Научном већу Института за физику у Београду

Предмет: Молба за покретање поступка за стицање звања истраживач-сарадник

На основу испуњености услова предвиђених Правилником о стицању истраживачких и научних звања, прописаног од стране ресорног Министарства, молим Научно веће Института за физику у Београду да покрене поступак за мој избор у звање истраживач сарадник.

У прилогу достављам:

1. Потписани Захтев кандидата за покретање поступка;
2. Мишљење руководиоца лабораторије са предлогом комисије која ће писати извештај. Комисија треба да се састоји од најмање три члана у научном или наставном звању, при чему бар један није, а бар половина јесте запослена у Институту;
3. Кратка стручна биографија кандидата (до 1 стране);
4. Кратак преглед научне активности кандидата (до 1 стране);
5. Списак објављених радова и других публикација, разврстан по важећим категоријама прописаним Правилником;
6. Потврда о уписаним докторским студијама;
7. Потврда о просеку на основним и мастер студијама (диплома или уверење о дипломирању), који мора бити већи од 8;
8. Потврда о пријављеној теми докторске дисертације. За кандидате који су на докторским студијама на Физичком факултету Универзитета у Београду може се приложити потврда да је тема дисертације одбрањена на Колегијуму докторских студија. За кандидате уписане на другим факултетима треба приложити потврду одговарајућег тела факултета, потврду факултета или потврду универзитета;
9. Копије објављених радова и других публикација (верзије из часописа, зборника апстраката, итд.).

С поштовањем,

Јелена Митић
Истраживач приправник

Научном већу Института за физику у Београду

Београд, 23. мај 2025. године

Предмет: Мишљење руководиоца лабораторије о избору Јелене Митић у звање истраживач сарадник

Јелена Митић је запослена у Лабораторији за физику животне средине Института за физику у Београду од децембра 2022. године. Докторска дисертација колегинице Митић под називом „Испитивање различитих сценарија за процену ризика по здравље људи услед излагања потенцијално токсичним елементима и полицикличним ароматичним угљоводоницима из земљишта са депонија у Србији" је прихваћена за израду од стране Наставно-научног већа Хемијског факултета Универзитета у Београду под менторством др Дубравке Релић, ванредне професорке Хемијског факултета Универзитета у Београду и др Тијане Милићевић, више научне сараднице Института за физику у Београду. У досадашњем ангажовању Јелена Митић је објавила један научни рад у часопису категорије М21, и учествовала на две националне и једној међународној конференцији.

С обзиром да испуњава све услове предвиђене Правилником о стицању истраживачких и научних звања, сагласан сам са покретањем поступка за избор Јелене Митић у звање истраживач сарадник.

За избор Јелене Митић у звање истраживач сарадник предлажем комисију у следећем саставу:

1) др Тијана Милићевић, виша научна сарадница, Институт за физику у Београду
2) др Мира Аничић Урошевић, научна саветница, Институт за физику у Београду
3) др Дубравка Релић, ванредна професорка, Хемијски факултет Универзитета у Београду

Зоран Мијић

др Зоран Мијић, виши научни сарадник

Руководилац Лабораторије за физику животне средине

Биографија

Јелена Митић (рођена Ђорђевић) је рођена у Пироту, где је завршила основну школу и гимназију - билингвални смер (математички смер на српском и француском језику). Основне академске студије на Хемијском факултету Универзитета у Београду уписала је школске 2017/2018. године, на студијском програму Хемија животне средине, а дипломирала је 2021. године са просечном оценом 8,09. Завршни рад под насловом „Квалитет амбијенталног ваздуха Србије у односу на садржај макро и микроелемената процењен пасивним биомониторингом, студија 2020“ одбранила је са оценом 10. Мастер академске студије уписала је школске 2021/2022. године на Хемијском факултету Универзитета у Београду, на студијском програму Хемија животне средине. Мастер академске студије је завршила 2022. године са просечном оценом 9,25. Завршни мастер рад под насловом „*In vitro* екстракција елемената из узорака мајчиног млека“ одбранила је са оценом 10. Докторске академске студије уписала је школске 2022/2023. године на Хемијском факултету Универзитета у Београду, на студијском програму Хемија. Положила је све испите предвиђене планом и програмом докторских академских студија са просеком оцена 10,00. Од децембра 2022. године запослена је у Лабораторији за физику животне средине на Институту за Физику у Београду, Институту од националног значаја за Репбублику Србију, као истраживач приправник. Од тада, похађала је различите студијске курсеве и радионице из области хемије животне средине: „*Water Workshop 2023*“, „*Organic soil amendments impact on soil organic matter and nutrient characteristics and dynamics*“ радионица, „IMPTOKS радионица: *Navigating the Invisible Currents – Micro and Nanoplastics' Water Odysseyand*“, и “Тренинг за писање идеја пројеката, Фонда за науку РС”, радионица „*PFAS* у Србији: Тренутно стање, научни и регулаторни изазови и будући кораци“. Учествовала је на две националне конференције „*EnviroChem* 2023” и „9. Конференција младих хемичара Србије“, и једној међународној конференцији „Advances in Solid State Physics and New Materials“. Као члан тима, учествовала је на билатералном пројекту са Факултетом за агрономију и прехрамбену индустрију (*Animal and Functionality of Animal Products Unit Research – UR AFPA*, *National Superior School of Agronomy and Alimentary Industries – ENSAIA, INRAE*), Универзитет у Лорени, Нанси, Француска (337-00-93/2023-05/10), у оквиру програма „Павле Савић“, у оквиру ког је посетила Универзитет у Лорени. Члан је организационог одбора „*The International Association for Biomonitoring of Environmental Pollution– IABEP* 2025“ међународне конференције која ће се одржати у Београду, октобра 2025. године.

Преглед научне активности

Истраживачки рад Јелене Митић, првенствено је усмерен на истраживању у области хемије животне средине и процену ризика по здравље људи на основу концентрација органских и неорганских загађивача у узорцима животне средине. У оквиру истраживања за њен завршни рад, испитивала је загађење ваздуха уз помоћ маховина, а назив завршног рада гласио је: „Квалитет амбијенталног ваздуха Србије у односу на садржај макро и микроелемената процењен пасивним биомониторингом, студија 2020“. За мастер тезу, испитивала је биоприступачне концентрације елемената из узорака хуманог млека, а назив тезе је био: „*In vitro* екстракција елемената из узорака хуманог млека“. До сада се бавила применом пасивног биомониторинга са маховинама за процену загађености ваздуха, као и применом *in vitro* метода за процену ресорпције токсичних и канцерогених елемената у гастро-интестиналном тракту човека и процену ризика по људско здравље на основу концентрације загађујући́х супстанци из животне средине. Похађала је различите курсеве и радионице из области хемије животне средине. Учествовала је на две националне конференције „EnviroChem 2023” и „9. Конференција младих хемичара Србије”, и на једној међународној конференцији „Advances in Solid State Physics and New Materials”.

Фокус њене тренутне научне активности је на испитивању утицаја загађујућих супстанци из земљишта са различитих типова депонија на здравље људи. Њено истраживање обухвата одређивање садржаја потенцијално токсичних елемената (ПТЕ) и полицикличних ароматичних угљоводоника (ПАУ) у узорцима земљишта са депонија, и процену ризика по здравље људи који могу бити хронично изложени овим супстанцама. Такође, бави се и *in vitro* симулацијом гасто-интестиналног тратка, уз помоћ које долази до биоприступачних концентрација, које омогућавају процену реалног ризика по здравље људи. Њено истраживање о биоприступачности и ризику по здравље радника у пољу са земљишта дивљих депонија у пољопривредним подручјима, под називом „The oral bioaccessibility of potentially toxic elements of illegal landfills’ soil and health risk assessment for field workers”, објављено је у часопису *Chemosphere*.

Списак публикација

Јелена Митић (рођена Ђорђевић)

М21 – Радови публиковани у врхунском међународном часопису:

1. **Mitić, J.,** Relić, D., Pucarević, M., Stojić, N., Štrbac, S., Ninkov, J., Milićević, T. 2025. The oral bioaccessibility of potentially toxic elements of illegal landfills' soil and health risk assessment for field workers. Chemosphere, 373, 144173. https://doi.org/10.1016/j.chemosphere.2025.144173

Саопштења са међународног скупа штампана у изводу (М34)

1. Milićević, T., Aničić Urošević, M., **Mitić, J.**, Popović, M., Aćimović, J., Popović, A., Samson, R. Saturation Isothermal Remanent Magnetization of Grapevine Leaves as a Proxy for Environmental Pollution. Advances in Solid State Physics and New Materials, Book of Abstracts, 19-23th May, 2025, Belgrade, Serbia, p. 178.

Саопштења са скупа националног значаја штампано у изводу (М64)

1. Milićević, T, **Đorđević J.**, Herceg Romanić, S., Dojčinović, B., Matek Sarić, M., Popović, A., Relić, D. The element concentrations in human milk samples from Croatia and *in vitro* bioaccessibility assay. 9th Symposium Chemistry and Environmental Protection „EnviroChem2023" with international participation, Book of Abstracts, 4-7th June, 2023, Kladovo, Serbia, p. 149-150.
2. **Đorđević, J.**, Pucarević, M., Stojić, N., Milićević, T. Human health risk assessment based on the element concentrations in landfills' soil. 9th Conference of Young Chemists of Serbia, Book of Abstracts, 4th November 2023, Novi Sad, Serbia, p. 88.

Универзитет у Београду - Хемијски факултет
Студентски трг 12-16 * П. фах 51 * 11158 Београд 118 * ПАК: 105104 * Тел/факс: 011-2184330 * http://helix.chem.bg.ac.rs/

Број: ДХ17/2022
У Београду, 22. 5. 2025. године

На основу члана 29. Закона о општем управном поступку и службене евиденције издаје се

У В Е Р Е Њ Е

Јелена (Дејан) Митић, рођена **10. 9. 1998.** године у месту **Пирот**, општина **Пирот**, **Република Србија**, број индекса **ДХ17/2022**, уписана је школске **2024/2025.** године на студијски програм докторских академских студија **Хемија**, укупног обима 180 ЕСПБ, као **студент који се финансира из буџета**.

Студент је први пут уписан на наведени студијски програм школске **2022/2023.** године. По статуту високошколске установе студије трају **6 семестара**, односно **3 године**. Рок за завршетак студија јесте двоструко трајање студија.

Уверење се издаје на лични захтев студента.

Овлашћено лице високошколске установе

Ђорђе Петрић

Република Србија
Универзитет у Београду
Оснивач: Република Србија
Дозволу за рад број 612-00-02666/2010-04 од 12. октобра 2011. године је издало Министарство просвете и науке Републике Србије

УБ

Хемијски факултет, Београд
Оснивач: Република Србија
Дозволу за рад број 612-00-00725/2010-04 од 27. децембра 2010. године је издало Министарство просвете Републике Србије

Диплома

Јелена, Дејан, Ђорђевић

рођена 10. септембра 1998. године, Пирот, Република Србија, уписана школске 2017/2018. године, а дана 28. септембра 2021. године завршила је основне академске студије, првог степена, на студијском програму Хемија животне средине, обима 240 (двеста четрдесет) бодова ЕСПБ са просечном оценом 8,09 (осам и 9/100).

На основу тога издаје јој се ова диплома о стеченом високом образовању и стручном називу

дипломирани хемичар

Број: 13159100
У Београду, 28. децембра 2021. године

Декан
Проф. др Горан Роглић

Ректор
Проф. др Владан Ђокић

00131845

УБ

Република Србија

Универзитет у Београду

Оснивач: Република Србија

Дозволу за рад број 612-00-02666/2010-04 од 12. октобра 2011. године је издало Министарство просвете и науке Републике Србије

Хемијски факултет, Београд

Оснивач: Република Србија

Дозволу за рад број 612-00-00725/2010-04 од 27. децембра 2010. године је издало Министарство просвете Републике Србије

Диплома

Јелена, Дејан, Ђорђевић

рођена 10. септембра 1998. године, Пирот, Република Србија, уписана школске 2021/2022. године, а дана 15. септембра 2022. године завршила је мастер академске студије, другог степена, на студијском програму Хемија животне средине, обима 60 (шездесет) бодова ЕСПБ са просечном оценом 9,25 (девет и 25/100).

На основу тога издаје јој се ова диплома о стеченом високом образовању и академском називу

мастер хемичар

Број: 14513600

У Београду, 29. децембра 2022. године

Декан
Проф. др Горан Роглић

Ректор
Проф. др Владан Ђокић

00145471

340/2

На основу члана 46. Статута Хемијског факултета и чланова 20-22. Правилника о докторским академским студијама на Универзитету у Београду – Хемијском факултету, Наставно-научно веће Хемијског факултета је дана 9. 5. 2025. године донело следећу

О Д Л У К У

Члан 1.

Прихвата се пријава теме за израду докторске дисертације **Јелене (Дејан) Митић**, мастер хемичара, под насловом:

„Испитивање различитих сценарија за процену ризика по здравље људи услед излагања потенцијално токсичним елементима и полицикличним ароматичним угљоводоницима из земљишта са депонија у Србији“

Члан 2.

Именује се Комисија за оцену научне заснованости теме: **др Дубравка Релић**, ванредни професор Универзитета у Београду – Хемијског факултета, **др Тијана Милићевић**, виши научни сарадник Универзитета у Београду – Института за физику, **др Александар Поповић**, редовни професор Универзитета у Београду – Хемијског факултета.

Члан 3.

Председник комисије, на основу мишљења чланова комисије, у року од 30 дана од дана именовања подноси извештај о научној заснованости теме докторске дисертације Наставно-научном већу на разматрање.

Члан 4.

Извештај комисије се ставља на увид јавности објављивањем на интернет страници Факултета најмање 10 дана пре седнице Већа на којој се разматра.

Члан 5.

Одлука ступа на снагу даном доношења.

Члан 6.

Одлуку доставити члановима Комисије, докторанту и Архиви Факултета.

ДЕКАН ХЕМИЈСКОГ ФАКУЛТЕТА

проф. др Горан Роглић

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

The oral bioaccessibility of potentially toxic elements of illegal landfills' soil and health risk assessment for field workers

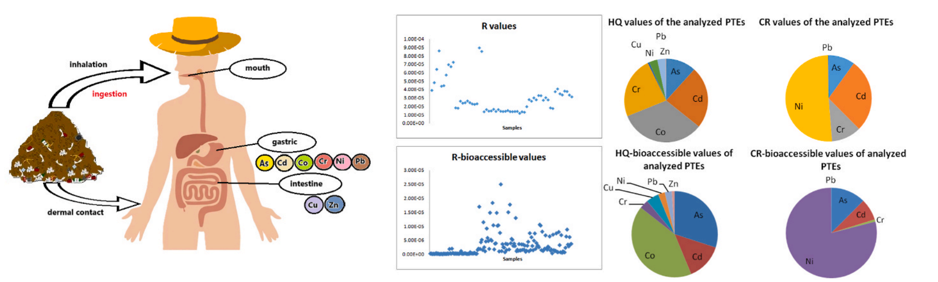
Jelena Mitić [a], Dubravka Relić [b], Mira Pucarević [c], Nataša Stojić [c], Snežana Štrbac [d], Jordana Ninkov [e], Tijana Milićević [a,*]

[a] University of Belgrade, Institute of Physics Belgrade (Environmental Physics Laboratory), National Institute of the Republic of Serbia, Pregrevica 118, 11080, Belgrade, Serbia
[b] University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, Belgrade, Serbia
[c] EDUCONS University, Faculty for Environmental Protection, Vojvode Putnika 87, 21208, Sremska Kamenica, Serbia
[d] University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000, Belgrade, Serbia
[e] Institute of Field and Vegetable Crops, National Institute of the Republic of Serbia, Maksima Gorkog 30, 21101, Novi Sad, Serbia

HIGHLIGHTS

- Potentially toxic elements (PTEs) were investigated in illegal landfills' soil.
- Bioaccessibility of the PTEs was assessed by using *in vitro* UBM test.
- The highest bioaccessibility was observed for Cu at 40.54%, in the gastric phase.
- Increased carcinogenic risk for field workers near illegal landfills was observed.
- Based on the oral bioaccessible PTE concentrations, there is an increased risk for field workers.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on their adverse impact on the environment and human health, landfills represent one of the biggest environmental issues. In this study, the soil samples (two depths, 0–30 and 30–60 cm) from 6 illegal landfills located in the agricultural areas in the Autonomous Vojvodina (AP) Province in Serbia were investigated to assess the bioaccessibility of potentially toxic elements (PTEs: As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) and health risk for field workers. All PTEs, except Pb, in some of the studied soils exceeded the threshold value (TV) prescribed by the national regulation. To assess their bioaccessibility, *in vitro* gastrointestinal test, the Unified BARGE Method (UBM), was used. The UBM test simulates the three phases of the gastrointestinal tract: saliva (S), gastric (GE), and intestinal (IE) by the appropriate fluids. For most of the analyzed PTEs, higher concentrations were extracted in the gastric (GE) phase due to the acidity of the fluid. The bioaccessibility of the investigated PTEs does not exceed 50%, and the highest bioaccessibility from the soil was observed for Cu (40.54%). The workers' health risk assessment (WHRA) indicated no high risk (HI < 1) for developing non-carcinogenic illness for workers in agricultural fields, while there was moderate carcinogenic risk based on both pseudo-total ($R = 2.60 \times 10^{-5}$) and bioaccessible ($R = 1.58 \times 10^{-6}$) concentrations. The highest influence on the workers' health has oral exposure to the soil (HI_o: 8.82×10^{-2} > HI_d: 9.24×10^{-3} > HI_i: 1.09×10^{-3}; R_o: 1.89×10^{-5} > R_d: 6.97×10^{-6} > R_i: 3.86×10^{-8}). Utilizing Both scenarios, the worst-case scenario and the "more realistic" based on bioaccessible

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concentrations, showed that exposure of the field workers to these soil samples has adverse effects on their health.

Abbreviations

PTE –	potentially toxic element
PTEs -	potentially toxic elements
TV -	threshold value
S -	saliva
GE –	gastric extraction
IE -	intestinal extraction
WHRA –	workers' health risk assessment
BARGE -	BioAccessibility Research Group of Europe
UBM -	Unified BARGE Method
AP -	Autonomous Province
ICP-OES -	Inductively Coupled Plasma–Optical emission spectrometry
C -	concentration
EF -	exposure frequency
ED -	exposure duration
IRing -	ingestion rate
IRinh -	inhalation rate
RBA -	risk-benefit assessment
CF -	conversion factor
BW -	body weight
AT -	average exposure time
PEF -	particulate emission factor
SA -	exposed skin area
AF -	soil adherence factor
ABS -	fraction of the applied dose absorbed across the skin
CDI -	Chronic daily intake rate
RfD -	Reference dose
CSF -	carcinogenic slope factor
GIABS -	gastrointestinal absorption factor
HQ -	hazard quotient
HI -	hazard index
CR -	carcinogenic risk
R -	total carcinogenic risks

1. Introduction

Comunal landfills are the easiest and most economical way to manage waste, thus they represent the most common places worldwide for waste disposal (Karimian et al., 2021; Wang et al., 2022). Anyhow, the open waste disposal poses adverse effects to the environment and human health. The emerging environmental problem is generating illegal (wild) landfills that are not controlled and that usually are located near houses, playgrounds, agricultural areas, and rivers. Municipal solid waste in landfills (both communal and illegal) includes household, agricultural, medical, and industrial waste that contains various toxic and dangerous substances.

Potentially toxic elements (PTEs), such as As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, due to their persistence, represent one of the most significant problems in landfills (Karimian et al., 2021). Humans can be exposed to PTEs through inhalation, ingestion, or dermally (Thongyuan et al., 2021; Vongdala et al., 2019). Their bioaccumulation in human tissues can adversely affect the functions of the nervous, cardiovascular, endocrine, and immune systems (Karimian et al., 2021).

PTE influences on human health are frequently studied in the past, and the health effects of most of them are known (Kabata-Pendias and Mukherjee, 2007). Arsenic may cause cardiovascular and respiratory diseases. Cadmium can cause renal damage and hypertension. Chromium, especially Cr^{6+}, leads to liver and kidney failure and anaemia. Copper toxicity disrupts cellular functions, contributing to oxidative stress and Wilson's disease. Nickel exposure can result in developmental and neurological effects. Lead is associated with neurological damage, anaemia, and impaired mental development, especially in children. Increase of Zn concentrations can cause gastrointestinal issues, such as diarrhoea and fever. Long-term exposure to the increased concentrations of As, Cd, Cr, and Ni may cause the development of the cancer (Kabata-Pendias and Mukherjee, 2007). Thus, continuous monitoring of PTE concentrations and human health risk assessments are necessary to obtain safe living and working environments and to protect human health (Vongdala et al., 2019). Human health risk assessment is a method for determining the probability of adverse effects (carcinogenic and non-carcinogenic) on human health that may affect the wider population in case of exposure to harmful chemicals (RAIS, 2013).

The ingested amount of a certain PTE from soil is not equal to the amount that reaches the human bloodstream. Calculating the risk based on the pseudo-total concentrations may represent the overestimation of the risk (Intawongse and Dean, 2006; Guan et al., 2023), while assessment of health risk based on the bioaccessible PTE fractions may represent the "more real" risk assessment. The most important factors influencing bioaccessibility include the source of contamination, physical and chemical properties of the soil, chemical form, and solid phase distribution of the analyzed element (Billmann et al., 2023). Bioaccessibility refers to the fraction of the pollutant, soluble in digestive fluids, that represents the maximum amount of pollutant available for intestinal absorption (Wragg et al., 2011). *In vivo* bioaccessibility assays are long-term, expensive, and require ethical permissions, while *in vitro* are cost-benefit, less time-consuming, strictly controlled, and have a significant correlation with the results obtained *in vivo* (Qian et al., 2024; Denys et al., 2012). Currently, various *in vitro* bioaccessibility assays that simulate oral bioaccessibility are in use (Wragg et al., 2011; Xiao et al., 2024). The bioaccessibility test developed by the BioAccessibility Research Group of Europe (BARGE), known as the Unified BARGE Method (UBM), simulates three phases of the gastrointestinal tract and it was validated by the *in vivo* tests (Billmann et al., 2023; Wragg et al., 2011; Denys et al., 2012), thus this method was chosen in our study as appropriate for the PTE oral bioaccessibility assessment.

Until now, various studies investigating PTEs at landfills have been published (Adelopo et al., 2018; Barbieri et al., 2014; Bartkowiak et al., 2016; Critto et al., 2003; Hiller et al., 2024; Karimian et al., 2021; Obiri-Nyarko et al., 2021; Osibote and Oputu, 2020). Most of the studies investigated the human health risk caused by the municipal solid waste landfills (Adelopo et al., 2018; Hiller et al., 2024; Karimian et al., 2021; Obiri-Nyarko et al., 2021; Osibote and Oputu, 2020). Finally, only a few tests have been conducted on illegal landfills to assess the potential human health risks associated with humans' exposure to the soil of illegal landfills (Bešta-Gajević et al., 2022; Štrbac et al., 2024; Wang et al., 2022). The only research on the bioaccessibility of PTE from municipal solid waste landfill soil was conducted by Hiller et al. (2024). However, according to the available literature, no study has yet investigated in parallel the health risk assessment for field workers near illegal landfills, oral bioaccessibility and bioaccessibility-corrected health risk of PTEs. Thus, the aims of this study are to assess the health risk for field workers (agricultural producers working at the field during the vegetation season of fruits, vegetables, and crops) near illegal landfills. By using the UBM assay, the bioaccessibility of the PTEs from the illegal landfill soils in AP Vojvodina was studied. The worst-case scenario and the more-real risk (bioaccessibility-corrected) for field workers were assessed.

2. Material and method

2.1. Study area

Soil samples from six locations in Autonomous Province (AP) Vojvodina, the northern part of the Republic of Serbia, were investigated. Vojvodina is very rich in fertile land that covers 1.6 million ha, which constitutes 90% of its territory (Agribussines, 2024). Out of a total of 1.6 million ha of the agricultural area in Vojvodina, 91.13% is used as arable land, 7.13% for meadows and pastures, 1.05% for fruit plantations, 0.36% for kitchen gardens, 0.31% for vineyards, and 0.03% for nurseries. On arable land, the most represented are cereals 66.58% (of which wheat is 33.83% and grain maize is 62.52%), industrial crops 23.66% (of which sunflower is 48.47% and soya is 47.92%), and sugar beets 4.48%. On fruit plantations, the most represented continuous fruits are 77.97% (Republican Bureau of Statistics, 2024).

The soils of the Autonomous Province (AP) Vojvodina are extremely susceptible to wind erosion due to the region's physical and geographical characteristics, including its flat topography, lack of forest cover, intensive agriculture, and wind patterns. Vojvodina is the least forested region in Europe, with only 6.37% forest cover, rendering its landscape an agrarian desert (Baumgertel et al., 2019). Agriculture is the largest global employer, particularly in developing countries. In Serbia, with a total population of 6,623,183, the agricultural sector involves 1,157,319 people in the workforce (Republican Bureau of Statistics, 2024).

2.2. Sampling sites and sample collection

Soil samples were collected from 6 illegal landfills (L1, L2, L3, L4, L5, and L6) located in the vicinity of agricultural areas in the Vojvodina Province (Fig. 1). The locations were identified using the Register of Illegal Landfills of the AP Vojvodina, managed by the Provincial Secretariat for Environmental Protection of AP Vojvodina. At each investigated landfill, five subsamples were collected from two depths (topsoil 0–30 cm and subsoil 30–60 cm layers). Given the relatively small surface areas of the observed illegal landfills, subsamples were systematically collected as follows: one from the centre of the landfill (with surface waste removed, if present, before sampling) and four from the landfill periphery, aligned with the cardinal directions (north, east, south, and west), in the nearest areas not covered by waste material. The investigated soils surrounding the illegal landfills are predominantly calcareous, exhibiting an alkaline reaction. The coordinates of sampling sites were determined by GPS and are given in Table S1.

Landfill L1 is located near *Beočin* (Fig. 1). In its surroundings, there are several manufacturers (producing mechanical equipment, concrete, and animal food). It is located along a dirt road, surrounded by arable land. The distance from the road and some manufacturers is about 200 m. Landfill L2 is located near *Bukovac* (Fig. 1). It is located next to a dirt road, surrounded by arable land. The nearest object of unknown purpose is located about 100 m from it, while it is about 250 m from the company that produces carpentry. Landfill L3, with waste scattered over a larger area, is located next to the *Lalić* (Fig. 1). It is located next to a dirt road, surrounded by arable land. Landfill L4 is located near *Manđelos* (Fig. 1), close to the road, surrounded by arable land, about 100 m from the stream. The distance from the village is about 500 m. Landfill L5 is located near *Radenković* (~1 km) (Fig. 1). It is surrounded by dirt roads and arable land. The nearest house is about 200 m away. Landfill L6 is located near *Jamena* (Fig. 1). It is scattered over a larger area, located along the road, surrounded by arable land. The nearest houses are located at a distance of about 200 m, while the Sava River is about 800 m away.

2.3. Sample preparation and chemical analysis of PTEs

2.3.1. Pseudo-total PTE concentrations

Soil samples were dried at room temperature. Each soil sample was gently sieved through a 2 mm sieve (in accordance with ISO 11464, 2006) and placed in paper bags. From each sample of sieved soil, 0.4 g was measured for further analysis for pseudo-total PTE concentrations. The pH value was determined in 1 M KCl soil suspension by the potentiometric method (ISO 10390, 2021). The free $CaCO_3$ content was determined by the volumetric method (ISO 10693, 1995). Organic matter content was measured using the Tyurin method (Shamrikova

Fig. 1. Sampling sites of analyzed soil of illegal landfills in AP Vojvodina. L1 – *Beočin*, L2 – *Bukovac*, L3 – *Lalić*, L4 – *Manđelos*, L5 – *Radenković*, L6 – *Jamena*.

et al., 2022). Total organic carbon (TOC) was determined by elementary analysis (CHNSO VarioEL III) after dry combustion (ISO 10694, 1995). Cation exchange capacity (CEC) was determined by ammonium acetate (Chapman, 1965). The sieved soil samples (0.4 g) were then digested by 7 mL of 65% HNO_3 and 2 mL of 30% H_2O_2 using a microwave digestion system (ETHOS 1, Advanced Microwave Digestion System, MILESTONE, Italy). Samples were diluted to a volume of 50 mL with deionized water. The PTEs (As, Cd, Cr, Co, Cu, Ni, Pb, and Zn) concentrations were determined by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES system Thermo iCAP 6500 Duo). The instrument was calibrated before each set of measurements. Samples were analyzed in triplicates. The blanks and certified soil reference materials (BCR-141R) were used for method validation. The procedure used to detect soil PTE concentrations was relatively accurate; the relative standard deviation was less than 5%, and the recovery percentages were within 90–110%. More details for the analytical technique of analysis of the pseudo-total PTE concentrations are given in a previously published paper by Štrbac et al. (2024).

2.3.2. In vitro bioaccessibility assay

For bioaccessibility assessment, each soil sample was gently sieved through a 250 μm sieve. From each sample, 0.6 g was measured to simulate gastrointestinal extraction using the Unified Barge Method (UBM) (Roussel et al., 2010). The simulation consisted of three steps: the mouth, stomach, and small intestinal cavities. The mouth phase represents the saliva solution (S). The 'stomach' phase (GE) begins after the removal of the supernatant released by extraction with a saliva solution, adding the stomach fluid consisting of gastric juice. The "intestine" (IE) phase begins after removing the supernatant released in the GE phase and adding an extraction solution consisting of duodenal juice and bile (Wragg et al., 2011). After simulating all three phases, the samples were diluted with distilled water, acidified with concentrated HNO_3 and then analyzed on an inductively coupled plasma optical emission spectrometer (ICP-OES system Thermo iCAP 6500 Duo). All the samples were analyzed in triplicates, the blanks were measured, and the calibrations of ICP-OES for the analyses of saliva, gastric, and intestinal soil extracts were done by the matrix matching method with annulling the effects of the matrix to the element determination. As there are not any available certified reference materials for the UBM bioaccessibility method, we used certified reference materials (ERM CC135a Sample 102, Soil ground SARM 42 SAVM, BCR 143R, 2711a Montana II) that have certified values for pseudo-total or total PTE fractions, and % of bioaccessible concentrations are shown in the supplementary material (Table S2).

2.4. Data analysis and human health risk assessment

Statistical analyses were performed using SPSS software version 21 for Windows and Statistic 8 (Stat Soft Inc., Tulsa, OK, USA). The data normality ($p < 0.05$) was tested by applying the Kolmogorov-Smirnov test. The Mann-Whitney *U* test was applied to determine differences in the PTE concentrations between two soil layers. Advanced Principal Component Analysis (PCA biplot) was used to indicate associations between the PTEs and physico-chemical parameters of the investigated soil. The Friedman test ($p < 0.05$) was used to compare the concentrations between saliva, gastric (GE), and intestinal (IE) phases. The descriptive statistics were given in tables and shown with boxplots. The outliers and extremes were identified on the boxplot. The bioaccessibility of PTEs was assessed by the following Equation:

$$Bioaccessibility\ (\%) = \frac{C_{bioaccessible}}{C_{pseudo-total}} \times 100 \quad (1)$$

The PTEs with Reference doses (RfD) and Cancer slope factors (CSF) were used to assess health risk for field workers. Chronic daily intake rate (CDI), non-carcinogenic (HQ – hazard quotient; HI – hazard index) and carcinogenic (CR) and total carcinogenic risks (R) were calculated using the exposure scenario models (RAIS, 2013). To assess the health risk for field workers, the models developed by the US Environmental Protection Agency (RAIS, 2013) were used, but they were adapted to the conditions of work in the field, specifically for agricultural producers (working in the field during the vegetation season of fruits, vegetables, and crops). This model of workers' health risk assessment was adapted previously for the workers in the agricultural areas (Milićević et al., 2018a). Pseudo-total concentrations were used to calculate the total risk (oral + inhalation + dermal) of PTEs for the health of field workers, while bioaccessible concentrations were used to calculate a more realistic oral risk.

Humans could be exposed to PTEs through the following routes: (1) ingestion, (2) inhalation, and (3) dermal contact. Equations (2)–(4) were used to determine the chronic daily intake (CDI) of PTEs via these exposure routes in order to enable an assessment of the health risk for field workers (Relić et al., 2019; Obiri-Nyarko et al., 2021).

$$CDIo = \frac{C/C_b \times EF \times ED \times IR_o \times RBA \times CF}{AT \times BW} \quad (2)$$

$$CDIinh = \frac{C \times IR_{inh} \times EF \times ED}{BW \times AT \times PEF} \quad (3)$$

$$CDIderm = \frac{C \times EF \times ED \times SA \times AF \times ABS \times CF}{AT \times BW} \quad (4)$$

CDI_o, CDI_{inh}, and CDI_{derm} are the chronic daily intake of PTEs via ingestion, inhalation and dermal contact (mg kg^{-1} day^{-1}); C is pseudo-total concentration of PTEs in landfills soil (mg kg^{-1}); C_b is bioaccessible concentration of PTEs in landfills soil (mg kg^{-1}); IR_o is the ingestion rate (mg day^{-1}); RBA is relative bioavailable fraction; EF is the exposure frequency (day yr^{-1}); ED is the exposure duration (yr); BW is the body weight of the exposed individual (kg); AT is the average exposure time (day); CF is the conversion factor; IR_{inh} is inhalation rate (m^3 day^{-1}); PEF is the particulate emission factor (m^3 kg^{-1}); SA is exposed skin area (cm^2); AF is soil adherence factor (mg cm^{-2} day^{-1}); ABS is the fraction of the applied dose absorbed across the skin. Table S3 shows the parameters and the corresponding values used to calculate the CDI of the PTEs via the different exposure pathways.

Based on CDI values, carcinogenic and non-carcinogenic health risks for field workers were calculated. The non-carcinogenic HQ for each PTE and all routes of exposure was first determined using the appropriate Equations (5)–(7). To estimate the overall potential non-carcinogenic health hazard, all HQs were summed and expressed as a HI (Equation (8)). For PTEs capable of causing carcinogenesis, the CR was calculated by multiplying the CDI with the corresponding values to produce the carcinogenic risk for that PTE and for that route of exposure (Equations (9)–(11)). The total carcinogenic risk (R) was determined as the sum of all CR values (Equation (12)).

$$HQo = \frac{CDIo}{RfDo} \quad (5)$$

$$HQinh = \frac{CDIinh}{RfDinh} \quad (6)$$

$$HQderm = \frac{CDIderm}{RfDo \times GIABS} \quad (7)$$

$$HI = \Sigma HQ = HQo + HQinh + HQderm \quad (8)$$

$$CRo = CDIo \times CSFo \quad (9)$$

$$CRinh = CDIinh \times CSFinh \quad (10)$$

$$CRderm = CDIderm \times \frac{CSFo}{GIABS} \quad (11)$$

$$R = \Sigma CR = CRo + CRinh + CRderm \quad (12)$$

The RfD (mg kg^{-1} day^{-1}) refers to the reference dose; CSF (kg day mg^{-1}) to the carcinogenic slope factor; GIABS – to the gastrointestinal absorption factor. These values are shown in Table S4. According to USEPA (2001), there are no non-carcinogenic health hazards if HI < 1, but if HI > 1, there may be a concern for potential human health hazards. The range of acceptable total carcinogenic risk for regulatory purposes is 1.0×10^{-6} to 1.0×10^{-4}. In regulatory terms, $R \leq 1.0 \times 10^{-6}$ represents virtual safety, and $R \geq 1.0 \times 10^{-4}$ indicates a potentially great risk (Huang et al., 2019). In the absence of CSF values for the other analyzed PTEs, the carcinogenic risk was calculated only for As, Cd, Cr, Ni, and Pb. For the purposes of this study, for health risk assessment, the values for Cr^{6+} were used (1/6 of pseudo-total and bioaccessible concentration).

Also, the ratio between HQo and HQo-bioaccessible was calculated (Equation (13)).

$$HQ(\%) = \frac{HQ_{o-bioaccessible}}{HQ_o} \times 100 \quad (13)$$

3. Results and discussion

3.1. Potentially toxic elements in soils of the illegal landfills

3.1.1. Pseudo-total concentrations of PTEs in illegal landfills soil

Across all locations, the chemical properties vary slightly between the topsoil (0–30 cm) and subsoil (30–60 cm) layers, but the overall trends remain consistent. pH values range from 6.88 to 7.78, indicating neutral to slightly alkaline soil conditions. The highest pH values were observed at landfill L3, while the lowest were measured at landfill L5. Calcium carbonate ($CaCO_3$) content also varies significantly, from as low as 0.92 at L5 (0–30 cm) to 24.26% at L1 (30–60 cm). The sites with higher $CaCO_3$ levels suggest a calcareous nature of the soils in these areas. Organic matter content ranges from 1.47 to 3.83%. The highest values were measured in the topsoil at L4, while the subsoil layers generally exhibited lower organic matter content across all sites. Total organic carbon (TOC) closely follows the trend of organic matter, ranging from 0.85 to 2.22%. Cation exchange capacity (CEC) shows wide variation across the sites, ranging from 27.25 to 74.28 meq 100g $^{-1}$. The highest CEC was observed at L3 (0–30 cm), likely linked to higher organic matter content and soil texture. Observing the descriptive statistics (Fig. 2; Table S5), it can be seen that the median concentrations of PTEs (mg kg^{-1}) decrease in the following order: Cr > Ni > Zn > Cu > Pb > Co > As > Cd (Fig. 2). Two soil samples from landfill L3 have extreme concentrations of As (Fig. 2). Concentrations of As (Fig. S2; Table S5) in other samples do not exceed the threshold value for soil (TV) (Official Gazette of the RS, 30/2018 and 64/2019). The highest concentrations of As are present at landfill L2 (Fig. S1). In our study, As concentrations were higher compared to the concentrations measured in most landfills from Table S6. In the literature, besides the geogenic origin of As in the soil of the Balkan Peninsula (Dangić and Dangić, 2007), an additional increase in the total concentrations may be a consequence of the fuel combustion and agricultural activities, such as treatment with pesticides, fertilizers, sludge, and manure (Kabata-Pendias and Mukherjee, 2007; Poznanović Spahić et al., 2019). Cadmium concentrations exceed the TV in all analyzed samples from landfills (Fig. S2; Table S5), and some outliers and extremes originate from landfills L3, L4, and L6 (Fig. 2). The highest concentrations of Cd are present at landfill L6 (Fig. S1). The concentrations of Cd in our study are higher compared to Cd concentrations measured in half of the studies in Table S6, while they are lower compared to the other half of the studies. The main sources of Cd in soil are atmospheric deposition and P-fertilizers, but it can also originate from batteries, pigments, coatings, and plastics (Kabata-Pendias and Mukherjee, 2007). Most of the samples have Co concentrations higher than the TV (Fig. S2; Table S5). The outliers (Fig. 2) originate from landfill L3, while the highest concentrations come from landfill L1 (Fig. S1). Cobalt concentrations from our study are higher compared to concentrations measured in landfills from Table S6. The results indicate that these concentrations may originate from anthropogenic sources such as the fossil fuel combustion in machines used on agricultural land, the use of P-fertilizers, and the disposal of various waste (spent batteries) in the landfills (Jiang et al., 2022). The outliers of Cr concentrations were determined in samples from landfill L1, while in the samples from landfills L1, L3, L5, and L6 were found concentrations (Fig. 2) that exceeded the TV (Fig. S2; Table S5). The highest Cr concentrations originate from landfill L1, which is close to manufacturers of mechanical equipment and animal food (Fig. S1). Wang et al. (2022) reported that 90% of landfill soil samples worldwide exceed urban soil standard Cr values. In our study, Cr concentrations (mg kg^{-1}) were several times higher compared to Cr concentrations measured in most landfills from Table S6. It can be found in different forms depending on whether it is used for electronic products, plastics, food additives, wood preservatives, batteries, and P-fertilizers (Wang et al., 2022; Wu et al., 2024; Poznanovič Spahić et al., 2018). It can also be found in sewage sludge used in agricultural environments (Kabata-Pendias and Mukherjee, 2007). It is estimated that about 30% of Cr originates from plastic packaging (Jung et al., 2006). Therefore, it can be assumed that the mentioned sources are the reason for such elevated concentrations of Cr at these landfills in the investigated agricultural areas of the Province of Vojvodina. The outliers and extreme concentrations of Cu originate from landfills L2, L4, and L3 (Fig. 2). Some soil samples (including outliers and extremes) from landfills L1, L2, L3, and L4 have concentrations higher than TV (Fig. S2; Table S5). The highest Cu concentrations originate from landfill L2 (Fig. S1). Compared to the Cu concentrations presented in Table S6, in our research, most of the Cu concentrations were lower. Among a wide range of uses, Cu is also used in agriculture in fertilizers and pesticides, but it can also be found in manure, sewage sludge, and batteries (Kabata-Pendias and Mukherjee, 2007; Oorts, 2013). It can be assumed that these residues of fertilizers, pesticides, and other Cu-containing products used in agricultural environments end up in such landfills and thereby contribute to an additional increase in Cu concentrations (Kabata-Pendias and Mukherjee, 2007). The outliers for Ni concentration (Fig. 2) are the soil samples from landfill L1, while concentrations higher than the TV are also present in other samples from landfill L1, in all samples from landfill L2 (except one sample), in samples from landfill L3, and in all analyzed samples from landfills L5 and L6 (Fig. S2; Table S5). Much higher concentrations of Ni compared to other landfills are found at landfill L1, which is near several manufacturers (Fig. S1). In contrast to Cu concentrations, Ni concentrations determined in this study are higher than the amounts of this metal in most of soil samples shown in Table S6. Nickel is used in various industries, magnetic

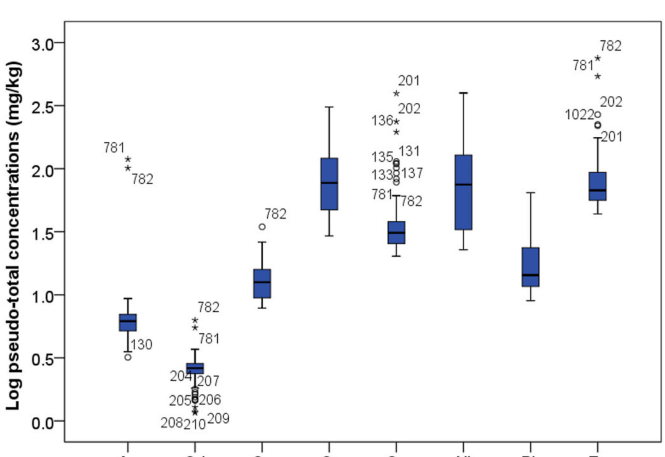

Fig. 2. Pseudo-total PTE concentrations (mg kg^{-1}) in the soil from illegal landfills. Box plots represent the range of these concentrations, asterisks represent extreme values, while circles represent outliers.

components, electrical equipment, stainless steel, various tools and vessels, batteries, P-fertilizers, and sewage sludge (Kabata-Pendias and Mukherjee, 2007). Elevated concentrations of Ni may be a consequence of the use of P-fertilizers as well as other Ni-containing products used in agricultural environments (Kabata-Pendias and Mukherjee, 2007). The Pb concentrations marked as extremes represent the samples from L1 and L2 landfills, which were sampled near the dirt roads (Fig. 2). Higher concentrations of Pb originate from landfill L5 (Fig. S1). However, in the investigated soil samples, concentrations of Pb are not higher than the TV (Fig. S2; Table S5). In our study, Pb concentrations were lower than those in most of the soil samples presented in Table S6. This could be a consequence of the reduced use of Pb in the last decade in the Republic of Serbia. Lead can be found in batteries, leaded gasoline residues, cable covers, pesticides, fertilizers, and pigments (Obiri-Nyarko et al., 2021). For Zn, the outliers originate from landfills L1 and L6, while samples from landfills L3, L4, and L6 represent extreme values (Fig. 2), and only these concentrations exceeded TV (Fig. S2; Table S5). The highest Zn concentrations originate from landfill L5 (Fig. S1). The main source of the waste in this area could be agricultural production, and the main sources of Zn as a pollutant in the agricultural environment could be fertilizers, pesticides, batteries, cable covers, and other waste (Kabata-Pendias and Mukherjee, 2007; Panero et al., 1995; Obiri-Nyarko et al., 2021). Certain Zn concentrations are higher in half of the studies from Table S6, while in half of the studies, they are lower compared to the concentrations from our study. In this study, it can be observed that all analyzed PTEs in the soil, except Pb, exceed the TV prescribed by the national regulation (Fig. S2; Table S5). Such results indicate the anthropogenic influence of waste on the soil in the agricultural areas in Vojvodina Province. The concentrations of analyzed PTEs differ between landfills, and no trend is observed (Fig. S1), which may be a consequence of differences in their composition and environment. As the landfills are illegal, the composition of the landfills cannot be known, thus the potential reasons for such results can be quite diverse.

A comparison of the studied landfills in our study with other landfills from different countries shows great variability in all analyzed PTEs (Table S6). The concentration ranges mostly have partial overlap, with the maximum/minimum values contributing to a greater difference in values, especially for illegal landfills. The PTEs whose concentrations are higher in our study compared to most of the mentioned studies (Table S6) are As, Cr, Cu, and Ni (from all the mentioned studies). This may be due to the agricultural environment of the landfills in our study, because these PTEs are abundant in the agricultural environment (section 3.1.1). The concentrations of Pb in our study are significantly lower compared to most of the mentioned studies, while for Cd, Co, and Zn, there are the variations in concentrations in the published studies, both higher and lower than we measured in landfills' soil (Table S6). These differences in the concentrations of PTEs between landfills are due to the type of waste, the type, size, surroundings, age of the landfill, and local geology (Hiller et al., 2024).

Finally, the pseudo-total concentrations of As, Cd, Co, Cr, Cu, Ni, and Zn in our study are in most of the investigated samples higher than TV, thus harmful effects to the environment and human health can be expected.

3.1.2. *Bioaccessibility of PTEs from landfill soils*

Bioaccessible concentrations from all phases of UBM gastrointestinal extraction are presented in Fig. 3 and Table S7. Medians (mg kg^{-1}) of bioaccessible PTE concentrations decrease in the following order: Zn (11 mg kg^{-1}) > Cu (7 mg kg^{-1}) > Ni (1.7 mg kg^{-1}) > As (0.5 mg kg^{-1}) > Co (0.4 mg kg^{-1}) > Cr (0.34 mg kg^{-1}) > Pb (0.3 mg kg^{-1}) > Cd (0.10 mg kg^{-1}). This descending order of bioaccessible PTE concentrations differs from their pseudo-total concentrations (Figs. 2 and 3). This difference indicates that a higher pseudo-total concentration of ingested PTEs does not necessarily mean that its bioaccessible concentration will be higher. It depends on several factors, such as the physical and chemical

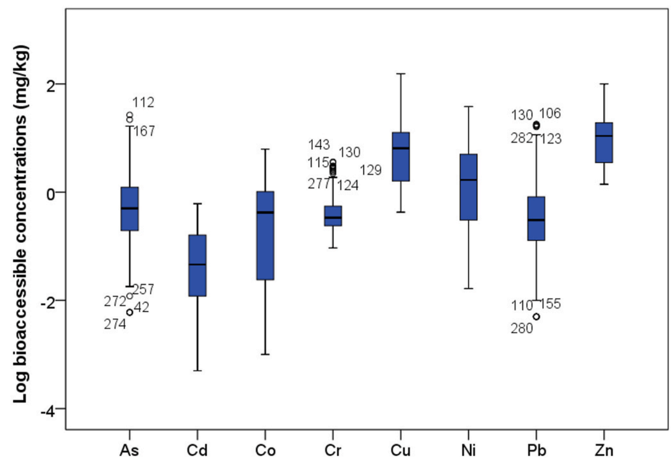

Fig. 3. The total bioaccessible PTE concentrations (mg kg^{-1}) from all phases (sum of saliva, gastric, and intestinal PTEs phases) from the landfill soil. Box plots represent the range of these concentrations, asterisks represent extreme values, while circles represent outliers.

properties of the landfill soil, the chemical form and solid phase distribution of the analyzed PTEs (Billmann et al., 2023), as well as the composition of extraction agents that simulate the gastrointestinal tract.

The Friedman test was used to compare the concentrations between saliva, gastric (GE), and intestinal (IE) phases, and based on it, it showed ($p < 0.05$) differences between the phases for all analyzed PTEs. The PTE that has the highest percentage of bioaccessibility (S + GE + IE) is Cu (Fig. 4e). In the Cao et al. (2020) study, the bioaccessible values for Cu range from 1.3% to 57.7% in the GE phase, while in the IE phase from 7% to 100%; this range is comparable with our results. In almost half of the published studies, As bioaccessibility was below 30% in both the GE and IE phases (Billmann et al., 2023, and references therein). The value for bioaccessibility (%) for As in the GE phase obtained in this study does not exceed 30%, while it is slightly higher in the IE phase (Fig. 4a). More than half of the published studies found bioaccessible values for Pb lower than 50% in the GE and lower than 30% in the IE phase, while for Cd, lower than 60% in the GE phase and lower than 40% in the IE. The bioaccessibility (%) for Pb and Cd in both phases (GE and IE) obtained in our study (Fig. 4g–b) is significantly lower compared to other studies that were described in the study published by Billmann et al. (2023). For Ni and Cr, it was published that the bioaccessibility is lower than 20% and 30% in the GE phase, while in the IE phase, it is 30% and 20%, respectively (Billmann et al., 2023 and references therein). In this study, the same bioaccessibility (%) was also obtained in the case of Ni and Cr (Fig. 4f–d). The bioaccessibility varied significantly among the analyzed PTEs and showed variance between GE and IE phases (Fig. 4). The bioaccessibility tended to be higher in the GE phase than in the IE phase for Ni, As, Co, Cr, Pb, and Cd. The reason for the better extraction of most PTEs in the GE phase is the acidic stomach environment. Besides, bile salts and pancreatin in the IE phase can lead to reabsorption and precipitation of dissolved PTEs (Guan et al., 2023). The increased bioaccessibility of Cu and Zn in the IE compared to the GE can be attributed to the presence of pepsin in the GE, which forms stable complexes with Cu and Zn ions, thus reducing their bioavailability (Wu et al., 2024). The lowest percentage of bioaccessible concentrations is released in the saliva phase, as in this phase soil retention is the shortest. In order to optimize soil sample preparation, this extraction step, if it is not specifically important to analyze for some specific samples, may be excluded or combined with the gastric phase.

3.1.3. *Principal component analysis (PCA) of PTE concentrations*

The Mann-Whitney *U* test showed that there is no statistically significant difference in PTE concentrations between topsoil and subsoil layers, thus results from both soil layers were statistically analyzed and

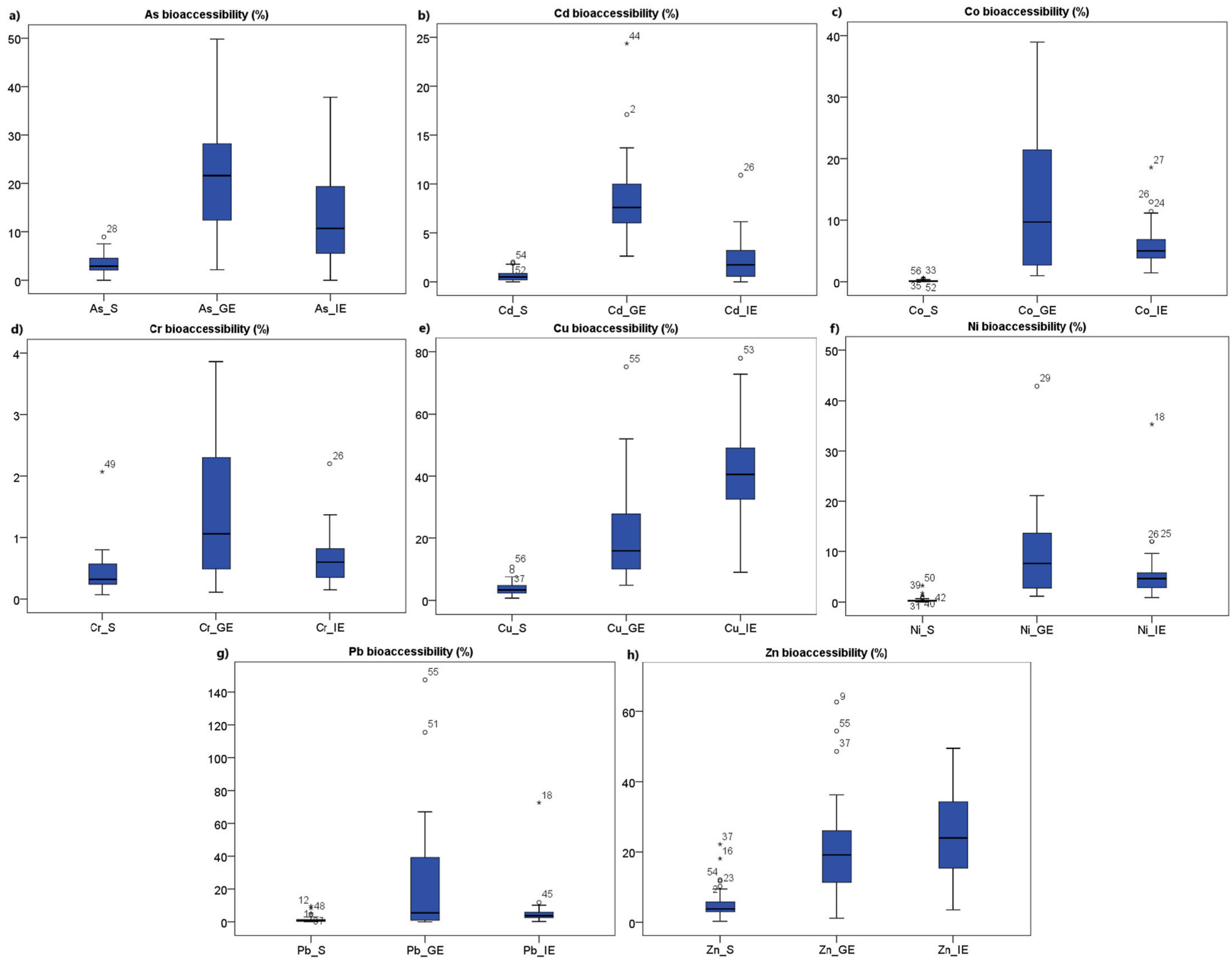

Fig. 4. Bioaccessibility (%) of PTEs in saliva (S), gastric (GE) and intestinal (IE) phase. Box plots represent the range of these concentrations, asterisks represent extreme values, while circles represent outliers.

were used for human health risk assessment. This phenomenon may be caused by the mixing of the soil layers in the surrounding area of the landfills during agricultural activities or by the leaching of some PTE quantities from topsoil to subsoil. Also, the soil samples investigated in this study have been collected from 6 different locations, and the Kolmogorov-Smirnov test indicates that the data is not normally distributed. The PCA biplot (Fig. 5) was used to determine interaction within the PTE concentrations in the illegal landfill soils. The pseudo-total concentrations of the Co, Cd, Cr, Pb, and Ni grouped in one quadrant with both positive PC loadings (PC1: 21.4 and PC2: 16.3%). Between these PTE concentrations, significant relations were observed (Fig. 5). The positive PC1 and high positive PC2 loadings have pseudo-total concentrations of Cr, Co, Cd, Pb, and Ni concentrations, and their concentrations higher than TV probably indicate the occurrence of anthropogenic pollution at investigated locations, by both the leather industry and cement plant (Poznanović Spahić et al., 2019). Common sources for Ni and Cr may be electrical components and sewage sludge, while pesticides may be additional sources of As, Zn, and Cu (Wang et al., 2022; Wu et al., 2024; Poznanović Spahić et al., 2018; Kabata--Pendias and Mukherjee, 2007; Obiri-Nyarko et al., 2021). The use of P-fertilizers on surrounding arable land and their disposal in landfills (Kabata-Pendias and Mukherjee, 2007; Jiang et al., 2022; Poznanović Spahić et al., 2018; Obiri-Nyarko et al., 2021) and different types of batteries can be the source of all the above-mentioned elements on the landfill (Kabata-Pendias and Mukherjee, 2007; Jiang et al., 2022; Poznanović Spahić et al., 2018; Obiri-Nyarko et al., 2021). In parallel, As, Cu, and Zn pseudo-total concentrations are grouped in another quadrant on PCA (with negative PC1 loadings), and in the same quadrant are grouped OM, pH, and $CaCO_3$ and TOC of soil (Fig. 5). This implies that the mentioned physico-chemical soil parameters highly influenced these pseudo-total concentrations in the soil. It should be noted that at the Balkan Peninsula, the geological formations and ore deposits may be one of the most important natural sources of As (Dangić and Dangić, 2007; Milićević et al., 2018b), especially in AP Vojvodina, which is part of the Pannonian Basin (Ružičić et al., 2023; Bašić, 2013). Additionally, at some sites in AP Vojvodina located near the cement factory, the increased total As concentrations may originate from both geogenic and anthropogenic sources (Poznanović Spahić et al., 2019), and at the sites we investigated these elements (Cu, Zn, and As) may have additional sources originating from agricultural practice.

Observing the PCA biplot (Fig. 5), PTEs extracted with gastric fluid associated in the upper part of PCA with positive loadings on both PC1 and PC2. In this upper part of PCA, with positive PC2 loadings the soil samples from L5 and L6 are grouped (Fig. 5). The largest number of significant correlations was in the GE phase; this could be due to the effect of better extraction of PTEs in acidic, gastric medium. In this

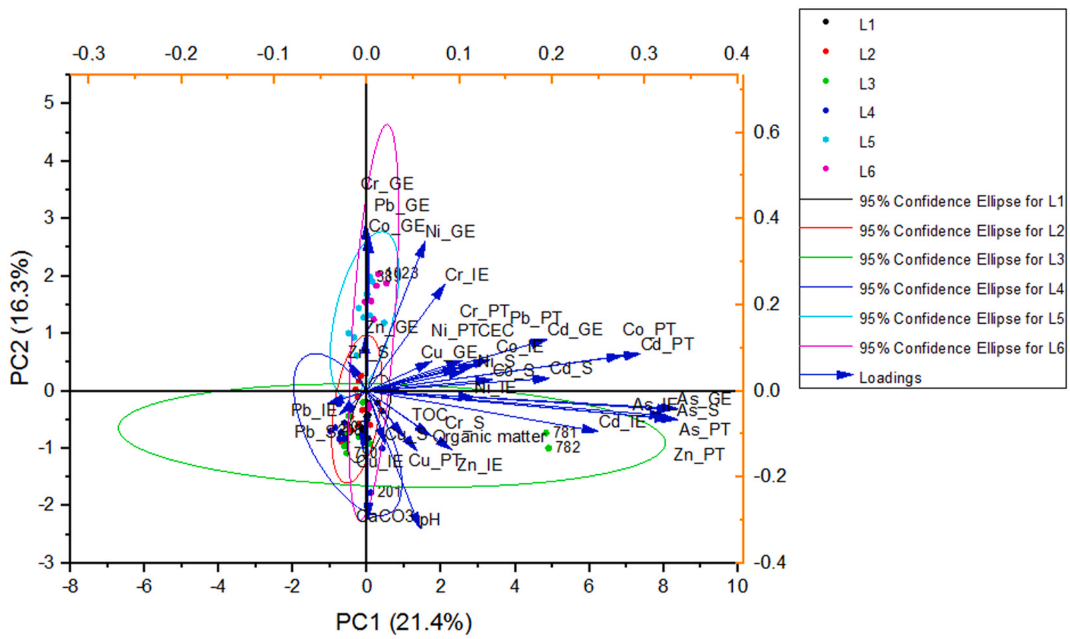

Fig. 5. Principal Component Analysis (PCA) with PC1 (21.4%) and PC2 (16.3%) observing the distribution of soil samples (coloured dots represent the samples from different landfills) and variables (pseudo-total, saliva, gastric and intestinal concentrations and physicochemical parameters of soil).

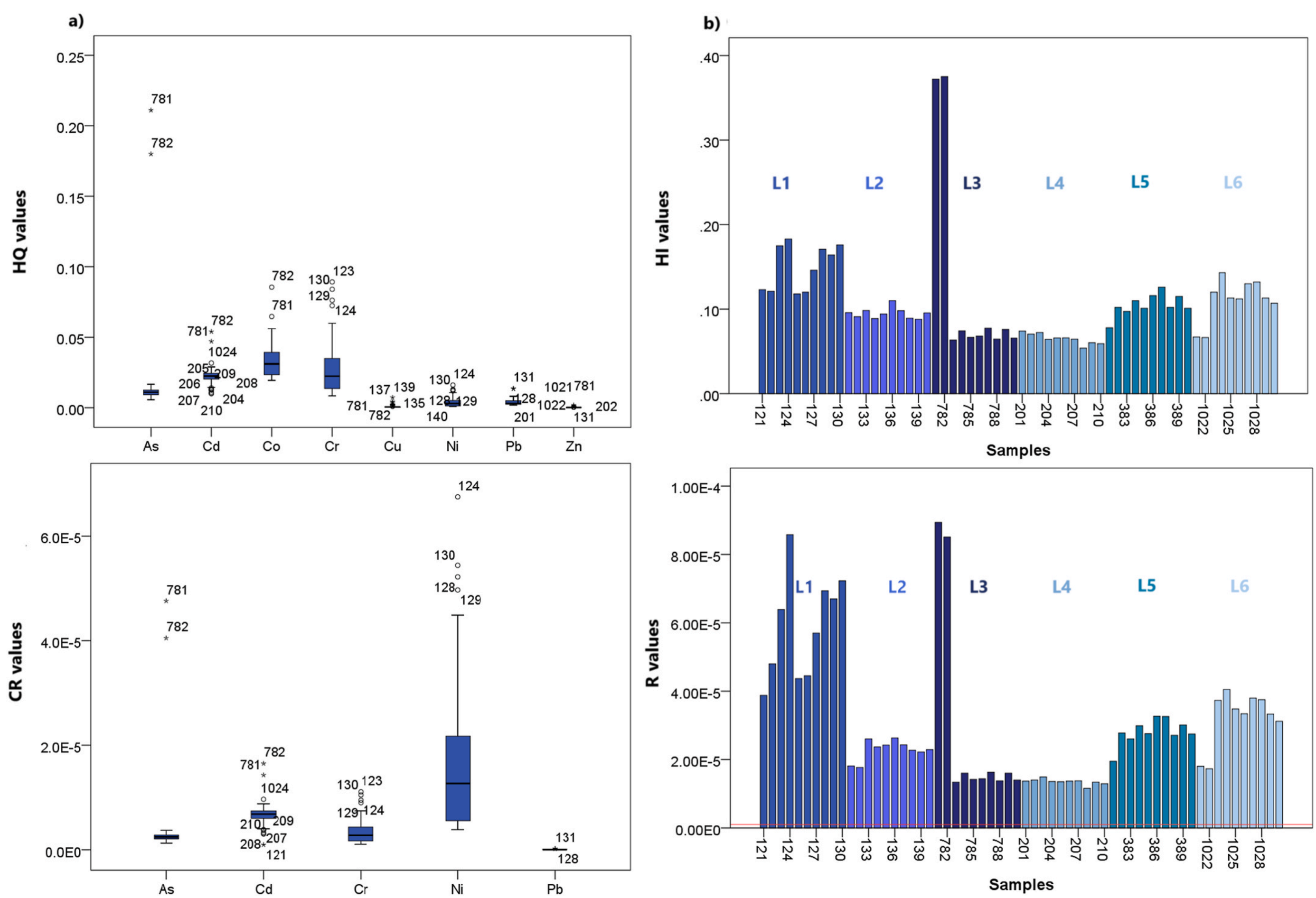

Fig. 6. a) Hazard quotient (HQ); b) Total non-carcinogenic risk (HI) values; c) CR values and d) R values for pseudo-total concentrations of analyzed PTEs. In Fig. 6a–c box plots represent the range of HQ (Fig. 6a) and CR (Fig. 6c) values for each PTE separately. Asterisks represent extreme values, and circles represent outliers. In Fig. 6b–d, the columns represent HI (Fig. 6b) and R (Fig. 6d) values for each sample.

quadrant, with most of the pseudo-total and gastric PTEs, is grouped cation exchange capacity (CEC) which probably has the major influence on the release of the PTEs in acid solutions such as HNO_3 with H_2O_2 and gastric fluid. As it was previously mentioned, the variation of soil CEC probably has a major influence on the gastric and pseudo-total PTE concentrations in the investigated soil. Significant associations were noticed between all three gastrointestinal phases (S, GE, and IE) and pseudo-total As concentrations (Fig. 5). These concentrations have high positive PC1 loadings and are grouped with samples from landfill L3 (*Lalić* landfill, which is the most northern sample site in this study), implying the higher As concentrations in this landfill soil (Fig. S2). In this quadrant are grouped Cu, Zn, Cd, and As from the intestinal phase and Cr, Cu, and As from the saliva phase; also in this quadrant are grouped gastric-extracted As and pseudo-total As, Cu, and Zn (Fig. 5). As previously stated, TOC, OM, pH, and $CaCO_3$ can affect pseudo-total concentrations of As, Cu, and Zn. Since these physicochemical parameters are within this quadrant, it is possible that they also affect the amounts of these elements that are extracted by the intestinal and saliva extractants that are applied. Observing the PCA biplot (Fig. 5), may be seen that only Pb extracted with saliva and intestinal fluid grouped separately in a quadrant with negative PC1 and PC2 plots, which may indicate that these are not aggressive enough extractants to isolate low quantities of Pb from soil and that their isolation mechanism was similar.

3.2. Human health risk assessment for field workers exposed to illegal landfills soil

3.2.1. Human health risk assessment based on PTE pseudo-total concentrations

To assess the health risk for field workers, non-carcinogenic (HQ, HI) and carcinogenic (CR, R) risks were calculated for each of the analyzed PTE concentrations. Three routes of exposure (oral ingestion, inhalation, and dermal) to PTEs in the soil were assessed. The HQ and HI (Fig. 6a and b) results represent the non-carcinogenic effects of PTEs on human health, and the CR and R (Fig. 6c and d) results represent the carcinogenic effects on human health (Tables S8 and S9). Observing the results (Fig. 6), it can be noticed that the risk of each PTE (HQ) as well as the total risk (HI) are notably lower than the limit value of 1 (RAIS, 2013). Thus, the results indicate that there is no high risk to the development of the non-carcinogenic illnesses of field workers in the surroundings of illegal landfills. Anyhow, for most of the investigated landfills (L1, L3, L5, and L6), HI is higher than 0.1, which indicates these locations as a priority for detail and frequent PTEs monitoring for human health risk and environmental implication assessments. Based on the HQ values (Fig. 6a), the highest risk originates from Co, followed by Cr and Cd concentrations. The highest total non-carcinogenic risk (HI) was observed for workers near landfill L1 (near *Beočin*), with the exception of two samples from landfill L3 (Fig. 6b), where the concentrations of Co contribute the most to the increase of the field workers' health risk. The reason for this may be the proximity of various manufacturers in the surroundings of their location (Fig. 1) which was in detail described in section 2.2. For Cd, the largest contribution to the total risk comes from oral intake (Fig. S3). The oral route of intake contributes the most to the total non-carcinogenic risk of Co, while inhalation and dermal contact contribute significantly less to the non-carcinogenic risk of Co (Fig. S3). For Cr, the results also indicate that oral ingestion contributes the most to the increase of the non-carcinogenic health hazards to field workers, while inhalation and ingestion of Cr contribute less to the non-carcinogenic risk (Fig. S3).

In the investigated soil, pseudo-total concentration of Ni contributed the most to the cancer risk (Fig. 6c). The median CR value for Ni is 1.27 x 10^{-5} which is higher than the acceptable limit of 1.0 x 10^{-6} (RAIS, 2013). The existence of a carcinogenic risk to field workers (outdoor workers in the agricultural fields) due to Ni exposure to the soil is worrying. Carcinogenic risk values for As, Cd, and Cr slightly exceed the threshold values (RAIS, 2013). The total carcinogenic risk (R), representing the sum of the carcinogenic risks, exceeds the acceptable limit, and its median is 2.6 x 10^{-5} (Table S9). If we exclude two extreme values from landfill L3 (Fig. 6d), the highest carcinogenic risk was observed for landfill L1 (near *Beočin*; Fig. 1). The reason for this can be the proximity of various manufacturers that can additionally increase the concentrations of the carcinogenic PTEs in soils but also on the type of the waste in the illegal landfills.

3.2.2. Human health risk assessment based on the oral exposure to PTEs from illegal landfill soil — in vitro bioaccessibility assay

As it was shown, in the case of the worst-case scenario of human health risk assessment, oral exposure to the PTE concentrations mostly contributed to the increase of workers' health risk. Thus, the oral exposure was investigated by using an *in vitro* UBM bioaccessibility assay to assess the more real oral exposure and human health risk. The ingested content of certain PTEs is not equal to the amount that reaches the bloodstream; by calculating the risk based on the pseudo-total ingested PTE concentrations, the human health risk may be overestimated. For a more realistic assessment of the health risk, the bioaccessible concentrations were used in risk assessment (Tables S10 and S11).

It is observed that the HQ-bioaccessible (Fig. 7a) of the analyzed PTEs and the total non-carcinogenic bioaccessible risk (HI-bioaccessible) (Fig. 7b) are lower than the threshold value of 1 (RAIS, 2013). Observing HQ-bioaccessible, Co has slightly higher values than the other investigated PTEs, followed by As, Cd, and Cu. Anyhow, some of the investigated soil samples have As and Co HQ-bioaccessible values (extremes in Fig. 7b) higher than 0.1 which may suggest their higher bioaccessibility and risk than other PTEs. Similar to the HQ calculated based on the pseudo-total concentrations, there are outliers for As originating from landfill L3 (soil samples from the central part of the landfill). The impact of Co on human health has already been discussed in the previous section (3.2.1).

Although only the median of Ni CR-bioaccessible value (Fig. 7c) exceeds the limit value of 1.0 x 10^{-6} (RAIS, 20113) proposed for pseudo-total and total concentrations, in some samples field workers' health risk exposed to the bioaccessible As and Cd from landfills soil exceeds the limit value (Fig. 7c). CR-bioaccessible values for Ni contributed the most to R-bioaccessible (Fig. 7d), whose median is 1.6 x 10^{-6}. This value indicates the existence of a carcinogenic risk for field workers from bioaccessible concentrations that represent the amount of PTEs that enter the bloodstream and can accumulate in organs and directly affect human health.

Comparing HQ values calculated for oral intake using pseudo-total and bioaccessible concentrations (Table S12), HQ-bioaccessible represents 8.12% of the HQ-pseudo-total for As, 1.76% for Cd, 3.34% for Co, 0.44% for Cr, 20.86% for Cu, 2.25% for Ni, 2.14% for Pb, and 16.23% for Zn. The total oral bioaccessible non-carcinogenic risk represents 3.75% of the total oral non-carcinogenic risk (worst-case scenario). It should be noted that the risk calculated based on the bioaccessible PTEs fractions can be more accurate in identifying the more hazardous elements that are bioaccessible to humans and to which human exposure should be more carefully considered. CR-bioaccessible represents 8.12% of the CR-pseudo-total for As, for Cd 1.76%, for Cr 0.44%, for Ni 13.52%, and for Pb 2.14%, while the total oral bioaccessible carcinogenic risk represents 8.34% of the total oral carcinogenic risk. As the assessment of bioaccessible risk is based only on the risk from the oral intake of PTEs, a more sensitive scale should be developed compared to the one used for pseudo-total concentrations.

4. Conclusion

In this study, the bioaccessible and worst-case scenario health risk for workers in the field who are exposed to the As, Cd, Co, Cr, Cu, Ni, Pb, and Zn concentrations in illegal landfills' soils in AP Vojvodina were

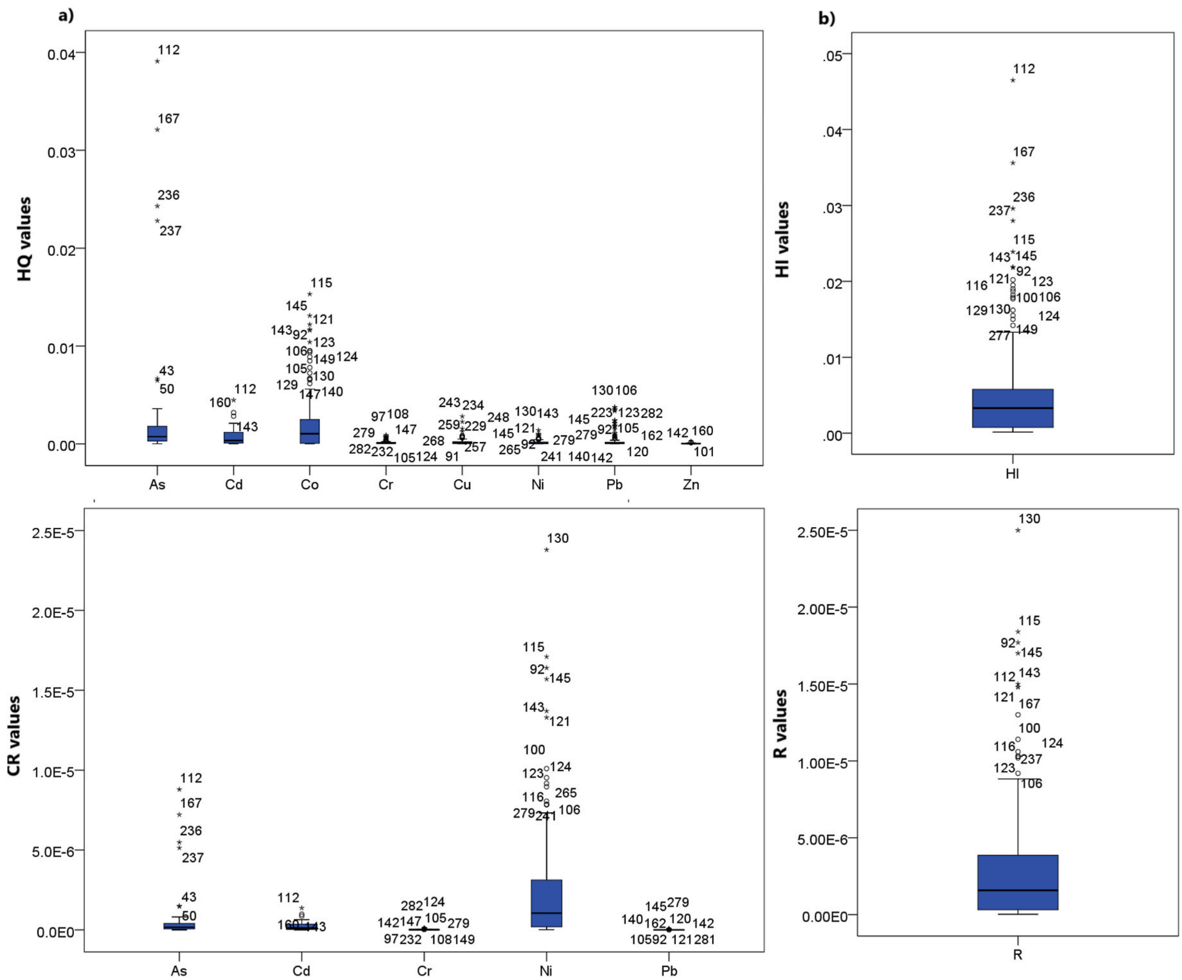

Fig. 7. a) Bioaccessible hazard quotient (HQ); b) Total oral bioaccessible non-carcinogenic risk (HI) values; c) bioaccessible carcinogenic risk (CR) values and d) total oral carcinogenic risk (R) values for oral bioaccessible concentrations of analyzed PTEs. In Fig. 7a–c box plots represent the range of HQ (Fig. 7) and CR (Fig. 7c) values for each PTE separately. Asterisks represent extreme values, and circles represent outliers. In Fig. 7b–d, box plots represent the range of HI (Fig. 7b) and R (Fig. 7d) values for each sample. Asterisks represent extreme values, while circles represent outliers.

studied. In some of the investigated samples, all analyzed PTEs, except Pb, exceed the TV prescribed by the national regulation. However, the findings of the pseudo-total concentration-based health risk assessment for field workers suggest that there isn't presently a high risk for developing the non-carcinogenic illnesses by exposure to PTEs, while with long-term exposure there is a carcinogenic risk for field workers. The results show that the highest non-carcinogenic and carcinogenic risk for field workers mostly originates from landfill L1 (in the vicinity of *Beočin*) and landfill L3 (in the vicinity of *Lalić*). Bioaccessibility has large variations between phases and analyzed PTEs. The bioaccessibility values (medians) of the analyzed PTEs do not exceed 50%, and Cu has the highest bioaccessibility. Higher values for bioaccessibility were determined in the GE phase than in the IE phase for all PTEs, except Cu and Zn. As the bioaccessibility in the salivary solution (S) is very low, this phase may not be separate from the GE phase in further research to optimize the analysis and sample preparation. The health risk assessment for field workers based on bioaccessible PTE concentrations shows that there is currently no high risk for developing non-carcinogenic illnesses, while there is an acceptable risk of developing carcinogenic illnesses. The risk from pseudo-total concentrations represents the worst-case scenario, while the risk from bioaccessible concentrations represents a more realistic scenario. The bioaccessible concentrations of PTEs are more realistically representative of the concentrations that enter the bloodstream and remain in the human body; therefore, our study suggests the use of bioaccessible concentrations for calculating the risk to human health in order to avoid overestimation of health risk. The scale for ranging the risk was developed for models using total and pseudo-total concentrations. Therefore, a specific scale should be developed for further research on risk assessment based on bioaccessible concentrations. The long-term exposure to PTEs from the landfill soils may cause carcinogenic adverse effects to the health of field workers. Finally, the studies like this may be the first step in making the priorities to sanitise the illegal landfills that were developed by the local communities and that may adversely affect their health. The awareness of the health risks associated with pollution exposure should be increased to prevent the creation of harmful illegal landfills near areas where people live, work, or grow food.

CRediT authorship contribution statement

Jelena Mitić: Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization. **Dubravka Relić:** Writing – review & editing, Supervision, Investigation, Conceptualization. **Mira Pucarević:** Writing – review & editing, Supervision, Resources, Project administration, Formal analysis, Data curation. **Nataša Stojić:** Writing – review & editing, Project administration, Data curation. **Snežana Štrbac:** Writing – review & editing, Project administration, Formal analysis, Data curation. **Jordana Ninkov:** Writing – review & editing, Resources, Project administration, Formal analysis, Data curation. **Tijana Milićević:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2025.144173.

Data availability

No data was used for the research described in the article.

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EA PP 09

Human health risk assessment based on the element concentrations in landfills' soil

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Landfills represent the simplest and cheapest way of waste management, however, this way of waste disposing significantly contributes to environmental pollution [1]. Among landfills, special attention should be paid to illegal landfills located in agricultural areas. In addition to polluting the surrounding soil, groundwater, and even the air, such landfills lead to the pollution of the surrounding crops and thus contribute to a greater negative impact on human health.

For our study, 6 illegal landfills from northern Serbia were analyzed and 5 samples were taken from each landfill. The aim of our study was to assess the risk to human health due to inhalation, oral or dermal intake of contaminated soil from landfills. Both carcinogenic (R) and non-carcinogenic risk (HQ) were investigated. The following potentially toxic elements (PTEs) were analyzed: As, Cd, Co, Cr, Cu, Ni, Pb, Zn and Hg. Samples were prepared by microwave digestion and the PTE concentrations were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The results showed the following order of HQ levels (median) of PTEs in landfills' soil: Pb (5.49E+02) > Cr (3.21) > Ni (2.93E-01) > Co (1.61E-01) > Hg (9.37E-02) > As (1.10E-02) > Cu (2.97E-03) > Cd (2.28E-03) > Zn (8.62E-04). These values show that there is a high risk of damage to the brain and central nervous system due to chronic exposure to high concentration of Pb, in addition to other diseases that can occur due to the synergistic toxic effect of other PTEs. For carcinogenic risk values (median), the order is as follows: Cr (8.01E-04) > As (2.90E-06) > Pb (4.22E-07). The results show that there is a medium to high risk to human health because of the chronic exposure to soil from landfills in agricultural areas. The potential non-carcinogenic risks followed the order of inhalation > ingestion > dermal absorption, but the order of exposure routes for carcinogenic risk was ingestion > dermal absorption > inhalation.

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The element concentrations in human milk samples from Croatia and *in vitro* bioaccessibility assay

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Human milk represents the most significant food and source of nutrients for the newborn. It has immunological and health effects on the baby which is of major importance. Human milk samples were collected from healthy volunteer mothers from the general population living in urban or semi-urban areas in Zadar in Croatia. Each participant gave informed consent before donating the milk samples for the experiment. In our study 50 milk samples from healthy mothers were investigated. The aim of our study was to determine macro elements as nutrients in milk samples and to monitor the potentially toxic elements (PTEs) in human milk since they pose health risk for infants. Also, the *in vitro* bioaccessibility assay simulating gastrointestinal tract (GIT) was used for the assessment quantity of dissolution of PTEs in infant GIT [1, 2].

Milk samples were stored frozen before the analysis. The microwave digestions of milk samples, 10 mL of each sample, were done by using HNO_3 and H_2O_2 and concentration of 24 elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Se, Sr, Zn) were determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma –Mass Spectrometry (ICP-MS). The skimmed milk powder ERM certified Reference Material (ERM®-BD150) was used and the blank samples were analysed. In parallel, the bioaccessibility assay was performed at the controlled temperature of 37 °C with solutions simulating gastric (GE) and gastro-intestinal (GIE) fluids to simulate the GIT (stomach and small intestine, respectively) of infants [1, 2]. In the solutions GE and GIE we also analysed the PTE concentrations by ICP-OES and ICP-MS. GE simulates bioaccessibility in the infant's stomach and GIE in the small intestine. The macro elements were not determined in bioaccessible fraction because the solutions for the simulation GE and GIE contain salts and enzymes, and salts in the extracts make this procedure inappropriate for nutrients bioaccessibility assessment.

Observing the pseudo-total element content the macro element concentrations were determined in highest concentrations in the following order K > Ca > Na > P > S > Zn > Mg > Fe > Cu > Li > Al > Se > Sr > B > As > Mn > Ba > Cd > Pb. Concentrations of Co, Cr, Hg and Ni were not determined in human milk samples (concentrations were lower than the limit of the detection). Some of the measured elements are of an essential role in infant health and their concentrations were similar with nutritional studies and WHO reports, while the other elements such As, Cu, B, Cd and Pb can mostly originate from food consumption or environmental exposure of mothers. For As, Cd and Pb there are some pseudo-total extreme values in milk samples from mothers who consume cigarettes but also in some samples from mothers who do not consume cigarettes were extreme or outlier values. Thus, we cannot have a clear connection because probably many of them can be indirectly exposed to the different sources of these toxic elements. Anyhow for further investigation, more details in observing the habits of mothers will be included (such as identification of the exposure, type of food they mostly consume, potential metal pollution sources at the home and in the working place etc).

Bioaccessibility assay was appropriate for the determination the bioaccessibility of elements Al, As, B, Ba, Cd, Cu, Fe, Mn, Pb, Sr and Zn. The median values of bioaccessible element fractions in GE compared to the pseudo-total concentration (%) are Al (0.19 %), As (0.41 %), B (0.19 %), Ba (10.6 %), Cd (12.1 %), Cu (13.3 %), Fe (7.99 %), Mn (25.4 %), Pb (2.67×10^{-6} %) Sr (0.07 %) and Zn (8.25 %). The median values of bioaccessibility of elements in GIT compared to the pseudo-total content of elements in milk samples are Al (0.04 %), As (0.07 %), B (0.04 %), Ba (0.98 %), Cd (2.29 %), Cu (19.25 %), Fe (1.88 %), Mn (4.83 %), Pb (4.6×10^{-5} %) Sr (0.08 %) and Zn (8.25 %). The bioaccessibility of Al, As, B, Ba, Cd, Fe, and Mn is higher in GE (stomach) where the GE fluids were more acidic than in GIT. Similar bioaccessibility in GE and GIE fractions were obtained for Sr and Zn, but higher bioaccessibility of Cu and Pb were obtained in the small intestine than in the stomach. The highest bioaccessibility, among the investigated elements, were obtained for Ba, Cd, Cu, Fe, Mn, and Zn in the stomach, and Cu, Mn and Zn in the small intestine. Thus, mothers should avoid uncontrolled exposure to the Ba, Cd, Cu, Fe, Mn, and Zn in lactation periods, because their accumulation in milk and bioaccessibility to the infant is higher and can affect the infant's health.

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Saturation Isothermal Remanent Magnetization of Grapevine Leaves as a Proxy for Environmental Pollution

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Abstract. Magnetic particulate matter (PM) monitoring can be realized by magnetic parameters' determination. The magnetic parameters' measurements can represent the alternative method for identification of PM and potentially toxic elements (PTE) pollution in the environmental studies. Determination of magnetic parameters such as saturation isothermal remanent magnetization (SIRM) has been described as cost-effective, sensitive and non-destructive method for PTE pollution assessment which allows fast screening of magnetic PM pollution over large areas [1, 2]. Content of SIRM on leaf surface (an indicator of current pollution) was assessed in agricultural areas (conventional and organic vineyards). Main aim of our study [3] was to explore whether SIRM can be a proxy for magnetic PM pollution and associated potentially toxic elements (PTEs) in agricultural areas. Saturation isothermal remanent magnetization may represent a reliable proxy for assessing the ambient PTE pollution in the agricultural environment, and there were some differences between the distributions of SIRM throughout the grapevine season [3]. The leaf SIRM could pinpoint site-specific pollution in the vineyard ambient, suggesting that grapevine leaves can be used as biomonitors of PTE ambient pollution and leaf SIRM as a reliable representation for magnetic PM and some PTEs. The advanced principal component analysis showed that leaf SIRM was associated with PTEs of those sampling sites where higher concentrations were observed (near a metal foundry in a conventional vineyard and parcels not surrounded by the natural barriers and near the river in an organic one). Measurements of SIRM parameter can be recommended as user-friendly, fast and eco-sustainable techniques for determining magnetic PM and PTE pollution hotspots in agricultural ambient as pre-screening before more detail PTE pollution research.

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