynamics of $PM_{2.5}$ and PM_{10} concentrations on the basis of a regular monitoring of data over a three-year period. As shown, the particulate matter time series possess a long-term memory of distant past events and require a large number of exponents, the so-called fractal dimensions, to be described. The presented analysis provides essential information for better understanding of the PM behaviour and the underlying factors, as well as for more accurate and reliable pollutant forecasting and efficient mitigation policy.

ACKNOWLEDGEMENTS

This study was performed as part of the projects Grant No III43007 and No III41011, which were supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2017. The publication was supported by the project GEO-CRADLE (Coordinating and integRating state-of-the-art Earth Observation Activities in the regions of North Africa, Middle East, and Balkans and Developing Links with GEO related initiatives towards GEOSS), Grant Agreement No. 690133, funded under European Union Horizon 2020 Programme - Topic: SC5-18b-2015, Integrating North African, Middle East and Balkan Earth Observation capacities in GEOSS.

REFERENCES

1. Dong, Q., Wang, Y. and Li, P. 2017. Multifractal behaviour of an air pollutant time series and the relevance to the predictability, Environmental Pollution 222, 444-457.
2. Gierałtowski, J., Żebrowski, J. J. and Baranowski, R. 2012. Multiscale multifractal analysis of heart rate variability recordings with a large number of occurrences of arrhythmia, Physical Review E 85(2), 021915.
3. Glushkov, A. V., Svinarenko, A. A., Buyadzhi, V. V., Zaichko, P. A. and Ternovsky, V. B. 2014. Chaosgeometric attractor and quantum neural networks approach to simulation chaotic evolutionary dynamics during perception process, Advances in Neural Networks, Fuzzy Systems and Artificial Intelligence, Series: Recent Advances in Computer Engineering, Ed. J. Balicki. Gdansk, WSEAS Pub.
4. Koçak, K., Şaylan, L. and Şen, O. 2000. Nonlinear time series prediction of O_3 concentration in Istanbul, Atmospheric Environment 34(8), 1267-1271.
5. Kumar, U., Prakash, A. and Jain, V. K. 2008. Characterization of chaos in air pollutants: A Volterra-Wiener-Korenberg series and numerical titration approach, Atmospheric Environment 42(7), 1537-1551.
6. Lalwani, A. 2016. Long-Range Correlations in Air Quality Time Series: Effect of Differencing and Shuffling, Aerosol and Air Quality Research 16(9), 2302-2313.
7. Liu, Z., Wang, L. and Zhu, H. 2015. A time-scaling property of air pollution indices: a case study of Shanghai, China, Atmospheric Pollution Research 6(5), 886-892.
8. Lorenz, E. N. and Haman, K. 1996. The essence of chaos, Pure and Applied Geophysics 147(3), 598-599.
9. Sivakumar, B., Wallender, W. W., Horwath, W. R. and Mitchell, J. P. 2007. Nonlinear deterministic analysis of air pollution dynamics in a rural and agricultural setting, Advances in Complex Systems 10(04), 581-597.
10. Stojić, A., Stojić, S. S., Šoštarić, A., Ilić L., Mijić Z. and Rajšić S. 2015a. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling, Environmental Science and Pollution Research 1-16.
11. Stojić, A., Stojić, S. S., Mijić, Z., Šoštarić, A. and Rajšić S. 2015b. Spatio-temporal distribution of VOC emissions in urban area based on receptor modelling, Atmospheric Environment 106, 71-79.
12. Stojić, A., Stojić, S. S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M. and Mijić, Z. 2016. Comprehensive analysis of PM_{10} in Belgrade urban area on the basis of long-term measurements, Environmental Science and Pollution Research 23(11), 10722-10732.
13. Stojić, S. S., Stanišić, N., Stojić, A., and Šoštarić, A. 2016a. Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia, Journal of Toxicology and Environmental Health, Part A 79(1), 17-27.
14. Stojić, S. S., Stanišić, N., and Stojić, A. 2016b. Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area, Environmental Health 15(1), 73.
15. Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z. and Rajšić, S. 2015. Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data, Air Quality, Atmosphere & Health 8(4), 379-389.
16. Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z. and Stojić, A. 2017. Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation, Air Quality, Atmosphere & Health 10(1), 93-103.
17. Xue, Y., Pan, W., Lu, W. Z. and He, H. D. 2015. Multifractal nature of particulate matters (PMs) in Hong Kong urban air, Science of the Total Environment 532, 744-751.
18. Yu, B., Huang, C., Liu, Z., Wang, H. and Wang, L. 2011. A chaotic analysis on air pollution index change over past 10 years in Lanzhou, Northwest China, Stochastic Environmental Research and Risk Assessment 25(5), 643-653.

8.1. CONCENTRATION WEIGHTED BOUNDARY LAYER HYBRID RECEPTOR MODEL FOR ANALYZING PARTICULATE MATTER ALTITUDE DISTRIBUTION

A. Stojić (1), S. Stanišić Stojić (2)
(1) Institute of Physics, University of Belgrade, Belgrade, Serbia, (2) Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia
andreja.stojic@ipb.ac.rs

ABSTRACT

The aim of this study is to present the first analysis of PM_{10} altitude distribution in Belgrade using the innovative concentration weighted boundary layer hybrid receptor model. The model employs a two-dimensional grid and a planetary boundary layer height as a frame of reference. The results indicate that the PM_{10} concentrations were highest in the ground layer throughout the year and exhibited a rapid decrease with height. Although similar patterns were observed for all seasons, the significant differences in winter and summer planetary boundary layer height are reflected in the PM_{10} altitude profiles. It can be concluded that the CWBL-derived pollutant altitude profiles exhibit the complexity of several factors that affect the pollutant behavior and distribution in the atmosphere, and provide the possibility for more accurate estimations of the urban or regional background levels.

INTRODUCTION

The studies dealing with coarse particulate matter (PM_{10}), its atmospheric reactions and transport pathways in urban environments have practical and scientific significance because it has been proven that these particles affect human life and the environment. Due to deteriorating air quality, urban residents in Serbia experience pollution-related health burdens on a daily basis (Stanišić Stojić et al, 2016a). Our previous studies published over the past few years were aimed at better understanding of the origin and the spatio-temporal distribution of coarse and fine aerosol fractions, as well as their relationship with mortality caused by circulatory, respiratory and malignant diseases in the Belgrade area (Stojić et al, 2016, Stanišić Stojić et al, 2016b, Perišić et al, 2017).

This study represents the first analysis of the PM_{10} altitude distribution in Belgrade and was performed using the new hybrid receptor model: concentration weighted boundary layer (CWBL). The three-dimensional (3D) versions of conventionally applied hybrid receptor models, potential source contribution function (Stojić and Stanišić Stojić, 2017, Kim et al, 2016) and concentration weighted trajectory (Stojić and Stanišić Stojić, 2017) are used for the identification of potential source regions as defined by longitude, latitude and altitude, without providing information on altitude distribution of pollutant concentrations. CWBL is designed to fill this gap and enable the analysis of pollutant vertical profile along the transport pathway and within the planetary boundary layer (PBL), or any height in general.

METHODOLOGY

The concentration weighted boundary layer is designed to provide information on pollutant altitude distribution along the transport pathway, and above the receptor site by coupling the planetary boundary layer (PBL) height with pollutant concentrations obtained at the receptor site. For the purpose of this study, we used PM_{10} concentrations measured from January 2011 to December 2015 at the New Belgrade urban site by the Institute of Public Health Belgrade and PBL heights at the receptor site calculated using GDAS1 (Global Data Assimilation System, 2017) and MeteoInfo software (Wang, 2014).

As explained in Stojić and Stanišić Stojić (2017), the estimated contribution of transport to pollutant concentrations measured at the receptor site is attributed to all volume cells within the PBL at each endpoint location along the corresponding trajectory that arrives at the receptor site (Figure 1, left). The calculation of the CWBL is illustrated in Figure 1, right. As can be seen, the CWBL value at each 2D grid cell is obtained by averaging the transport contribution to pollutant levels that correspond to all endpoints falling into the selected cell (i,j) within the corresponding PBL heights, as follows:

$$CWBL_{ijh} = mean(C^{e}_{l|PBLH^{e}_{ijl} \geq h})$$

where C_l^e is the concentration attributed to each endpoint e of trajectory l, and $PBLH_{ijl}^e$ refers to the PBL height at each endpoint at the moment when the air parcel passed grid cell (i, j).

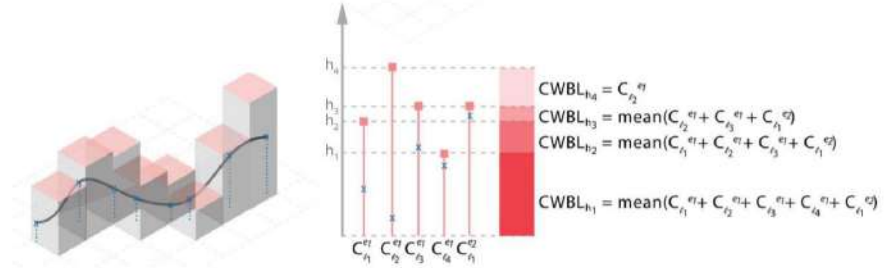


Figure 1. *The concept of CWBL hybrid receptor model (left) and CWBL graphical illustration (right) (Stojić and Stanišić Stojić, 2017).*

RESULTS AND DISCUSSION

As defined by Stull (1988), the PBL represents a part of the troposphere that typically responds to surface emissions with a timescale of about 1 hour or less. Its height fluctuations, which can range from several tens to several thousands of meters, determine the volume of air where mixing controls the vertical dispersion of pollutants. According to our results, the variations of the seasonal PBL height were in the range from 800 m agl in winter to over 2000 m agl in summer, with an average value of 1600 m. The PBL height distribution for the measurement period is presented in Figure 2.

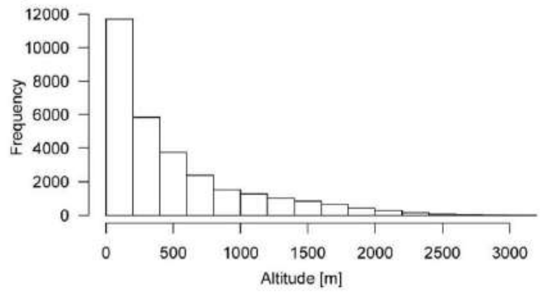


Figure 2. *PBL height distribution obtained for the period from January 2011 to December 2015 in New Belgrade.*

As can be noted, PM_{10} concentrations remained high in the ground layer of the troposphere throughout the year and exhibited a rapid decline with height, reaching the minimum values for the highest PBL (Figures 2 and 3). These findings comply with the aerosol altitude distribution described by Stull (1988), as well as with the findings of some recent empirical studies. In the study of Tao et al. (2016), the altitude profile of $PM_{2.5}$ concentrations within the PBL was retrieved by a new measurement technology combining a charge-coupled device (CCD) side-scatter LIDAR with simultaneous ground level measurements. It has been shown that the empirically evidenced altitude distribution of $PM_{2.5}$ depicts a similar declining tendency in pollutant levels with height, with maximum values being registered in the near-surface layer.

In addition, the pollutant altitude profiles obtained using CWBL display the complexity of several factors that govern spatio-temporal PM_{10} distribution. As described by Bravo-Ananda et al. (2017), the PM_{10} concentrations in the ground layer are directly influenced by spatial distribution of emission sources and their activities, whereas the concentrations and residence time of particles in the upper levels are additionally affected by topography, meteorological conditions, as well as by complex atmospheric reactions, further leading to the formation of secondary aerosol species. Similarly, Wu et al. (2015), who examined the contributions of different emission sources to pollutant concentrations at a specific height within the PBL, have concluded that the near-ground height (5-10 m) pollutant concentrations are extensively influenced by anthropogenic emissions, whereas the concentrations at greater heights could be representative of urban or regional horizontal scales. The latter observation might be important given the regional background cannot be measured directly and choosing the appropriate values is sometimes challenging because background concentrations are dependent on several factors, including regional anthropogenic and natural emissions, as well as long-range transport. In the study of Han et al. (2015), the nocturnal $PM_{2.5}$ concentrations at a height of 220 m were used for estimating the aerosol background concentrations associated with the regional-scale pollution within 100 km of the receptor site. This suggests that the pollutant altitude profiles obtained using CWBL can be useful for estimating the urban or regional background levels and their contributions to total pollutant concentrations.

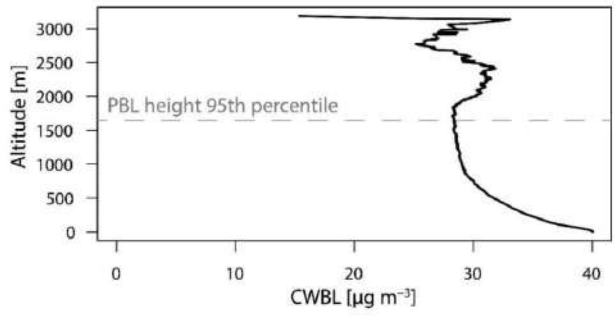


***Figure 3**. CWBL derived PM_{10} altitude distribution.*

According to Pecorari et al. (2013), the local source contributions account for 70% of total pollutant concentrations in summer, while the impact of regional sources becomes equally important during the cold season. However, the authors pointed out that the reported results were due to specific meteorological conditions in the research area. If the PM_{10} concentrations at the top of the PBL were representative of the background, it could be concluded that the major contribution to the total PM_{10} concentrations in Belgrade area was associated with an urban or regional background.

The impact of PBL height on pollution distribution, in the context of seasonal variations is illustrated in the Figure 4. As shown, the significant differences in winter and summer PBL heights is reflected in the PM_{10} altitude profiles. Although similar patterns within PBL were observed for all seasons, the gradient of pollutant concentrations was most pronounced in the cold season, whereas the lower spring and summer concentrations registered near the surface seem to remain more stable throughout the altitude profile due to increase in PBL height.

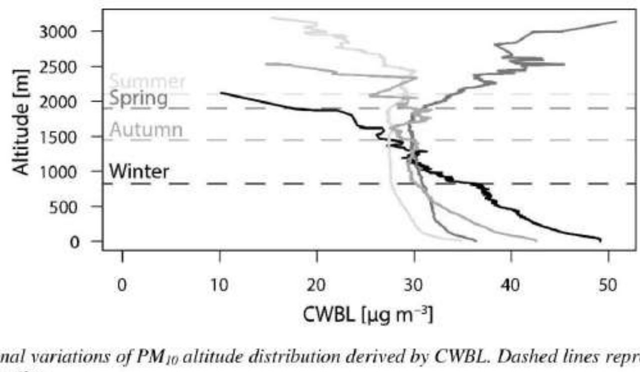


***Figure 4**. Seasonal variations of PM_{10} altitude distribution derived by CWBL. Dashed lines represent PBL height in the 95^{th} percentiles.*

CONCLUSIONS

It can be concluded that the presented CWBL model can be successfully applied for analysing the altitude profile of PM_{10} concentrations. Moreover, this approach enables estimating the impact of the PBL height on pollutant distribution, especially in the context of diurnal or seasonal changes. High PM_{10} concentrations in the ground layer of the troposphere exhibit a rapid decrease with height, and the CWBL-obtained altitude distribution follows the findings of recent empirical studies. We strongly believe that future methodological enhancements of hybrid receptor models are of vital importance for better understanding the complex factors that govern spatio-temporal PM_{10} distribution and for more accurate estimates of regional background concentrations.

ACKNOWLEDGEMENTS

This study was performed as part of the projects Grant No III43007 and No III41011, which were supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2017. The publication was supported by the project GEO-CRADLE (Coordinating and integRating state-of-the-art Earth Observation Activities in the regions of North Africa, Middle East, and Balkans and Developing Links with GEO related initiatives towards GEOSS), Grant Agreement No. 690133, funded under European Union Horizon 2020 Programme - Topic: SC5-18b-2015, Integrating North African, Middle East and Balkan Earth Observation capacities in GEOSS.

REFERENCES

1. Global Data Assimilation System, 2017 https://www.ready.noaa.gov/gdas1.php. Accessed: 8th February, 2017.
2. Kim, I. S., Wee, D., Kim, Y. P. and Lee, J. Y. 2016. Development and application of three-dimensional potential source contribution function (3D-PSCF), Environmental Science and Pollution Research 23(17), 16946-16954.
3. Stojić, A. and Stanišić Stojić, S. 2017. The innovative concept of three-dimensional hybrid receptor modeling, Atmospheric Environment 164, 216-223.
4. Stull, R. B. 1988. Mean boundary layer characteristics, In: An Introduction to Boundary Layer Meteorology. Springer Netherlands.
5. Wang, Y. Q. 2014. MeteoInfo: GIS software for meteorological data visualization and analysis, Meteorological Applications 21(2), 360-368.
6. Stojić, S. S., Stanišić, N., Stojić, A. and Šoštarić, A. 2016. Single and combined effects of air pollutants on circulatory and respiratory system-related mortality in Belgrade, Serbia. Journal of Toxicology and Environmental Health, Part A 79(1), 17-27.
7. Stojić, S. S., Stanišić, N. and Stojić, A. 2016. Temperature-related mortality estimates after accounting for the cumulative effects of air pollution in an urban area, Environmental Health 15(1), 73.
8. Stojić, A., Stojić, S. S., Reljin, I., Čabarkapa, M., Šoštarić, A., Perišić, M. and Mijić, Z. 2016. Comprehensive analysis of PM10 in Belgrade urban area on the basis of long-term measurements, Environmental Science and Pollution Research 23(11), 10722-10732.
9. Perišić, M., Rajšić, S., Šoštarić, A., Mijić, Z. and Stojić, A. 2017. Levels of PM_{10}-bound species in Belgrade, Serbia: spatio-temporal distributions and related human health risk estimation, Air Quality, Atmosphere & Health 10(1), 93-103.
10. Bravo-Aranda, J. A., de Arruda Moreira, G., Navas-Guzmán, F., Granados-Muñoz, M. J., Guerrero-Rascado, J. L., Pozo-Vázquez, D., Arbizu-Barrena, C., Reyes, F. J. O., Mallet, M. and Arboledas, L. A. 2017. A new methodology for PBL height estimations based on lidar depolarization measurements: analysis and comparison against MWR and WRF model-based results, Atmospheric Chemistry and Physics 17(11), 6839.
11. Wu, H., Zhang, Y. F., Han, S. Q., Wu, J. H., Bi, X. H., Shi, G. L., Wang, J., Yao, Q., Cai, Z. Y. and Feng, Y. C. 2015. Vertical characteristics of $PM_{2.5}$ during the heating season in Tianjin, China, Science of the Total Environment 523, 152-160.
12. Pecorari, E., Squizzato, S., Masiol, M., Radice, P., Pavoni, B. and Rampazzo, G. 2013. Using a photochemical model to assess the horizontal, vertical and time distribution of PM2.5 in a complex area: relationships between the regional and local sources and the meteorological conditions, Science of the Total Environment 443, 681-691.
13. Han, S., Zhang, Y., Wu, J., Zhang, X., Tian, Y., Wang, Y., Ding, J., Yan, W., Bi, X., Shi, G. and Cai, Z. 2015. Evaluation of regional background particulate matter concentration based on vertical distribution characteristics, Atmospheric Chemistry and Physics 15(19), 11165-11177
14. Tao, Z., Wang, Z., Yang, S., Shan, H., Ma, X., Zhang, H., Zhao, S., Liu, D., Xie, C. and Wang, Y. 2016. Profiling the $PM_{2.5}$ mass concentration vertical distribution in the boundary layer, Atmospheric Measurement Techniques 9(3), 1369-1376.

PHYSICAL CHEMISTRY 2016

13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

B E L G R A D E
September 26 - 30, 2016

ISBN 978-86-82475-34-7
Title: Physical Chemistry 2016 (Proceedings)
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.
Publisher: Society of Physical Chemists if Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan", Printing and Publishing Company; 200 Copies.
Number of pages: 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

200 - *Copy printing*

CONTENT

PHYSICAL CHEMISTRY 2016

13th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by

The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of Russian Academy of Sciences

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry
Institute of Chemistry, Technology and Metallurgy
Vinča Institute of Nuclear Sciences
Faculty of Pharmacy
Institute of General and Physical Chemistry, Belgrade, Serbia

SPONSORS

Ministry of Education, Science and Technological Development
University of Belgrade, Belgrade
Institute of General and Physical Chemistry, Belgrade
PRIMALAB d.o.o., Serbia

RELATIONSHIP BETWEEN ISOPRENE, RELATED GASEOUS POLLUTANTS AND METEOROLOGICAL FACTORS IN AN URBAN AREA

S. Stanišić Stojić[1], A. Stojić[2] and M. Perišić[2]

[1]*Singidunum University, 32 Danijelova St., 11010 Belgrade, Serbia.*
(sstanisic@singidunum.ac.rs)
[2]*Institute of Physics Belgrade, University of Belgrade, 118 Pregrevica St., 11080 Belgrade, Serbia.*

ABSTRACT

In this paper we used multivariate regression methods to examine the relationships between isoprene, related volatile organic compounds (VOC), inorganic gaseous pollutants (NO_x, NO, NO_2, SO_2 and CO), PM_{10} and meteorological data.The concentrations of 36 VOC-related masses were measured in Belgrade urban area during a two-month campaign by the use of a proton transfer reaction mass spectrometer.The results have shown that isoprene exhibited significant associations with several volatile species, including propyne, 1,3-butadiene, isoprene oxidation products, hexenal and monoterpene fragments, styrene, ethylbenzene and xylenes. Conversely, the associations between meteorological factors and inorganic gaseous pollutants with isoprene variations were estimated as less significant.

INTRODUCTION

Isoprene, as a globally dominant biogenic VOC, is mostly emitted by deciduous vegetation, while in urban areas it can also originate from anthropogenic sources. Known for its high reactivity, isoprene can undergo either photolysis or oxidation by ozone, OH and NO_3 radicals, with a number of resulting degradation products, oxidant species and intermediates, e.g. organic peroxy radicals and secondary organic aerosols, which can affect atmospheric radical chemistry and the oxidizing capacity of the atmosphere. Previous findings have shown that the first-generation photochemical products are more toxic than isoprene itself [1].

EXPERIMENTAL

The concentrations of 36 VOC-related protonated masses (m) were measured in real time using a proton transfer reaction mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria). Additionally, the concentrations of inorganic gases (IG) including NO_x, NO, NO_2, SO_2 and CO,

PM_{10}, and meteorological data were obtained from the standard automatic monitoring station of the Institute of Public Health Belgrade. The measurements were conducted in Belgrade urban area in the period from January 23rd to March 24th 2014 as described in Stojić et al., 2015 [2]. In order to investigate the relationships between isoprene, related gaseous pollutant species and meteorological data, three regression MVA methods including Linear Regression method (LR), Multilayer Perceptron (MLP) and Support vector machine (SMO SVM),implemented in Weka [3], were applied.

RESULTS AND DISCUSSION

According to the results, high correlation coefficients (r>0.8) were calculated between isoprene and several volatile species, including propyne, 1,3-butadiene, isoprene oxidation products, hexenal and monoterpene fragments, styrene, ethylbenzene and xylenes, registered at m 41, 55, 71, 81, 105 and 107, respectively (Figure 1). Conversely, correlation coefficients between meteorological data and isoprene were in the range from 0.19 to 0.30, thus suggesting that meteorology plays a relatively small role in spatio-temporal distribution of isoprene in the urban environment, which could be explained by its high reactivity.

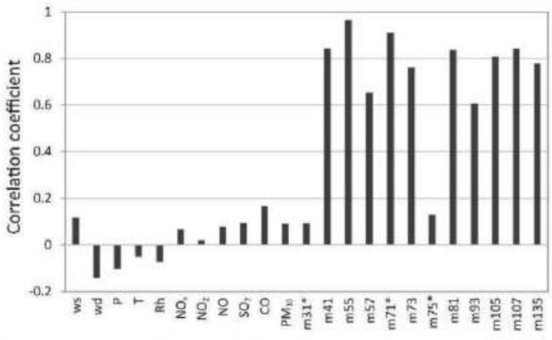


Figure 1. Correlation coefficients (r) between isoprene and meteorological parameters, inorganic gaseous pollutants, PM_{10}, potential isoprene oxidation products (*) and highly correlated VOC (r>0.6).

Regression analysis performed on isoprene and highly correlated VOC concentrations resulted in the relative errors ranging from 9.9 to 12.8%, whereas the correlation coefficients between the modelled and observed isoprene levels were in the range from 0.97 to 0.99 for all three applied methods (Table 1). Furthermore, three species alone, including 1,3-butadiene, isoprene oxidation product at m71 and styrene, explained the concentrations of isoprene with the relative error ranging between 11.5 and 13.8%.

Vehicular exhaust is often the single most dominant source of anthropogenic isoprene and 1,3-butadiene. Previous studies have shown that the regression analysis with 1,3-butadiene gives the greatest estimation of the anthropogenic fraction of isoprene [4]. In addition to their known traffic-related origin, styrene, 1,3-butadiene and isoprene are used in rubber and polymer industry, and thus, another potential source is one of the leading producers of petrochemical feedstock, plastic and rubber polymers in the region, located in the industrial zone about 13 km from the measurement site.

Table 1. MVA method performance for highly correlated VOC, meteorological parameters (Meteo) and inorganic gaseous pollutants (IG) used as inputs.

Method	VOC		VOC+Meteo		VOC+Meteo+IG	
	Rel. error	Corr.	Rel. error	Corr.	Rel. error	Corr.
LR	12.84	0.98	9.54	0.99	9.51	0.99
SMO	11.52	0.97	8.80	0.98	8.79	0.99
MLP	9.91	0.99	7.16	0.99	6.94	0.99

As regards isoprene oxidation products at m71, the OH-initiated oxidation is complicated by the fact that OH radical may attach to isoprene at four different positions, resulting in peroxy radical isomers that further undergo atmospheric reactions and produce methyl vinyl ketone (MVK), methacrolein (MACR), both registered at m71, and 3-methylfuran [5]. Conversely, the reactions with ozone are of secondary importance for isoprene oxidation, with major products including MVK, MACR and formaldehyde, whereas the reactions between isoprene and NO_3 radicals are least understood and their occurrence is mostly expected at night.

Inclusion of meteorological data in the analysis resulted in a decrease in the relative error of only 3%, whereas accounting for IG and second-generation photooxidation isoprene product, hydroxyacetone registered at m 75, led to an increase in the relative error. Based on the results of LR and SMO, only CO was associated with isoprene. In compliance with this, previous studies aimed at investigating the importance of hydrocarbons for CO tropospheric distribution, have shown that oxidation of isoprene only contributes with 10% to the global tropospheric CO burden [6].

The best performing method used highly correlated VOC, IG and meteorological data and provided relative error of 6.94% (MLP), with the correlation coefficient of 0.99% (Figure 2).

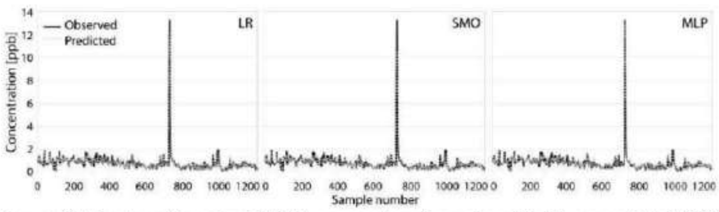


Figure 2. Best performing MVA regression based on highlycorrelatedVOC, inorganic gaseous pollutants and meteorological parameters as inputs.

CONCLUSION

Volatile organic compounds are known for their detrimental effects on human health and the environment, although the factors and complex atmospheric reactions that affect their spatio-temporal distribution are still the matter of scientific research. According to the results, isoprene exhibited strong associations with several volatile species, while its associations with meteorological factors and inorganic gaseous pollutants were estimated as less significant.

Acknowledgement

This paper was realized as part of projects No III43007 and III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-2016.

REFERENCES

[1] M. Doyle, K. G. Sexton, H. Jeffries, K. Bridge, I. Jaspers, Environ health persp., 2004, 1488-1495.
[2] A. Stojić, S. Stanišić Stojić, A. Šoštarić, L. Ilić, Z. Mijić, S. Rajšić, Environ Sci Poll Res., 2015, **22**(17), 13137-13152.
[3] M. Hall, E. Frank, G. Holmes, B. Pfahringer, P. Reutemann, I. H. Witten, (2009). SIGKDD Explor, 2009, **11**(1), 10-18.
[4] J. L. Wang, C. Chew, C. Y. Chang, W. C. Liao, S. C. C. Lung, W. N. Chen, P. J. Lee, P. H. Lin, C. C. Chang, Atmos Environ., 2013, **79**, 369-379.
[5] P. Warneck, Chemistry of the natural atmosphere, 1999, Academic press. K. M. Spencer, M. R. Beaver, J. M. St Clair, J. D. Crounse, F. Paulot, P. O. Wennberg, AtmosChem Phys Discuss., 2011, **11**, 23619-23653.
[6] C. Granier, G. Pétron, J. F. Müller, G. Brasseur, Atmos. Environ., 2000, **34**(29), 5255-5270.

IMPACT OF REMOTE SOURCES ON CHROMIUM CONCENTRATIONS IN BELGRADE AND THE RELATED HEALTH RISK

M. Perišić[1], A. Stojić[1] and S. Stanišić Stojić[2]

[1]*University of Belgrade, Institute of Physics Belgrade, Pregrevica 118, 11000 Belgrade, Serbia* (mirjana.perisic@ipb.ac.rs)
[2]*Singidunum University, 32 Danijelova St., 11010 Belgrade, Serbia*

ABSTRACT

In this paper we investigated the impact of transported air pollution onchromium concentrations and estimated the associated population health riskat three different locations in Belgrade areafor the period 2011-2013. According to the results, chromium levels were associated with significant carcinogenic risk, especially in the suburban area affected by industrial pollution. The contribution of transported pollution to the observed chromium concentrations was assessed by the use of hybrid multireceptor models, revealing major potential emission sources located in the neighboring countries ofSE Europe.

INTRODUCTION

The levels of air pollutants in Belgrade are higher than in most European cities. The factors associated with poor air quality include the growth in the number of inhabitants, significant number ofpoorly-maintainedvehicles and outdated technologies in all economysectors, as well as polluted air masses coming from the neighboring industrial countries[1]. According to the results of long-term measurements, the mean annual PM_{10} levels in Belgrade ranged from 30.0 to 58.9 μg m^{-3}, with a significant number of EU AQS limit (40 μg m^{-3}) exceedances [2]. In addition to PM_{10} concentrations, chemical composition is also implicated in particles' relative toxicity. For instance, inhalation of chromiumcontaining aerosols is recognized to induce a wide range of adverse health effects[3].The emissions from two main anthropogenic Cr sources, coal combustion and metallurgical processes, result in particles of very small diameter (< 1 μm)that may be transported over long distances [4]. The aim of this study was to investigate potential remote emission sources contributing to Cr loadings in Belgrade which are reported to be high [5] and to estimate the related human health risk associated with exposure to the observed concentrations.

EXPERIMENTAL

Chromiumconcentrations were determined by the use of inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500) in PM_{10}daily samples collected during the period 2011-2013 at three locations in Belgrade (Serbia)using referent Sven Leckel samplers. The sampling procedure and measurements were conductedaccording to standards EN 12341 and EN 14902, respectively.Two urban sampling sites includedBojanska,located in highly populated residential area ofthe city central zone,andTrg JNA,exposed to intense traffic, whileVeliki Crljeni,situated in the vicinity ofthe coal minewas assigned assuburban-industrial type.

The carcinogenic health riskassociated with exposure to the observed Cr levels was calculated in accordance with the US EPA health risk model[6]. The obtained parameter, incremental lifetime cancer risk (ILCR),represents an incremental probability of an individual developing cancer over lifetime as a result of exposure to a carcinogenic compound.The acceptable, baseline risk level is considered to be below 10^{-6}, while 10^{-4} is considered as the upper limit and the reason for public health concern [7].

The potential non-local emission sources and their impact on the observed Cr concentrations were analyzed by the use of 72-h air mass trajectories, calculatedas described inPerišić et al. [4],and advanced multireceptor trajectory ensemble models (TEM), including potential source contribution function (PSCF), concentration weighted trajectory (CWT), residence time weighted concentration (RTWC) and simplified quantitative transport bias analysis (sQTBA), all implemented in MetCor statistical software (MetCor v.1.0, revision 30) [8].

RESULTS AND DISCUSSION

The toxicity of Crcompounds is mainly associated with metal oxidation state. For instance, hexavalent Cr, mainly originating from anthropogenic sources, is the form considered highly carcinogenic. As no information on Cr oxidation state could be obtained, ILCR was calculated based on one seventh of the measured Cr concentrations, as proposed by the US EPA. The results reveal that ILCR was higher than10^{-5} at all sampling sites, with the maximum value of 3.74×10^{-5},as estimated for the suburban-industrial site (Figure 1) [5].Traffic emissions and fuel burning for heating purposes in cold season were recognized as dominant Cr local sources in urban, residential areas, whereas dust resuspension and coal burning had major impact on Cr concentrations at the suburban-industrial site,located in the vicinity of the lignite mine and thermal power plant Kolubara A [5].

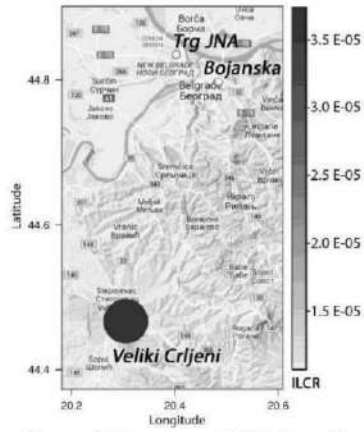


Figure 1. Incremental lifetime Cr cancer risk for the period 2011-13.

Nevertheless, air pollution is not only a local and time-limited issue, and our previous studies have confirmed the significant contribution of long-range transport (up to 16%) to locally registered PM_{10}[5]. As regards the non-local origin of chromium,the results of multireceptor PSCF model have shown that the potential Cr emission sources were located in NE and SW areas of Belgrade, as well as in the neighboring countries (Figure 2). Additionally, the results of multireceptor CWT and RTWC analysis revealed that the examined sites were influenced by strong Cr emission sources from Eastern Europe, located in the vicinity of the Black Sea. The prevailing impact of regional sources and sources in Eastern Romania was clearly distinguished by the use of sQTBA.

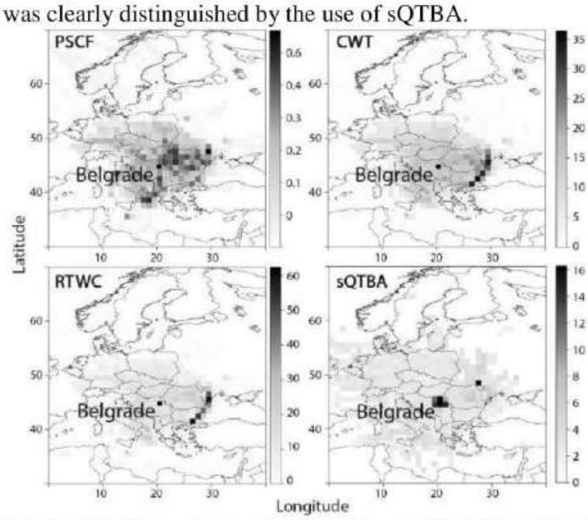


Figure 2. Potential Cr sources resolved by the use of multireceptor PSCF (probability), CWT, RTCW and sQTBA [$\mu g\ m^{-3}$] forthe period 2011-2013.

CONCLUSION

Population exposure to chromium compounds in Belgrade is estimated to be associated with high carcinogenic health risk, particularly in the suburban area affected by industrial emissions. According to the results of hybrid multireceptor models, the major potential Cr emission sources were located in NE, E and SW areas of Belgrade, as well as in the neighboring countries.

Acknowledgement

This paper was realized as part of projects No III43007 and III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-2016.

REFERENCES

[1] A.Stojić, S.S.Stojić, I.Reljin, M.Čabarkapa, A.Šoštarić, M.Perišićand Z.Mijić,Environ Sci Pollut Res., 2016, **23**(11), 10722-10732.
[2] M.Perišić, A. Stojić, S. S.Stojić, A. Šoštarić, Z. Mijić, S. Rajšić, S. Estimation of required PM_{10} emission source reduction on the basis of a 10-year period data. Air Qual, Atmos& Health, 2015, **8**(4), 379-389.
[3] S.Langard, M.Costa,in: Handbook on the toxicology of metals,Nordberg G (Eds.), 4th edn. Elsevier, London, UK, 2014.
[4] N.O. Jerome and E. Nieboer, Chromium in the natural and human environments. Vol. 20. John Wiley & Sons, 1988.
[5] M.Perišić, S.Rajšić, A.Šoštarić, Z. Mijić, A.Stojić,Air Qual, Atmos& Health, 2016, 1-11.doi:10.1007/s11869-016-0411-6
[6] United States Environmental Protection Agency (US EPA), Integrated Risk Information System (IRIS), http://www.epa.gov/iris, 2013.
[7] United States Environmental Protection Agency (US EPA), Methods to Develop Inhalation Cancer Risk Estimates for Chromium and Nickel Compounds, 2011.
[8] U.Sofowote, Y.Su, E.Dabek-Zlotorzynska, A.Rastogi, J.Brook, F. Hopke, Atmos Environ., 2015, **108**, 140-150.

WeBIOPATR2015

Particulate Matter: Research and Management

Proceedings from the
5th WeBIOPATR
Workshop & Conference
Belgrade, Serbia
14.-16.10.2015.

Milena Jovašević-Stojanović
and Alena Bartoňová, eds.

Belgrade 2016.

The 5th WeBIOPATR Workshop and Conference,
Particulate Matter: Research and Management,
WEBIOPATR2015 is organized by:

Vinča Institute of Nuclear Sciences, Serbia
Public Health Institute of Belgrade, Serbia
NILU Norwegian Institute for Air Research, Norway

with contribution by
World Health Organization, Regional Office Europe

The 5th WeBIOPATR Workshop and Conference,
Particulate Matter: Research and Management,
WEBIOPATR2015 is supported by:

Ministry of Education, Science and Technological
Development of
Republic of Serbia

PROCEEDINGS FROM THE 5TH WEBIOPATR WORKSHOP & CONFERENCE

The Fifth International WeBIOPATR Workshop & Conference
Particulate Matter: Research and Management
WeBIOPATR2015

14 – 16 October 2015
Belgrade, Serbia

Editors
Milena Jovašević-Stojanović
Alena Bartoňová

Publisher
Vinča Institute of Nuclear Sciences
Dr Borislav Grubor, Director
Mike Petrovića Alasa 12-14, Vinča
P. O. Box 522, 11001 Belgrade, Serbia, 11000

Technical assistance
Miloš Davidović

Printed by
Vinča Institute of Nuclear Sciences

Number of copies
50

ISBN 978-86-7306-139-9

Vinča Institute of Nuclear Sciences
www.vinca.rs

SCIENTIFIC COMMITTEE

Dr Alena Bartoňová, Norway
Dr Aleksandra Stanković, Serbia
Mr Bjarne Sivertsen, Norway
Dr Bojan Radak, Serbia
Prof. Dr David Broday, Israel
Dr Dorota Jarosinska, WHO
Dr Med Elizabeta Paunović, WHO
Dr Eva Csobod, Hungary
Dr Fintan Hurley, UK
Prof. Dr Ivan Gržetić, Serbia
Prof. Michael Jerrett, USA
Dr Milena Jovašević-Stojanović, Serbia
Prof. Dr Nenad Živković, Serbia
Prof. Dr Radim Sram, Czech Republic
Prof. Dr Simone Barreira Morais, Portugal
Dr Viša Tasić, Serbia
Prof. Dr Zoran Ristovski, Australia
Dr Zorana Jovanović-Andersen, Denmark
Dr Zoran Mijić, Serbia

ORGANIZING COMMITTEE

Vinča Institute of Nuclear Sciences, Belgrade, Serbia
Dr Aleksandra Stanković
Ms Dušan Topalović, (Secretary)
Ms Ivan Lazović
Ms Marija Živković
Dr Maja Živković
Dr Milena Jovašević-Stojanović (Co-chair)
Dr Miloš Davidović, (Secretary)

NILU – Norwegian Institute for Air Research, Kjeller
Dr Alena Bartoňová (Co-chair), Norway

Public Health Institute of Belgrade, Belgrade, Serbia
Dr Anka Cvetković
Ms Andrej Šoštarić
Dr Vesna Slepčević

Ministry of Education, Science and Technological Development of Republic of Serbia
Dr Snežana Pašalić

Ministry of Agriculture and Environmental Protection of Republic of Serbia
Ms Biljana Filipović

Serbian Environmental Protection Agency
Mr Dejan Lekić
Mr Tihomir Popović

National Institute of Public Health "Dr Milan Jovanović-Batut", Belgrade, Serbia
Dr Med Branislava Matić

Faculty of Applied Ecology "Futura", Singidunum University, Belgrade, Serbia
Prof. Dr Dragan Marković

Military Medical Academy, Belgrade, Serbia
Prof. Dr Jasmina Jović-Stošić

Institute of Physics, Belgrade, Serbia
Dr Mira Aničić Urošević

Faculty of Occupational Protection, University of Niš
Prof dr Nenad Živković, Serbia

Institute of Metallurgy and Mining, Bor, Serbia
Dr Renata Kovačević

CONFERENCE TOPICS

ATMOSPHERIC PARTICULATE MATTER: PHYSICAL AND CHEMICAL PROPERTIES

- *sources and formation of particulate matter*
- *particulate matter composition and levels outdoors and indoors*
- *environmental modeling*
- *nanoparticles in the environment*

PARTICULATE MATTER AND HEALTH

- *exposure to particulate matter*
- *health aspects of atmospheric particulate matter*
- *full chain approach*

PARTICULATE MATTER AND REGULATORY ISSUES

- *issues related to monitoring of particulate matter*
- *legislative aspects*
- *abatement strategies*

PREFACE

The International Workshop and Conference, Particulate Matter: Research and Management – WeBIOPATR is a biennial event held in Serbia since 2007. The conference rationale stems from the fact that particulate matter is the air quality constituent that currently is responsible for most instances of non-compliance with air quality directives in Europe. Particulate matter, arising both from primary emissions and as a result of secondary formation in the atmosphere, is also one of the least well understood issues.

The 1st WeBIOPATR Workshop was held in Beograd, 20.-22. May 2007. The workshop was attended by more than 70 participants presenting 35 contributions, and received media attention (newspaper article and TV coverage on national TV). In addition to providing information about latest research in Serbia and internationally, the workshop has contributed to communication within the research community in Serbia, and between the research community and the responsible authorities (Ministry of Health, Ministry of Environment, and the Serbian Environmental Agency).

The 2nd WeBIOPATR workshop was held in Mecavnik, Serbia, 28.8.-1.9. 2009. It has attracted over 40 participants, including participants from the neighboring countries and EU. The participants discussed air quality issues, research needs and management tools and strategies currently used in Serbia. The workshop also had a section on health issues related to particulate matter, recognizing that the legislation is based on health considerations, and that the PM are an important health determinant in adults and in children. Proceedings are available at http://www.nilu.no/index.cfm?ac=publications&folder_id=4309&publication_id=24659&view=rep. Selected extended contributions are published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING QUARTERLY Vol: 16 No 3 (2010).

The 3rd event, WeBIOPATR2011, held in Beograd 14.-17- November 2011, had wider international audience, and own student workshop. Forty three presentations were given (for book of abstracts see http://www.vin.bg.ac.rs/webiopatr/3rd-workshop/). Selected extended contributions are published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING Vol 18, No 4/II (2012).

The 4th event, WeBIOPATR2013, was held in Beograd 2.-4. October 2013. It covered the traditional PM research and management issues as well as topics that aim to encourage citizens to contribute to environmental governance. Ways to provide the citizens and authorities with a range of tools and services related to the environment including PMs, and developing participatory sensing methods and tools utilizing smaller and less expensive monitoring devices and advanced ITC technologies, were one of the foci. The book of abstracts can be downloaded at http://www.vin.bg.ac.rs/webiopatr/3rd-workshop/. Selected extended contributions were published in CHEMICAL INDUSTRY & CHEMICAL ENGINEERING Vol 21, No 1/II (2015).

This proceedings contains 38 papers and abstracts 6 of all presentations of the WeBIOPATR-2015 workshop and conference, the fifth event of the series. In all, 9 invited keynote lectures, 18 oral presentations and 15 poster presentations are presented by speakers from 12 countries, the most from Serbia but also from countries all over the Europe and Australia. We hope that this event will continue to be an important forum for the Serbian scientists and other professionals to meet and discuss, and for the Serbian professional community to meet with professionals dealing with similar issues elsewhere.

We hope that next event, that will be 10 years after the first one, will continue the success from the past. We wish to again provide the professional community from Western Balkans region with a suitable meeting platform, and the global professional community with an arena where we can draw on each other's experiences and scientific insights.

Milena Jovašević-Stojanović and Alena Bartoňová

CONTENTS

3.5 TRANSPORT CONTRIBUTION TO $PM_{2.5}$ MASS CONCENTRATIONS IN BELGRADE SUB-URBAN AREA

M.Perišić (1), A. Stojić (1), M. Todorović (1), Z.Mijić (1), A. Šoštarić (2)
(1)Institute of Physics, University of Belgrade, Pregrevica 118, Serbia
(2) Institute of Public Health of Belgrade, Boulevard of Despot Stefan 54a, Belgrade, Serbia
mirjana@ipb.ac.rs

ABSTRACT

In the present study, hourly $PM_{2.5}$ mass concentrations obtained from the monitoring station in the Belgrade sub-urban area were analyzed for the 2013. The contribution of local and remote pollution sources on measured concentrations were considered. The contribution of transported $PM_{2.5}$ pollution to the observed concentrations was determined by the use of trajectory sector analysis (TSA). A certain proximity sources were identified by means of conditional bivariate probability function (CBPF), while potential source contribution function (PSCF) and concentration weighted trajectory (CWT) hybrid receptor models were used for the identification of potential non-local source regions. Trajectory cluster analysis (TCA) was applied to assess representative pathways of air masses affecting the sampling site. The results suggest significant influence of transport processes in examined area, and potential remote $PM_{2.5}$ sources in neighboring countries and countries of North and East Europe.

INTRODUCTION

Particulate matter (PM) is emitted from a variety of sources including the industrial activities, heat and power generation plants, traffic exhaust and agricultural processes (Heal et al, 2012). Because of adverse effects on human health and environment, fine particles $PM_{2.5}$ (with aerodynamic diameter < 2.5 μm) have become one of the main concerns in highly populated urban areas (WHO, 2013). Air Quality Directive (EU, 2008), establishing the 25 μg m^{-3} as annual limit value for $PM_{2.5}$ to be met in 2015, will become progressively more restrictive in 2020. Although environmental policies have led to significant improving of air quality, in some European cities particle levels still exceed prescribed limit value (Guerreiro et al, 2014). Besides local sources, low wind speed and stable meteorological conditions are important factors leading to air pollution episodes (Engler et al, 2012). The most worrying situations occurred in urban and sub-urban areas during the cold season, where high air pollution may cause serious risks for human health (Pant et al, 2015).

Significant input of $PM_{2.5}$ is provided through the transport processes affecting the air quality all over the Europe (Makra et al, 2011). For deciding any effective abatement measure, knowing the relationship between the local atmospheric circulation and the regional and long-range transport processes in contributing to $PM_{2.5}$ levels, has become very important.

METHODOLOGY

In this study, hourly $PM_{2.5}$ mass concentrations and meteorological parameters (wind speed and direction, temperature, relative humidity and atmospheric pressure) during 2013 were obtained from the Institute of Public Health Belgrade automatic monitoring station Ovča (44°53' N, 20°31' E) located in the Belgrade sub-urban area. The sampling site was chosen because the area is characterized by rather flat landscape with an average altitude of about 70 m, entirely exposed for the influence of different air masses. In order to identify local potential emission sources, conditional bivariate probability function (CBPF) analysis was performed with the statistical software R, using the Openair package (Carslaw and Ropkins, 2012). Considering intervals of concentration, it provides more information on emission strength and location in examined area.

To differentiate the shares of transported and background $PM_{2.5}$ pollution to the observed mass concentrations, a pronounce local contribution was excluded from the time series by the use of frequency differentiated non-linear digital filtering algorithm implemented in the function baseline.RollingBall (wm=8, ws=6) of the Baseline package (Kneen and Annegarn, 1996) of the statistical software R, thus providing a baseline. Subsequently, trajectory sector analysis (TSA) was applied to the derived baseline in order to obtain the monthly mean background levels and time series of transported $PM_{2.5}$ pollution according to Stojić and coauthors (2015a). The whole area with the center at the receptor site was divided into 16 22.5°-sectors and the contribution of the least polluted sector was taken as a background level.

Trajectory cluster analysis (TCA) was applied to the transported $PM_{2.5}$ time series to reveal the major pathways of air masses affecting the sampling site. Furthermore, the estimation of the origin of non-local emission sources and their impacts to the observed concentrations were performed by the use of potential source contribution function (PSCF) and concentration weighted trajectory (CWT) models (Hsu, 2003) according to Stojić and coauthors (2015b). Three days air mass back-trajectories used for the transport analyses were computed every hour UTC for the height of 200 m above the measuring point at the ground level by the use Openair and Opentraj (2015) packages of the statistical software R.

RESULTS AND DISCUSSION

Based on 97% available data, mean annual $PM_{2.5}$ mass concentrations was 39.3 µg m^{-3}, which is significantly higher than the prescribed limit value. The highest concentrations were observed through the colder part of year, with the highest monthly mean of 80.4 µg m^{-3} in December. Summer and spring were characterized with sporadic, short term peaks in the time series, but with the lowest average concentrations (monthly mean in July was 18.2 µg m^{-3}). In order to locate potential emission sources near the sampling site, CBPF analysis was carried out in the four percentile intervals of $PM_{2.5}$ mass concentration (Figure 1). The most probable source of emission in the lowest concentrations range (0-25th percentile) was located in the SW direction which reflects the Belgrade urban area. In the range from 25-50th percentile locations of the most probable source was in the SE direction, which may be related to steel factory located in the suburban area of Smederevo, about 40 km from the measurement site. These sources showed their maximum influence in concentration regions under the 50th percentile and at higher wind speed, which may be related to the distance from the measuring site (Uria-Tellaetxe and Carslaw, 2014). The sources in SE and W direction were dominant between 50th and 75th percentile of concentrations. First one may be associated with industrial complex near Pančevo while second reflects the positions of large agriculture and food production complexes located about 10 kilometers far from the sampling site. The highest concentrations (75-100th percentile) were measured during the calm weather conditions, indicating the main contribution of proximate sources.

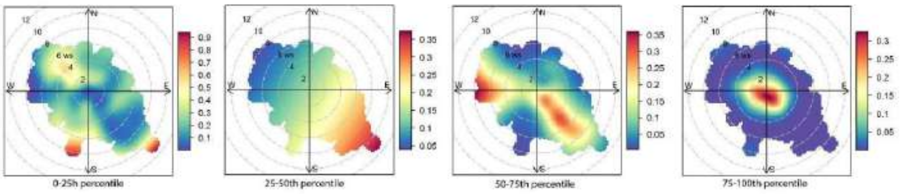


***Figure 1.** CBPF plots of $PM_{2.5}$ mass concentrations within four percentile intervals*

Time series of measured and transported concentrations, and average monthly contribution variability of local production, background and transport to the observed mass concentrations during 2013 were presented in Figure 2. The contributions of transport and background were the largest during the winter. During the colder part of year, intensive fossil fuel usage in individual heating units and traffic activity increase significantly contribute to the background concentration in this area. The influence of strong local sources was high in winter, but their maximum contributions were observed in May, Jun and August (60-70%). Droughty summer season characterize intensive agriculture activates and diesel fuel usage in rural environment of the sampling site, which might be the reason for occasional concentration level increase.

TCA derived six representative clusters, with the percent of trajectories belonging to a particular cluster and contribution to transported concentrations presented in Figure 3 (left).The most frequent transport pathways were N and NE, clusters C5 and C6 respectively, but the highest contribution to the observed concentrations was associated with the air masses coming from the SW direction, cluster C3. Monthly average contribution of six representative clusters are presented in Figure 4. The contribution of the remote pollution sources has proved to be highest during winter and spring, with the dominant influences of NW and W directions, with the exception in February, when the largest impact was from E/SE region (cluster C1).

The results of PSCF analysis, presented at the same figure, show potential distant sources of $PM_{2.5}$ located along the direction of the cluster C3, in neighboring countries (Bosnia and Hercegovina and Croatia). CWT analysis (Figure 3, right) shows the additional sources of fine particulates in the countries of North and East Europe, Lithuania and Ukraine. Results of TSA are also shown in Figure 3 (right). Combining the frequency of arriving air masses with transported concentrations, the contribution of long-range transport to the measured concentrations was estimated. The maximum impact of the long-range transport was from W, SW and E sectors about 10 μg m^{-3}.

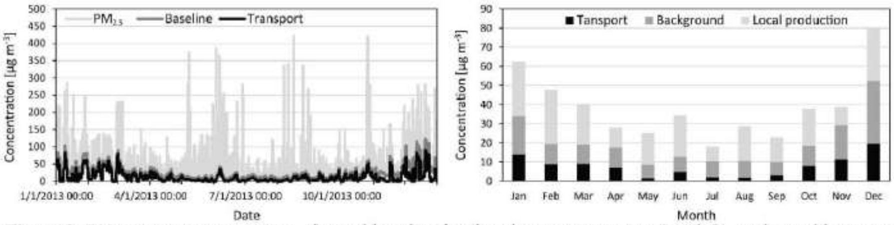


Figure 2. *$PM_{2.5}$ mass concentrations, derived baseline level and transport time series (left), and monthly average transport, background and local production shares in the observed concentrations (right)*

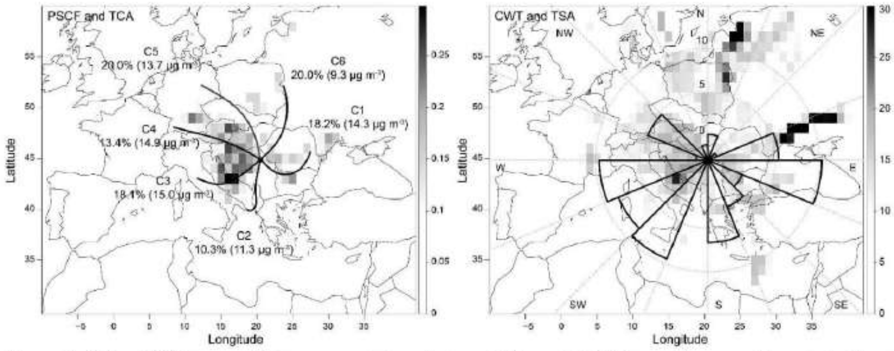


Figure 3. *$PM_{2.5}$ PSCF map and six representative clusters (left), and CWT [μg m^{-3}] map with contribution of transport from different regions (right)*

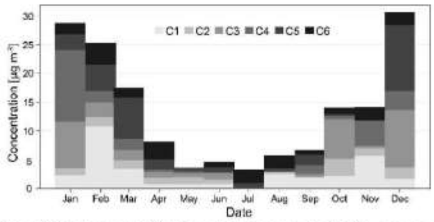


Figure 4. *Time series of cluster contributions to transported $PM_{2.5}$ mass concentrations*

CONCLUSIONS

Annual mean $PM_{2.5}$ concentrations exceed prescribed limit value during the 2013 in the Belgrade sub-urban area, at the sampling site Ovča. Hybrid receptor models were applied in order to distinguish impacts of local production and long-range transport on measured concentrations. CBPF analysis, carried out in the four percentile intervals, allowed the identification of different nearby sources. According to the results of PSCF and CWT analyses, the main remote sources of emission are located in bordering countries, East and North Europe. Summer characterizes the influence of dominant local sources, while transport contribution and background concentrations were higher during the winter. TSA estimated the transport contribution up to 10 μg m^{-3}, which suggest its significant impact on air quality in this area. In order to reach prescribed limit values for $PM_{2.5}$ in Belgrade sub-urban area, potential environmental regulation measures may not be effective if restricted to mitigating the emission from local sources only.

ACKNOWLEDGMENTS

This paper was realized as a part of the project "Studying climate change and its influence on the environment: impacts, adaptation and mitigation" (III43007) financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2016.

REFERENCES

1. Carslaw, D.C. and Ropkins, K., 2012. Openair—an R package for air quality data analysis. Environ. Modell. Softw. 27, 52-61.
2. Engler, C., Birmili, W., Spindler, G. and Wiedensohler, A., 2012. Analysis of exceedances in the daily PM_{10} mass concentration (50 μg m^{-3}) at a roadside station in Leipzig, Germany. Atmos. Chem. Phys. 12, 10107-10123.
3. EU, 2008. Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of European Communications. L152/1, 11/6/2008.
4. Guerreiro, B., Cristina, B., Foltescu, V., de Leeuw, F., 2014. Air quality status and trends in Europe. Atmos. Environ. 98, 376-384.
5. Heal, R.M., Kumarb, P. and Harrison R.M, 2012. Particles, air quality, policy and health. Chem. Soc. Rev. 41, 6606–6630.
6. Hsu, Y.-K., Holsen, T.M. and Hopke, P.K., 2003. Comparison of hybrid receptor models to locate PCB sources in Chicago. Atmos. Environ. 37, 545-562.
7. Kneen, M.A. and Annegarn, H.J., 1996. Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds. Nucl. Inst. Meth. B 109, 209-213.
8. Makra, L., Matyasovszky, I., Guba, Z., Karatzas, K. and Anttila, P., 2011. Monitoring the long-range transport effects on urban PM_{10} levels using 3D clusters of backward trajectories. Atmos. Environ. 45, 2630-2641.
9. Opentraj, 2015. https://cran.r-project.org/web/packages/opentraj/opentraj.pdf, accessed June 2015.
10. Pant, P., Shukla, A., Kohl, S.D., Chow, J.C., Watson, J.G. and Harrison, R.M. 2015. Characterization of ambient $PM_{2.5}$ at a pollution hotspot in New Delhi, India and inference of sources. Atmos. Environ. 109, 178-189.
11. R Core Team, 2012. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org
12. Stojić, A., Stojić, S. S., Mijić, Z., Šoštarić, A., Rajšić, S. , 2015b. Spatio-temporal distribution of VOC emissions in urban area based on receptor modeling. Atmos. Environ. 106, 71-79.
13. Stojić, A., Stojić, S. S., Šoštarić, A., Ilić, L., Mijić, Z. and Rajšić, S., 2015a. Characterization of VOC sources in an urban area based on PTR-MS measurements and receptor modelling. Environ. Sci. Pollut. R. 22(19) 13137-13152.
14. Uria-Tellaetxe, I. and Carslaw, C. D., 2014. Conditional bivariate probability function for source identification. Environ. Mod. Softw. 59, 1-9.
15. WHO, 2013. Review of Evidence on Health Aspects of Air Pollution e REVIHAAP Project. Technical Report, World Health Organization, Regional Office for Europe, Copenhagen, Denmark.

8.2 THE ASSOCIATION BETWEEN SHORT-TERM PM10 EXPOSURE AND MORTALITY CAUSED BY RESPIRATORY SYSTEM DISEASES IN THE BELGRADE AREA

S. Stanišić Stojić (1), N. Stanišić (1), A. Šoštarić (2), A. Stojić (3) and S. Mladenović (2)
(1) Singidunum University, 32 Danijelova St., 11010 Belgrade, Serbia
(2) Institute of Public Health Belgrade, 54 Despota Stefana Blvd., 11000 Belgrade, Serbia
(3) Institute of Physics Belgrade, University of Belgrade, 118 Pregrevica St., 11080 Belgrade, Serbia
andrej.sostaric@zdravlje.org.rs

ABSTRACT

In this study, we evaluated the association between the observed PM_{10} concentrations and mortality caused by respiratory diseases in the Belgrade area (Serbia). The estimated health-related risk for the two-year period (2010-2011) is expressed as % increase in respiratory system-related mortality per unit increase in daily PM_{10} levels. According to the results, a 30-day moving average is found to be a stronger predictor of death rate than a single day's exposure. The effects were mostly pronounced for the middle-aged population, whereas the lower estimated increase in respiratory system-related mortality of 3.13% for elderly males is more significant due to a higher number of observed cases. Better understanding of the relationship between air pollution and health outcomes provides a solid basis for the establishment of new environmental legal framework in developing countries which could significantly reduce exposure and related public health hazards.

INTRODUCTION

Considerable research attention has been devoted to the role of particulate matter (PM_{10}) in the impairment of the respiratory system function, aggravation of the pre-existing chronic obstructive pulmonary disease and increase of the respiratory-related death rate among the susceptible groups. According to Pope and Dockery (2006), the shape of the exposure-response function across the broad range of PM_{10} pollution is found to be linear with no safe threshold level, which indicates that further refinement of air quality standards would result in public health improvements. Therefore, numerous epidemiological studies conducted worldwide are aimed at evaluating the health effects of PM_{10} exposure and revealing the specific features of particles that pose the greatest risk (Gray et al, 2015). The present study was conducted in Belgrade, a city of 1 600 000 citizens, which experiences high levels of air pollution. As previously reported, high PM_{10} loadings in Belgrade pose a significant threat, partly due to long-range and regional pollutant transport, but mainly due to outdated technology, the use of sulfur-containing fuels, emission sources located in industrial suburban zones and considerable portion of old, poorly-maintained vehicles (Perišić et al, 2014). Hence, studies aimed at exploring the growing public health burden in Serbia would yield a solid basis for the new environmental policy design and human welfare improvement.

METHODOLOGY

Mortality statistics including total and respiratory system related mortality (J00-J99 according to the International Classification of Diseases, 10^{th} Revision, ICD-10), were retrieved from the Institute of Public Health, Belgrade for the two-year period (2010-2011). The deaths attributed to injuries, poisoning and external causes were excluded from the overall death rate. Daily PM_{10} concentrations were provided by the automatic monitoring network comprising 7 stations. Meteorological data obtained from the Global Data Assimilation System with spatial resolution of 1 degree were averaged over a 24-hour periods to provide a mean, median, maximum, minimum and range for temperature, relative humidity and pressure. Daily counts of respiratory system-related mortality were modeled using quasi-Poisson regression, selected in order to compensate for overdispersion (*i.e.* residual deviance is larger than residual degrees of freedom). The confounding factors, including days of the week, seasonal trends and meteorological conditions, were selected on the basis of previous studies (Schwartz, 1995; Samet et al, 2000a; Samet et al, 2000b; Dominici et al, 2006; Bell et al, 2008; Peng and Dominici, 2008).

The model was specified as follows:

$$E(Y_t) = \exp\{\beta_1\, PM\Delta3_t + \beta_2\, PM\Delta7_t + \beta_3\, PM30MA_t + \beta_4\, PRSS_t + \beta_5\, RH2M_t + S(time, \lambda_1) + S(temp, \lambda_2) + \alpha\, DOW_t\}$$

Y_t – the expected number of respiratory disease-related deaths on day t; $PM\Delta3_t$ – difference between 3-day simple moving average and 7-day simple moving average of mean concentration ($\mu g\ m^{-3}$) of PM_{10} ending on day t; $PM\Delta7_t$ – difference between 7-day simple moving average and 30-day simple moving average of mean concentration (μg m^{-3}) of PM_{10} ending on day t; $PM30MA_t$ – 30-day simple moving average of mean concentration (μg m^{-3}) of PM_{10} ending on day t; $PRSS_t$ – daily range of pressure at surface (hPa) on day t; $RH2M_t$ – daily range of relative humidity at 2m AGL (%) on day t; $S(.,\lambda)$ – natural cubic spline of time with λ degrees of freedom (five/year for time and three in total for temperature); DOW_t – day of the week on day *t*; β_n – regression coefficients relating covariate levels to number of deaths; and α – regression coefficient relating the day of the week to the number of deaths.

As presented in Dominici et al (2003), the smooth function $S(.,\lambda)$ was applied to adjust fluctuations in mortality over time so that only short-term variations in mortality and pollutant concentrations are used to estimate β.

RESULTS AND DISCUSSION

During the study period 37,540 deaths occurred, out which 1,342 cases were attributed to respiratory failure. The daily mean concentrations of PM_{10} were in the range from 10.36 to 276.43 μg m^{-3}, with 229 days exceeding the 50 μg m^{-3} level threshold. The pollutant levels exhibited seasonal variations with the lowest values recorded during the spring and summer months (Figure 1). The number of death cases caused by respiratory diseases is ranked third in Serbia, immediately after circulatory and malignant-related mortality. The majority of deaths are detected among the population aged 65 and older. According to the data obtained from the Statistical Office of the Republic of Serbia (2015), the death rate in Belgrade area ranged between 28 and 60 per 100 000 inhabitants over the period 2000-2014, which is comparable to the levels registered in the surrounding countries, namely in Bulgaria (54.0), Hungary (62.5), and Croatia (44.3) available at The European Detailed Mortality Database (WHO, 2014).

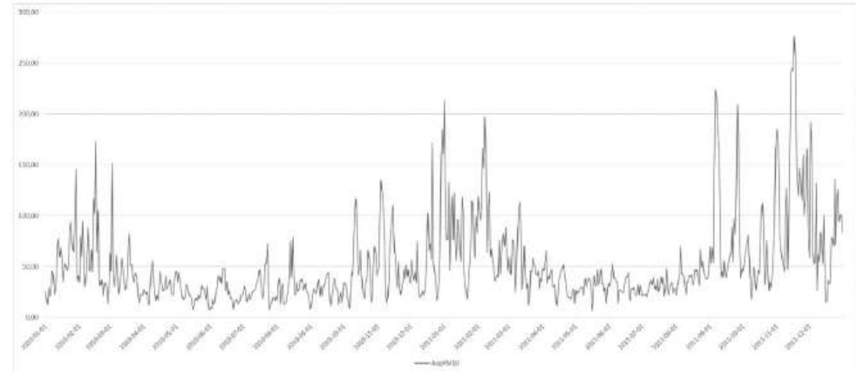


Figure 1. *Seasonal variations of PM_{10} concentrations during the study period.*

The model estimates of the association between PM_{10} concentrations and respiratory system-related mortality are shown in Table 1. As can be seen, the statistical significance of the estimated association between PM_{10} concentrations and respiratory-related mortality is not high probably due to the limited number of observations (1,342) over the specified two-year period. Accordingly, the effects on young population (<30) and people of non-identified age are not presented and discussed in this paper.

Relative risks calculated for 10-μg m^{-3} increase in PM_{10} concentrations are shown in Table 2. It can be seen that an increase of 10 μg m^{-3} of PM_{10} levels was related to a significant rise in the number of daily deaths, particularly after a cumulative exposure over the last 30 days. The effects were mostly pronounced for the middle-aged population, which could be explained by the fact that younger people have higher minute ventilation, intense physical activity and spend more time outdoors. During the exposition, the coarse particles deposited in the upper airways or larger lower airways may cause the disruption of lung endothelial barrier integrity via oxidative stress which further leads to their transfer from lungs to blood (Wang et al, 2010). Unlike the middle-aged group, the estimated change in mortality of 3.13% for elderly males associated with 30-day average concentrations is lower, but still more significant due to a higher number of the observed cases.

Table 1. Model estimate of the association between PM_{10} and respiratory system-related mortality.

	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM_{10} 3 days delta	-0.001	-0.003	0.0004	0.001	-0.004
	(-0.004, 0.002)	(-0.012, 0.005)	(-0.011, 0.012)	(-0.004, 0.006)	(-0.010, 0.001)
PM_{10} 7 days delta	0.001	0.004	0.012**	-0.0004	-0.001
	(-0.002, 0.004)	(-0.004, 0.011)	(0.002, 0.022)	(-0.004, 0.004)	(-0.006, 0.004)
PM_{10} 30 days MA	0.003	0.01	0.015	0.003	-0.001
	(-0.002, 0.008)	(-0.004, 0.024)	(-0.005, 0.036)	(-0.004, 0.010)	(-0.009, 0.007)
PRSS range	-0.008	-0.024	0.071	-0.013	-0.013
	(-0.032, 0.016)	(-0.096, 0.049)	(-0.020, 0.162)	(-0.050, 0.024)	(-0.054, 0.029)
RH2M range	-0.002	0.003	-0.017	0.001	-0.004
	(-0.008, 0.004)	(-0.017, 0.022)	(-0.043, 0.008)	(-0.009, 0.010)	(-0.015, 0.007)
Tuesday	-0.112	-0.105	0.017	-0.062	-0.228
	(-0.318, 0.093)	(-0.725, 0.514)	(-0.843, 0.876)	(-0.366, 0.242)	(-0.588, 0.132)
Wednesday	-0.097	0.096	-0.301	-0.122	-0.119
	(-0.302, 0.109)	(-0.496, 0.689)	(-1.236, 0.634)	(-0.431, 0.186)	(-0.470, 0.232)
Thursday	-0.067	-0.182	0.357	-0.216	0.07
	(-0.271, 0.136)	(-0.820, 0.456)	(-0.445, 1.159)	(-0.531, 0.100)	(-0.264, 0.404)
Friday	-0.063	0.072	-0.09	-0.043	-0.119
	(-0.266, 0.141)	(-0.527, 0.671)	(-0.974, 0.794)	(-0.344, 0.259)	(-0.469, 0.231)
Saturday	-0.087	0.069	-0.274	-0.08	-0.122
	(-0.292, 0.117)	(-0.532, 0.669)	(-1.186, 0.637)	(-0.385, 0.226)	(-0.472, 0.229)
Sunday	0.039	-0.03	0.346	-0.005	0.095
	(-0.160, 0.237)	(-0.641, 0.581)	(-0.442, 1.134)	(-0.305, 0.296)	(-0.236, 0.426)
nsTime1	-0.056	-1.651	3.657*	0.282	-0.577
	(-1.088, 0.977)	(-4.417, 1.115)	(-0.518, 7.832)	(-1.337, 1.901)	(-2.346, 1.191)
nsTime2	-0.2	-3.515*	4.003	0.165	-0.433
	(-1.511, 1.111)	(-7.172, 0.143)	(-1.515, 9.522)	(-1.872, 2.202)	(-2.664, 1.797)
nsTime3	0.151	-1.32	1.355	0.695	-0.121
	(-0.989, 1.290)	(-4.365, 1.725)	(-3.441, 6.150)	(-1.090, 2.480)	(-2.063, 1.820)
nsTime4	-0.123	-2.602*	2.009	0.323	-0.44
	(-1.178, 0.933)	(-5.401, 0.197)	(-2.435, 6.453)	(-1.336, 1.982)	(-2.249, 1.369)
nsTime5	0.797	-0.99	1.572	1.088	0.847
	(-0.270, 1.863)	(-3.811, 1.831)	(-2.927, 6.071)	(-0.589, 2.765)	(-0.972, 2.665)
nsTime6	-0.002	-2.725	4.942*	0.402	-0.35
	(-1.215, 1.212)	(-6.040, 0.590)	(-0.134, 10.017)	(-1.490, 2.293)	(-2.416, 1.716)
nsTime7	-0.423	-2.299	1.02	0.018	-0.729
	(-1.647, 0.800)	(-5.619, 1.021)	(-4.310, 6.350)	(-1.889, 1.924)	(-2.807, 1.350)
nsTime8	-0.143	-1.691	1.074	0.062	-0.148
	(-0.926, 0.639)	(-3.860, 0.477)	(-2.382, 4.529)	(-1.154, 1.278)	(-1.478, 1.181)
nsTime9	0.473	-5.486*	3.242	1.81	0.069
	(-1.768, 2.715)	(-11.732, 0.761)	(-6.289, 12.774)	(-1.665, 5.285)	(-3.769, 3.906)
nsTime10	0.587**	-0.285	0.128	0.774**	0.634
	(0.130, 1.044)	(-1.776, 1.206)	(-2.062, 2.318)	(0.101, 1.446)	(-0.162, 1.431)
nsTemp1	0.196	0.071	-0.651	0.195	0.338
	(-0.309, 0.700)	(-1.389, 1.530)	(-2.691, 1.390)	(-0.568, 0.958)	(-0.539, 1.214)
nsTemp2	0.717	-0.699	-0.534	0.424	1.692*
	(-0.333, 1.767)	(-3.419, 2.022)	(-4.438, 3.370)	(-1.185, 2.033)	(-0.231, 3.615)
nsTemp3	0.837***	0.529	-0.888	0.885**	1.180***
	(0.316, 1.359)	(-1.098, 2.156)	(-3.104, 1.328)	(0.101, 1.669)	(0.303, 2.058)
Constant	0.266	0.506	-4.995**	-0.839	-0.728
	(-0.850, 1.383)	(-2.412, 3.425)	(-9.714, -0.276)	(-2.583, 0.905)	(-2.659, 1.202)

Note: *$p<0.1$; **$p<0.05$; ***$p<0.01$. Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

Similar effect estimates for PM_{10} exposure were reported by Hoek et al (2013), who found a 4.5% increase in respiratory system-related mortality for a 10 µg m^{-3} increase in PM_{10} concentrations. The gender-differences can be explained by a smaller diameter of upper airways in females due to which particles are deposited in the trachea and bronchioles and later on swallowed or expelled by coughing (Gehr and Heyder, 2000).

The majority of previous studies have estimated the PM_{10} effects at multiple lag days (0-day to 3-day lags were mostly examined) and according to their findings, the relative risk estimates are shown to be highest over 3 days of exposure (Anderson et al, 2012). However, our results indicate that the period longer than just a few days might play an important role in the aggravation of the pre-existing respiratory conditions and related mortality. This is in compliance with the study of Zanobetti et al (2003), who reported that, during the first 40 days after exposure, the effect size estimate becomes five times higher. According to their findings, a 10 μg m^{-3} increase in PM_{10} concentrations was associated with a 4.2% increase in respiratory mortality, whereas the effects of pollutant exposure observed for the same day and the day preceding the fatal outcome were considerably lower (0.74%).

Dockery and Pope (1994) summarized the results of several studies with the conclusion that the PM_{10} exposure was followed by an increase in mortality attributed to respiratory diseases ranging from 1.5% to 3.7%. It is worth noting that some of these studies, particularly those with lower estimated effect size, were conducted in the regions where PM_{10} concentrations were considerably lower compared to those registered in Belgrade area.

Table 2. *The percent changes in respiratory system-related mortality with a 10-μg m^{-3} increase in pollutant concentrations.*

Model 1	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM10 3 days delta	-1.24%	-3.47%	0.38%	0.91%	-4.31%
PM10 7 days delta	1.01%	3.51%	11.92%	-0.39%	-0.86%
PM10 30 days MA	3.16%	10.13%	15.50%	3.13%	-0.83%
PRSS range	-0.81%	-2.33%	7.36%	-1.33%	-1.25%
RH2M range	-0.19%	0.26%	-1.73%	0.09%	-0.38%

Note: Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

One of the major limitations of the retrospective epidemiological studies is associated with the possibility of misinterpretation of the health outcomes due to neglecting the underlying causes of death. For instance, the respiratory-related death rate might even be higher when taking into account that patients with chronic obstructive pulmonary disease are often removed by cardiovascular failure (Pope et al, 2004). Furthermore, it has been argued that true pollutant effects might remain underestimated since the information obtained from the ambient monitoring networks is not always correlated with the personal exposure levels on the days preceding the fatal outcome (Tellez-Rojo et al, 2001). Nevertheless, despite the potential uncertainties mentioned in the literature, the evidence derived from the retrospective epidemiological studies is still a useful indicator of public health burden.

CONCLUSIONS

This study is focused on the quantification of health risks associated with PM_{10} exposure in the Belgrade area, Serbia. Unlike previous studies that estimated PM_{10} effects at multiple lag days, this study focuses on cumulative pollutant exposure during the 3, 7 or 30 days preceding the death. The presented findings confirm that high pollutant loadings, which are nowadays common in many urban areas, pose a significant risk factor for mortality caused by respiratory diseases. Due to the fact that the problem of air pollution in Serbia is severe, the introduction of clean technologies in the industry, energy production and transportation sectors, as well as the development of new environmental regulations, shall remain a key target for the future public-health action. Further studies in the region are also needed to gain better insight into the effects of real life exposure and to help policy makers to determine acceptable risk levels.

ACKNOWLEDGEMENTS

This study was carried out as part of projects No III43007 and No OI171002, funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-2016.

REFERENCES

1. Anderson, J. O., Thundiyil, J. G., Stolbach, A., 2012. Clearing the air: a review of the effects of particulate matter air pollution on human health. *Journal of Medical Toxicology*, *8*(2), 166-175.
2. Bell, M. L., Ebisu, K., Peng, R. D., Walker, J., Samet, J. M., Zeger, S. L., & Dominici, F., 2008. Seasonal and regional short-term effects of fine particles on hospital admissions in 202 US counties, 1999–2005. *American Journal of Epidemiology*, *168*(11), 1301-1310.
3. Dockery, D. W., & Pope, C. A., 1994. Acute respiratory effects of particulate air pollution. *Annual Review of Public Health*, *15*(1), 107-132.
4. Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L., & Samet, J. M.,(2006. Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *Jama*, *295*(10), 1127-1134.
5. Dominici, F., Sheppard, L., & Clyde, M., 2003. Health effects of air pollution: a statistical review. *International Statistical Review*, *71*(2), 243-276.
6. Gehr, P., & Heyder, J. (Eds.)., 2000. *Particle-lung interactions*. CRC Press.
7. Gray, D. L., Wallace, L. A., Brinkman, M. C., Buehler, S. S., & La Londe, C., 2015. Respiratory and Cardiovascular Effects of Metals in Ambient Particulate Matter: A Critical Review. In *Reviews of Environmental Contamination and Toxicology* (pp. 135-203). Springer International Publishing.
8. Hoek, G., Krishnan, R. M., Beelen, R., Peters, A., Ostro, B., Brunekreef, B., & Kaufman, J. D., 2013. Long-term air pollution exposure and cardio-respiratory mortality: a review. *Environmental Health*, *12*(1), 43.
9. Peng, R. D., Dominici, F., 2008. Statistical methods for environmental epidemiology with R. In *R: A Case Study in Air Pollution and Health*. Springer Publishing Company New York, NY.
10. Perišić, M., Stojić, A., Stojić, S. S., Šoštarić, A., Mijić, Z., & Rajšić, S. (2014). Estimation of required PM10 emission source reduction on the basis of a 10-year period data. *Air Quality, Atmosphere & Health*, 1-11.
11. Pope III, C. A., & Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. *Journal of the Air & Waste Management Association*, *56*(6), 709-742.
12. Pope, C. A., Burnett, R. T., Thurston, G. D., Thun, M. J., Calle, E. E., Krewski, D., Godleski, J. J., 2004. Cardiovascular mortality and long-term exposure to particulate air pollution epidemiological evidence of general pathophysiological pathways of disease. *Circulation*, *109*(1), 71-77.
13. Samet, J. M., Dominici, F., Zeger, S. L., Schwartz, J., Dockery, D. W. ,2000a. The National Morbidity, Mortality, and Air Pollution Study. Part I: Methods and methodologic issues. *Research Report (Health Effects Institute)*, (94 Pt 1), 5-14.
14. Samet, J. M., Zeger, S. L., Dominici, F., Curriero, F., Coursac, I., Dockery, D., ... & Zanobetti, A., 2000b. The National Morbidity, Mortality, and Air Pollution Study (HEI project no. 96-7): morbidity and mortality from air pollution in the United States. *Cambridge, MA: Health Effects Institute*. Available at: http://www.ncbi.nlm.nih.gov/pubmed/11354823
15. Schwartz, J., 1995. Short term fluctuations in air pollution and hospital admissions of the elderly for respiratory disease. *Thorax*, *50*(5), 531-538.
16. Statistical Office of the Republic of Serbia, 2015. The additionally processed mortality data, Vital statistics
17. Tellez-Rojo, M. M., Romieu, I., Ruiz-Velasco, S., Lezana, M. A., & Hernandez-Avila, M. M., 2001. Daily respiratory mortality and PM10 pollution in Mexico City. *European Respiratory Journal*, *18*(6), 1076-1076.
18. Wang, T., Chiang, E. T., Moreno-Vinasco, L., Lang, G. D., Pendyala, S., Samet, J. M., ... & Garcia, J. G., 2010. Particulate Matter Disrupts Human Lung Endothelial Barrier Integrity via ROS-and p38 MAPK–Dependent Pathways. *American Journal of Respiratory Cell and Molecular Biology*, 42(4), 442-449.
19. World Health Organization, Regional Office for Europe, 2014. Detailed Mortality Database, Division of Information, Evidence, Research and Innovation, Copenhagen, available at: http://data.euro.who.int/dmdb/ (last change July 2016.)
20. Zanobetti, A., Schwartz, J., Samoli, E., Gryparis, A., Touloumi, G., Peacock, J., ... & Katsouyanni, K. , 2003. The temporal pattern of respiratory and heart disease mortality in response to air pollution. *Environmental Health Perspectives*, *111*(9), 1188.

8.6 THE ASSOCIATION BETWEEN SHORT-TERM EXPOSURE TO PM10 AND SOOT AND CIRCULATORY SYSTEM-RELATED MORTALITY IN BELGRADE AREA

S. Stanišić Stojić (1), N. Stanišić (1), A. Šoštarić (2), A. Stojić (3), S. Mladenović (2)
(1) Singidunum University, 32 Danijelova St., 11010 Belgrade, Serbia;
(2) Institute of Public Health Belgrade, 54 Despota Stefana Blvd., 11000 Belgrade, Serbia ;
(3) Institute of Physics Belgrade, University of Belgrade, 118 Pregrevica St., 11080 Belgrade, Serbia
andrej.sostaric@zdravlje.org.rs

ABSTRACT

In this study we estimated the relationship between exposure to particulate matter and daily mortality counts attributed to circulatory system diseases in Belgrade area (Serbia). The analysis is based on the 2-year pollutant monitoring (2010-2011) and the corresponding administrative records on mortality. A slightly modified methodological approach is introduced in order to estimate the impact of increased pollutant exposure over the last few days preceding death. The circulatory system-related-mortality rates for the observed period in Belgrade area were among the highest in the EU region. According to the results, a 10-µg m^{-3} increase in PM_{10} concentrations is followed by an increase in cardiovascular outcomes in the range from 1.28 to 1.47% in elderly population. The impact of air pollution on health is well documented, and thus it is necessary to introduce rigorous emission control regulations in developing countries to ensure improvement of ambient air quality and public health indicators.

INTRODUCTION

Epidemiological studies have provided convincing evidence in support of a positive causal relationship between particulate matter (PM_{10}) and mortality occurring as a result of ischemic heart disease, cardiac arrhythmia, cardiac arrest, increased blood markers of risk and subclinical atherosclerosis (Künzli et al,, 2005). Thereby, vulnerable young and elderly populations in urban areas, along with the people with low educational attainment and socioeconomic status, disproportionately experience a pollution-related health burden (Barret, 2015). The principal purpose of this study is to examine the effects of short-term exposure to PM_{10} and soot on cardiovascular mortality in the urban area of Belgrade based on the 2-year pollutant monitoring and the corresponding administrative records on mortality. Mortality rate is chosen as an indicator since it represents a clear outcome which is not likely to be misinterpreted and unregistered like subtle health conditions (Bell et al,, 2011). Unlike previous studies that dealt with the short-term effects using lags of 0, 1, and 2 days, the present one introduces a slightly modified methodological approach in order to estimate the effects of cumulative pollutant exposure during the 3, 7 or 30 days preceding death. According to the data obtained from the Statistical Office of the Republic of Serbia (2015), circulatory system diseases were the leading cause of death in the Belgrade area with high related rates in the range from 635 to 677 per 100 000 inhabitants over the last 15 years. Comparable rates have been registered in the neighbouring countries, namely in Romania and Hungary, and are among the highest values in the EU region (The European Detailed Mortality Database).

METHODOLOGY

Daily time series data on total mortality and mortality trends due to circulatory system diseases for the years 2010 and 2011 were obtained from the Institute of Public Health in Belgrade. The concentrations of PM_{10} and soot were measured at 7 and 17 monitoring stations, respectively, uniformly distributed over the city area. Meteorological data obtained from the Global Data Assimilation System with spatial resolution of 1 degree were collapsed over a 24-hour period to provide a mean, median, maximum, minimum and range for temperature, relative humidity and atmospheric pressure. The relationship between daily counts of circulatory system related mortality and the levels of air pollutants were modeled using quasi-Poisson regression. Based on the previous studies (Samet et al, 2000a; Samet et al, 2000b; Le Tertre et al, 2002; Dominici et al, 2006; Bell et al, 2008; Peng and Dominici, 2008; Brook et al, 2010; Shah et al, 2015), the selected major confounding factors included days of the week, seasonality, nonlinear function of temperature, pressure and relative humidity.

Two separate models were specified; one for PM_{10} and the other one for soot.

The models were specified as follows, respectively:

$$E(Y_t) = \exp\{\beta_1 \, PM\Delta3_t + \beta_2 \, PM\Delta7_t + \beta_3 \, PM30MA_t + \beta_4 \, PRSS_t + \beta_5 \, RH2M_t + S(time, \lambda_1) + S(temp, \lambda_2) + \alpha \, DOW_t\}$$

$$E(Y_t) = \exp\{\beta_1 \, Soot\Delta3_t + \beta_2 \, Soot\Delta7_t + \beta_3 \, Soot30MA_t + \beta_4 \, PRSS_t + \beta_5 \, RH2M_t + S(time, \lambda_1) + S(temp, \lambda_2) + \alpha \, DOW_t\}$$

Y_t – the expected number of circulatory disease related deaths on day t; $PM\Delta3_t$ ($Soot\Delta3_t$) – difference between 3-day simple moving average and 7-day simple moving average of mean concentration (µg m^{-3}) of the air pollutant ending on day t; $PM\Delta7_t$ ($Soot\Delta7_t$) – difference between 7-day simple moving average and 30-day simple moving average of mean concentration (µg m^{-3}) of the air pollutant ending on day t; $PM30MA_t$ ($Soot30MA_t$) – 30-day simple moving average of mean concentration (µg m^{-3}) of the air pollutant ending on day t; $PRSS_t$ – daily range of pressure at surface (hPa) on day t; $RH2M_t$ – daily range of relative humidity at 2m AGL (%) on day t; $S(.,\lambda)$ – natural cubic spline of time with λ degrees of freedom (five/year for time and three in total for temperature); DOW_t – day of the week on day *t*; β_n – regression coefficients relating covariate levels to the number of deaths; and α – regression coefficient relating the day of the week to the number of deaths.

The smooth function $S(.,\lambda)$ in the model is used to adjust smooth fluctuations in mortality over time so that only short-term variation in mortality and air pollution is used to estimate β (Dominici et al, 2003).

RESULTS AND DISCUSSION

The daily mortality counts in Belgrade area for the years 2010 and 2011 included 37,540 deaths, out of which 20,081 were attributed to circulatory diseases. In general, the lowest circulatory related-death rates registered in the spring and autumn season are followed by a steady increase and prominent peaks in the middle of summer and the start of winter period. The model estimates of the association between pollutant concentrations and related mortality are shown in Table 1 and Table 2. In the presented solution, PM_{10} and soot were modelled as separate air quality indicators. Their effects on young people (<30) and individuals of non-identified age are not considered herein due to a relatively small number of observations. In the case when both pollutants were included in the model, soot has taken over explanatory power, probably due to the fact that it includes the combustion-related PM_{10} fraction originating from traffic, solid fuel burning, shipping and industrial sources, which proved to be more harmful than the secondary organic aerosol formed through photochemical reactions (Janssen et al, 2011).

The percent changes in circulatory system-related mortality with a 10-µg m^{-3} increase in PM_{10} and soot concentrations are shown in Table 3. According to the results, the death outcomes triggered by air pollution events are not immediate, but may take few days to occur. This is in compliance with the previous studies reporting that PM_{10} effects on cardiovascular mortality usually occur after a time lag of about two days (Pope and Dockery, 2006). The short-term effects of exposure to elevated PM_{10} concentrations are observed to be particularly significant in elderly population, as this group is generally more susceptible to the effects of air pollution. For them, the 10-µg m^{-3} increase in PM_{10} concentrations is followed by a moderate increase in cardiovascular outcomes ranging from 1.28 to 1.47%. Similarly, the daily number of circulatory-related deaths among all age groups increased by 1.33% for the same increment in pollutant concentrations. The higher effects of PM_{10} exposure (2.12%) over the period of 3 and 7 days preceding the fatal outcome are observed solely for the middle-aged male group. As regards soot, the higher levels do not appear to be statistically significant with the exception of elevated concentrations over the last 30 *i.e.* 7 days preceding the fatal outcome (30-day moving average and 7-day delta values) that also exert the pronounced effects on middle-aged males.

The observed impact of increased pollutant concentrations on males aged 30-65 can be explained by two factors. Firstly, unlike the elderly people who spend more time indoors, the younger population is more active and their activity patterns might have a substantial impact on timing, location and degree of pollutant exposure (Klepeis et al, 2001). Secondly, the observed gender-dependent difference in size effect of both particles for the middle-aged group may be explained by a larger diameter of upper respiratory airways and higher respiratory minute volume in males (Gehr and Heyder, 2000).

Table 1. *Model estimate of the association between PM_{10} and circulatory system-related mortality.*

	Total	**Middle-aged males**	**Middle-aged females**	**Elderly males**	**Elderly females**
PM_{10} 3 days delta	0.001***	0.002	-0.001	0.001**	0.001**
	(0.0005, 0.002)	(-0.001, 0.004)	(-0.005, 0.004)	(0.0001, 0.003)	(0.0001, 0.002)
PM_{10} 7 days delta	0.001*	0.002*	-0.003	0.001*	0.0002
	(-0.0001, 0.001)	(-0.0002, 0.004)	(-0.007, 0.001)	(-0.0001, 0.002)	(-0.001, 0.001)
PM_{10} 30 days MA	0.0004	0.003	-0.003	0.0001	0.0004
	(-0.001, 0.002)	(-0.001, 0.007)	(-0.010, 0.003)	(-0.002, 0.002)	(-0.001, 0.002)
PRSS range	-0.006*	-0.005	0.008	-0.009*	-0.005
	(-0.012, 0.0002)	(-0.026, 0.016)	(-0.021, 0.038)	(-0.019, 0.001)	(-0.014, 0.004)
RH2M range	-0.001	-0.006**	-0.001	-0.001	-0.001
	(-0.003, 0.0005)	(-0.012, -0.001)	(-0.009, 0.007)	(-0.004, 0.002)	(-0.003, 0.002)
Tuesday	-0.052*	-0.183*	-0.141	0.03	-0.087**
	(-0.106, 0.002)	(-0.371, 0.005)	(-0.402, 0.120)	(-0.055, 0.116)	(-0.164, -0.010)
Wednesday	-0.055**	-0.04	-0.123	-0.029	-0.076*
	(-0.109, -0.001)	(-0.221, 0.142)	(-0.382, 0.137)	(-0.116, 0.058)	(-0.152, 0.001)
Thursday	-0.085***	-0.029	-0.191	-0.059	-0.106***
	(-0.139, -0.031)	(-0.209, 0.152)	(-0.455, 0.074)	(-0.147, 0.028)	(-0.183, -0.029)
Friday	-0.085***	-0.158*	-0.217	-0.072	-0.073*
	(-0.139, -0.030)	(-0.345, 0.029)	(-0.483, 0.050)	(-0.160, 0.016)	(-0.149, 0.003)
Saturday	-0.060**	-0.049	-0.017	-0.021	-0.093**
	(-0.114, -0.006)	(-0.230, 0.132)	(-0.269, 0.236)	(-0.108, 0.066)	(-0.170, -0.016)
Sunday	-0.044	0.04	-0.138	-0.04	-0.055
	(-0.097, 0.010)	(-0.137, 0.217)	(-0.399, 0.122)	(-0.127, 0.047)	(-0.131, 0.021)
nsTime1	-0.197	-0.003	-0.139	-0.317	-0.165
	(-0.451, 0.057)	(-0.860, 0.854)	(-1.403, 1.124)	(-0.720, 0.086)	(-0.527, 0.197)
nsTime2	-0.729***	-0.202	-1.093	-0.898***	-0.703***
	(-1.054, -0.403)	(-1.310, 0.905)	(-2.696, 0.509)	(-1.416, -0.380)	(-1.165, -0.240)
nsTime3	-0.08	-0.312	-0.029	-0.244	0.057
	(-0.359, 0.199)	(-1.265, 0.640)	(-1.404, 1.346)	(-0.688, 0.200)	(-0.340, 0.454)
nsTime4	-0.274**	0.042	-0.291	-0.343*	-0.29
	(-0.526, -0.022)	(-0.821, 0.904)	(-1.531, 0.949)	(-0.742, 0.056)	(-0.649, 0.069)
nsTime5	0.019	-0.258	0.183	-0.164	0.16
	(-0.241, 0.278)	(-1.152, 0.637)	(-1.092, 1.458)	(-0.577, 0.248)	(-0.209, 0.529)
nsTime6	-0.337**	-0.034	-0.942	-0.409*	-0.308
	(-0.639, -0.034)	(-1.067, 0.998)	(-2.458, 0.574)	(-0.889, 0.071)	(-0.738, 0.122)
nsTime7	-0.686***	-0.807	-0.731	-0.846***	-0.584***
	(-0.988, -0.385)	(-1.840, 0.226)	(-2.225, 0.763)	(-1.324, -0.367)	(-1.013, -0.155)
nsTime8	-0.228**	0.18	-0.748	-0.226	-0.281**
	(-0.422, -0.034)	(-0.468, 0.827)	(-1.741, 0.245)	(-0.534, 0.081)	(-0.559, -0.004)
nsTime9	-0.493*	-0.333	-0.791	-0.805*	-0.324
	(-1.033, 0.046)	(-2.180, 1.514)	(-3.447, 1.866)	(-1.661, 0.052)	(-1.091, 0.444)
nsTime10	-0.059	-0.07	0.311	-0.152	-0.015
	(-0.188, 0.070)	(-0.509, 0.369)	(-0.308, 0.930)	(-0.361, 0.058)	(-0.196, 0.166)
nsTemp1	-0.052	0.458**	0.064	-0.051	-0.142
	(-0.184, 0.081)	(0.014, 0.902)	(-0.587, 0.715)	(-0.263, 0.162)	(-0.330, 0.046)
nsTemp2	0.221	1.210**	-0.398	0.351	0.036
	(-0.049, 0.491)	(0.251, 2.170)	(-1.684, 0.888)	(-0.083, 0.784)	(-0.344, 0.417)
nsTemp3	0.360***	0.279	0.259	0.338***	0.406***
	(0.220, 0.499)	(-0.195, 0.753)	(-0.429, 0.948)	(0.115, 0.562)	(0.209, 0.603)
Constant	3.675***	0.52	0.9	2.747***	3.030***
	(3.403, 3.946)	(-0.413, 1.453)	(-0.444, 2.245)	(2.317, 3.178)	(2.644, 3.416)

Note: *p<0.1; **p<0.05; ***p<0.01. Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

Table 2. *Model estimate of the association between soot and circulatory system-related mortality.*

	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
Soot 3 days delta	0.002	0.006	-0.005	-0.001	0.003
	(-0.001, 0.005)	(-0.004, 0.015)	(-0.020, 0.010)	(-0.005, 0.004)	(-0.001, 0.007)
Soot 7 days delta	0.002	0.009*	-0.008	0.001	0.002
	(-0.002, 0.005)	(-0.001, 0.018)	(-0.023, 0.008)	(-0.004, 0.006)	(-0.003, 0.006)
Soot 30 days MA	0.001	0.030***	-0.002	0.0001	-0.004
	(-0.006, 0.007)	(0.008, 0.052)	(-0.034, 0.029)	(-0.010, 0.011)	(-0.013, 0.005)
PRSS range	-0.007**	-0.008	0.009	-0.011**	-0.005
	(-0.013, -0.0003)	(-0.029, 0.013)	(-0.021, 0.039)	(-0.021, -0.0003)	(-0.014, 0.004)
RH2M range	-0.001	-0.006**	-0.0004	-0.0005	-0.0004
	(-0.003, 0.001)	(-0.012, -0.001)	(-0.008, 0.008)	(-0.003, 0.002)	(-0.003, 0.002)
Tuesday	-0.051*	-0.187*	-0.14	0.032	-0.085**
	(-0.105, 0.003)	(-0.374, 0.001)	(-0.401, 0.121)	(-0.054, 0.118)	(-0.162, -0.009)
Wednesday	-0.051*	-0.04	-0.121	-0.024	-0.072*
	(-0.106, 0.003)	(-0.220, 0.141)	(-0.381, 0.138)	(-0.111, 0.063)	(-0.149, 0.004)
Thursday	-0.080***	-0.026	-0.189	-0.053	-0.102***
	(-0.135, -0.026)	(-0.206, 0.154)	(-0.454, 0.076)	(-0.140, 0.035)	(-0.179, -0.025)
Friday	-0.080***	-0.155	-0.215	-0.065	-0.069*
	(-0.134, -0.025)	(-0.341, 0.032)	(-0.481, 0.051)	(-0.154, 0.023)	(-0.145, 0.007)
Saturday	-0.055**	-0.046	-0.014	-0.013	-0.091**
	(-0.110, -0.001)	(-0.227, 0.135)	(-0.267, 0.239)	(-0.101, 0.074)	(-0.168, -0.014)
Sunday	-0.042	0.04	-0.137	-0.038	-0.054
	(-0.096, 0.012)	(-0.137, 0.217)	(-0.398, 0.124)	(-0.125, 0.050)	(-0.129, 0.022)
nsTime1	-0.199	-0.028	0.029	-0.319	-0.173
	(-0.444, 0.046)	(-0.853, 0.798)	(-1.178, 1.236)	(-0.707, 0.068)	(-0.520, 0.175)
nsTime2	-0.741***	0.202	-0.972	-0.943***	-0.765***
	(-1.083, -0.399)	(-0.959, 1.364)	(-2.645, 0.700)	(-1.487, -0.400)	(-1.247, -0.282)
nsTime3	-0.076	-0.33	0.113	-0.236	0.05
	(-0.352, 0.200)	(-1.273, 0.612)	(-1.231, 1.457)	(-0.674, 0.201)	(-0.340, 0.440)
nsTime4	-0.273**	0.145	-0.311	-0.363*	-0.287
	(-0.527, -0.019)	(-0.727, 1.018)	(-1.553, 0.931)	(-0.765, 0.038)	(-0.647, 0.072)
nsTime5	0.02	0.315	0.174	-0.207	0.1
	(-0.267, 0.308)	(-0.670, 1.299)	(-1.233, 1.581)	(-0.664, 0.250)	(-0.307, 0.506)
nsTime6	-0.332**	0.419	-0.8	-0.414	-0.378
	(-0.654, -0.010)	(-0.675, 1.513)	(-2.398, 0.799)	(-0.925, 0.097)	(-0.833, 0.077)
nsTime7	-0.687***	-0.285	-0.618	-0.879***	-0.655***
	(-1.015, -0.359)	(-1.402, 0.832)	(-2.232, 0.997)	(-1.399, -0.358)	(-1.118, -0.191)
nsTime8	-0.189*	0.752**	-0.895	-0.196	-0.311**
	(-0.405, 0.028)	(0.025, 1.478)	(-1.984, 0.194)	(-0.540, 0.149)	(-0.617, -0.005)
nsTime9	-0.483*	0.255	-0.798	-0.861*	-0.36
	(-1.037, 0.070)	(-1.638, 2.147)	(-3.515, 1.918)	(-1.738, 0.017)	(-1.142, 0.423)
nsTime10	-0.048	0.224	0.189	-0.177*	-0.019
	(-0.166, 0.070)	(-0.164, 0.613)	(-0.392, 0.769)	(-0.367, 0.013)	(-0.185, 0.146)
nsTemp1	-0.1	0.337	0.141	-0.109	-0.178*
	(-0.234, 0.035)	(-0.103, 0.777)	(-0.522, 0.805)	(-0.323, 0.105)	(-0.368, 0.011)
nsTemp2	0.122	0.774	-0.28	0.234	-0.01
	(-0.151, 0.395)	(-0.181, 1.730)	(-1.583, 1.024)	(-0.205, 0.672)	(-0.393, 0.372)
nsTemp3	0.346***	0.241	0.258	0.330***	0.391***
	(0.205, 0.487)	(-0.233, 0.715)	(-0.437, 0.953)	(0.105, 0.555)	(0.192, 0.589)
Constant	3.729***	0.21	0.614	2.820***	3.154***
	(3.442, 4.016)	(-0.777, 1.196)	(-0.782, 2.009)	(2.365, 3.274)	(2.749, 3.558)

Note: *p<0.1; **p<0.05; ***p<0.01. Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

Table 3. *The percent changes in circulatory system-related mortality with a 10-µg m⁻³ increase in pollutant concentrations.*

Model 1	Total	Middle-aged males	Middle-aged females	Elderly males	Elderly females
PM10 3 days delta	1.33%	1.52%	-0.54%	1.47%	1.28%
PM10 7 days delta	0.62%	2.12%	-2.58%	1.09%	0.24%
PM10 30 days MA	0.40%	3.24%	-3.34%	0.06%	0.39%
PRSS range	-0.61%	-0.47%	0.83%	-0.90%	-0.52%
RH2M range	-0.12%	-0.62%	-0.07%	-0.09%	-0.05%
Model 2	**Total**	**Middle-aged males**	**Middle-aged females**	**Elderly males**	**Elderly females**
Soot 3 days delta	1.52%	5.64%	-5.04%	-0.60%	2.89%
Soot 7 days delta	1.59%	8.60%	-7.66%	0.91%	1.50%
Soot 30 days MA	0.62%	30.61%	-2.14%	0.10%	-3.82%
PRSS range	-0.67%	-0.79%	0.88%	-1.06%	-0.46%
RH2M range	-0.10%	-0.63%	-0.04%	-0.05%	-0.04%

Note: Middle-aged – 30-65 years; Elderly - >65 years; PRSS – pressure at surface; RH2M – relative humidity at 2 m AGL.

It is worth noting that retrospective studies have certain limitations. For instance, the exposure measurements resulting from a number of centrally located monitors can affect the estimated health risk in a way that is difficult to predict because these data do not reflect the individual exposure. An additional source of uncertainty for health risk estimation lies in the fact that, in uncontrolled retrospective studies, conclusions are made under the assumption that negligible variations in people's lifestyle occurred during the observation period, which doesn't have to be the case in the real world.

CONCLUSIONS

In this study, we calculated the relative rate (expressed as % increase) in circulatory system related-mortality per unit increase in daily PM_{10} and soot concentrations. These findings reflect not only the harvesting or aggravation of the pre-existing conditions among the most vulnerable group of people, but they also point to the importance of the day to day accumulation effect during the long-term PM_{10} and soot exposure. In order to better understand the air pollution effects on healthy people, as well as its long-term consequences, further attempts should include longer time-series and if possible, data for separate regions that could reflect the individual exposure more precisely. Further studies in the area are also required to fully understand the complex biological responses elicited by potentially additive and/or synergistic combinations of air pollutants. The results obtained could provide useful information for establishing environmental legal framework in developing countries.

ACKNOWLEDGEMENTS

This study was carried out as part of the projects No III43007 and No OI171002, funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-2016.

REFERENCES

1. Barrett, J. R., 2015. "Exported" Deaths and Short-Term PM10 Exposure: Factoring the Impact of Commuting into Mortality Estimates. *Environmental Health Perspectives*, *123*(1), A22.
2. Bell, M. L., Ebisu, K., Peng, R. D., Walker, J., Samet, J. M., Zeger, S. L., Dominici, F., 2008. Seasonal and regional short-term effects of fine particles on hospital admissions in 202 US counties, 1999–2005. *American Journal of Epidemiology*, *168*(11), 1301-1310.
3. Bell, M. L., Morgenstern, R. D., & Harrington, W., 2011. Quantifying the human health benefits of air pollution policies: Review of recent studies and new directions in accountability research. *Environmental Science & Policy*, *14*(4), 357-368.
4. Brook, R. D., Rajagopalan, S., Pope, C. A., Brook, J. R., Bhatnagar, A., Diez-Roux, A. V., ... & Kaufman, J. D., 2010. Particulate matter air pollution and cardiovascular disease an update to the scientific statement from the American Heart Association. *Circulation*, *121*(21), 2331-2378.

5. Detailed Mortality Database, World Health Organization, Regional Office for Europe, available at: http://data.euro.who.int/dmdb/
6. Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L., Samet, J. M., 2006. Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *Jama, 295*(10), 1127-1134.
7. Dominici, F., Sheppard, L., & Clyde, M., 2003. Health effects of air pollution: a statistical review. *International Statistical Review, 71*(2), 243-276.
8. Gehr, P., & Heyder, J. (Eds.), 2000. *Particle-lung Interactions*. CRC Press.
9. Janssen, N. A., Hoek, G., Simic-Lawson, M., Fischer, P., Van Bree, L., Ten Brink, H., ... & Cassee, F. R. , 2011. Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2. 5. *Environmental Health Perspectives, 119*(12), 1691-1699.
10. Klepeis, N. E., Nelson, W. C., Ott, W. R., Robinson, J. P., Tsang, A. M., Switzer, P., ... & Engelmann, W. H. , 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *Journal of Exposure Analysis and Environmental Epidemiology, 11*(3), 231-252.
11. Künzli, N., Jerrett, M., Mack, W. J., Beckerman, B., LaBree, L., Gilliland, F., ... & Hodis, H. N., 2005. Ambient air pollution and atherosclerosis in Los Angeles. *Environmental Health Perspectives*, 201-206.
12. Le Tertre, A., Medina, S., Samoli, E., Forsberg, B., Michelozzi, P., Boumghar, A., ... & Katsouyanni, K., 2002. Short-term effects of particulate air pollution on cardiovascular diseases in eight European cities. *Journal of Epidemiology and Community Health, 56*(10), 773-779.
13. Peng, R. D., & Dominici, F., 2008. Statistical methods for environmental epidemiology with R. In *R: A Case Study in Air Pollution and Health*. Springer Publishing Company New York, NY.
14. Pope III, C. A., & Dockery, D. W., 2006. Health effects of fine particulate air pollution: lines that connect. Journal of the Air & Waste Management Association, 56(6), 709-742.
15. Samet, J. M., Dominici, F., Zeger, S. L., Schwartz, J., & Dockery, D. W. ,2000a. The National Morbidity, Mortality, and Air Pollution Study. Part I: Methods and methodologic issues. *Research Report (Health Effects Institute)*, (94 Pt 1), 5-14.
16. Samet, J. M., Zeger, S. L., Dominici, F., Curriero, F., Coursac, I., Dockery, D., ... & Zanobetti, A.,2000b. The National Morbidity, Mortality, and Air Pollution Study (HEI project no. 96-7): morbidity and mortality from air pollution in the United States. *Cambridge, MA: Health Effects Institute*. Available at: http://www.ncbi.nlm.nih.gov/pubmed/11354823
17. Shah, A. S., Lee, K. K., McAllister, D. A., Hunter, A., Nair, H., Whiteley, W., Langrish J.P., Newby D.E., Mills, N. L., 2015. Short term exposure to air pollution and stroke: systematic review and meta-analysis. *bmj, 350,* h1295., doi: http://dx.doi.org/10.1136/bmj.h1295
18. Statistical Office of the Republic of Serbia, 2015. The additionally processed mortality data, Vital statistics

XIX INTERNATIONAL
ECO-CONFERENCE® 2015
23rd - 25th SEPTEMBER

ENVIRONMENTAL PROTECTION OF URBAN AND SUBURBAN SETTLEMENTS

ЕКОЛОШКИ ПОКРЕТ НОВОГ САДА

PROCEEDINGS

NOVI SAD, SERBIA

Publisher
ECOLOGICALMOVEMENT OF NOVI SAD
21000 Novi Sad, Vojvođanskih brigada 17/I
Phone/Fax: (+381 21) 529-096
Phone: (+381 21) 420-175
E-mail: ekopokretns@gmail.com
www.ekopokret.org.rs

Academician Rudolf Kastori, President
Nikola Aleksić
Ljubica Aleksić
Prof. dr Desanka Božidarević
Prof. dr Biserka Dimiskovska
Prof. dr Imre Kadar
Prof.dr Rodoljub Oljača
Prof. dr Radmila Šovljanski
Dr Djordje Okanović
Mr Sladjana Djuranović

Project Editor
Nikola Aleksić

Copy Editor
Ljubica Aleksić

Layout and Formatting
Ljubica Aleksić

For the Publisher
Nikola Aleksić, Direktor

Print
Futura doo

Circulation
300 copies

Publication year: 2015

XIX INTERNATIONAL
ECO-CONFERENCE®
23-25th SEPTEMBER 2015
NOVI SAD, SERBIA

ENVIRONMENTAL PROTECTION OF URBAN AND SUBURBAN SETTLEMENTS

PROCEEDINGS
2015

Organizer:
- Ecological Movement of Novi Sad

Co-organizers:
- Vojvodina Academy of Sciences and Arts
- University of Novi Sad
- Russian State Agrarian University-MTAA, Moscow, Russian Federation
- International Independent University of Environmental and Political Sciences, Moscow, Russian Federation
- Institute of Field and Vegetable Crops Novi Sad
- Institute for Food Technology, Novi Sad
- Institute of Lowland Forestry and Environment in Novi Sad
- Legambiente d'Italia (National environmental organization)

Patronage:
- Matica srpska, Novi Sad

Host:
- Institute for Nature Conservation of Vojvodina Province, Novi Sad

Official water of XIX International Eco-Conference® 2015
MINAQUA

Honorary Committee:

President:
- **Prof. dr Dragan Stanić,** President of Matica Srpska

Vice-presidents:
- **Academician Julian Tamaš,** President of the Vojvodina Academy of Art and Science
- **Prof. Dr. Zoran Kovačević,** President of the Serbian Academy of Science and Art, Serbia
- **Prof. Dr Radovan Pejanović** , Rector of the University of Novi Sad
- **Prof. Dr. Vladimir Bautin,** Rector at the Russian State Agrarian University-MTAA, Moscow, Russian Federation
- **Prof. Dr. Stanislav A. Stepanov,** Rector of the International Independent Ecological-Politicology University in Moscow,
- **Dr. Jegor Miladinović,** Director of the Institute for Field and Vegetable Crops in Novi Sad
- **Dr. Olivera Djuragić,** Institute for Food Technology of Novi Sad
- **Prof. Dr. Saša Orlović,** Director of the Institute of Lowland Forestry and Environment in Novi Sad,
- **Prof. Dr. Biljana Panjkovic,** Director of the Institute for Nature Protection of Vojvodina region
- **Vittorio Cogliati Dezza,** President of Legambiente d' Italia

Scientific Committee:

President:

- **Academician Rudolf Kastori,** Academy of Science and Art of Vojvodina, Novi Sad, Serbia and Hungarian Academy of Sciences, Budapest, Hungary

Vice-presidents:

- **Prof. Dr. Pavle Sekeruš,** Vice-Chancellor for Science at the University of Novi Sad
- **Prof. Dr. Marfenin N.N.,** Russian Federation, Vice-Chancellor for Science at the International Independent Ecological-Politicology University in Moscow
- **Prof. Dr Evgenij Ivanovich Koshkin,** Vice-Chancellor for International Cooperation at the Russian State AgrarianUniversity-MTAA, Moscow, Russian Federation
- **Dr. Marijana Sakač,** Institute for Food Technology of Novi Sad
- **Dr. Dragana Miladinović,** Assistant Director for Science at the Institute for Field and Vegetable Crops in Novi Sad
- **Prof. Dr. Baccichet Moreno,** University of Ferrara, Faculty of Philology and Philosophy, Italy

Secretary:

- **Ljubica Aleksić,** Organizer of the Ecological Movement of Novi Sad

Members:

- **Academician Vaskrsija Janjić,** University of Belgrade, Faculty of Agriculture, Serbia
- **Academician Vukadin Leovac,** University of Novi Sad, Faculty of Mathematics and Natural Sciences, Serbia
- **Prof. Dr. Ištvan Bikit,** Faculty of Mathematics and Natural Sciences, Department for Physics, University of Novi Sad
- **Prof. Dr. Desanka Božidarević,** University of Novi Sad, Resident Professor at the Agricultural Faculty, retired.
- **Prof. Dr. Ilija Ćosić,** Resident Professor at the Faculty of Technical Sciences, University of Novi Sad
- **Prof. Dr. Biserka Dimiskovska,** University of „St. Cyril and Methodius", Institute for Eartquake Engineering and Engineering Seismology (IZIIS), Skopje, Republic of Macedonia
- **Prof. Dr. Ivana Đujić,** University of Belgrade, Resident Professor of FoodChemistry at Biological Faculty, retired.
- **M. Sc. Aleš Golja,** Prof. of Physical Education, Lecturer, University of Ljubljana, Faculty of Civil and Geodetic Engineering, Slovenia
- **Prof. Dr. Vladan Joldžić,** University of Belgrade, Biological and Chemical Faculty, Institute for Criminological and Sociological Research, Serbia
- **Prof. Dr. Kadar Imre,** Research Institute for Soil Science and Agricultural Chemistry, Hungarian Academy of Sciences, Budapest, Hungary

Organizing Committee:

President:
- **Nikola Aleksić,** Director of the Ecological Movement of Novi Sad

Vice-president:
- **Angelo Mancone,** Legambiente Veneto, Rovigo, Italy

Secretary:
- **Zoran Kovačević,** Organizer of the Ecological Movement of Novi Sad

Members:
- **Marina Bajić,** Organizer of the Ecological Movement of Novi Sad
- **Stevan Domazet,** Scientific Institute for Field and Vegetable Crops in Novi Sad
- **MA Slađana Đuranović,** Professor of English language and literature
- **Milenko Košutić,** Engineer, expert assistant at the Institute for Food Technologies (FINS), Novi Sad
- **Slobodan Mišić,** Organizer of the Ecological Movement of Novi Sad
- **Marina Samsonov,** translator and interpreter
- **Marija Stepanović,** Organizer of the Ecological Movement of Novi Sad
- **Željko Štrbac,** Web administrator of the Ecological Movement of Novi Sad
- **Luka Vujasinović,** Web administrator of the Ecological Movement of Novi Sad
- **Petar Vukić,** Technical Director of Ecological Movement of Novi Sad
- **Milan Vurdelja,** Rector's Office, University in Novi Sad

CIP - Каталогизација у публикацији
Библиотека Матице српске, Нови Сад

502:711.4(082)

INTERNATIONAL Eco-Conference (19 ; 2015 ; Novi Sad)
Environmental protection of urban and suburban settlements : proceedings / XIX International Eco-Conference, 23-25th September 2015, Novi Sad ; [organizer Ecological Movement of Novi Sad ; project editor Nikola Aleksić]. - Novi Sad : Ecological Movement of Novi Sad, 2015 (Novi Sad : Futura). - 420 str. : ilustr. ; 23 cm

Tiraž 300. - Bibliografija uz svaki rad. - Rezime na srp. jeziku uz svaki rad. - Registar.

ISBN 978-86-83177-49-3
1. Ecological Movement of Novi Sad
а) Животна средина - Заштита - Градови - Зборници
COBISS.SR-ID 299458055

ECO-CONFERENCE® 2015
ECOLOGICAL MOVEMENT OF NOVI SAD

Zoran Mijić, Mirjana Perišić, Andreja Stojić, Maja Kuzmanoski, Luka Ilić
Institute of Physics, Belgrade

ESTIMATION OF ATMOSPHERIC AEROSOL TRANPORT BY GROUND-BASED REMOTE SENSING AND MODELING

Abstract

Potential source regions of $PM_{2.5}$ and transport pathways were investigated based on backward trajectories and mass concentrations measured in Belgrade, Serbiain 2013. A study of airflow characteristics was performed using cluster analysis of backward trajectories of air masses arriving at 200 m vertical level above Belgrade. Potential source contribution function and concentration weighted trajectory models were used for identification of source regions. Regional and long – range transport from north and northeast pathways was evident and sporadically associated with African dust outbreaks. Case study of elastic backscatter LIDAR observation and complementary prediction of Saharan dust aerosols by the DREAM model were also carried out.

Keywords:*PM, Transport, PSCF, CWT, LIDAR*

INTRODUCTION

Atmospheric aerosols are of major scientific interest due to their confirmed role in climate change (Seinfeld and Panadis, 2012;IPCC, 2007) and their effect on human health (WHO, 2003; Dockery and Pope, 2006). In order to protect public health and the environment i.e. to control and reduce particulate matter (PM) levels, air quality standards were issued and limit values for annual and daily mean $PM_{2.5}$ (particles below 2.5 μm in diameter) mass concentrations were established.Since air pollution is both a local and trans-boundary problem, studies of spatial and temporal variation of atmospheric aerosol particles are essential for an understanding of particle formation, transport, transformation and deposition mechanisms (Perez et al. 2006).In the field of atmospheric sciences receptor models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants based on ambient data measured at the monitoring sites (Hopke, 2003).For pollutant sources that are unknown, hybrid receptor models that incorporate wind trajectories Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT) (Hsu et al., 2003) can be used to resolve source locations. In this paper these models were applied on $PM_{2.5}$ data set from Belgrade in order to provide a map of source potential of geographical areas.In addition, transport paths of air masses with similar history and origin were obtained by trajectory cluster analysis.Having in mind that practically all long-range transport occurs at elevated layers, decoupled from the ground, the requirement for improved observations of the aerosol vertical distribution is evident. Thus, particular attention is devoted to Saharan dust transport events monitoring using LIDAR (Light Detection and Ranging) an active ground based optical remote sensing technique (Nicolaeand Talianu, 2010). The case study LIDAR measurement of Saharan dust intrusion over Belgrade is shown related to DREAM (Dust REgional Atmospheric Model) model prediction.

METODOLOGY

Based on $PM_{2.5}$ data set obtained from the automatic monitoring station "Ovca" bythe Institute of Public Health of Belgrade, from January 2013 to July 2014, possible transport processes over the Belgrade were investigated. As a part of the monitoring network inBelgrade area, this sampling site was established to enable continuous monitoring of pollutant levels and to estimate influence of different emission sources. A few kilometres away from the Belgrade city centre, it is placed in the rural environment, with mainly lowland characteristics.

In order to explorethe origin oftransported $PM_{2.5}$ mass concentrations in this area, dominant local contribution was excluded from the time series.Baseline concentration levels were determined using a frequency differentiated non-linear digital filtering algorithm implemented in the function *baseline.RollingBall* (*wm*=8, *ws*=6) of the Baseline package (Kneen and Annegarn, 1996) of the statistical software environment R (Team 2012). For the purpose of transport ánalysis air-mass back trajectories were computed using the HYSPLIT model (Draxler and Rolph, 2015). Three-day backward trajectories, starting from the sampling site every hour UTC each day, were evaluated for heightof 200 m above ground level, and each trajectory reaching the ground level was excluded from the analysis (49.5%). The influence of non-local source regions and pollution transport pathways was investigated by the use of potential sources contribution function, concentration weighed trajectory(Hsu et al., 2003) and trajectory cluster analysis (TCA) models.

To calculate PSCF, the whole geographic region of interest is divided into an array of grid cells whose size is dependent on the geographical scale of the problem so that PSCF is a function of location, as defined by the cell indices i and j.Air parcel back trajectories, ending at the receptor site, are represented by segment endpoints.

Each endpoint has two coordinates (latitude and longitude) representing the central location of an air parcel at a particulate time. If a trajectory end point lies in a cell of address (i, j), the trajectory is assumed to collect material emitted in the cell. Once aerosol is incorporated into the air parcel, it can be transported along the trajectory to the receptor site. The PSCF value can be understood as a conditional probability that describes the spatial distribution of probable source locations(Ashbaugh et al., 1985). The staying time of all trajectories in a single grid cell is n_{ij}, and m_{ij} is the staying time in the same cell that corresponds to the trajectories that arrived at the receptor site with pollutant concentrations higher than a pre-specified criterion value (average $PM_{2.5}$ concentration was used in this study). The PSCF value for the ij-th cell is then defined as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (1)$$

Cells related to the high values of potential source contribution function are the potential source areas. However, the potential source contribution function maps do not provide an emission inventory of a pollutant but rather show those source areas whose emissions can be transported to the measurement site.To remove the large uncertainty caused when a grid cell has small staying time and large PSCF values, the PSCF value is usually multiplied by a weight function $W(n_{ij})$ to better reflect the uncertainty in the values for these cells (Wang et al., 2008). The weighting function reduced the PSCF values when the total number of the endpoints in a particular cell was less than about two times the average value of the end points per each cell. In this study the grid covers area of interest defined by (30^0- 70^0)N and (-15^0- 50^0)E with cells $1^0{}'1^0$ latitude and longitude. In the current PSCF method, grid cells having the same PSCF values can result from samples of slightly higher concentrations than defined by the criterion or extremely high concentrations. As a result, larger sources cannot be distinguished from moderate sources. Therefore, a method of weighting trajectories with associated concentrations CWT was developed(Hsu et al., 2003). In this procedure, each grid cell gets a weighted concentration obtained by averaging sample concentrations that have associated trajectories that crossed that grid cell as follows:

$$C_{ij} = \frac{1}{\sum_{l=1}^{M} \tau_{ijl}} \sum_{l=1}^{M} C_l \tau_{ijl} \quad (2)$$

C_{ij} is the average weighted concentration in the grid cell(i,j), C_l is the baseline level of $PM_{2.5}$ concentration observed on arrival of trajectory$l$, τ_{ijl} is the number of trajectory endpoints in the grid cell (i,j) associated with the C_l sample, and M is the total number of trajectories. Similarly to the PSCF method, CWT method also employs the arbitrary weight function to eliminate grid cells with few endpoints. Weighted concentration fields show concentration gradients across potential sources. This method helps to determine the relative significance of potential sources.

For vertical profiling and remote sensing of atmospheric aerosol layers the RamanLIDARsystem at the Institute of Physics Belgrade (44.860 N, 20.390 E) was used. It is bi-axial system with combined elastic and Raman detection designed to perform continuousmeasurements of suspended aerosols particles in theplanetary boundary layer and the lower free troposphere. It is based on thethird harmonic frequency of a compact, pulsedNd:YAG laser, emitting pulses of 65 mJ output energy at 355 nm witha 20Hz repetition rate.The optical receiver is a Cassegrainianreflecting telescope with a primary mirror of 250mm diameterand a focal length of 1250 mm. Photomultiplier tubes are used to detect elastic backscatter LIDARsignal at 355 nm and Raman signal at 387 nm The detectors are operatedboth in the analog and photon-counting mode and thespatial raw resolution of the detected signals is 7.5 m.AveragingtimeoftheLIDARprofiles was of the order of1mincorresponding to 1200 lasershots.LIDAR measurements can be used in synergy with numerical models in order to validate and compare information about aerosols. In this paper DREAM model is used to analyse dust transport. DREAM is a regional model designed to simulate and/or predict the atmospheric cycle of mineral dust aerosol (Nickovic et al., 2001). Once injected into the air, dust aerosol is driven by the atmospheric model variables: by turbulent parameters in the early stage of the process when dust is lifted from the ground to the upper levels; by model winds in the later phases of the process when dust travels away from the sources; finally, by thermodynamic processes (atmospheric water phase changes producing clouds, rain and dust wet scavenging) of the atmospheric model and land cover features which provide wet and dry deposition of dust over the Earth surface.

RESULT AND DISCUSSION

Based on trajectory cluster analysis of the whole trajectory data set, sixrepresentative directions of air mass flows over Belgrade were resolved (Figure 1, left).

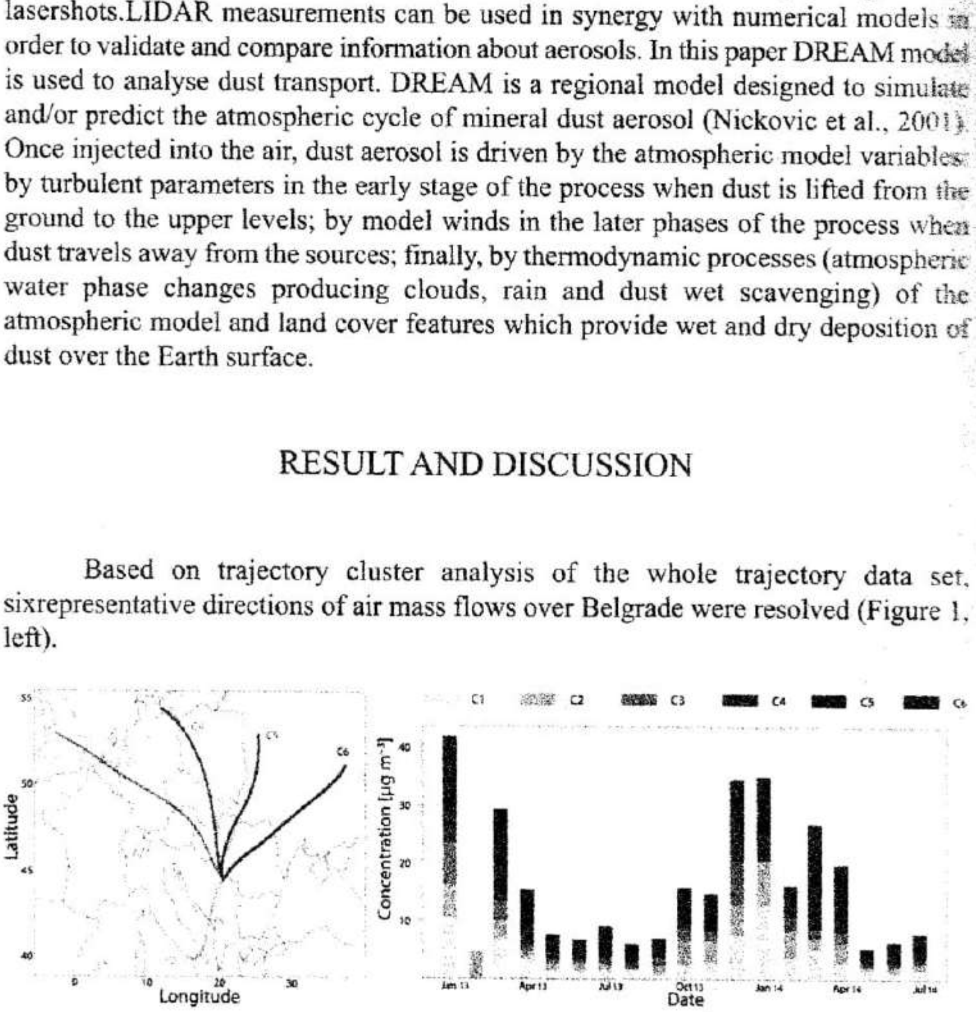


Figure 1. Representative clusters for 72-hours backward trajectories (left) and time series of cluster contributions to transported concentrations (right)

The main directions of air mass flows over Belgrade were therefore grouped into classes named: (C1) north; (C2) south-southwest; (C3) northwest; (C4) north-northwest; (C5) north-northeast; (C6) northeast. The most frequently arriving directions are C4 (22%), C1 (19%) and C5 (18%) thus suggesting the sampling site might be under the main influence of north source regions. Trajectories within different classes of airflow had distinct effects on the $PM_{2.5}$ concentrations. The highest $PM_{2.5}$baseline concentrations were associated with classes C5(24μg m^{-3}) and C6 (22μg m^{-3}), while the lowest $PM_{2.5}$ concentrations were found in class C3 (12μg m^{-3}).Transport contribution to $PM_{2.5}$mass concentrations at the sampling site was the largest during the winter season (Figure 1 - right). Trajectories from west-northwest directions (cluster C3) were crossing over England, Germany, Austria and Hungary with higher potential contribution to $PM_{2.5}$ during the winter season, with anexception during the February of 2013 when the dominant air mass direction was from south-southeastregion (cluster C2).

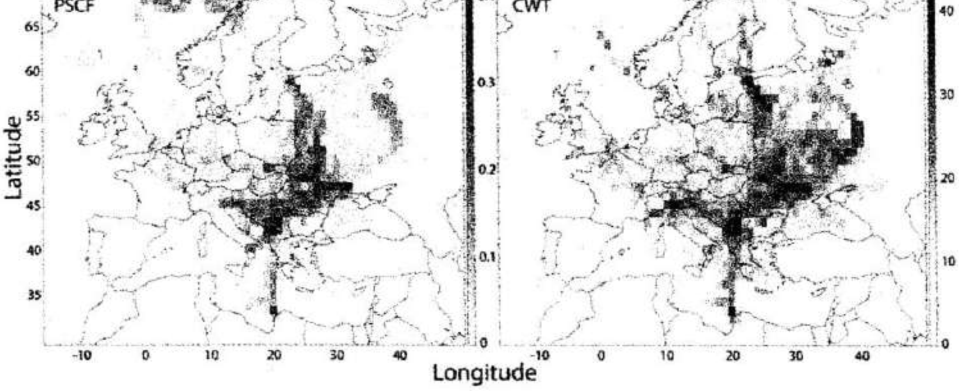


Figure 2. PSCF (left) and CWT [μg m^{-3}] (right) maps for $PM_{2.5}$

According the derived PSCF and CWT maps (Figure 2) the sampling site was under the influence of several possible source regions of $PM_{2.5}$. The mainareas were located in the neighbouring countries (Montenegro, Bosnia and Hercegovina, and Croatia), as well as in north Italy, Romania, Bulgaria and Ukraine.Potential sources in south regioncould be associated with the long-rangetransport of Saharan dust.Higherlevels of particulate matter occurring as a consequence of transport processes were observed during spring and autumnin the area of the southern European countries(Remoundaki et al., 2013). Saharan dustparticlestransport to Serbiamainly follow southwest direction represented by cluster C2.

Fine particulates can be transported at different altitude ranges affecting the local aerosol content when it reaches very low altitude and the planetary boundary layer. LIDAR measurements are very useful tool for investigation of dust transport thanks to the capability to provide high quality aerosol vertical profiles.Figure 3shows an example of LIDAR measurements during a Saharan dust event observed on 19 February, 2014 over Belgrade, and the correspondingdust load predicted by the DREAM model.A dust layer was observed at altitudes between 4 and 6 km at 12:00 UTC, and at descended to lower altitudes later during the measurements.

directions are C4 (22%), C1 (19%) and C5 (18%) thus suggesting the sampling site might be under the main influence of north source regions. Trajectories within different classes of airflow had distinct effects on the $PM_{2.5}$ concentrations. The highest $PM_{2.5}$baseline concentrations were associated with classes C5(24μg m^{-3}) and C6 (22μg m^{-3}), while the lowest $PM_{2.5}$ concentrations were found in class C3 (12μg m^{-3}).Transport contribution to $PM_{2.5}$mass concentrations at the sampling site was the largest during the winter season (Figure 1 - right). Trajectories from west-northwest directions (cluster C3) were crossing over England, Germany, Austria and Hungary with higher potential contribution to $PM_{2.5}$ during the winter season, with anexception during the February of 2013 when the dominant air mass direction was from south-southeastregion (cluster C2).

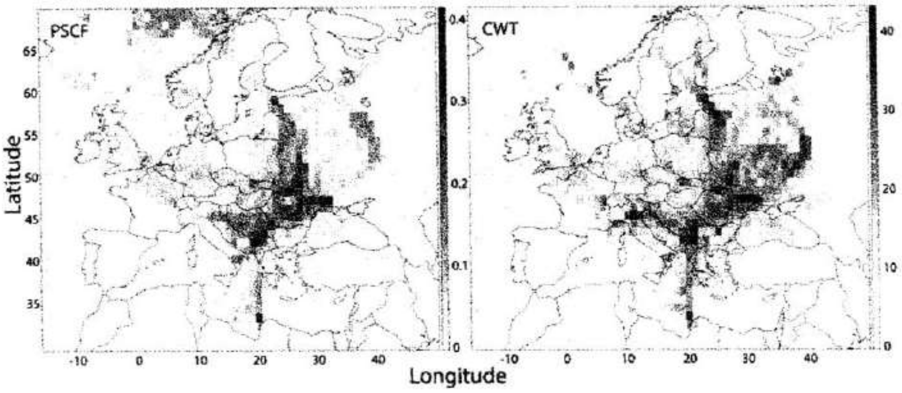


Figure 2. PSCF (left) and CWT [μg m^{-3}] (right) maps for $PM_{2.5}$

According the derived PSCF and CWT maps (Figure 2) the sampling site was under the influence of several possible source regions of $PM_{2.5}$. The mainareas were located in the neighbouring countries (Montenegro, Bosnia and Hercegovina, and Croatia), as well as in north Italy, Romania, Bulgaria and Ukraine.Potential sources in south regioncould be associated with the long-rangetransport of Saharan dust.Higherlevels of particulate matter occurring as a consequence of transport processes were observed during spring and autumnin the area of the southern European countries(Remoundaki et al., 2013). Saharan dustparticlestransport to Serbiamainly follow southwest direction represented by cluster C2.

Fine particulates can be transported at different altitude ranges affecting the local aerosol content when it reaches very low altitude and the planetary boundary layer. LIDAR measurements are very useful tool for investigation of dust transport thanks to the capability to provide high quality aerosol vertical profiles.Figure 3shows an example of LIDAR measurements during a Saharan dust event observed on 19 February, 2014 over Belgrade, and the correspondingdust load predicted by the DREAM model.A dust layer was observed at altitudes between 4 and 6 km at 12:00 UTC, and at descended to lower altitudes later during the measurements.

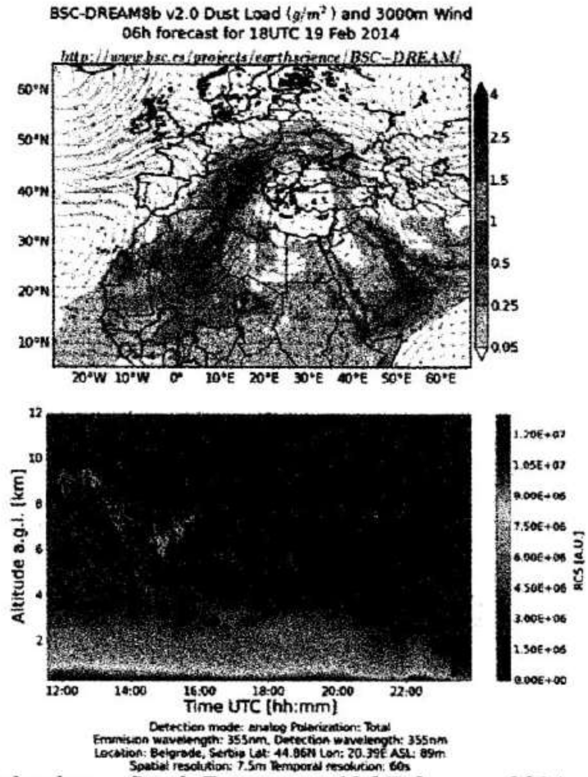


Figure 3.Dust load over South Europe, on 19thFebruary, 2014 estimated by the DREAM model (above) and LIDAR range corrected signal (below)

CONCLUSION

In the field of atmospheric sciences hybrid receptor models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants based on ambient data measured at the monitoring sites.The information provided by receptor models is key to the design of effective mitigation strategies of the pollutant on the local and meso-scale.In this paper PSCF and CWT hybrid receptor models are applied on $PM_{2.5}$ data sets measured in Belgrade. In addition, a case of active ground-based remote LIDAR technique measurement is presented. Comparison of DREAM model prediction of dust intrusion above Belgrade andLIDARmeasurement is presented as well.

ACKNOWLEDGEMENTS
This paper was realized as a part of the project "Studying climate change and its influence on the environment: impacts, adaptation and mitigation" (III43007) financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2015.

REFERENCES

1. AshbaughL.L., Malm W.C., Sadeh W.Z.:*A residence time probability analysis of sulfur concentration at ground canyon national park*, Atmos. Environ, 19, 1263-1270, 1985.
2. Dockery D.W. and Pope III, C.A.:*Critical Review: Health Effects of Fine Particulate Air Pollution: Lines that Connect*, Jour. AirWast. Manage. Ass., 56, 709-742,2006.
3. Draxler R.R. and Rolph G.D.:*HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory)*, NOAA Air Resources Laboratory, Silver Spring, MD,2015,http://ready.arl.noaa.gov/HYSPLIT.php
4. Hopke K.P., *Recent developments in receptor modeling*, Journal of chemometrics, 17 255-265, 2003
5. Hsu Y-K; Holsen M.T. andHopke, K.P.:*Comparison of hybrid receptor models to locate PCB sources in Chicago*. Atmos. Environ., 37, 545-562,2003.
6. IPCC, Climate change 2007: the physical science basis. *Contribution of Working Group I to the Fourth Assessment Report of the IPCC*, 2007.
7. Kneen, M. A. andAnnegarn, H. J.: *Algorithm for fitting XRF, SEM and PIXE X-ray spectra backgrounds, Nuclear Instruments and Methods in Physics Research Section B*, 209-213, 1996.
8. Nickovic S., Kallos G., Papadopoulos A., Kakaliagou O.:*A model for prediction of desert dust cycle in the atmosphere*, J. Geophys. Res. 106, 18 113-18 129, 2001.
9. Nicolae D. and TalianuC.:*Atmospheric LIDAR and retrieval of aerosol optical characteristics*, Book Chapter in Recent Advances in Atmospheric LIDARS, INOE Publishing House, 2010.
10. Perez C., Nickovic S., Baldasano J. M., Sicard M., Rocadenbosch F., Cachorro V. E., *A long Saharan dust event over the western Mediterranean: LIDAR, Sun photometer observations, and regional dust modeling*, Journal of Geophysical Research, 111, D15214, 2006.
11. RemoundakiE.,Papayannis A., Kassomenos P., Mantas E., Kokkalis P. and TsezosM., *Influence of Saharan Dust Transport Events on $PM_{2.5}$ Concentrations and Composition over Athens*, Water Air and Soil Pollution, 224:1373, 2013.
12. Seinfeld J.H. andPandisS.N.,*Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Published by John Wiley &Sons, Inc., Hoboken, New Jersey, 2012.
13. Team 2012, R Core Team: *A language and environment for statistical computing. R Foundation for Statistical Computing*, Vienna, Austria, 2012, http://www.R-project.org/
14. Wang Y.Q., Zhang X.Y., Draxler R., 2008. TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environ. Model. Soft. 24, 938-939.

15. WHO 2003, World Health Organization, *Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide*, Report on a WHO Working Group, Regional Office for Europe; Bonn, Germany, 2003.

Зоран Мијић, Мирјана Перишић, Андреја Стојић, Маја Кузманоски, Лука Илић
Институт за физику, Београд

ПРОЦЕНА ТРАНСПОРТА АТМОСФЕРСКИХ АЕРОСОЛА ПОМОЋУ ДАЉИНСКЕ ДЕТЕКЦИЈЕ И МОДЕЛИРАЊА

Апстракт

На основу концентрација измерених током 2013. године и трајекторија кретања ваздушних маса, извршена је процена потенцијалних извора емисије и главних праваца транспорта честица ($PM_{2.5}$). Кластер анализа трајекторија уназад, које на мерно место долазе на висину 200м изнад земље, коришћена је за одређивање карактеристика и начина кретања ваздушних маса. Функција потенцијалних доприноса и модел трајекторија отежињених концентрацијама употребљени су да се идентификују географске области емисије. Уочен је транспорт честица на регоналном нивоу као и из удаљених извора из северног и североисточног правца, који је повремено у вези са продором афричког песка. Пример лидарских осматрања и комплементарне прогнозе присуства честица сахарског песка *DREAM* моделом је такође приказан у овом раду.

Кључне речи: *PM, Транспорт, PSCF, CWT, LIDAR*

Учешће на пројектима

УНИВЕРЗИТЕТ У БЕОГРАДУ
ИНСТИТУТ ЗА ФИЗИКУ БЕОГРАД
Прегревица 118, 11080 Земун - Београд, Србија
Телефон: +381 11 3713000, Факс: +381 11 3162190, www.ipb.ac.rs
ПИБ: 100105980, Матични број: 07018029, Текући рачун: 205-66984-23

РЕПУБЛИКА СРБИЈА УНИВЕРЗИТЕТ У БЕОГРАДУ ИНСТИТУТ ЗА ФИЗИКУ
Орг. бр. 1007/1
20-07-2017 20 год.

Београд, 20. 07. 2017.

Др Братислав Маринковић
Национални COST координатор
Институт за физику у Београду
Универзитет у Београду
Телофон: +381 11 316-0882
E-mail: ncc-serbia@ipb.ac.rs

Проф. др Виктор Недовић
Помоћник министра за међународну сарадњу и европске интеграције
Немањина 22-26, Београд
Телефон: +381 11 265-7655

Предмет: Молба за укључење истраживача са Института за физику у Београду, Универзитета у Београду у COST акцију CA16202 под називом: *InDust – International Network to Encourage the Use of Monitoring and Forecasting Dust Product*.

Молимо вас, као националног координатора COST-а, да подржите укључивање истраживача из Института за физику у Београду у COST акцију CA16202 *InDust – International Network to Encourage the Use of Monitoring and Forecasting Dust Product*. Такође вас молимо да за заменика члана Management Committee-ја именујете:

Др Зорана Мијића
Виши научни сарадник
Институт за физику у Београду
Лабораторија за физику животне средине
11080 Београд, Прегревица 118, Србија
mailto: zoran.mijic@ipb.ac.rs
http://www.envpl.ipb.ac.rs/

Од истраживача из Института за физику, поред др Зорана Мијића, предвиђено је учешће др Маје Кузманоски, научног сарадника, др Андреје Стојића, научног сарадника, др Мирјане Перишић, истраживача сарадника и Луке Илића, истраживача сарадника.

Истраживања групе из Института за физику се ослањају на пројекат интегралних индердисциплинарних истраживања ИИИ43007 "Истраживање климатских промена и њиховог утицаја на животну средину-праћење утицаја, адаптација и ублажавање". Истраживања у оквиру COST акције CA16202 су компатибилна са истраживањима у Институту за физику у Београду.

Циљ ове акције је успостављање мреже истраживача са различитим експертизама ради бољег разумевања атмосферског процеса транспорта честица песка и њихове улоге у климатском систему, као и интеграција и координација постојећих сателитских и *in-situ* капацитета за осматрања са посебним акцентом на асимилацију података и побољшање прогнозе модела. Учешће наших истраживача је виђено кроз сарадњу две групе, групе физичара која има екпертизу мерења и даљинске детекције атмосферских аеросола помоћу лидар система, и групе метеоролога са експертизом у нумеричком моделирању транспорта честица песка и валидацији модела.

Са поштовањем,

Др Александар Богојевић
директор Института за физику у Београду

РЕПУБЛИКА СРБИЈА УНИВЕРЗИТЕТ У БЕОГРАДУ ИНСТИТУТ ЗА ФИЗИКУ

УНИВЕРЗИТЕТ У БЕОГРАДУ
ЕЛЕКТРОТЕХНИЧКИ ФАКУЛТЕТ
Број 2383
29 OCT 2018 20 год.
БЕОГРАД

УНИВЕРЗИТЕТ У БЕОГРАДУ
ИНСТИТУТ ЗА ФИЗИКУ | БЕОГРАД
ИНСТИТУТ ОД НАЦИОНАЛНОГ ЗНАЧАЈА ЗА РЕПУБЛИКУ СРБИЈУ

Прегревица 118, 11080 Земун - Београд, Република Србија
Телефон: +381 11 3713000, Факс: +381 11 3162190, www.ipb.ac.rs
ПИБ: 100105980, Матични број: 07018029, Текући рачун: 205-66984-23

УНИВЕРЗИТЕТ СИНГИДУНУМ
Бр. 1056
29. 10. 2018 год.
БЕОГРАД, Данијелова 32

УГОВОР О ПАРТНЕРСКОЈ САРАДЊИ

Закључен између:

1. **Института за физику у Београду** са седиштем на адреси Прегревица 118, Земун, 11080 Београд, кога заступа директор института др Александар Богојевић (у даљем тексту **Носилац пројекта**),

2. **Електротехничког факултета, Универзитет у Београду** са седиштем на адреси Булевар Краља Александра 73, 11120 Београд, кога заступа декан факултета др Мило Томашевић (у даљем тексту **Партнер на пројекту 1**)

и

3. **Универзитета Сингидунум** са седиштем на адреси Данијелова 32, 11010 Београд, кога заступа председник универзитета др Милован Станишић (у даљем тексту **Партнер на пројекту 2**).

ПРЕДМЕТ УГОВОРА

Члан 1.

Предмет овог Уговора о партнерској сарадњи (у даљем тексту **Уговор**) је дефинисање уговорних обавеза и утврђивање определеног износа средстава у буџету сваке уговорне стране на пројекту **„Мапирање извора токсичних, мутагених и канцерогених испарљивих органских једињења на територији Града Београда“** за који је носилац пројекта добио средства на *Јавном конкурсу за доделу средстава Зеленог фонда за подстицање образовних истраживачких и развојних студија и пројеката у области заштите животне средине у 2018. години* (у даљем тексту **Јавни конкурс**), који је расписало Министарство заштите животне средине Републике Србије (у даљем тексту **Министарство**).

Члан 2.

На основу Одлуке број 401-00-698/3/18-05 о утврђивању коначне ранг листе студија и пројеката за суфинансирање из средстава Зеленог фонда у оквиру Јавног конкурса, Носиоцу пројекта су додељена средства у износу од [redacted] ([redacted] РСД.

Члан 3.

Руководилац пројекта испред Носиоца пројекта је научни сарадник др Андреја Стојић, (чланови тима Носиоца пројекта су: др Мирјана Перишић, др Гордана Вуковић и др Зоран Мијић; чланови тима Партнера на пројекту 1 су: др Александар Нешковић, др Горан Марковић и др Милан Чабаркапа; чланови тима Партнера на пројекту 2 су др Светлана Станишић и др Драган Марковић).

ЦИЉЕВИ САРАДЊЕ

Члан 4.

Током реализације пројекта за који је обезбеђено суфинансирање из средстава Зеленог фонда за 2018. годину, Носилац пројекта и Партнери на пројекту ће извршити развој и примену јединствене методологија за мапирање и карактеризацију извора токсичних, мутагених и канцерогених једињења у ваздуху на основу постојеће базе података концентрација и метеоролошких параметара са аутоматске мониторинг станице урбаног типа у Београду.

Резултати пројекта ће обезбедити:

- интерактивне мапе загађења бензеном, толуеном и ксиленима у делу урбане зоне Београда;
- карактеризацију доминантних и појединачних извора загађујућих супстанци у блиским и удаљеним областима, које нису покривене станицама за мониторинг;
- развој иновативне интегрисане методологије за прогнозу просторне и временске динамике загађујућих супстанци, засноване на алгоритмима вештачке интелигенције имплементиране кроз методе машинског учења;
- истраживање утицаја фактора животне средине на квалитет ваздуха у урбаном окружењу;
- боље сагледавање и разумевање проблема загађења ваздуха на фундаменталном нивоу.

Члан 5.

Носилац пројекта је обавезан да у складу са Захтевом за доделу средстава на Јавном конкурсу:

- координира свим пројектним активностима;
- врши усклађивање активности тимова партнерских институција;
- учествује са Партнерима у развоју иновативне методологије за мапирање, карактеризацију и прогнозу извора токсичних, мутагених и канцерогених једињења у ваздуху;
- креира интернет страну на којој ће бити приказани резултати пројекта;
- заједно са Партнерима на пројекту и ангажованим спољним сарадницима ради на дисеминацији резултата пројекта и информисању јавности.

Члан 14.

Уговорне стране могу једнострано раскинути овај Уговор услед неиспуњења уговорних обавеза једне од уговорних страна или уколико наступе такве околности које доводе уговорну страну у неравноправан положај и које битно повређују интересе уговорне стране без њене кривице, са отказним роком од 10 (десет) дана од дана достављања писменог захтева о раскиду Уговора.

Члан 15.

У случају раскида Уговора послови и активности чија је реализација у току, морају се завршити у договореним роковима и захтеваним квалитетом.

Члан 16.

Уговорне стране су сагласне да спорове који би могли да настану у току реализације обавеза решавају споразумно.

У случају спора надлежан је суд у Београду.

Члан 17.

Овај Уговор је сачињен у 7 (седам) истоветних примерака, од којих свака уговорна страна задржава по 2 (два) примерка и 1 (један) Министарсво заштите животне средине Републике Србије.

У Београду, 29. oктобар 2018. године

Институт за физику у Београду,
Универзитет у Београду

ДИРЕКТОР

Др Александар Богојевић, научни саветник

01 1582/1
29. 10. 2018

Електротехнички факултет,
Универзитет у Београду

ДЕКАН

Др Мило Томашевић, редовни проф.

Универзитет Сингидунум, Београд

ПРЕДСЕДНИК

Др Милован Станишић, редовни проф.

Table of Contents

List of Tables

List of Figures

4 MEMBERS OF THE CONSORTIUM

4.1 PARTICIPANTS (APPLICANTS)

The GEO-CRADLE consortium brings together 19 partners representing leading research institutes and universities, highly-esteemed international associations and service providers with a strong regional presence, combining a strong background in GEO-related coordination activities with proven excellence in the field of Earth Observation. The consortium capabilities relevant for GEO-CRADLE are summarized in the following table.

Table 12: GEO-CRADLE capability matrix

Skills / Partner	Proven scientific excellence and expertise in relation to the global challenges addressed by GEO and Copernicus	Strong international and/or regional engagement promoting the vision of GEO and Copernicus for the uptake of EO services and applications	Extensive experience from coordination of and/or involvement in GEO, GEOSS and Copernicus-related projects	Solid experience in maintaining, operating and integrating high-performance, large coverage infrastructures	Strong representation and links with EO stakeholders across the whole value chain (scientific community, service and data providers, end-users and decision makers)
NOA	XXX	XXX	XX	XXX	XXX
IBEC	XXX	XXX	XX	XX	XXX
CEDARE	XX	XXX	X		XXX
CERT	X	XX	XX	X	X
TAU	XX	X	XX	X	XX
CUT	XX			XX	X
UZAY	XXX	X	XXX	XXX	XX
SRTI	X				X
INOE	X			XXX	XX
USCM	X		XX		XX
INCA	X				XX
IPB	X			XX	X
CIMA	XXX	XX	XX	X	XX
AOA	XXX	XX	XX	X	X
INS	XXX	XX	XXX		XX
EARSC	XXX	XXX	XX		XXX
EURISY	XXX	XXX	X		XXX
EGS	XX	XXX	XX	XXX	XX
PMOD/WRC	XX			XXX	X

The profiles of the companies and organisations involved in the project are provided hereafter. Additional information is provided in the Annexes.

The Institute of Physics Belgrade (IPB) http://www.ipb.ac.rs/index.php/en/ currently employs 120 senior researchers from which 80 are doctoral and post-doctoral students. IPB researchers make up 1% of Serbia's research sector, producing roughly 10% of the country's scientific output. IPB leads Serbian participation in international projects and collaborations. The majority of these international collaborations are within the European Research Area (ERA). IPB covers an expertise various research areas, organizing the scientific activities through different laboratories.
The **Environmental Physics Laboratory (EPL)** participates in this proposal as a partner. The activities of the EPL (http://www.envpl.ipb.ac.rs/) include fundamental and applied studies related to atmospheric processes, transport and transformation of pollutants (particulate matter and gaseous species) and their impact on environment. The Laboratory staff especially has a leading role in atmospheric, aerosol and hydrology modelling. The Institute of Physics is a partner of the South East European Virtual Climate Change Center – SEEVCCC (www.seevccc.rs/) in which it participates in the implementation of the regional earth modeling studies, focused to the aerosol impacts on weather, climate and environment, including: a regional Earth Modelling System (EMS) by integrating the modelling components for the atmosphere, aerosol, ocean, hydrology and soil; implementation of regional climate models for seasonal and climate assessment. In addition, IPB has a high level expertise in the following observations: suspended particulate matter, PM10 (< 10 micrometers in diameter) and PM2.5 (< 2.5 micrometers in diameter); ozone and VOCs (volatile organic compounds) concentration; trace metals and other elements content in PM10 and PM2.5, vegetation, soil and atmospheric bulk deposition; plant biomonitoring (tree leaves, moss) of the trace elements atmospheric deposition; natural Pb isotopes in deciduous tree leaves for atmospheric Pb source identification; active moss biomonitoring of trace element distribution in canyon streets, tunnels and public garages using moss bags; source apportionment using receptor models; active ground-based lidar remote sensing of atmospheric aerosols.
Concerning its modelling expertise, IPL/IPB finally has a human capacity with high skills in the regional climate change studies done through its contribution through SEEVCCC. Here, development activities are mostly related to the numerical modeling of the Earth system components (coupling the atmosphere, ocean, aerosol, soil, hydrology Earth systems), and their application in agriculture, forestry, energy sector, and other economy components. The earth modeling is driven by the NCEP/NMM atmospheric model developed used by the US Weather Service for its regional operation weather predictions. Use of NMM is realized through a bilateral agreement between SEEVCC and NCEP. The climate regional system to which EPL/IPB contribute through SEEVCCC provides the following climate monitoring functions: every month regional long range forecast for 7 months: dynamical downscaling ECMWF 41 ensemble with Regional Climate Model RCM-SEEVCC. Occasionally, IPCC-type scenarios are done with the RCM to assess decadal climate assessments. The scenarios outputs are available for the wider Euro-Mediterranean region, including North Africa.
In the *observational monitoring,* EPL/IPB has long-term skills in use of lidar technology. The newest lidar equipment installed in 2014, provided EPL/IPB to perform aerosol measurements at its site and the observations are used to study variability of aerosol loading and to characterize vertical distribution of these aerosol properties over Belgrade. Particular focus is given to measurements during Saharan dust intrusions and validation of outputs of the DREAM dust model using lidar measurements. To increase performance of the DREAM model forecasts, techniques used for atmospheric data assimilation in numerical weather prediction systems will be applied for assimilation of LIDAR observations of aerosol parameters into our modeling system.

Contributions of IPB to GEO/GEOSS:

- A EPL/IPB staff member is a member of the Steering committee of the GEO/WMO/WHO project *The Meningitis Environmental Risk Information Technologies* (MERIT). He is also the architect of the WMO SDS-WAS project supported by GEO and collaborating in the GEO health-aerosol tasks.
- Two members of the EPL/IPB team are members (one is Chair) of the Regional Steering Group for N. Africa – Europe – Middle East.
- A EPL/IPB staff member is member of the GEIA: Global Emissions InitiAtive Steering Committee. GEIA and Earth Observing System of Systems (GEOSS), cooperate on the interoperability between two in using the pollution emission data.
- A EPL/IPB staff is a Member, Advisory Board, EU project: Aerosol, Clouds, and Trace Gases Research Infrastructure (ACTRIS), also a Member, Scientific Advisory Committee, EU project: Building Capacity for a

Centre of Excellence for EO-based monitoring of Natural Disasters (BEYOND).

Contributions of IPB to international (or national) initiatives and networks:

- EPL/IPB is member of the WMO SDS-WAS initiative.
- EPL/IPB is associate member of: the EARLINET lidar network (***http://earlinet.org/***) and the associate ACTRIS atmospheric network (***http://www.actris.net/***).

Role in GEO-CRADLE

IPB contributes to several tasks of GEO-CRADLE. IPB will lead **T2.3** and contribute to **T2.4, T3.1, T4.1, T4.2, T6.2** and **T6.3.**

Capabilities Matching GEO-CRADLE Tasks

- Operational regional dust forecast facilities based on DREAM model; participation in the WMO SDS-WAS project dust model intercomparison initiative.
- Stand-by emergency system for volcano ash transport predictions.
- Stand-by regional modelling system for prediction of pollen transport; participation in a NASA funded pollen transport project.
- Near-real time system for hydrology flash-flood predictions.
- Operating lidar measurements in Belgrade; associate partner in ACTRIS and EARLINET projects.

Short CVs

<table>
<tr><td>Slobodan Nickovic (male)
IPB

Senior Researcher, PhD</td><td>Role in GEO-CRADLE: Primarily Responsible for carrying out IPB's work, Leader of T2.3, and contributor across the other activities carried out by IPB.
• PhD in meteorology from the University of Belgrade.
• Adjunct Professor at University of Arizona.
• Responsible at IPB for conducting the atmospheric, aerosol, and hydrology modelling including aerosol model transport developments, dust mineralogy, and impacts of aerosol on the climate and environment.
• Coordination and/or participation in more 30 international scientific/technology projects, including those funded by EU, FAO, and NASA.
• Senior advisor in the Republic Hydrometeorological Service of Serbia.
• Participation in the National Project of the Serbian Ministry for Education and Science "Research of climate changes and their impact on the environment: monitoring, adaptation and mitigation".
• Developed or contributed to developments of original modelling systems and/or numerical methods such as Dust Regional Atmospheric model (DREAM) and Hydrology Prognostic Model (HYPROM).
• Former scientific officer in the World Meteorological Organization (WMO) (2005-2013), and the architect of the WMO Sand and Dust Warning Advisory and Assessment System.
• Author of more than 100 peer review scientific articles, with more than 2500 article citations.</td></tr>
<tr><td>Goran Pejanovic (male)
IPB</td><td>Role in GEO-CRADLE: Contributor across the activities carried out by IPB.
• Coordinator of the operational implementation of the DREAM dust model.
• Conductor and architect of the seasonal weather forecasts and climate assessments within the the South East European Virtual Climate Change Center – SEEVCCC network (www.seevccc.rs).</td></tr>
</table>

	• Member of the Working group of the WMO Sand and Dust Warning Advisory and Assessment System. • Participation in more than 10 international scientific/technology projects, including those funded by EU and NASA. • Contributed to developments of the Hydrology Prognostic Model (HYPROM). • Author of 15 peer review scientific articles.
Vladimir Djurdjevic (male) **IPB**  **Senior Researcher, PhD**	**Role in GEO-CRADLE: Contributor across the activities carried out by IPB.** • PhD in meteorology from the University of Belgrade. • Assistant Professor in the University of Belgrade. • Coordination and/or participation in more then 20 international/national projects, including those funded by EU, GEF, and NSF. • Research and developments in regional climate modelling and climate change impacts and vulnerability. • External associate in the South East European Virtual Climate Change Center, participating in climate change scenarios downscaling, operational system for regional seasonal forecast, system for medium range global forecast with NMMB model. • Main contributor to the development of coupled regional climate model EBU-POM. • Contributor as an expert to preparation of the vulnerability and adaptation chapter in the National communication to the UNFCCC for Serbia, Bosnia and Herzegovina and Montenegro. • Participation in the Med-CORDEX initiative. • Author of 5 book chapters and 16 peer review scientific articles, with more than 150 article citations.
Zoran Mijic (male) **IPB**  **Assistant Research Professor, PhD**	**Role in GEO-CRADLE: Contributor across the activities carried out by IPB.** • PhD in Physics. • Assistant Research Professor at IPB. • Responsible for the operation of ground based lidar system operating in Serbia, hosted by IPB. • PI of Belgrade lidar station within EARLINET. • Participation in several EU and bilateral projects related to atmospheric research. • Representative of IPB as Associated Partner in the ACTRIS Project (FP7-Infrastructures-2010-1). • Co-leader of national project Investigation of Climate Change and its Influences on Environment Monitoring: the Influences, Adaptations, and Offsets. • Experience in statistical modeling in atmospheric physics, multivariate receptor modeling, laser remote sensing, mass spectrometry. • 12 papers in peer review journals, more than 40 papers in conference proceedings, 6 book chapters and numerous technical reports.
Maja Kuzmanoski (female) **IPB**  **Assistant Research Professor, PhD**	**Role in GEO-CRADLE: Contributor across the activities carried out by IPB.** • PhD in Atmospheric Physics from the University of New South Wales, Sydney, Australia. • Assistant Research Professor at IPB. • Participation in the National Project of the Serbian Ministry for Education and Science "Research of climate changes and their impact on the environment: monitoring, adaptation and mitigation". • Research topics: characterization of aerosol optical properties, through modeling and remote sensing studies, and their radiative effects. • 12 publications in peer-reviewed journals and international conference peer-reviewed proceedings, 2 book chapters.

Luka Ilic (male) **IPB**  **Research Assistant, PhD student**	**Role in GEO-CRADLE: Contributor across the activities carried out by IPB.** • PhD student of meteorology at the University of Belgrade. • Research Assistant at IPB. • DREAM model simulations of atmospheric transport of Saharan dust and ground based LIDAR remote sensing of aerosols. Regional dust re-analysis, studies related to particular dust cases/events and comparison of modeled and observed lidar profiles of dust. • Participation in the SEE-GRID-SCI FP7 project – porting of multi model, multi analysis numerical weather prediction system to a GRID infrastructure. • Development of MOS methodology for wind power site assessment and wind forecasts. • More than 5 years of experience in private sector in operational numerical weather forecasting.
Andreja Stojić (male) **IPB**  **Research Assistant, PhD student**	**Role in GEO-CRADLE: Contributor across the activities carried out by IPB.** • PhD student at the Faculty of Physics, University of Belgrade. • Research Assistant at IPB. • Proton-transfer-reaction mass spectrometry (PTR-MS) and air pollution research. Volatile organic compounds (VOC) and other gaseous pollutants research, aerosol research, source apportionment, VOC and PM10 transport analysis. • Participation in two EU projects and five national (interdisciplinary, fundamental and technological) projects. • More than 7 years of experience.

RELEVANT PROJECTS

IPB 01 – DRIHM - Distributed Research Infrastructure for Hydro-Meteorology; Contract No: RI-283568; Project type: CP-CSA

Client	Volume	Period
European Commission	4.809.938€	2011-2015

Relevance to GEO-CRADLE

- Fostering the development of new hydro-meteorological research (HMR) models.
- Generating HM observational archives for the study of severe hydro-meteorological events.
- Applying advanced integrated meteorological and hydrological models to improve the accuracy of flood predictions.
- Networking of HMS organizations in the SEE region to avoid overlapping of human and technical resources in activities for HM risk reduction.

Description

Context & objectives

The DRIHM project is a European initiative running from 1st September 2011 to 28th February 2015 aiming at providing an open, fully integrated workflow platform for predicting, managing and mitigating the risks related to extreme weather phenomena.

The objectives of DRIHM are to lead the definition of a common long-term strategy, to foster the development of new HMR models and observational archives for the study of severe hydro-meteorological events, to promote the execution and analysis of high-end simulations, and to support the dissemination of predictive models as decision analysis tools. DRIHM combines the European expertise in HMR, in Grid and High Performance Computing (HPC). Joint research activities will improve the efficient use of the European e-Infrastructures, notably Grid and HPC, for HMR modeling and observational databases, model evaluation tool sets and access to HMR model results. Networking activities will disseminate DRIHM results at the European and global levels in order to increase the cohesion of European and possibly worldwide HMR communities and increase the awareness of ICT potential for HMR. Service activities will deploy the end-to-end DRIHM services and tools in support of HMR networks and virtual organizations on top of the existing European e-Infrastructures.

DRIHM intends to develop a prototype e-Science environment to facilitate this collaboration and provide end-to-end HMR services (models, datasets and post-processing tools) at the European level, with the ability to expand to global scale. The objectives of DRIHM are to lead the definition of a common long-term strategy, to foster the development of new HMR models and observational archives for the study of severe hydrometeorological events, to promote the execution and analysis of high-end simulations, and to support the dissemination of predictive models as decision analysis tools.

DRIHM combines the European expertise in HMR, in Grid and High Performance Computing (HPC). Joint research activities will improve the efficient use of the European e-Infrastructures, notably Grid and HPC, for HMR modeling and observational databases, model evaluation tool sets and access to HMR model results. Networking activities will disseminate DRIHM results at the European and global levels in order to increase the cohesion of European and possibly worldwide HMR communities and increase the awareness of ICT potential for HMR. Service activities will deploy the end-to-end DRIHM services and tools in support of HMR networks and virtual organizations on top of the existing European e-Infrastructures.

IPB 02 – OrientGate - A network for the integration of climate knowledge into policy and planning.
Funded by the EU South East Europe Transnational Cooperation Programme

Client	Volume	Period
European Commission		2012-2015

Relevance to GEO-CRADLE

- Developing transnational partnerships in climate research and services.
- Improving territorial, economic and social integration process in reducing climate risks.
- Contribute, through networking, to cohesion, stability and competitiveness of the region in the climate adaptation.

Description

Context & objectives

The OrientGate project is made to foster concerted and coordinated climate adaptation actions across the SEE region. The project will explore climate risks faced by coastal, rural and urban communities; contribute to a better understanding of the impact of climate variability and change on water regimes, forests and agro-ecosystems; and analyse specific adaptation needs in the hydroelectricity, agro-alimentary and tourism sectors. The principal scope of the project is to convey the up-to-date climate knowledge to policy makers who may best benefit from it, that is urban planers, nature protection authorities, regional and local development agencies, territorial and public works authorities. The principal project results include six pilot studies of specific climate adaptation exercises, a data platform connected to the EU Clearinghouse on Climate Adaptation, capacity enhancing seminars and workshops, working partnership among the hydro-meteorological offices of the SEE countries.

The main objective of the project is to communicate up-to-date climate knowledge for the benefit of policy makers, including urban planners, nature protection authorities, regional and local development agencies, and territorial and public works authorities.

Partner Countries: Italy, Austria, Croatia, Bosnia and Herzegovina, Serbia, Montenegro, Albania, the former Yugoslav Republic of Macedonia, Greece, Bulgaria, Romania, and Chech Republic.

IPB 03 – SEERISK - Joint Disaster Management risk assessment and preparedness in the Danube macro-region

Client	Volume	Period
South East Europe Transnational Cooperation Programme	1,974,605.16 EUR	2012-2014

Relevance to GEO-CRADLE

- Developing and testing a Common Risk Assessment Methodology for the SEE.
- Enhancement of joint preparedness in order to strengthen awareness and efficiency of action in emergencies caused by climate change.
- To formulate common methodology for the assessment of natural hazards.
- Reveal the similarities and distinctions between the institutional framework of risk assessment and disaster management.
- Put in local practice the European Commission risk assessment guidelines.
- Reveal the gap between risk experts and communities' understanding of climate change.
- Close gap between risk exposure and preparedness.

Description

Context & objectives

The main purpose of this project is to improve coherence and consistency among risk assessments undertaken by the countries at national and local level, and especially in case of disasters intensified by climate change. The project builds on the EU Council conclusions on "Further Developing Risk Assessment for Disaster Management within the European Union" adopted in 2011, that aims for a common approach and harmonisation on the prevention of natural and man-made disasters setting out an overall disaster prevention framework. The EC is called to prepare this cross-sectoral overview of the major natural and man-made risks taking into account, where possible, the future impact of climate change and the need for climate mitigation.

SEERisk is therefore established to test and adapt the EC guildelines to selected pilot areas in the SEE region, focusing on two main activities: risk assessment and the enhancement of joint preparedness in order to strengthen awareness and efficiency of action in emergencies caused by climate change.

Partner Countries: Austria, Bosnia and Herzegovina, Bulgaria, Hungary, Romania, Serbia, Slovakia.

IPB 04 – CARPATCLIM - Climate of the Carpathian Region

Client	Volume	Period
South East Europe Transnational Cooperation Programme	1,974,605.16 EUR	2012-2014

Relevance to GEO-CRADLE

- Development of technologies, international co operations and environmental management require climatological databases covering large area.
- Homogenizing measuring networks, instruments, data management tools and data quality control methods for performing climatological studies.
- Improving the availability and accessibility of a homogeneous and spatially representative time series of climatological data.
- Ensuring Carpathian countries data harmonization with special emphasis on across-country harmonization and production of gridded climatologies per country.

• Developing a Climate Atlas as the basis for climate assessment.
Description
Context & objectives The development of technologies, international co operations and environmental management require climatological databases covering large area. It causes problems especially in smaller countries, because the national (hydro)meteorological services have different measuring networks, instruments, data management tools and data quality control methods. These differences could lead to inhomogeneities in the climatological fields and they could bias the results. The main aim of the project is to improve the basis of climate data in the Carpathian Region for applied regional climatological studies such as a Climate Atlas and/or drought monitoring, to investigate the fine temporal and spatial structure of the climate in the Carpathian Mountains and the Carpathian basin with unified methods. Therefore, a freely available, high resolution gridded database would be produced for the Larger Carpathian Region (LCR). Partner Countries: Italy, Hungary, Croatia, Ukraine, JRC, Austria, Romania, Serbia, Poland, Slovakia.

IPB 05 – A series of FP7 SEE-GRID based projects (SEE-GRID-2, SEE-GRID-SCI, HP-SEE)

Client	Volume	Period
Relevance to GEO-CRADLE		
• Providing computer resources to support extensive GEO-modelling activities in the SEE region, which are highly demanding in terms of processing power. • Sharing computing and data resources across various domains. • Setting up e-Infrastructures in South East European region.		
Description		
Context & objectives The establishment of collaborative models for use of computing and data resources across various domains all over Europe and worldwide is currently being pursued through several e-Infrastructure efforts. In this context, the SEE-GRID regional initiatives has demonstrated that a geographically-independent, common-pool of computing resources can be of substantial scientific value to a widely distributed, less-resourced region like South-East Europe (SEE). SEE-GRID-SCI infrastructure was used as a HPC resource for numerical weather models runs which are highly demanding in terms CPU needs. Dozens of ensemble runs were distributed across the Grid to make use of its resources. This provided the necessary CPU power to reduce the time needed to produce ensemble forecast outputs in operational forecasting environment. SEE-GRID projects have objective to contribute to the regional cooperation and stability, in order to demonstrate the importance of collaborative efforts in science and technology areas like e-Infrastructures, and help add one more element in the continuing EU efforts to ease the SEE digital divide and aid the integration of the region with the rest of the continent.		

RELEVANT PUBLICATIONS

- **Nickovic, S., G. Pejanovic, V. Djurdjevic, J. Roskar, and M. Vujadinovic** (2010), HYPROM hydrology surface-runoff prognostic model, Water Resour. Res., 46, W11506, doi: 10.1029/2010WR009195.
- **Nickovic, S., G. Kallos, A. Papadopoulos, O. Kakaliagou,** 2001: A model for prediction of desert dust cycle in the atmosphere J. Geophys. Res. 106, 18113-18130.
- **Ruml M, Vukovic A, Vujadinovic M, Djurdjevic V, Rankovic-Vasic Z, Atanackovic Z, Sivcev B, Markovic N, Matijasevic S, Petrovic N,** 2012, On the use of regional climate models: Implications of climate change for viticulture in Serbia, Agric. Forest. Meteorol. 158-159, 53-62, doi: j.agrformet.2012.02.004.

УНИВЕРЗИТЕТ У БЕОГРАДУ
ИНСТИТУТ ЗА ФИЗИКУ БЕОГРАД
ИНСТИТУТ ОД НАЦИОНАЛНОГ ЗНАЧАЈА ЗА РЕПУБЛИКУ СРБИЈУ

Прегревица 118, 11080 Земун - Београд, Република Србија
Телефон: +381 11 3713000, Факс: +381 11 3162190, www.ipb.ac.rs
ПИБ: 100105980, Матични број: 07018029, Текући рачун: 205-66984-23

УНИВЕРЗИТЕТ У БЕОГРАДУ ИНСТИТУТ ЗА ФИЗИКУ БЕОГРАД
ИНСТИТУТ ОД НАЦИОНАЛНОГ ЗНАЧАЈА ЗА РЕПУБЛИКУ СРБИЈУ
www.ipb.ac.rs
0801 Број 1929/1
Датум 09. 12. 2019

ПОТВРДА О УЧЕШЋУ У МЕЂУНАРОДНОМ ПРОЈЕКТУ

Овим потврђујем да научни сарадник **др Андреја Стојић** из Лабораторије за физику животне средине Института за физику у Београду, учествује у пројекту NI4OS-Europe (National Initiatives for Open Science in Europe, Grant number 857645), финансираном од стране Европске комисије у оквиру програма Хоризонт 2020. На овом пројекту др Стојић ради на пројектном задатку под називом: EML Comp Techniques Service for highly sophisticated machine learning and interpretation frameworks deployment aimed at delivering analytics solutions.

др Антун Балаж, научни саветник
члан Управног одбора (Project Management Board)
пројекта NI4OS-Europe

УНИВЕРЗИТЕТ У БЕОГРАДУ
ИНСТИТУТ ЗА ФИЗИКУ БЕОГРАД
ИНСТИТУТ ОД НАЦИОНАЛНОГ ЗНАЧАЈА ЗА РЕПУБЛИКУ СРБИЈУ
Прегревица 118, 11080 Земун - Београд, Република Србија
Телефон: +381 11 3713000, Факс: +381 11 3162190, www.ipb.ac.rs
ПИБ: 100105980, Матични број: 07018029, Текући рачун: 205-66984-23

УНИВЕРЗИТЕТ У БЕОГРАДУ
ИНСТИТУТ ЗА ФИЗИКУ БЕОГРАД
ИНСТИТУТ ОД НАЦИОНАЛНОГ ЗНАЧАЈА ЗА РЕПУБЛИКУ СРБИЈУ
www.ipb.ac.rs
0801 Број 1928/1
Датум 09. 12. 2019

ПОТВРДА О УЧЕШЋУ У МЕЂУНАРОДНОМ ПРОЈЕКТУ

Овим потврђујем да је научни сарадник **др Андреја Стојић** из Лабораторије за физику животне средине Института за физику у Београду, учествовао на пројекту „*ACTRIS-2 - Aerosols, Clouds, and Trace gases Research InfraStructure, Integrated Activities European Union's Horizon 2020 research and innovation programme*" (No 654109).

др Зоран Мијић

контакт особа Института за физику у Београду
у оквиру пројекта *ACTRIS-2*

РЕПУБЛИКА СРБИЈА
ГРАДСКИ ЗАВОД ЗА ЈАВНО ЗДРАВЉЕ, БЕОГРАД
11000 БЕОГРАД, Булевар деспота Стефана 54-а
Централа: 20 78 600 e-mail: info@zdravlje.org.rs www.zdravlje.org.rs
Директор – тел: 32 33 976, факс: 32 27 828 e-mail: direktor@zdravlje.org.rs
Центар за хигијену и хуману екологију
Тел/факс: 32 39 207; 32 35 080; 32 38 230 e-mail: slavisa.mladenovic@zdravlje.org.rs

Жиро рачун: 840 – 627667 – 91
ПИБ 100044907 Матични број 07041152

Датум: 02.12.2019.
Озн: II-8
Број: 6073/2

Предмет: Потврда о учешћу у пројекту„Израда Плана квалитета ваздуха у Београду“

Овим потврђујем да су научни сарадник др **Андреја Стојић,** научни сарадник др **Мирјана Перишић** и виши научни сарадник др **Зоран Мијић** из Лабораторије за физику животне средине Института за физику у Београду, као стручни сарадници учествовали на пројекту „Израда Плана квалитета ваздуха у Београду“, на основу уговора закљученог између ГРАДСКОГ ЗАВОДА ЗА ЈАВНО ЗДРАВЉЕ, БЕОГРАД и ГРАД БЕОГРАД – ГРАДСКА УПРАВА ГРАДА БЕОГРАДА, Секретаријат за заштиту животне средине.

за **Помоћник директора**
за област хигијене и екотоксикологије

Др Славиша Младеновић,
спец.хигијене

1

Награде – сертификат

PROTON TRANSFER REACTION - MASS SPECTROMETRY

HANDS-ON PTR-MS 2019

> Training Certificate

hands-on PTR-MS 2019,
February 2-3, 2019

IONICON hereby certifies that

Andreja Stojic

has participated in a comprehensive PTR-MS training, covering the following subjects:

Theory on
Analytical Mass Spectrometry
PTR-MS, TOF and Related Topics

Practice on
Professional Maintenance Training,
Measurement Set-up, Calibration and
PTR-TOF Instrument Optimization

Innsbruck, February 3, 2019

Dr. Alfons Jordan
Principal Scientist

THE SOLUTION FOR REAL-TIME TRACE GAS ANALYSIS

IONICON

Активност у научним и научно-стручним друштвима

Gmail

Andreja Stojic <[redacted]>

Reviewer Invitation for ENVINT-D-16-00117

1 порука

Yong-Guan Zhu <[redacted]> 06. март 2016. 14:10

Коме: andreja.stojic@ipb.ac.rs

Ms. Ref. No.: [redacted]

Title: [redacted]

Environment International

Dear Dr. Andreja Stojic,

We have received the following manuscript for possible publication in the Journal Environment International:

"[redacted]"

Having looked at the paper myself I feel it is suitable for detailed assessment and your name has been suggested as a possible reviewer.

The review process is extremely important to ensure that scientific quality is maintained. If you would be willing to provide an assessment of this work please let me know promptly.

To view the ABSTRACT, please click on this link:

[redacted]

To view the manuscript, please click on this link:

View Submission

If you are willing to review this manuscript, please click on the link below:

Agree to Review

If you are NOT able to review this manuscript, please click on the link below. We would appreciate receiving suggestions for alternative reviewers:

Decline to Review

Alternatively, you may also register your response by accessing the Elsevier Editorial System for Environment International as a REVIEWER using the logon credentials below:

http://ees.elsevier.com/envint/

Your username is: [redacted]

If you can't remember your password please click the "Send Password" link on the Login page.

If you accept this invitation, I would be very grateful if you would return your review by Mar 27, 2016.

You may submit your comments online at the above URL. There you will find spaces for confidential comments to the editor, comments for the author and a report form to be completed.

To assist you in the reviewing process, I am delighted to offer you full access to Scopus* for 30 days. With Scopus you can search for related articles, references and papers by the same author. You may also use Scopus for your own purposes at any time during the 30-day period. If you already use Scopus at your institute, having this 30 day full access means that you will also be able to access Scopus from home. Access instructions will follow once you have accepted this invitation to review

*Scopus is the world's largest abstract and citation database of research information and quality internet sources.

Thanking you in advance

Your sincerely,

Yong-Guan Zhu
Editor
Environment International

Reviewer Guidelines are now available to help you with your review: http://www.elsevier.com/wps/find/reviewershome.reviewers/reviewersguidelines

****
For any technical queries about using EES, please contact Elsevier Reviewer Support at reviewersupport@elsevier.com

Gmail Andreja Stojic <[redacted]>

Review invitation for ENVPOL_2017_2555

1 порука

Kimberly Hageman (Environmental Pollution) <EviseSupport@elsevier.com> 13. јул 2017. 05:57
Одговор на: [redacted]
Коме: andreja.stojic@ipb.ac.rs

Ref: [redacted]
Title: [redacted]
Journal: Environmental Pollution
Corresponding [redacted]
Co-authors: [redacted]

Dear Dr Stojic,

I would like to invite you to review the above-referenced manuscript. To maintain our journal's high standards we need the best reviewers, and given your expertise in this area I would greatly appreciate your contribution.

I kindly ask you to give this review invitation the same consideration that you would want one of your own manuscripts to receive.

Please find the abstract of the manuscript at the end of this email.

If you have any concerns about potential conflicts of interest, please consult the Editor.

If you are willing to review this manuscript, please click on the link below:
Accept Invitation

If you accept this invitation, I would appreciate your submitting your review within 21 days.

Please submit your review via EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=ENVPOL.

If you cannot review this manuscript, please click on the link below. I would also appreciate your suggestions for alternate reviewers.
Decline

I look forward to receiving your response.

Kind regards,

Kimberly Hageman
Associate Editor
Environmental Pollution

Abstract:

[redacted]

[redacted]

Free access to ScienceDirect and Scopus

To assist you with reviewing this manuscript it is our pleasure to offer you 30 days of free access to ScienceDirect and Scopus. Your complimentary access can be accessed at any time within 6 months of the day you accept this review invitation and will ensure that you can access ScienceDirect and Scopus both from home and via your institute. Just click on the 'Go to Scopus' tab on your main menu.

Have questions or need assistance?

For more information on the review process, please visit the Reviewer Support site.

For further assistance, please visit our Customer Support site. Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about EVISE® via interactive tutorials. You can also talk 24/5 to our customer support team by phone and 24/7 by live chat and email.

Gmail Andreja Stojic <[redacted]>

Review invitation for ENVPOL_2018_1034

1 порука

Maria Cristina Fossi (Environmental Pollution) <EviseSupport@elsevier.com> 02. мај 2018. 16:01
Одговор на: [redacted]
Коме: andreja.stojic@ipb.ac.rs

Ref: ENVPOL_2018_1034
Title: [redacted]
Journal: Environmental Pollution
Corresponding Author: [redacted]
Co-authors: [redacted]

Dear Dr Stojic,

I would like to invite you to review the above-referenced manuscript. To maintain our journal's high standards we need the best reviewers, and given your expertise in this area I would greatly appreciate your contribution.

I kindly ask you to give this review invitation the same consideration that you would want one of your own manuscripts to receive.

Please note: Reviews are subject to a confidentiality policy.

Please find the abstract of the manuscript at the end of this email.

If you have any concerns about potential conflicts of interest, please consult the Editor.

If you are willing to review this manuscript, please click on the link below:
Accept Invitation

If you accept this invitation, I would appreciate your submitting your review within 21 days.

Please submit your review via EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=ENVPOL.

If you cannot review this manuscript, please click on the link below. I would also appreciate your suggestions for alternate reviewers.
Decline

Please also note that authors have been invited to convert their supplementary material into a Data in Brief article (a data description article). You may notice this change alongside the revised manuscript. You do not need to review this, but may need to look at the files in order to confirm that any supporting information you requested is present there.

Please also note that authors have been invited to convert their supplementary material into a MethodsX article (a method description article). You may notice this change alongside the revised manuscript. You do not need to review this, but may need to look at the files in order to confirm that any supporting information you requested is present there.

I look forward to receiving your response.

Kind regards,

Maria Cristina Fossi
Associate Editor
Environmental Pollution

Abstract:

[redacted]

Free access to ScienceDirect and Scopus

To assist you with reviewing this manuscript it is our pleasure to offer you 30 days of free access to ScienceDirect and Scopus. Your complimentary access starts from the day you accept this review invitation and will ensure that you can access ScienceDirect and Scopus both from home and via your institute. Just click on 'Go to Review' and then on the 'Go to Scopus' link under the Useful links section on the My Review tab or click here for more information.

Have questions or need assistance?

For more information on the review process, please visit the Reviewer Support site.

For further assistance, please visit our Customer Support site. Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about EVISE® via interactive tutorials. You can also talk 24/5 to our customer support team by phone and 24/7 by live chat and email.

Gmail **Andreja Stojic <[redacted]>**

Reviewer Invitation for JFUE-D-17-04869R1

1 порука

John Patrick <eesserver@eesmail.elsevier.com> 09. јул 2018. 10:52
Одговор на: John Patrick <[redacted]>
Коме: andreja.stojic@ipb.ac.rs

Fuel
Ref: [redacted]
Title: [redacted]
Authors: [redacted]

Dear Andreja Stojić,

You are invited to review the above-mentioned manuscript that has been submitted for publication in Fuel. The abstract is shown at the end of this e-mail.

Our goal is to provide as rapid a response as possible to our authors. Therefore, please register your response as soon as your schedule allows.

We look forward to receiving your referee report online within 21 days from the day you accept the invite.

If you are willing to review this manuscript, please click on the link below:
[redacted]

After acceptance you will be able to access the full copy of the article to review.

If you are unable, please click on the link below. We would appreciate receiving suggestions for alternative reviewers:
[redacted]

Alternatively, you may register your response by accessing the Elsevier Editorial System for Fuel as a REVIEWER using the login credentials below:
https://ees.elsevier.com/jfue/
Your username is: andreja.stojic@ipb.ac.rs

Note: If you reply by email, please note you may receive an automated reminder before we can register your reply.

If you need to retrieve password details, please go to: http://ees.elsevier.com/jfue/automail_query.asp

Click on 'Reviewer Login' and then "New Invitations"

You may submit your comments online at the above URL. There you will find spaces for confidential comments to the editor, comments for the author and a report form to be completed.

As a reviewer you are entitled to complimentary access to Scopus and ScienceDirect for 30 days. Full instructions and details will be provided upon accepting this invitation to review.

In addition to accessing our subscriber content, you can also use our Open Access content. Read more about Open Access here: http://www.elsevier.com/openaccess
Please also note that authors have been invited to convert their supplementary material into a Data in Brief article (a data description article). You may notice this change alongside the revised manuscript. You do not need to review this, but may need to look at the files in order to confirm that any supporting information you requested is present there.

With kind regards,

Bill Nimmo, PhD, CEng, FEI
Associate Principal Editor
Fuel

Reviewer Guidelines are now available to help you with your review: http://www.elsevier.com/wps/find/reviewershome.reviewers/reviewersguidelines

[redacted]

****

For further assistance, please visit our customer support site at http://help.elsevier.com/app/answers/list/p/7923. Here you can search for solutions on a range of topics, find answers to frequently asked questions and learn more about EES via interactive tutorials. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

Please note: Reviews are subject to a confidentiality policy, http://service.elsevier.com/app/answers/detail/a_id/14156/supporthub/publishing/

Gmail

Andreja Stojic <[redacted]>

Reviewer Invitation for STOTEN-D-19-02335

1 порука

Jose Julio Ortega-Calvo <eesserver@eesmail.elsevier.com> 28. фебруар 2019. 19:24
Одговор на: Jose Julio Ortega-Calvo <[redacted]>
Коме: andreja.stojic@ipb.ac.rs

Dear Andreja Stojić,

We are mindful of the demands on your time, and in light of your considerable expertise in this field we would be pleased if you would consider reviewing for the journal, Science of the Total Environment (STOTEN), the manuscript titled "[redacted]".

The manuscript has already been subject to editorial screening and considered to be of sufficient quality to be sent out for review. If you are unfamiliar with our journal, please visit our website (http://www.journals.elsevier.com/science-of-the-total-environment) and review our Aims and Scope. The Abstract provided by the author is at the end of the email. If you wish to review this manuscript but have any conflicts of interest can you please let me know. Additionally, please remember that peer review is a confidential process, and any information associated with this manuscript should not be discussed or shared with anyone. If you are too busy to review this paper I would appreciate it if you could recommend an alternate reviewer with appropriate expertise.

We would like the review to be completed in no more than 21 days from the date you receive it.

If you are willing to accept this invitation and to review this manuscript, please click on the following link:

[redacted]

If you are not available to review this manuscript, please click on the link below:

[redacted]

To view reviewer PDF: [redacted]

If you must Decline, may I ask you to please use the text box provided online to suggest possible alternative reviewers for this paper.

As a reviewer you are entitled to complimentary access to Scopus and ScienceDirect for 30 days. Full instructions and details will be provided upon accepting this invitation to review.

Please also note that authors have been invited to convert their supplementary material into a Data in Brief article (a data description article). You may notice this change alongside the revised manuscript. You do not need to review this, but may need to look at the files in order to confirm that any supporting information you requested is present there.

With thanks,
Jose Julio Ortega-Calvo
Associate Editor

Science of the Total Environment

Reviewer Guidelines are now available to help you with your review: http://www.elsevier.com/wps/find/reviewershome.reviewers/reviewersguidelines (http://www.elsevier.com/wps/find/reviewershome.reviewers/reviewersguidelines)

ABSTRACT:

[redacted]

[redacted]

For further assistance, please visit our customer support site at http://help.elsevier.com/app/answers/list/p/7923 (http://help.elsevier.com/app/answers/list/p/7923) . Here you can search for solutions on a range of topics, find answers to frequently asked questions and learn more about EES via interactive tutorials. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

Please note: Reviews are subject to a confidentiality policy,

http://service.elsevier.com/app/answers/detail/a_id/14156/supporthub/publishing/

Gmail

Andreja Stojic <[redacted]>

EES-18-3359: Request to Review

1 порука

EES (ELS) <eesserver@eesmail.elsevier.com> 10. новембар 2018. 19:47
Одговор на: "EES (ELS)" <ees2@elsevier.com>
Коме: andreja.stojic@ipb.ac.rs

Ms. No.: EES-18-3359
Title: [redacted]
Corresponding Author: [redacted]
Authors: [redacted]

Dear Dr. Stojic,

Because of your substantial expertise related to the paper listed above, I would like to ask your assistance in determining whether the above-mentioned manuscript is appropriate for publication in Ecotoxicology and Environmental Safety. External reviews are the single most important element in critically evaluating a manuscript and we almost invariably follow the advice of the Reviewers.

The manuscript abstract appears below.

If you are willing to review this manuscript, please click on the link below:
[redacted]

If you are unable, please click on the link below. We would appreciate receiving suggestions for alternative reviewers:
[redacted]

Alternatively, you may register your response by accessing the Elsevier Editorial System for Ecotoxicology and Environmental Safety as a REVIEWER using the login credentials below:

https://ees.elsevier.com/ees/
Your username is: [redacted]
If you need to retrieve password details, please go to: http://ees.elsevier.com/ees/automail_query.asp

NOTE: If this is your first time reviewing for us in the Elsevier Editorial System for Ecotoxicology and Environmental Safety, please update your personal contact information and classifications at:
http://ees.elsevier.com/ees/info_update.asp
Classifications are used in the reviewer selection process, and will ensure that you are only invited to review if the manuscript is in your own field.

We would appreciate it if you could respond to this invitation within 7 days. Once you accept to review this paper, you will find this manuscript in your "Pending Reviews" menu and will be allowed to complete your review online. Please note the invitation will be active for 7 days. If there is no response until 7 days, the invitation will automatically expire.

In order to get a decision to the authors as soon as possible, we ask that reviews be returned to this office within 21 days of your agreement to review. However, we realize that the most qualified reviewers often have many obligations, and since the editor has chosen you specifically based on your expertise, we are willing to work with your schedule. If time constraint should be the only factor in your decision to decline, please reply to this e-mail and let us know when you would otherwise be willing to return a review.

If you are unable to review this manuscript, we would appreciate your suggestions of alternate reviewers (contact information would be helpful).

As a reviewer you are entitled to complimentary access to Scopus and ScienceDirect for 30 days. Full instructions and details will be provided upon accepting this invitation to review.

Please also note that authors have been invited to convert their supplementary material into a Data in Brief article (a data

description article). You may notice this change alongside the revised manuscript. You do not need to review this, but may need to look at the files in order to confirm that any supporting information you requested is present there.
Thank you in advance for your assistance.

Sincerely,

Fernando Barbosa Jr, PhD
Associate Editor

Reviewer Guidelines are now available to help you with your review:http://www.elsevier.com/wps/find/reviewershome.reviewers/reviewersguidelines

Ecotoxicology and Environmental Safety
Elsevier
525 B Street Suite 1900
San Diego, CA 92101-4495, USA
Phone: 619-699-6407
Fax: 619-699-6855
Email: ees2@elsevier.com

Abstract:
[redacted]

****
For further assistance, please visit our customer support site at http://help.elsevier.com/app/answers/list/p/7923 Here you can search for solutions on a range of topics, find answers to frequently asked questions and learn more about EES via interactive tutorials. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

Please note: Reviews are subject to a confidentiality policy,
http://service.elsevier.com/app/answers/detail/a_id/14156/supporthub/publishing/

Gmail

Andreja Stojic <[redacted]>

Review invitation for APR_2019_18

1 порука

Atmospheric Pollution Research <EviseSupport@elsevier.com> 30. јануар 2019. 19:28
Одговор на: apr@elsevier.com
Коме: andreja.stojic@ipb.ac.rs

Ref: [redacted]
Title: [redacted]
Journal: Atmospheric Pollution Research
Corresponding Author: [redacted]
Co-authors: [redacted]

Dear Dr Stojic,

I would like to invite you to review the above-referenced manuscript. To maintain our journal's high standards we need the best reviewers, and given your expertise in this area I would greatly appreciate your contribution.

I kindly ask you to give this review invitation the same consideration that you would want one of your own manuscripts to receive.

Please note: Reviews are subject to a confidentiality policy.

Please find the abstract of the manuscript at the end of this email.

If you have any concerns about potential conflicts of interest, please consult the Editor.

If you are willing to review this manuscript, please click on the link below:
Accept Invitation

If you are NOT able to review this manuscript, please click on the link below. We would appreciate receiving suggestions for alternative reviewers:
Decline

If you accept this invitation, I would appreciate your submitting your review within 21 days.

Please submit your review via EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=APR.

I look forward to receiving your response.

Kind regards,

Mustafa Odabasi
Editor-in-Chief
Atmospheric Pollution Research

Abstract:

[redacted]

[redacted]

Free access to ScienceDirect and Scopus

To assist you with reviewing this manuscript it is our pleasure to offer you 30 days of free access to ScienceDirect and Scopus. Your complimentary access starts from the day you accept this review invitation and will ensure that you can access ScienceDirect and Scopus both from home and via your institute. Just click on 'Go to Review' and then on the 'Go to Scopus' link under the Useful links section on the My Review tab or click here for more information.

Have questions or need assistance?

For more information on the review process, please visit the Reviewer Support site.

For further assistance, please visit our Customer Support site. Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about EVISE® via interactive tutorials. You can also talk 24/5 to our customer support team by phone and 24/7 by live chat and email.

Gmail Andreja Stojic <[redacted]>

Invitation to review BAE-D-19-01309

1 порука

Bert Blocken <eesserver@eesmail.elsevier.com> 29. мај 2019. 17:53
Одговор на: Bert Blocken <[redacted]>
Коме: andreja.stojic@ipb.ac.rs

Ms. Ref. No.: [redacted]

[redacted]

Building and Environment

Dear Andreja M. Stojić,

Given your expertise in this area, I would appreciate your comments on the above paper. I have included the abstract of the manuscript below to provide you with an overview.

If you are unable to act as a reviewer at this time, I would greatly appreciate your suggestions for alternate reviewers.

To accept this invitation, please click here:

[redacted]

To decline this invitation, please click here:

[redacted]

As you are not registered to EES yet, upon accepting this invitation you will be prompted to complete a registration procedure.

I look forward to hearing from you in the near future.

[redacted]

Yours sincerely,

Bert Blocken Civil Engineer, PhD, MSc
Editor
Building and Environment

ABSTRACT:

[redacted]

[redacted]

Reviewer Guidelines are now available to help you with your review:
http://www.elsevier.com/wps/find/reviewershome.reviewers/reviewersguidelines

For further assistance, please visit our customer support site at http://help.elsevier.com/app/answers/list/p/7923 Here you can search for solutions on a range of topics, find answers to frequently asked questions and learn more about EES via interactive tutorials. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

Please note: Reviews are subject to a confidentiality policy,
http://service.elsevier.com/app/answers/detail/a_id/14156/supporthub/publishing/

Subject	**6387508: Review Request**
From	Arkady Serikov <stni@hindawi.com>
To	<andreja.stojic@ipb.ac.rs>
Reply-To	<[redacted]>
Date	2019-11-04 14:29

Dear Dr. Stojic,

An article titled "[redacted]" by [redacted] has been submitted for consideration in Science and Technology of Nuclear Installations. As the Academic Editor handling the manuscript, I would be delighted if you would agree to review it and let me know whether you feel it is suitable for publication.

Please use the following link to view the article's abstract, and respond to the request. Once you have agreed to review, you will be able to download the full article PDF.

[redacted]

If a potential conflict of interest exists between yourself and either the authors or the subject of the manuscript, please decline to handle the manuscript. If a conflict becomes apparent during the review process, please let me know at the earliest possible opportunity. For more information about our conflicts of interest policies, please see: https://www.hindawi.com/ethics/#coi.

If you are able to review the manuscript, I would be grateful if you could submit your report by Monday, November 25, 2019.

With many thanks and best regards,

Arkady Serikov
arkady.serikov@kit.edu

Subject	**[IJERPH] Manuscript ID: [redacted] - Review Request**
From	IJERPH Editorial Office <ijerph@mdpi.com>
Sender	<[redacted]>
To	Andreja Stojić <andreja.stojic@ipb.ac.rs>
Cc	IJERPH Editorial Office <ijerph@mdpi.com>, Cristina Yu <cristina.yu@mdpi.com>
Reply-To	Cristina Yu <[redacted]>
Date	2019-11-22 04:46

Dear Dr. Stojić,

We have received the following manuscript to be considered for publication in International Journal of Environmental Research and Public Health (https://www.mdpi.com/journal/ijerph/) and kindly invite you to provide a review to evaluate its suitability for publication:

Type of manuscript: Article
Title: [redacted]

The abstract is available at the end of this message. Please click on the link below to access the manuscript and review report form, and inform us whether or not you will be able to provide a review.

[redacted]

If you accept this invitation we would appreciate receiving your comments within 1 week. Please let us know if you will need more time. Advice for completing your review can be found at: https://www.mdpi.com/reviewers. We would like to stress that we rely on the critical reviews of external experts to maintain the quality of IJERPH. Along with the authors, we would greatly value your contribution to the peer-review process.

If you are not able to review this manuscript, we kindly ask you to decline by clicking on the above link so that we can continue processing this submission. We would also appreciate any suggestions for alternative expert reviewers.

MDPI partners with Publons (https://publons.com/in/mdpi/) to provide recognition for reviewers. Your credit will appear on Publons after a final decision on the paper and once you have claimed your review on the Publons website. For well-prepared review reports submitted in a timely manner, we also provide APC discount vouchers for publication in any MDPI journal.

Please note that this peer-review request and the contents of the manuscript are highly confidential. You must not distribute the manuscript in part or whole to a third party, including other members of your research group, without explicit permission from the editorial office. You must also disclose if you have a conflict of interest with the content of the manuscript or the authors. We discourage reviewers from recommending citation of their own work when not clearly necessary to improve the quality of the manuscript under review. Please state in your comments to the editor if you recommend citation of your own work and the reason for this recommendation.

IJERPH is one of MDPI's open access journals (available in Web of Science and PubMed, current Impact Factor 2.468). Our aim is to process manuscripts quickly and publish them shortly after peer-review. Some high quality manuscripts have been peer-reviewed and published in less than four weeks from submission.

Thank you very much for your consideration and we look forward to hearing from you.

Kind regards,

Cristina Yu
Assistant Editor, MDPI
Room 701, Jincheng Center
Tongzhou District, Beijing, China
www.mdpi.com

[redacted]

[redacted]

Gmail

Andreja Stojic <andrejastojicepl@gmail.com>

Thank you for reviewing for Atmospheric Environment

1 порука

My Elsevier Reviews Profile <journals@mail.elsevier.com> 27. јануар 2017. 12:13
Одговор на: Elsevier Journals <stjnlsemarketing@elsevier.com>
Коме: andreja.stojic@ipb.ac.rs

Can't see this email properly? **Click here to view an online version**

Thank you for reviewing for *Atmospheric Environment*

>> Access your Reviews Profile

We want to make it easier for reviewers to be recognized for the important contribution they make to Elsevier's and other publishers' journals and so have created a personalized page where, for Elsevier titles you can:

- Track your reviewer status
- Access your annual review history report
- Claim reviewer discounts
- Collect your certificate
- Volunteer to review for more journals

Should you wish to do so, via your personalized profile page to which only you have access, you can also create a public profile which automatically includes your reviews for Elsevier journals and allows you to claim your peer reviews for non-Elsevier journals.

When you take the time to help others improve their papers, you are instrumental in enabling the progress of science, technology and medicine. Our aim is to create a standard way of recording and acknowledging your efforts, providing you with a means to make your contribution more widely visible.

ACCESS YOUR PROFILE

Your Latest Elsevier Title Review:

Atmospheric Environment
October 2016

Based on your contribution, you have been awarded Recognized Reviewer Status. You are awarded this status as you have completed at least one manuscript review in the last two years for *Atmospheric Environment*.

Gmail

Andreja Stojic <[redacted]>

Welcome to AIS3 website

1 порука

AIS3 <ais3@rect.bg.ac.rs> 14. мај 2015. 10:08
Одговор на: infoais3@gmail.com
Коме: andreja.stojic@ipb.ac.rs

Dear AIS3 member,

Thank you for registering with the Association of Italian and Serbian Scientists and Scholars - AIS3. We received your request and our administrator will consider it.

After you receive an e-mail of approval you can log in on the AIS3 web site by accessing the following form.

Your username: [redacted]
Your password: [redacted]

Please fill-in your personal profile for full functionality of your account. You can access your personal data on the following address.

This is an automatically generated e-mail. Please do not reply, for all information you can contact us here.

Yours sincerely,
AIS3

Gmail

Andreja Stojic <andrejastojicepl@gmail.com>

[AIS3 official site] Registration approved

1 порука

AIS3 <ais3@rect.bg.ac.rs> 17. јул 2015. 11:19
Коме: andreja.stojic@ipb.ac.rs

Hi andreja-s,

Your registration for AIS3 web site has now been approved.

You can log in, using your e-mail address and password that you received when registering for our website, at the following URL: http://www.ais3.rs

If you have any questions, or problems, then please do not hesitate to contact us at URL: http://ais3.ac.rs/contact/.

Yours sincerely,
AIS3

Ангажованост у формирању научних кадрова

UNIVERZITET U BEOGRADU
HEMIJSKI FAKULTET

Andrej I. Šoštarić

Mehanizmi uklanjanja lako isparljivih monoaromatičnih ugljovodonika (BTEX) iz ambijentalnog vazduha mokrom depozicijom

doktorska disertacija

Beograd, 2017.

UNIVERSITY OF BELGRADE
FACULTY OF CHEMISTRY

Andrej I. Šoštarić

Mechanisms of scavenging monoaromatic hydrocarbons (BTEX) from ambient air by wet deposition

Doctoral Dissertation

Belgrade, 2017.

Članovi komisije:

____

Dr Ivan Gržetić, mentor
redovni profesor,
Hemijski fakultet, Univerzitet u Beogradu

____

Dr Aleksandar Popović,
redovni profesor,
Hemijski fakultet, Univerzitet u Beogradu

____

Dr Vele Tešević,
vanredni profesor,
Hemijski fakultet, Univerzitet u Beogradu

____

Dr Zoran Mijić,
viši naučni saradnik,
Institut za fiziku, Univerzitet u Beogradu

Datum odbrane: ________________

ZAHVALNICA

Ova doktorska disertacija rađena je na Katedri za primenjenu hemiju Hemijskog fakultetu Univerziteta u Beogradu, u Laboratoriji Centra za humanu ekologiju i ekotoksikologiju Gradskog zavoda za javno Zdravlje, Beograd i u Laboratoriji za fiziku životne sredine Instituta za fiziku Univerziteta u Beogradu.

Posebnu zahvalnost dugujem mentoru, profesoru dr Ivanu Gržetiću, na ukazanom poverenju, dragocenim savetima i bezrezervnoj podršci tokom svih etapa izrade ove doktorske disertacije.

Zahvalnost dugujem svojim kolegama zaposlenim u Centru za humanu ekologiju i ekotoksikologiju Gradskog zavoda za javno Zdravlje, Beograd na pomoći i razumevanju koje su iskazali, pre svega, tokom eksperimentalnih radnji vršenih u okviru ove doktorske disertacije.

Celokupnom kolektivu Laboratorije za fiziku životne sredine Instituta za fiziku Univerziteta u Beogradu, a pre svih, dr Andreji Stojiću zahvaljujem se na nesebičnoj podršci i saradnji u različitim fazama izrade ove doktorske disertacije.

Zahvalnost dugujem dr Svetlani Stanišić Stojić, dr Snežani Bajec i Ljiljani Ađanski Spasić.

Na podršci i interesovanju zahvaljujem se prijateljima.

Konačno, najveću zahvalnost na podršci, razumevanju i iznad svega strpljenju dugujem svojoj porodici.

Beograd, 2017.

Andrej Šoštarić

Show simple item record (/handle/123456789/6555)

Примена хибридних рецепторских модела у анализи квалитета ваздуха и транспорта загађујућих материја у Београду

Application of hybrid receptor models in the analysis of air quality and transport of pollutants in Belgrade

dc.contributor.advisor	Rajšić, Slavica
dc.contributor.other	Belić, Dragoljub
dc.contributor.other	Lazić, Lazar
dc.contributor.other	Stojić, Andreja
dc.creator	Perišić, Mirjana D.
dc.date.accessioned	2016-09-18T07:45:47Z
dc.date.available	2016-09-18T07:45:47Z
dc.date.issued	2016-07-12
dc.identifier.uri	http://eteze.bg.ac.rs/application/showtheses?thesesId=3894
dc.identifier.uri	https://fedorabg.bg.ac.rs/fedora/get/o:13071/bdef:Content/download
dc.identifier.uri	https://fedorabg.bg.ac.rs/fedora/get/o:13166/bdef:Izvestaj/download
dc.identifier.uri	http://vbs.rs/scripts/cobiss?command=DISPLAY&base=70036&RID=48206863
dc.identifier.uri	http://nardus.mpn.gov.rs/123456789/6555

dc.description.abstract | sr

У оквиру дисертације приказани су резултати анализе квалитета ваздуха на подручју града Београда уз посебан акценат на анализу резултата примене хибридних рецепторских модела у циљу одређивања просторне расподеле највероватнијих извора загађења. База података коришћених за анализу обухватала је средње дневне концентрације PM10 (масене концентрације и хемијски састав: As, Cd, Cr, Mn, Ni, Pb, Cl-, Na+, K+, Mg2+, Ca2+, NO3-, SO42-, NH4+ и бензо(а)пирен) и концентрације чађи, узорковане и анализиране у периоду од 2011. до 2015. године на 15 мерних места на територији града Београда. Други сет података за анализу укључивао је сатне вредности концентрација PM10 и PM2,5, неорганских гасовитих оксида (CO, NO, NO2, NOx, SO2 и O3), метеоролошке параметре и висину планетарног граничног слоја (ПГС) за исти период на седам мерних места у Београду. Комплексна анализа загађујућих материја, превасходно атмосферских аеросола урађена је коришћењем низа метода: рецепторског модела Unmix за идентификацију извора и процену њихових доприноса измереним концентрацијама; поларне кластер анализе и CBPF за одређивање утицаја и положаја извора емисије у близини мерног места; TSA, TCA, и хибридних рецепторских модела PSCF, CWT, RTWC и sQTBA у анализи утицаја и одређивања географских области удаљених извора; мултиваријационих модела за прогнозу концентрација PM10; функција расподеле за процену потребне редукције загађења и периода понављања екстремних вредности концентрација; и USEPA и CalEPA метода за процену здравственог ризика становништва. У дисертацији је приказан нов приступ за описивање кретања ваздушних маса чиме је анализа транспорта значајно унапређена. Први пут на овим просторима подаци о загађујућим материјама су анализирани применом хибридних рецепторских модела RTWC и sQTBA, као и мултифракталном и инверзном мултифракталном анализом. Резултати анализе атмосферских аеросола PM10 и њиховог хемијског састава указују на повећане вредности масених концентрација у областима под утицајем индустријских извора загађења, интензивних саобраћајних активности и локалних привредних активности. Сезонска варијабилност концентрација, са значајно вишим вредностима током јесени и зиме изражена је код PM10, али и код арсена и бензо(а)пирена. На локацијама у урбаном окружењу као главни извори загађујућих материја идентификовани су саобраћај и ложење, док су у индустријским области доминантни извори ископавање и сагоревање угља, и ресуспензија честица са пепелишта термоелектране. Највећи канцерогени здравствени ризик процењен је у околини рудника угља, док је у близини најпрометнијих градских саобраћајница изражен и канцерогени и неканцерогени утицај на здравље становника. На основу поларне кластер анализе, CBPF и TSA утврђено је да су доминантни извори на свим мерним местима локалног карактера, док се на појединим мерним местима бележи и значајан удео позадинског нивоа концентрација, као последица конфигурације мерног места или ресуспензије у близини рудника угља. Транспорт загађујућих материја доприноси до 30% измереним концентрацијама, са уочљивим осцилацијама током године, првенствено као последица различитих метеоролошких услова, а нарочито висине ПГС. Примена мултирецепторских варијанти хибридних рецепторских модела пружила је најкомплетнију слику утицаја и доприноса удаљених извора измереним концентрацијама. Мултиваријационе аналитичке методе употребљене су за прогнозу вредности масених концентрација PM10, са доста добрим слагањем између измерених и моделираних вредности. У оквиру дисертације је показано да примена великог броја метода уз довољно велику базу података омогућава разумевање порекла и динамике загађујућих материја, а такође пружа и могућност процене неопходне редукције и предвиђања повећаних концентрација честичног загађења у некој области.

dc.description.abstract	This dissertation presents an air quality study in the area of the city of Belgrade, with a special emphasis on the analysis of the results of hybrid receptor models implementation in order to determine spatial distribution of the most possible pollution sources. Database used for the study includes daily concentrations of PM10 (mass concentrations and chemical composition: As, Cd, Cr, Mn, Ni, Pb, Cl-, Na+, K+, Mg2+, Ca2+, NO3-, SO42-, NH4+, benzo(a)pyrene) and concentrations of black carbon, sampled and analyzed during the period 2011-15, at fifteen monitoring sites in Belgrade area. The second data set comprised hourly mass concentrations of PM10, PM2.5, inorganic gaseous pollutants (CO, NO, NO2, NOx, SO2 and O3), meteorological parameters and high of planetary boundary layer (PBL) during the same period at seven monitoring sites in Belgrade. A comprehensive analysis of the pollutants was performed by the use of variety of methods: receptor model Unmix in order to identify emission sources and estimate their contribution to measured concentrations; polar cluster analysis and CBPF to allocate PM10 and PM2.5 emission sources in the proximity of the sampling sites; TSA, TCA, and hybrid receptor models PSCF, CWT, RTWC and sQTBA to assess the influence and geographical area of remote sources; probability distribution functions to estimate the necessary reduction of the pollution emission and frequencies of extreme pollution episodes; and USEPA and CalEPA models to evaluate the inhabitants' health risk. The dissertation presents a new approach of air mass trajectory description, which significantly improves the transport analysis. For the first time in this region pollutants data were analyzed by the use of hybrid receptor models RTWC and sQTBA, and multifractal and inverse multifractal methods. Research results of atmospheric aerosols PM10 and their chemical composition indicate increased levels of concentrations in the areas affected by industrial pollution sources, intensive traffic and local production activities. Strong seasonal variability of PM10 and PM10-bounded arsenic and benzo(a)pyrene concentrations, with significantly higher levels during the autumn and winter, was obvious. In the urban environment, traffic and heating units are identified as the prevailing emission sources, while in the industrial area the main contributors are coal mining, coal combustion and dust resuspension from coal ash landfills. The highest carcinogenic health risk has been estimated in proximity of the coal mine, while both carcinogenic and non-carcinogenic impact on the residents' health were prominent near the busiest traffic routes. Polar cluster analysis, CBPF and TSA, show that the dominant emission sources are distributed mainly within proximity of the sampling sites, while, at some measurement points, a significant portion of background concentrations was evident as a consequence of sampling site configuration or particulate resuspension due to the vicinity of a coal mine. Pollutant transport contributes up to 30% of the measured concentrations, with observable fluctuations during the year, mostly as a result of different meteorological conditions, predominantly the PBL height. The multi-receptor option of the hybrid models gave a broad insight into the different influences and contributions of distant emission sources. Multivariate analytical methods have been applied to forecast values of PM10 mass concentrations, with very good correlation between measured and modelled values. Within the dissertation it has been shown that the application of multiple analytical methods in combination with a sufficiently large data set enables understanding of the atmospheric aerosols origin and the dynamics of pollutants concentration, and estimating necessary mitigation measures and forecasting of high aerosol mass concentrations in different environments.	en
dc.format	application/pdf	
dc.language	sr	
dc.publisher	Универзитет у Београду, Физички факултет	sr

dc.relation	info:eu-repo/grantAgreement/MESTD/Integrated and Interdisciplinary Research (IIR or III)/43007/RS//	
dc.rights	Autorstvo-Nekomercijalno-Bez prerade 3.0 Srbija (CC BY-NC-ND 3.0)	
dc.source	Универзитет у Београду	sr
dc.subject	квалитет ваздуха, PM10, рецепторски модели, MVA, транспорт аеросола, здравствени ризик	sr
dc.subject	air quality, PM10, receptor models, MVA, aerosol transport, health risk	en
dc.title	Примена хибридних рецепторских модела у анализи квалитета ваздуха и транспорта загађујућих материја у Београду	sr
dc.title	Application of hybrid receptor models in the analysis of air quality and transport of pollutants in Belgrade	en
dc.type	Thesis	
dcterms.abstract	Рајшић, Славица; Белић, Драгољуб; Лазић, Лазар; Стојић, Андреја; Перишић, Мирјана Д.; Primena hibridnih receptorskih modela u analizi kvaliteta vazduha i transporta zagađujućih materija u Beogradu;	

Files in this item

Name:
Disertacija4608.pdf
Size:
19.60Mb
Format:
PDF

(/bitstream/handle/123456789/6555/Disertacija4608.pdf?sequence=1&isAllowed=y)

View/Open
(/bitstream/handle/123456789/6555/Disertacija4608.pdf?sequence=1&isAllowed=y)

Name:
IzvestajKomisije4608.pdf
Size:
295.3Kb
Format:
PDF

(/bitstream/handle/123456789/6555/IzvestajKomisije4608.pdf?sequence=2&isAllowed=y)

View/Open
(/bitstream/handle/123456789/6555/IzvestajKomisije4608.pdf?

sequence=2&isAllowed=y)

This item appears in the following Collection(s)

- Физички факултет (/handle/123456789/228)

Show simple item record (/handle/123456789/6555)

Универзитет у Београду

Физички факултет

Мирјана Д. Перишић

Примена хибридних рецепторских модела у анализи квалитета ваздуха и транспорта загађујућих материја у Београду

Докторска дисертација

Београд, 2016. година

University of Belgrade

Faculty of Physics

Mirjana D. Perišić

Application of hybrid receptor models in the analysis of air quality and transport of pollutants in Belgrade

Doctoral Dissertation

Belgrade, 2016

Чланови комисије:

Др Славица Рајшић, научни саветник
Институт за физику у Београду, Универзитет у Београду, ментор

Др Драгољуб Белић, редовни професор
Физички факултет, Универзитет у Београду

Др Лазар Лазић, редовни професор
Физички факултет, Универзитет у Београду

Др Андреја Стојић, научни сарадник
Институт за физику у Београду, Универзитет у Београду

Докторска дисертација рађена је у Лабораторији за физику животне средине Института за физику у Београду под руководством др Славице Рајшић.

Велику захвалност дугујем својим менторима др Славици Рајшић, као и првом ментору др Мирјани Тасић, на руковођењу израдом дисертације, безрезервној подршци и стрпљењу током протеклих година.

Захваљујем се Градском заводу за јавно здравље у Београду на уступљеним подацима коришћеним за израду дисертације. Хвала колеги Андреју Шоштарићу на стручној помоћи током сређивања велике базе података концентрација загађујућих материја.

Хвала професору др Драгољубу Белићу са Физичког факултета Универзитета у Београду за успешно вођење докторских студија.

Овом приликом се захваљујем свим члановима Лабораторије за физику околине: др Зорану Мијићу, на руковођењу пројектом на коме учествујем, на дугогодишњој сарадњи и разумевању, др Милици Томашевић, др Мири Аничић, др Маји Кузманоски, Марији Тодоровић, др Гордани Вуковић, Луки Илићу и Тијани Милићевић, као и бившим члановима лабораторије др Велибору Новаковићу и Вери Ковачевић.

Желела бих да се захвалим колеги Зорану Великићу на великом интересовању, помоћи и корисним саветима.

Захвалност дугујем и др Невени Пуач за вишегодишњу сарадњу и успешно вођење пројекта на коме учествујем.

Посебну захвалност дугујем колеги др Андреји Стојићу чија су несебична помоћ, подршка и коментари у сваком сегменту мог рада допринели успешној реализацији ове дисертације.

Неизмерно хвала мојим родитељима Миланки и Драгославу, сестри Ани и њеној породици, мојој ивањичкој породици, и Петри, Станислави и Милутину на подршци и инспирацији за досадашњи и будући рад.

У Београду, 2016. године *Мирјана Перишић*

UNIVERZITET SINGIDUNUM

Departman za poslediplomske studije

MASTER RAD

KLIMATSKE PROMENE: MOGUĆI UTICAJ NA ZDRAVLJE I MORTALITET LJUDI U NOVOM SADU

Mentor:
prof. dr Jelena Milovanović

Kandidat:
Nataša Stanojković

Beograd, 2019. godina

SADRŽAJ

Veliku zahvalnost za nastanak ovog istraživanja kao i samog master rada, dugujem mom mentoru Prof. dr Jeleni Milovanović koja je od samog početka verovala u mene, pružila mi šansu i nesebično pomogla na svakom koraku koji je meni izgledao nedostižan. Hvala na podršci, savetima i pozitivnoj energiji koja je bila ključ našeg zajedničkog rada.

Posebnu zahvalnost dugujem i profesoru dr Andreji Stojiću na svim dobronamernim sugestijama i komentarima iz kojim sam puno naučila i koji su mi pomogli da rad dovršim na najbolji mogući način

Zahvaljujem se načelniku Centra za higijenu i humanu ekologiju Instituta za javno zdravlje Vojvodine, Prof. dr Sanji Bijelović na stručnim komentarima kao i na podršci na mom akademskom putu.

Želim da se zahvalim dr Miodragu Arsiću, načelniku Centra za informatiku i biostatistiku u zdravstvu Instituta za javno zdravlje Vojvodine, koji je ogromnu količinu podataka preveo u formu koju sam mogla da iskoristim u ovom istraživanju.

Poseban izraz zahvalnosti dugujem onima koji su mi najdraži u životu, suprugu Siniši i ćerkama Tijani i Tamari na ogromnoj podršci, pomoći, pažnji i ljubavi bez koje ne bih uspela da ostvarim svoj cilj, koji je postao naš zajednički cilj. Hvala vam što ste verovali u mene.

Математичка гимназија
школа од посебног националног интереса
Београд, Краљице Наталије 37
Тел. +381-11-3628-375, +381-11-3611-126, +381-11-3628-365
Факс. +381-11-3612-595
www.mg.edu.rs, mg@mg.edu.rs

ПОТВРДА

Потврђује се да је Андреја Стојић био ментор на изради матурског рада Лазару Златићу, матуранту Математичке гимназије, са темом: Примена метода машинског учења у физици животне средине, у јуну 2019. године.

Ова потврда се издаје на лични захтев Андреје Стојића, а у сврху прикупљања документације за избор у звање.

У Београду, 26.11.2019.

Директорка гимназије

Катић Мирјана

МАТЕМАТИЧКА ГИМНАЗИЈА БЕОГРАД II

УНИВЕРЗИТЕТ У БЕОГРАДУ
ИНСТИТУТ ЗА ФИЗИКУ БЕОГРАД
Прегревица 118, 11080 Земун - Београд, Србија
Телефон: +381 11 3713000, Факс: +381 11 3162190, www.ipb.ac.rs
ПИБ: 100105980, Матични број: 07018029, Текући рачун: 205-66984-23

Поштовани господине Поповићу

државни секретар за науку

Поштовани господине Лазаревићу

помоћник министра за технолошки развој

Овим Вам шаљемо извештај центра изузетних вредности Центар за неравнотежне процесе који је акредитован код министарства као центар изузетних вредности (ЦИВ). Извештај је за 2016. годину. Како смо средства за ЦИВ добили почетком децембра готово истовремено са датумом када је био рок да се предају извештаји било га је немогуће предати тада јер је требало утрошити средства.

Уз поздраве Зоран Љ Петровић

Центар за неравнотежне процесе

Извештај за 2016 годину

1. Увод и најважнији резултати 2016. године

Центар за неравнотежне процесе је ре-акредитован 21.10. 2014. године. И поред тешких услова за рад условљених неизвесним финансирањем и испоруком опреме Центар је у 2016. години остварио значајне резултате.

Истакнути резултати сарадника Центра у 2016. години су:

- Саша Дујко је током 2016. год. био гостујући уредник специјалног издања Кинетички методи у технолошким плазмама (*Kinetic Methods in Technological Plasmas*), часописа *Plasma Sources Science and Technology* чији је издавач Британски Институт за Физику.

- Зоран Љ Петровић је током 2017 био гостујући уредник специјалног издања *Advances in positron and electron scattering* часописа European Physical Journal D

- Ро позиву уредништва часописа *Journal of Physics D Applied Physics* сачињен је посебан сажетак рада (Bošnjaković et al, J. Phys. D: Appl. Phys. **49**, 405201, 2016) који је истакнут на *web* страници часописа (https://jphysplus.iop.org/2016/12/01/fluid-modeling-of-resistive-plate-chambers/) у оквиру секције *JPhys+* која обухвата радове и вести од нарочитог значаја.

- Ро позиву уредништва часописа *Plasma Sources Science and Technology* сачињен је посебан сажетак рада (Markosyan et al, Plasma Sources Sci. Technol. **24**, 065002, 2015) који је истакнут на *web* страници часописа (http://iopscience.iop.org/journal/0963-0252/labtalk/article/64938) у оквиру секције *LabTalk* која у кратким цртама приказује радове од нарочитог значаја.

- Саша Дујко је одржао предавање по позиву на Радионици (Workshop) *New directions of charged particle kinetics in low temperature plasmas: more precision, more exploration, more discovery* у оквиру 69. годишње Конференције Гасне Електронике Америчког Друштва Физичара (енгл. 69th Annual Gaseous Electronics Conference) која је оджана од 10 - 14 Октобра 2016. год. у Бохуму, Немачка.

Зоран Љ. Петровић и Гордана Маловић били су копредседавајући Радионице: Workshop on non-equilibrium processes одржане везано за програм конференције SPIG Belgrade 2016.

Зоран Љ. Петровић је био копредседавајући једнодневне Радионице (Workshop) *New directions of charged particle kinetics in low temperature plasmas: more precision, more exploration, more discovery* у оквиру 69. годишње Конференције Гасне Електронике Америчког Друштва Физичара (енгл. 69th Annual Gaseous Electronics Conference) која је оджана од 10 - 14 Октобра 2016. год. у Бохуму, Немачка.

Зоран Љ. Петровић је одржао предавање по позиву на Конференцији Европског Физичког друштва 2016 EPS Plasma Physics Conference у Лувену у Белгији 4.-8. јула под насловом: *Swarms as an exact representation of weakly ionized gases.*

- Саша Дујко је одржао предавање по позиву *Transport processes for electrons and positrons in gasses and liquids: Theory and Applications* у оквиру 3rd COST TD1208 Training School on Advanced Diagnostics of Discharges with Liquids and Plasma Treated Liquid Phase, 24 - 28 Септембар, Београд, Земун, Србија.

- Саша Дујко је одржао предавање по позиву *Kinetic and fluid description of charged particle swarms and its application in modeling of gaseous detectors* у оквиру RD51 Mini-Week Симпозијума, 6 - 9 Јуна 2016. год. CERN, Швајцарска.

- Данко Бошњаковић је одржао предавање по позиву *Microscopic and fluid modeling of resistive plate chambers* у оквиру RD51 Mini-Week Симпозијума, 6 - 9 Јуна 2016. год. CERN, Швајцарска.

- др Драгана Марић је одржала предавање по позиву на Gordon Research Conference on Plasma Processing Science: Plasmas with Complex Interactions – Exploiting the Non-Equilibrium (07/24/2016 - 07/29/2016 at Proctor Academy in Andover NH United States), под насловом "Atomic and Molecular Processes of interest for Modelling of Discharges in Liquids"
- др Никола Шкоро је на 23rd Europhysics Conference on Atomic and Molecular Physics of Ionized Gases (ESCAMPIG), која је била од 12.-16.7. 2016. у Братислави, Словачка одржао предавање по позиву (Topical Invited Lecture) са насловом "Heavy-particle collisions in water vapour discharges at low pressures"
- др Никола Шкоро је на 4th International Workshop on Non-Equilibrium Processes одржао предавање по позиву (Београд, 29.8.2016) са насловом "Heavy-particle processes in low-pressure water vapour discharge"

Др Мира Аничић Урошевић је била рецензент и члан комисије за одбрану докторске дисертације под називом: „*Elemental Analysis of Mosses and Lichens from the Western Cape (South Africa) using NAA and ICP-MS*" кандидата Ntombizikhona Beaulah Ndlovu (Stellenbosch University, Stellenbosch, South Africa) дана 19. маја 2016. године.

Др Мира Аничић Урошевић је била опонент на одбрани докторске дисертације под називом: „*Application of magnetic biomonitoring in air pollution research – Spatio-temporal properties of magnetic particle matter*" кандидата Hanna Salo (University of Turku, Turku, Finland) дана 9. децембра 2016. године.

Др Андреја Стојић је одржао предавање по позиву, под насловом „*Radon, ions and VOC as a source of indoor air pollution*" на *Green Building EXPO international exhibition and conference*, одржаној од 2. до 4. новембра 2016. године у Београду.

Зоран Љ. Петровић је био члан Панела за физику за оцењивање ERC пројеката (Европски савет за научна истраживања).

Зоран Љ Петровић је излагао уводно предавање под насловом: Plasma treatment of seeds and plant calli, аутора: Zoran Lj. Petrović, Kosta Spasić, Suzana Živković, Gordana Malović, Nevena Puač, на конференцији: 1st International Workshop on Plasma Agriculture May 15th–20th 2016, A.J. Drexel Plasma Institute 200 Federal Street, Suite 100, Camden, NJ 08103

Зоран Љ. Петровић је одржао предавање на Workshop on Application of Advanced Plasma Technologies in CE Agriculture 17th to 21th April 2016, Ljubljana, Slovenia

Зоран Љ. Петровић је одржао предавање: " Diagnostics of atmospheric pressure plasma jets and plasma needle and their application in biology and medicine" на GEM 2016 – 19th Gaseous Electronics Meeting. 14th-17th February Geelong Vic. Australia

Зоран Љ. Петровић је био један од чланова комитета конференције: 6th International Conference on Advanced Plasma Technologies (ICAPT-6) / Workshop on Industrial Application of Plasma Solutions, одржане 11th to 15th / 15th to 18th December 2016, у Siem Reap, Cambodia

Невена Пуач је одржала уводно предавање под насловом Plasma treatment in seed germination на конференцији 6th International Conference on Plasma Medicine (ICPM-6) Bratislava, Slovakia.

Невена Пуач је била члан комитета конференције ESCAMPIG, док је Марија Радмиловић Рађеновић била члан комитета конференције ICPIG. Драгана Марић је била члан комитета конференције SPIG 2016.

2. Пројекти Центра

НАТО пројекат 2013-2017

Крајем 2013.године добијен је НАТО пројекат: **EAP. SFPP 984555 "Atmospheric Pressure Plasma Jet for Neutralisation of CBW (Chemical Biological Weapons)"** чији су директори: др Урош Цвелбар (Институт Јожеф Штефан, Љубљана, Словенија) и проф. др Зоран Љ. Петровић; Учесници: Зоран Петровић, Невена Пуач, Гордана Маловић, Драгана Марић, Никола Шкоро, Андреја Стојић, Мирјана Перишић

Пројекти финансирани од Европске заједнице у оквиру H2020 програма

- GEO-CRADLE (Coordinating and integRating state-of-the-art Earth Observation Activities in the regions of North Africa, Middle East, and Balkans and Developing Links with GEO related initiatives towards GEOSS) пројекат, No. 690133 (2016-2018). Координатор пројекта за Институт за физику је др Зоран Мијић, а учесници на пројекту су др Маја Кузманоски, др Андреја Стојић и Лука Илић.
- ACTRIS-2 IA (Aerosols, Clouds, and Trace gases Research InfraStructure Network-Integrating Activities) пројекат, No. 654109 (2015-2019). Циљ ACTRIS-2 IA пројекта је интегрисање европских мерних станица опремљених уређајима за мерење физичких, оптичких и хемијских карактеристика атмосферских конституената. Координатор пројекта за Институт за физику је др Зоран Мијић, а учесници на пројекту су др Маја Кузманоски и Лука Илић.

COST Програми

TD1208 Electrical Discharges with Liquids for Future Applications

Учесници: Драгана Марић (руководилац радне групе), Зоран Петровић, Гордана Маловић, Невена Пуач, Марија Радмиловић-Рађеновић, Саша Дујко, Владимир Стојановић, Никола Шкоро, Јелена Сивош, Марија Савић

У оквиру ове акције др Драгана Марић је руководилац једне од четири радне групе и члан је управљачког одбора пројекта. Она је учествовала у формирању пројекта и покретању акција.

Билатерални пројекти и други пројекти међународне сарадње

- Билатерална сарадња са Словенијом:

Рад са младим талентима и популаризација науке:

- Марија Шиндик и Радоица Драшкић, сада студенти 2. године ФФ (Б.У.) су одрадили летњу праксу под менторством В. Дмитрашиновића.

-др Никола Шкоро: Рад са младим талентима и активности на популаризацији науке у сарадњи са Регионалним центром за таленте Земун. У оквиру ових активности, са две групе ученика 8. разреда основних школа, урађена су два експериментална рада која су успешно презентована и одбрањена на Регионалном такмичењу младих талената

5. Извештај о раду за 2016. и План активности за 2017. годину

Транспорт наелектрисаних честица (руководилац: Саша Дујко, Јасмина Мирић, Илија Симоновић, Зоран Љ. Петровић)

У домену гасних диелектрика, проучаван је транспорт електрона у јако елктронегативним гасовима, сумпор-хексафлуориду и трифлуорометил јодиду, где је посебан акценат стављен на разумевање кинетичких фиеномена индукованих захватом електрона. За ова истаживања је коришћен Монте Карло код са имплеметираним техникама за рескалирање електрона, а посебна пажња је посвећена развоју и тестовима континуалне технике рескалирања у којој је уводен фиктивни процес јонизације. Колизиона фреквенца овог фиктивног процеса не зависи од енергије електрона и изједначује се са колизионом фреквенцом за захват електрона у дикретним тренутцима времена, чиме се обезбеђује рескалирање роја не мењајући функцију расподеле. На основу нумеричких мулти терм решења Болцманове једначине и Монте Карло метода проучаван је транспорт електрона у живиним парама на високим температурама и притисцима. Показано је да коректна репрезентација димера атома живе и суперэластичних судара има кључну улогу за разумевање феномена негативне диференцијалне проводности. У домену временски промењљивих електричних и магнетских поља, Болцманова једначина и Монте Карло метод су коришћени за проучавање синергије ефеката временске нелокалности и циклотронске резонанце на загревање електрона у електронегативним гасовима који су од интереса за технолгију процесирања плазмом. Ове методе су употребљене за проучавање одзива електрона у доњим слојевима јоносфера планета Земље и Сатурна на електромагнетне импулсе (ЕМИ) који настају након муња. Временски профили ЕМИ су добијени на основу нумеричких решења Максвелових једначина. У Монте Карло симулацијама у којима се пажљиво разматрају ефекти кохерентног расејања у еластичним сударима и адекватно репрезентују нееластични и неконзервативни судари, проучаван је транспорт електрона у течном аргону, криптону и ксенону. Опажен је феномен негативне диференцијалне проводности индукован структурним ефектима. На основу флуидног модела првог реда који комбинује дрифт-дифузиону апроксимацију и апроксимацију локалног поља, проучавани су ефекти рекомбинације електрона и позитивних јона на динамику транзиције лавине у стример и пропагацију стримера у овим течностима.

Будући рад: Транспорт електрона, развој лавина и пропагација позитивних и негативних стримера биће проучавани у гасним диелектрицима, са посебним акцентом на повезивању макроскопских особина стримера и микроскопских особина електрона. За симулације стримера биће коришћени флуидни модели првог и вишег реда, како у бесконачном простору, тако и у условима који одговарају реалним експериментима. У домену транспорта електрона у неполарним течностима, транспортни коефицијенти ће бити израчунати у Монте Карло симулацијама у којима се разматрају ефекти индиректне јонизације, путем формирања јонизованог димера. Флуидним моделима првог и вишег реда ће бити разматран утицај различитог третмана нееластичних судара електрона и јонизације у неполарним течностима на пропагацију су пробојни напони и спектрално разложене просторне расподеле емисије за метанол, етанол, 2-пропанол и n-бутанол на међуелектродном растојању од 3,1 cm.

- Постављен је експеримент за проучавање пробоја у радиофреквентним пољима. У сарадњи са Проф. Антонијем Ђорђевићем, САНУ, дизајниран је капацитивни мост који омогућава да се из струјног сигнала елиминише струја помераја. Тиме се добја далеко поузданија детекција пробоја од стандардних метода мерења. Урађена су прва тест мерења
- Развијен је глобални модел за проучавање пражњења у смеши He/O2 са примесама влажног ваздуха. Проучавано је како облик функције расподеле енергије електрона утиче на резултате модела.
- Настављен је рад на одређивању сетова пресека за јоне и брзе неутрале у воденој пари – комплетиран је сет пресека за H2O+ и за брзе атоме водоника. Монте Карло симулација је коришћена и у моделовању просторних расподела емисије Балмер алфа линије у Таузендовом пражњењу у воденој пари.

Будући рад

- Проучавање пражњења у парама комплексинијих органиских течности и у смешама пара са гасовима које су од интереса за примене.
- Наставиће се са радом на унапређењу система за детекцију пробоја у радиофреквентним пољима. Очекује се и да ће бити урађена истематска мерења пробојних напона за више гасова. Експериментални резултати ће послужити као основа за моделовање радиофреквентног пробоја применом Монте Карло кода који је развијен у нашем Центру.
- Глобални модел пражњења са примесама водене паре ће бити примењен на већи број смеша гасова. Планира се укључивање протока гаса у модел, како би се описала кинетика стања за експерименте са плазма џетом на атмосферском притиску, који се користе у Центру.
- Наставиће се рад на моделовању емисије пражњења у воденој пари, а затим и на прикупљању и одређивању сетова пресека од интереса за моделовање емисије пражњења у парама алкохола.

Микро плазме (руководилац:Драгана Марић, Никола Шкоро и Гордана Маловић)

- Извршена су мерења у микропражњењу у воденој пари. Проучаван је пробој на милиметарским међуелектродним растојањима у широком опсегу притисака, од ниског притиска до услова када је притисак паре довољно висок да долази до кондензације и формирања капљица на површини електрода и на зидовима коморе. На притисцима изнад критичног, у присуству кондезоване паре, измерени су пробојни напони знатно виши од напона пробоја добијених у гасној фази.

- У сарадњи са групом из Словачке, моделовани су пробоји у микроплазмама код радио-фрекфентног пражњења у различитим гасовима и смешама гасова. Извршено је опсежно теоријско проучавање утицаја емисије електрона услед дејства јаког електричног има на карактеристике микропражњења.

Будући рад: Наставиће се рад на проучавању микропражњења на притисцима изнад критичног притиска паре.

- Наставиће се сарадња са групом из Словачке на моделовању микропражњења у радио-фреквентним пољима.

Утицаји фактора животне средине на квалитет ваздуха и здравље људи
(**руководилац: Андреја Стојић**, Мирјана Перишић, Зоран Мијић и Марија Тодоровић)

Извршена су симултана мерења концентрација испарљивих органских једињења (ИОЈ), аеросола ($PM_{2,5}$) и њиховог хемијског састава (метали, јони, органски/елементни угљеник и полициклични ароматични угљоводоници), неорганских гасних оксида (НГО; NO_x, NO_2, NO, SO_2, CO и O_3), радона и метеоролошких параметара (МП) у отвореном и затвореном простору урбане средине у

Београду. Спроведена је опсежна анализа квалитета ваздуха на подручју Београда у циљу бољег разумевања међусобне повезаности фактора животне средине и њиховог утицаја на атмосферске промене и здравље људи. Применом великог броја напредних статистичких метода извршена је детаљна анализа загађујућих супстанци у отвореном и затвореном простору урбане средине, као и карактеризација њихових просторно-временских расподела и извора. На основу резултата хибридних рецепторских модела и њихових мултирецепторских варијанти процењена је просторна расподела удаљених извора емисије и њихових доприноса измереним концентрацијама. Примена *MVA* за потребе прецизне прогнозе динамике извора загађујућих супстанци проширена је на атмосферске аеросоле. Динамички систем, развијен за одређивање расподела концентрација ИОЈ у мултифазним системима узорака из животне средине, коришћен је за анализу обогаћења кишнице једињењима *BTEX*. Применом модела *US EPA* и *CalEPA* анализиран је канцерогени и неканцерогени здравствени ризик на широј територији Београда. У циљу прецизнијег описа ефеката загађења ваздуха и екстремних атмосферских прилика на здравље људи и морталитет узрокован кардиоваскуларним, циркулаторним и малигним обољењима, унапређена је метода процене релативног ризика увођењем кумулативних ефеката загађујућих супстанци у модификован модел базиран на квази Поасоновој регресији и *DLNM*.

Будући рад: У наредном периоду наставиће се мерења ИОЈ, НГО, РМ и њиховог хемијског састава, радона и МП у амбијенталном ваздуху урбане и семи-урбане средине Београда. Одређивање концентрација ИОЈ у наредном периоду биће значајно унапређено коришћењем *Liquid Calibration Unit* (*LCU*). За анализу динамике и просторне расподеле загађујућих супстанци и њихових извора биће коришћене напредне статистичке, просторно-временске, мултифракталне и *MVA* методе, као и рецепторски и хибридни рецепторски модели. У циљу бољег разумевања транспорта загађења на регионалним скалама, извршиће се унапређење постојећих хибридних рецепторских модела развојем тродимензионалних *PSCF* и *CWT*, као и новог модела који ће омогућити процену вертикалне расподеле концентрација загађујућих супстанци. Наставиће се анализа расподела и интеракција ИОЈ у сложеним мултифазним системима узорака из животне средине уз развој комора за симулацију у контролисаним условима. У наредном периоду посебан акценат биће стављен на истраживања квалитета ваздуха у затвореном простору и утицај загађења и климатских фактора на осетљиве категорије становништва.

Даљинско мерење оптичких карактеристика и моделовање атмосферских аеросола (руководилац: Маја Кузманоски, Зоран Мијић, Лука Илић)

Током 2016. године настављен је рад на развоју алгоритма за анализу података добијених мерењем вертикалног профила аеросола *UV* Раман лидар системом. У оквиру процедуре за контролу квалитета података у *EARLINET* мрежи, извршена су мерења и анализа добијених података са циљем провере перформанси лидар система. Настављен је рад на анализи утицаја вертикалне структуре слоја аеросола на процену радијативних ефеката сахарског песка, коришћењем података о вертикалној расподели коефицијента екстинкције аеросола мерених лидаром. Започета су истраживања апсорбујућих карактеристика транспортованог сахарског песка на основу даљинских мерења аеросола и података о концентрацијама и минералном саставу песка добијених из *DREAM* (*Dust Regional Atmospheric Model*) модела. У току је рад на развоју нумеричке шеме за микрофизику облака у *DREAM* моделу, у сарадњи са Виртуелним центром за климатске промене за југоисточну Европу, са циљем анализе утицаја сахарског песка на нуклеацију леда у облацима. Док већина стандардних оперативних шема за прогнозу облака користи унапред дефинисан број честица које могу да учествују у нуклеацији леда (*#IN*), у *DREAM* моделу се *#IN* рачуна на основу прогнозе концентрације песка и термодинамичких величина. Резултати оперативне прогнозе и поређење са *SEVIRI* (*Spinning Enhanced Visible and InfraRed Imager*) осматрањима садржаја леда у стубу ваздуха су доступни на адреси: http://dream.ipb.ac.rs/ice_nucleation_forecast.html.

Универзитет
Сингидунум

На лични захтев ангажованог

УНИВЕРЗИТЕТ СИНГИДУНУМ
Бр. 1276
25.11. 2019 год.
БЕОГРАД, Данијелова 32

П О Т В Р Д А

да је др **Андреја Стојић**, стално запослен у Институту за физику у Београду, ангажован уговором о допунском раду на УНИВЕРЗИТЕТУ СИНГИДУНУМ, у периоду од 01.10.2019 до 30.09.2020. године као научни сарадник за студијски програм Животна средина и одрживи развој.

Потврда се издаје ради избора у звање виши научни сарадник и у друге сврхе се не може употребити.

С поштовањем,

Овлашћено лице

УНИВЕРЗИТЕТ СИНГИДУНУМ • БЕОГРАД •

Ул. Данијелова 32, 11000 Београд, Србија
Тел. +381 11 30 93 220, 30 93 209; 30 93 229; Факс. +381 11 30 93 294
office@singidunum.ac.rs
www.singidunum.ac.rs

Gmail

Andreja Stojic <andrejastojicepl@gmail.com>

Studentske prakse

3 поруке(а)

Prakse Za Studente <praksezastudente@gmail.com> 28. мај 2016. 13:04

Poštovani,

Želimo da Vam se zahvalimo u ime Studentskog parlamenta i svih studenata naseg fakulteta, na tome što ste predložili istraživački projekat - stručnu praksu za studente.

Lista ponuđenih praksi biće okačena na sajt Fakulteta u narednih par dana (uz dodatne komentareza studente, koji se tiču prijavljivanja). U prilogu se nalazi dokument sa svim ponuđenim praksama. Ukoliko primetite neku grešku sa praksom/istraživačkim projektom koju ste ponudili, molimo Vas da nas što pre kontaktirate.

Kao sto je već rečeno, zainteresovani studenti će Vas kontaktirati direktno na mejl adresu koju ste ostavili.

Rok za prijavu koji je dat studentima je 16. jun.

Broj studenata na Fizičkom fakultetu nije veliki, pogotovo na trećoj i četvrtoj godini, tako da verovatno neće biti prijavljenih studenata za svaku od ovolikog broja ponuđenih praksi. Ideja nam je da se studentima predstave oblasti istraživanja kojima se istraživači u Srbiji bave i da se studenti, shodno interesovanjima, dublje upoznaju sa određenom naučnom oblašću koja im se dopadne.

Ukoliko imate nekih pitanja ili komentara, u svakom trenutku nas mozete kontaktirati na ovu mejl adresu.

Srdačan pozdrav,

U ime radne grupe i Studentskog parlamenta,

Petar Bojović

Studentske prakse.pdf
660K

Prakse Za Studente <praksezastudente@gmail.com> 28. мај 2016. 14:03
Коме: Andreja Stojić <andreja@ipb.ac.rs>

Poštovani,

hvala Vama na podržanoj inicijativi i ponuđenoj praksi. Nadam se da će biti uspešna i pozitivna za sve učesnike.

Srdačan pozdrav,
Petar

2016-05-28 13:32 GMT+02:00 Andreja Stojić <andreja@ipb.ac.rs>:

> Poštovani Petre,
>
> zahvaljujem se na ovoj lepoj i korisnoj inicijativi.
>
> Srdačan pozdrav,
> Andreja
>
> ---
>
> **From:** Prakse Za Studente
> **Sent:** 5/28/2016 1:04 PM
> **Subject:** Studentske prakse
>
> [Цитирани текст је сакривен]

Prakse Za Studente <praksezastudente@gmail.com> 14. новембар 2016. 20:05

Poštovani,

Molimo Vas da popunite ovaj kratak upitnik o tome da li ste primili nekog na praksu:

[redacted]

Podaci o broju studenata će nam puno značiti u evaluaciji ove akcije, a komentari i predlozi će nam pomoći da u budućnosti ovu akciju podignemo na viši nivo.

Srdačan pozdrav,
U ime radne grupe i Studentskog parlamenta,
Petar Bojović

[Цитирани текст је сакривен]