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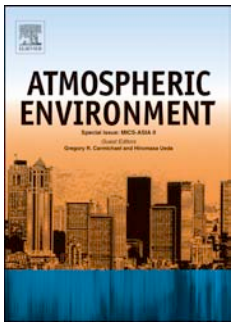

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AIR QUALITY IN URBAN PARKING GARAGES (PM_{10}, MAJOR AND TRACE ELEMENTS, PAHs): INSTRUMENTAL MEASUREMENTS *VS.* ACTIVE MOSS BIOMONITORING

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Abstract

This study was performed in four parking garages in downtown of Belgrade with the aim to provide multi-pollutant assessment. Concentrations of 16 US EPA priority PAHs and Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn were determined in PM_{10} samples. The carcinogenic health risk of employees' occupational exposure to heavy metals (Cd, Cr, Ni and Pb) and PAHs (B[a]A, Cry, B[b]F, B[k]F, B[a]P and DB[ah]A) was estimated. A possibility of using *Sphagnum girgensohnii* moss bags for monitoring of trace element air pollution in semi-enclosed spaces was evaluated as well. The results showed that concentrations of PM_{10}, Cd, Ni and B[a]P exceeded the EU Directive target values. Concentration of Zn, Ba and Cu were two orders of magnitude higher than those measured at different urban sites in European cities. Cumulative cancer risk obtained for heavy metals and PAHs was $4.51 \cdot 10^{-5}$ and $3.75 \cdot 10^{-5}$ in M and PP, respectively; upper limit of the acceptable US EPA range is 10^{-4}. In the moss, higher post-exposure than pre-exposure (background) element concentrations was observed. In comparison with instrumental monitoring data, similar order of abundances of the most elements in PM_{10} and moss samples was found. However, using of the *S. girgensohnii* moss bag technique in indoor environments needs further justification.

Key words: indoor air quality, active biomonitoring, moss bag, *Sphagnum girgensohnii*, health risk

1. Introduction

Under heavy traffic conditions, particulate matter (PM) concentrations were found to be about 10 % higher indoor than outdoor (Fischer et al., 2000). In a road tunnel, average particle mass concentrations were more than 30 times higher than in the outside urban background air (Oliveira et al., 2011). Also, PM concentrations measured inside a bus shelter were higher than those measured at the exposure site outside (Hess et al., 2010). Thus, like tunnels or tollbooths (Sapkota and Buckley, 2003), parking garage facilities are interesting for air quality assessment.

Parking garages represent hotspot microenvironments where employees and attendants are potentially exposed to elevated concentrations of traffic-related air pollutants due to very intensive vehicle activities and limited fresh air exchange. Both diesel and gasoline engine emissions have been considered as significant sources of PM. Additionally, wearing of brake linings and tires together with dust resuspension are the uppermost contributors to the increased PM concentrations during parking (e.g. Birmili et al., 2006). It should be noted that PM is a highly chemically complex mixture, consisting of various organic and inorganic compounds. Some heavy metals and polycyclic aromatic hydrocarbons (PAHs), adsorbed on the particle surface, determine its toxicological characteristics and have adverse effects on human health (De Kok et al., 2006; Kelly and Fussell, 2012). Because of its suspected carcinogenic nature, routine measurements of PAHs and some heavy metals in PM_{10} are recommended by EU legislation (Directive 2004/107/EC). Nevertheless, only a few studies have been carried out in parking garages including measurements of CO, VOCs and particle-bound PAH concentrations (Kim et al., 2007) as well as PM and element content (Obaidullah et al., 2012; Yaxuan and Xiang, 2012). Also, possible risk assessment of air quality in underground parking garage was done (Glorennec et al., 2008).

Over the past several decades, biomonitoring has been developed as a cost-effective, alternative way of instrumental air pollutant monitoring. Based on their morphological and physiological characteristics, mosses have proved to be suitable biomonitors for achieving information mainly about heavy metal and trace element air pollution. Between the two types of moss biomonitoring application, passive and active, the latter has been applied more often for intensive studies in urban areas where native mosses are scarce or completely absent. Active biomonitoring with so-called moss bags have been widely-used to define contamination trends of heavy metal and PAH content in industrial and urban areas (Aničić et al., 2009a; Ares et al., 2011; De Nicola et al., 2013). Also, active moss biomonitoring has been applied in semi-enclosed space such as a city tunnel (Zechmeister et al., 2006).

This study was designed to achieve: *(1)* multi-pollutant assessment of air contaminants (PM_{10}, trace elements and PAHs) in parking garages in Belgrade; *(2)* the carcinogenic health risk estimation of employees' occupational exposure in order to identify the analyzed pollutants that are of most concern as well as *(3)* evaluate the reliability of the use of *Sphagnum girgensohnii* moss bags for monitoring of trace element air pollution in parking garages. According to our knowledge, this would be the first time that study comprising instrumental measurements of both elements and PAHs content in PM was conducted in parking garage.

2. Materials and methods

2.1. *Study sites*

The study was performed in four parking garages in the downtown of the Belgrade city (φ = 44º49' N, λ = 20º27' E, H_s =117 m), the capital of the Republic of Serbia. The parking garages (Pionirski park — PP, Masarikova — M, Zeleni venac — ZV and Obilićev venac — OV) are situated in the heavy traffic street canyons with 619, 304, 460 and 472 parking spaces, respectively. The number of cars recorded during the experiment was 69,357; 46,482; 37,570 and 120,366 in PP, M, ZV and OV, respectively. They differ in size and conception: PP is an underground garage; M has three underground and six elevated levels, whereas ZV and OV consist of five to six above-ground levels. Garages M and ZV are semi-enclosed, while OV is an open one. For each garage there is only one gate that is used for cars entering and leaving the garage.

2.2. Experimental set-up

Only in two garages with inadequate funcionality of ventilation systems (according to data obtained from PUC "Parking services", City of Belgrade), instrumental measurements in M and PP were conducted. MiniVol portable air samplers (Springfield, OR, USA), provided with PM_{10} cut-off inlets with a flow rate of 5 L min^{-1}, were positioned near the tollgates. The sampler inlet was about 2 m above ground. The sites were chosen having in mind the highest traffic intensity in the vicinity of tollbooth and therefore increased health risk for employees. PM_{10} were collected on preconditioned (48 h) and preweighed Teflon-coated Quartz filters (Whatman, 47-mm diameter, 2-µm pore size). The sampling time was 24 hours, from 2 p.m. one day to 2 p.m. the next day. Due to practical constraints, PM filters were changed every other day for a period of 10 weeks. During the sampling, the total number of filter samples per one garage was 30. The PM_{10} mass concentrations were measured by gravimetric method.

Along with the instrumental measurements, the moss bag experiment was perfomed in all studied garages. Moss *Sphagnum girgensohnii* Russow was collected at the end of May 2011 from a pristine wetland area located near Dubna, Russian Federation. This background area was chosen on the basis of results obtained in previous studies (Aničić et al., 2009b; 2009c). In the laboratory, green upper part of moss was separated and manually carefully cleaned from soil particles and other foreign matter without any devitalized treatment. Notwithstanding washing by water or acid is recommended by some authors (Ares et al, 2012), the recent study (Giordano et al., 2013) reported that differences in element concentrations among the moss samples exposed after water washing and different devitalisation treatments (acid washing, oven drying and water boiling) was not significantly different.

After cleaning, moss material was air-dried at room temperature and then gently hand mixed to obtain homogeneous sample. About 3 g of the moss material was packed loosely in 10×10 cm nylon net bags with 2-mm mesh size.

Moss bags were exposed relatively uniformly in all garages, at two measuring positions: near the entrance and in the garage interior. Polyethylene string with 8 moss bags were suspended at each studied position at about 2.5 m above ground, for 10 weeks.The moss exposure site close to tollgates was chosen on the basis of the highest expected traffic flow. The other studied position inside the garage, far away from any openings, was characterized by similar traffic intensity to those near the entrance and expected poor air conditions. A schematic representation of a semi-enclosed parking garage indicating the location of air samplers and moss bags is shown in Figure 1.

Figure 1.

Both experiments referred to instrumental and active moss monitoring were performed for the same period during the autumn-winter 2011.

2.3. Major and trace element analysis

After the exposure periods, a half of each air filter, as well as 0.3 g of each air-dried homogenized moss sample (8 subsamples per exposure site), were digested for 45 min in a microwave digester (ETHOS 1 Advanced Microwave Digestion System, Milestone, Italy) with 7 mL of 65% HNO_3 (Sigma Aldrich) and 1 mL of 30% H_2O_2 (Sigma Aldrich) at 200°C. Digested samples were diluted with distilled water to a total volume of 50 mL. The concentrations of 16 elements were determined by inductively coupled plasma optical emission spectrometry (Thermo Scientific iCAP 6500 Duo, Thermo Scientific, UK). For calibration, multi-element stock solution (Merck) containing 1 000 µg mL^{-1} of each determined element was used to prepare intermediate multi-element standard solutions: 50, 25, 10, 1, 0.1 and 0.01 µg mL^{-1}. Limits of detection (µg L^{-1}) of determined elements were: Al- 0.12, Ba- 0.03, Ca- 0.003, Cd- 0.07, Co- 0.51, Cr- 0.21, Cu- 0.39, Fe- 0.25, K- 0.60, Mg- 0.01, Mn- 0.07, Na- 0.37, Ni- 0.36, Pb- 1.06 and Zn- 0.19. The quality control was performed using the standard reference material lichen-336 (IAEA).

2.4 PAH analysis

For the purpose of PAH determination, the other halves of the filter samples were stored in the refrigerator, at 4 ºC until three subsequent extractions by ultra-sonifications (sonicator 4GT,

Sonic, Niš, Serbia), each in 50 mL of dichloromethane (Carlo Erba, HPLC pure) for 5 min. The extracts were filtered and merged into one which was vacuum rotary evaporated to 1 mL. Analysis was performed by GC-MSD 7890A/5975C, Agilent, USA (with HP-5MS capillary column 30 mx0.25 mmx0.25 μm film thickness). Helium (5.0, Linde Gas) was used as a carrier gas at a constant flow rate of 1.5 mL min^{-1}. The oven temperature was programmed as follows: 50 ºC for 1 min, 25 ºC min^{-1} till 200 ºC, 8 C min^{-1} till 312 ºC and isotherm for 3 min. The temperature of injector was 300 ºC, and in all cases, 1 μl of sample was injected in splitless mode.

The US EPA 16 priority PAHs were determined: naphthalene (Nap), acenaphthylene (Acy), acenaphtene (Acp), fluorene (Fl), phenantrene (Phen), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (B[a]A), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), indeno[1,2,3-c,d]pyrene (I[cd]P), dibenzo-[a,h]anthracene (DB[ah]A) and benzo[ghi]perylene (B[ghi]P). The PAH Mix standard (Z-014G-R, AccuStandard, USA) was used for calibration. Following intermediate standard solutions were prepared: 3, 1, 0.5, 0.1 and 0.01 mg L^{-1}. Limit of detection and limit of quantification were 0.003 and 0.01 mg L^{-1}, respectively.

2.5. Data analysis

The data were processed using StatSoft STATISTICA 8.0 (StatSoft, Inc., Tulsa, OK, USA). Basic, non-parametric statistics (Mann-Whitney U test) was used to check for significance of differences between instrumental data. Significant differences among the moss element concentrations measured in four parking garages were tested by one way analysis of variance (ANOVA). All applied tests were performed at significant level of 0.05.

Element and PAH abundances (C) in PM_{10} samples were calculated following the equation:

$$C\ (ng\ m^3) = C_{determined}\ (ng\ mL^{-1}) \times 50\ mL / 7.2\ m^3,$$

where 7.2 m^3 represents volume of air sampling for 24 h and with a flow rate of 5 L min^{-1}.

We used the US EPA health risk assessment model for carcinogenic risk estimation associated with exposure to some analyzed pollutants (US EPA, 1989, 1991).

The assessment of carcinogenic health risk due to exposure to PM_{10}-bound elements and PAHs was conducted by calculating the incremental lifetime cancer risk (*ILCR*) value, according to:

$$ILCR = CDI \times SF.$$

Exposure to carcinogenic compounds, described by *CDI* - chronic daily intake (μg kg^{-1} day^{-1}), was calculated as follows:

$$CDI = (C \times IR \times ET \times EF \times ED) / (BW \times AT).$$

Here, *C* is concentration of the chemical in the air (μg m^{-3}), *IR* is the inhalation rate (20 m^3 day^{-1}), *ET* is the exposure time (8 hours day^{-1}), *EF* is the exposure frequency (235 days $year^{-1}$),

ED is the exposure duration (30 years), *BW* is the body weight (70 kg), and *AT* is the period over which the exposure is averaged (70 years for carcinogenic effects).

Slope factor (*SF*), as a parameter used to describe the toxicity of a carcinogenic chemical (i.e. the capacity of a chemical to cause negative health effect), was calculated from inhalation unit risk (UR), following the equation:

$$SF = (UR \times BW) / IR.$$

The assessment of non-carcinogenic health risk was carried out for Ba. The risk for non-cancer effects is typically quantified by comparing the exposure to the reference level via a ratio known as the hazard quotient (HQ). It is calculated according to formula:

$$HQ = CDI / RfD,$$

where *RfD* is the reference dose, used as a reference inhalation toxicity value. It was calculated from the chronic inhalation reference concentration (*RfC*) given in the RAIS database, as follows:

$$RfD = (RfC \times IR) / BW.$$

The parameters used in this study were obtained from US EPA Integrated Risk Information system (IRIS) and Risk Assessment Information System (RAIS) chemical toxicity databases (data are given in Table 4 shown in section Results and Discussion). Note that, in our health risk assessment, it is assumed that 100% of each considered chemical is bioavailable (Diaz and Dominguez, 2009).

3. Result and Discussion

3.1. Multi-pollutant assessment in PM_{10} samples

According to the obtained results, in 93% and 77% samples in PP and M, respectively, daily PM_{10} mass concentrations exceeded the air quality set value of 50 $\mu g\ m^{-3}$ (Directive 2008/50/EC) (Fig. 2). Due to lack of indoor air quality guideline, the prescribed value related to outdoor air quality could also be applicable to indoor (WHO, 2010). PM_{10} sampling was limited to a single location within the parking garage, so it is unknown how particle concentrations varied inside the whole parking garage. However, it is likely that the observed concentrations represent the worst case scenario for the garage microenvironment due to the most intense vehicle activities near the tollbooths where employees spend the working days. Also, PM_{10} concentrations higher than the limited value were reported in recent studies in car parks (Obaidullah et al., 2012; Li and Xiang, 2012).

Figure 2.

In general, the order of element abundances in PM_{10} samples, in both garages was: Na > Ca > Zn > Ba > K >Al > Mg > Fe > Sr > Cu > Mn > Pb > Ni > Cr > Co > Cd (Table 1). Surprisingly,

concentrations of Ba, Cu and Zn observed in PM_{10} were high, even two orders of magnitude higher than those measured at different urban sites in some European cities reviewed in previous studies (Johansson et al., 2009; Witt et al., 2010).

It is well-known that vehicle activities lead to road dust resuspension whose dominant components are major elements such as Al, Ca, Fe, K, and Na (Vianna et al., 2008). On the other side, in some studies (Gietl et al., 2010; Lawrence et al., 2013), Ba, Cu and Zn were reported as typical tracers of vehicle exhaust and/or so-called non-exhaust emissions. In this study, Ba and Zn are among the most abundant elements due to very intensive vehicle brake and tire wear which are probably dominant source of particles in enclosed parking garage. It was calculated, based on emission factors for break wear, that PM_{10} contains 98% of emitted break wear particles (Thorpe et al., 2008). Thus, poor air conditions in the parking garage studied here contribute to extremely elevated concentrations of brake dust-related elements - Ba, Cu and Zn.

Table 1

Nowadays, there are no standards or guidelines for air element concentrations in parking garages, as well as in other indoor areas. However, for outdoor air, Directive 2004/107/EC and WHO guideline (2000) recommended target values for several carcinogenic elements: As, Cd, Hg, Ni and Pb. Aiming to estimate possible effects of the exposure of employees and attendants to those elements, concentrations of Cd, Ni and Pb, determined in this study, were compared with their target values (Table 2). In all samples analyzed, Ni concentrations exceeded the set daily value − 20 ng m^{-3}. Nickel is used as main additive in fuels and can be emitted from vehicle exhaust in traffic (US EPA, 2000). Additionally, geological nature of Ni was also reported in Serbia (Environmental quality in the city of Belgrade, 2011), so the outdoor concentrations are elevated, as well (Mijić et al., 2010). Although Pb is still present in the urban environment notwithstanding the leaded gasoline was legally banned in Serbia in 2011, Pb concentrations did not exceed the daily air quality value.

Table 2

In general, the total PAH daily concentrations varied from 13 to 42 ng m^{-3} and from 10 to 29 ng m^{-3}, in PP and M, respectively. High molecular weight PAHs were dominated in PM_{10} samples (Table 3). The highest concentrations were measured for B[a]A, D[ah]A, B[b]F, B[k]F and B[ghi]P, which is expected if we take into account that the PM_{10} have shown to be the most enriched with the least volatile PAHs in the winter due to low temperatures and PAHs' low degree of volatilization (Callén et al., 2008; Vestenius et al., 2011). Increased concentration of B[ghi]P, B[k]F and B[b]F could be attributed to both diesel and gasoline vehicle emissions (Riddle at al., 2007; Bergvall and Westerholm, 2009).

Contributions of low molecular weight PAHs − Nap, Phen, Fl, Pyr and Chr to the total PAH content were slightly lower than the above-mentioned PAHs. As previous studies reported, those compounds occur in the gaseous phase rather than bound to the particulates (e.g. Wingfors et al., 2001). Acenaphthylene, Ant, Fl, Ant and I[cd]P were not identified in the filter samples at all.

Table 3

Certainly, B[a]P is one of the most important studied PAHs because of its carcinogenic effect. Also, it is the only one regulated by the Directive 2004/107/EC, although many other PAHs are listed in the European list of priority pollutants. For B[a]P, the target value of 1.0 ng m^{-3} for the total content in PM_{10} fraction, averaged over year, is established. In our study, average B[a]P concentrations were 1.3 ng m^{-3} in M and 1.6 ng m^{-3} in PP garages which exceeded the target value.

Comparing PM_{10} concentrations obtained for weekdays and weekends, statisticaly significant weekend effect became apparent as reflected in the reduction of the concentration of PM_{10} due to the lower number of vehicles on weekends (Fig. 3). Sharp increase in the number of vehicles on Sundays could be explained by the chosen sampling period which started at 2 p.m. on Sunday and finished at 2 p.m. on Monday and was consequently affected by increased traffic flow of the first working day.

Figure 3.

In general, concentrations of both PAHs and elements were in accordance with decreasing trend of PM_{10} concentrations. Concentrations of PAHs showed better correlations with vehicles flow in comparison with concentration of elements. Additionally, statistically significant difference between the concentration of PAHs among two garages was observed, whereas for the concentration of elements it was not the case. Given that traffic-related PAHs are mainly associated with particles, it is expected that their concentrations accompany decreasing trend of PM_{10} concentrations.

According to the results obtained, the traffic intensity may not be considered as a dominant factor affecting the differences in pollutant concentrations in semi-enclosed spaces such as parking garage. Poor air conditions give rise to the local pollution level. Ventilation systems are usually installed in larger enclosed and semi-enclosed garages to supply fresh air and to reduce air contaminants in order to maintain an acceptable level of air quality. Thus, the ventilation effectiveness, but also the possibility of pollutant accumulation due to closed structure, should be considered.

3.2. Health risk assessment

According to US EPA IRIS (2013), some of the determined pollutants (Cd, Cr, Ni, Pb and six PAHs: B[a]A, Cry, B[b]F, B[k]F, B[a]P and D[ah]A) have been classified as known and possible human carcinogens. In this study, the carcinogenic risk for these pollutants was characterized. It should be noted that other vehicle-related atmospheric pollutants, including gases (e.g. CO, NO, NO_2, SO_2, O_3), volatile organic compounds and platinum group elements may also exert adverse effects on human health. However, the analysis of these pollutants is beyond the scope of this work, and they were not considered in the health risk assessment.

The calculated ILCR values and cumulative cancer risks for PM_{10}-bound heavy metals and PAHs are shown in Table 4. ILCR value represents an incremental probability of an individual developing cancer over a lifetime as a result of exposure to these pollutants through inhalation. For instance 10^{-6} lifetime cancer risk means that there is one additional case of cancer during a lifetime in a population of a million persons. The ILCR level of 10^{-6} is usually the baseline level of risk that is acceptable, and 10^{-4} is typically at the high end of the range of acceptability (US EPA Cancer Risk Guideline, 2005). Individual ILCR values obtained for Cd, Cr, Ni and Pb as

well as PAHs was below the lower limit value of the acceptable ILCR range. On the other side, cumulative cancer risk obtained as sum of ILCR values for individual chemicals was in the acceptable range. Trace elements can be considered as the major contributors to the assessed cancer risks (about 98% in both PP and M). Hence, the risk evaluated for PAHs deemed to be insignificant in comparison with trace elements.

Table 4

Comparing the results from the two garages, it becomes apparent that cumulative cancer risk values are quite similar, with slightly lower value in PP. Although PP is completely underground garage as opposed to M, the lack of appropriate ventilation system with filters in M is a possible cause of this result.

In addition, non-carcinogenic health risk was calculated for Ba due to exposure to the excessive measured concentrations. The HQ value calculated for that purpose was found to be 14.7 and 17.4 in PP and M, respectively. Both values are significantly larger than the nominal value 1, suggesting significant non-carcinogenic health risk.

The assessment of non-carcinogenic health risk was not conducted for Zn, as reference concentration was not available for this element in RAIS and IRIS databases.

3.3. Active moss biomonitoring

The results of active moss biomonitoring, carried out in four parking garage, showed higher post-exposure element concentrations in *S. girgensohnii* moss than pre-exposure (background) values (Fig. 4). An order of element enrichment in the moss was: Ca > Al > Fe > Zn > Ba > Sr > Cu > Pb > Ni > Cr > Cd > Co. Concentrations of physiologically active elements - K, Mg, Mn and Na in the exposed moss which were close to their initial values in unexposed moss. This is in accordance with the previous research (Aničić et al. 2009b; Aničić et al. 2009c). In general, relative element content in the moss exposed in semi-enclosed space of parking garages was lower than in moss bags exposed previously at open space — street canyons (Vuković et al., 2013) where the parking garages are situated. Additionally, the relative moss element content was higher in the city tunnel experiment described in the previously mentioned study. Having in mind that moss may take up elements not only as particles, but also in ionic form, lower relative element moss enrichment in garage is probably a consequence of the indoor environment dry conditions limiting moss physiological activity and further element uptake.

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Figure 4.

ANOVA showed that concentration of the most elements measured in moss, exposed in four parking garages, were statistically different depending on diversity in the garage design: enclosed and open one (Fig. 4). Furthermore, moss exposed at the garage entrance showed significantly higher element concentrations than moss exposed in the interior, indicating that moss reflects changes in small-scale spatial variations in content of particle-bound elements.

Figure 4 shows that Al, Ba, Cd, Cr, Pb, Sr and Zn were more abundant in the moss exposed near the tollgate in comparison with moss suspended inside the following garages: M, PP and ZV. The exception was the moss content of Al, Ba, Fe and Sr in OV, where the element enrichment was lower in the vicinity of tollgate than in the interior. As previously mentioned,

PP, M and ZV are classified as underground and semi-enclosed, while OV is a completely open garage. Thus, the impact of air flow and consequently dilution of pollutant concentrations could be decisive parameters for garage air quality.

Therefore, the moss *S. girgensohnii* is moderated to intercept elements in enclosed spaces due to the absence of direct atmospheric deposition. The garage environment is usually characterized by stagnant ambient air because of poor air flow. In these conditions, moss element enrichment is a result of weak dust resuspension and/or movements caused by vehicle activities which are possibly predominant in above ground level (up to ≈ 1 m). Since, in this study, moss bags were exposed at about 2.5 m, further moss biomonitoring surveys are necessary in order to get information about the most representative height of moss bags exposure in indoor area.

3.4. Instrumental vs. moss monitoring

In two garages – PP and M, instrumental and active moss monitoring were performed in parallel. The comparison of the moss biomonitoring measurements with the data obtained by instrumental monitoring pointed out similar order of element abundances in PM_{10} and moss samples. Exception was concentrations of the elements usually depleted from moss tissue (K, Mg, Mn and Na). However, despite the fact that instrumental measurements recorded extremely elevated indoor concentration of brake dust-related elements – Ba, Cu and Zn, the moss did not reflect such increased element content in comparison with open space (Vuković et al., 2013). In our opinion, this suggests possible inappropriate moss bag exposure height.

Additionally, different air pollution level was expected due to diverse garage design: underground (PP) and above-ground (M). However, there was no statistically significant difference between the ambient element concentrations obtained by both the instrumental measurements and moss bag technique. In particular, it was observed that in the case of higher/lower certain element concentrations in moss exposed near the tollgate from one of the garages, the concentration of the same element was also higher/lower in the PM_{10} sampled from that garage (Fig. 5).

Figure 5.

Thus, the results suggest possible using of *S. girgensohnii* moss bag technique as complementary method to classical instrumental measurements of ambient element content in semi-enclosed spaces such as urban parking garages. However, this statement needs further justifications and future research could clarify representativeness of moss bag exposure height indoor. Also, a dry condition impact prevailing indoor environment, as a possible limited factor in moss vitality and element uptake, should be tested.

4. Conclusion

Instrumental monitoring of air quality assessment in parking garages showed elevated PM_{10} mass concentrations and increased content of carcinogenic heavy metals (Cd, Ni and Pb). Due to poor air conditions, particles, as well as pollutants bound to them, remain longer inside the garage depending on ventilation ineffectiveness. Individual cancer risk values calculated for both heavy metals and PAHs was below the lower limit value of the acceptable range of 10^{-4} to 10^{-6}. Cumulative cancer risk value obtained for Cd, Cr, Ni and Pb was 98% of the total assessed

cancer risk. Contrary, cumulative cancer risk value calculated for carcinogenic PAHs (B[a]A, Chr, B[b]F, B[k]F, B[a]P and D[ah]A) was only 2%. Therefore, heavy metals can be considered as the dominant contributors to the assessed cancer risks. According to the instrumental measurements and health risk assessment the need for setting indoor air quality guidelines is apparent.

The results of active moss biomonitoring survey performed in parking garages suggest that *S. girgensohnii* is capable to reflect small-scale variations in element content in enclosed spaces. This is supported by the evidence of statistically significant higher moss element concentrations in the vicinity of garage entrance than in the garage interior. However, the element content in moss exposed in parking garages was lower than in moss bags exposed at open space. Parking garage is characterized by an absence of atmospheric deposition, dry as well as poor air conditions. So, possible mechanism of moss element enrichment is weak dust resuspension caused by vehicle activities in above ground level. Comparing results of instrumental measurements with the data obtained by moss bag technique, similar order of abundances of the most elements in PM_{10} and moss samples was observed. Also, both monitoring techniques did not show statistically significant differences in ambient element concentrations in two compared garages.

It could be concluded that active moss biomonitoring can be applied as possible complementary method to routine instrumental measurements of trace element content in semi enclosed spaces such as parking garages. Further research should be focus on clarifying influence of dry indoor air conditions on moss element uptake. Also, a representativeness height of moss bag exposure in indoor area should be tested. It would be interesting to expand the number of exposure sites in order to examine various situations of indoor air pollution, as well.

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Figure Captions

Fig. 1. Scheme of semi-enclosed parking garage; the air sampler exposure site – AS, the moss bag exposure site near the tollgate – MB T, the moss bag exposure site in the garage interior – MB I

Fig. 2. Daily PM_{10} mass concentrations ($\mu g\ m^{-3}$) in two parking garages − Pionirski park (PP) and Masarikova (M); the daily limited value (LV) is marked with bolded line

Fig. 3. Average daily PM_{10} mass concentration ($\mu g\ m^{-3}$) in two parking garages – Pionirski park (PP) and Masarikova (M); the daily limited value (LV) and traffic flow are marked with dashed and dotted lines, respectively

Fig. 4. Average element concentrations ($\mu g\ g^{-1}$) in the moss (8 subsamples per site) with standard deviation bars after 10 week exposure in 4 parking garage; the element concentrations in unexposed moss – back (black line) with standard deviation (dashed line) are presented

Fig. 5. Average element concentrations with standard deviation bars in the moss exposed near the tollgate – *columns*, and PM_{10} – *dots*, sampled in two parking garages: Pionirski park (PP) and Masarikova (M)

Table 1 Average daily element abundances (ng m^{-3}) determined in PM_{10} samples in two parking garages – Masarikova i Pionirski park

	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
Masarikova																
Mon	21209	86530	141938	3.23	5.33	31.5	220	1636	49171	7809	102	163019	42.6	45.5	1516	72957
Tue	23393	93533	123372	4.24	3.68	37.1	264	2930	71285	9240	127	216330	66.1	41.8	2031	101960
Wed	23735	93197	159757	4.45	5.54	41.4	236	2345	89341	10467	128	270894	69.2	38.7	2294	129801
Thu	28951	108352	141294	3.67	6.96	46.9	261	2366	82010	9226	123	250730	41.7	45.6	2160	118520
Fri	23313	87984	129094	2.22	4.54	27.2	132	928	67233	8515	90	207398	57.4	14.5	1888	96201
Sat	24612	92965	131867	4.23	3.30	36.9	232	1091	74868	8713	96	217698	48.2	74.7	1952	104045
Sun	23026	99939	165315	3.62	4.19	31.1	170	2562	82013	11221	108	254311	61.4	33.3	2217	115446
Pionirski park																
Mon	18428	71072	124347	3.02	4.82	35.58	249	6304	51706	8495	100	166463	53.9	64.0	1722	76687
Tue	14686	69263	152192	4.50	3.92	23.88	247	2104	55190	8761	111	171029	56.1	80.2	1696	79117
Wed	14947	63915	131764	4.63	6.04	28.09	221	2118	49692	8769	134	164088	52.5	89.3	1516	73628
Thu	32285	123338	142617	4.01	4.03	42.18	264	2046	94874	10670	119	274015	67.1	76.3	2442	134115
Fri	17183	80652	127483	3.00	4.53	24.69	149	1334	64313	8365	98	198890	42.0	100.9	1832	93430
Sat	17679	76065	181425	6.81	5.08	30.87	281	1326	63271	10569	106	195204	70.1	119.4	1751	88034
Sun	11568	61764	102907	2.78	2.43	20.81	132	1607	46982	7172	81	139418	51.1	34.0	1475	65860

Table 2 Average element concentrations (ng m^{-3}) measured in PM_{10} for 10 weeks in two parking garages (Pionirski park - PP and Masarikova - M) and air quality target values (ng m^{-3})

	Average concentration (ng m^{-3})		Target value (ng m^{-3})
	PP	**M**	
Cd	5.1	3.7	5[a]
Ni	66	72	20[a]
Pb	144	78	500[b]

[a] EU Directive 2004/107/EC
[b] WHO, 2000

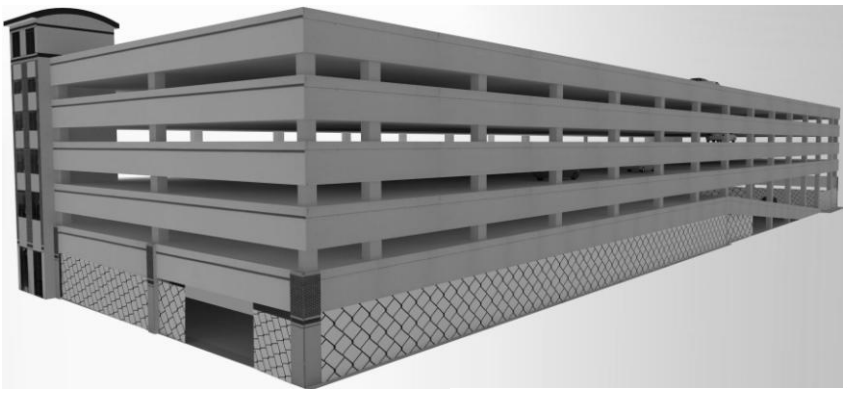
Table 3 Average daily total PAH concentrations (ng m^{-3}) and abundance of PAHs (ng m^{-3}) determined in the PM_{10} samples in two parking garages: Masarikova (M) and Pionirski park (PP)

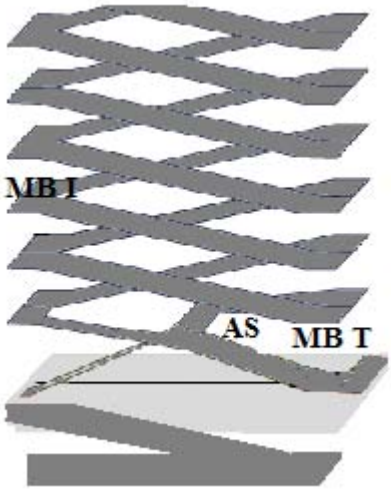
	Mon		Thu		Wed		Tue		Fri		Sat		Sun	
	M	**PP**	**M**	**PP**	**M**	**PP**	**M**	**PP**	**M**	**PP**	**M**	**PP**	**M**	**PP**
Nap	0.43	0.67	1.10	2.22	1.23	0.98	0.82	2.45	0.61	1.06	0.71	1.05	1.20	1.32
Phen	0.59	0.81	0.99	1.59	1.26	1.00	0.96	1.71	0.71	0.98	0.80	1.06	1.23	1.33
Fl	0.65	0.87	0.98	1.58	1.22	1.05	0.89	1.61	0.77	0.91	0.70	1.23	1.25	1.42
Pyr	0.84	1.11	1.20	1.75	1.40	1.26	1.04	1.81	0.89	1.09	0.89	1.54	1.46	1.63
Chr	0.74	0.96	1.17	1.77	1.40	1.20	1.03	1.80	0.90	1.07	0.87	1.41	1.38	1.55
B[a]A	1.76	2.16	2.55	3.46	3.00	2.72	2.41	3.61	2.20	2.44	1.98	3.13	2.84	3.10
B[b]F	1.79	2.18	2.58	3.56	3.01	2.77	2.40	3.69	2.32	2.49	2.06	3.17	2.91	3.19
B[k]F	1.66	1.74	2.46	3.41	2.70	2.50	2.23	3.55	2.09	2.35	1.96	2.87	2.82	3.06
B[a]P	1.01	1.19	1.35	1.91	1.50	1.28	1.20	2.01	1.00	1.23	1.14	1.67	1.49	1.59
D[ah]A	2.06	2.37	3.03	4.00	3.27	2.98	2.70	4.05	2.62	2.89	2.45	3.33	3.37	3.55
B[ghi]P	2.06	2.37	2.94	4.02	3.20	2.88	2.59	3.96	2.51	2.83	2.28	3.33	3.36	3.57
Σ PAHs	13.56	16.43	20.36	29.27	23.19	20.62	18.27	30.25	16.61	19.34	15.84	23.79	23.32	25.31

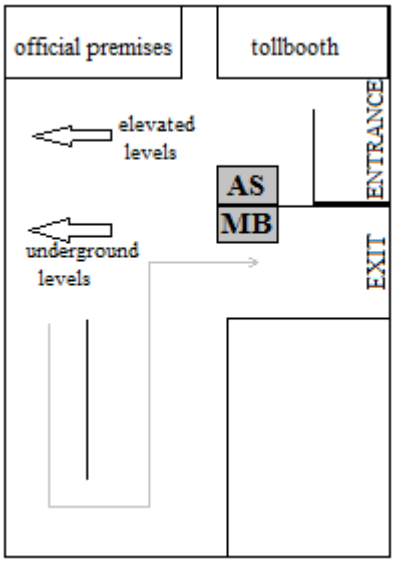
Table 4 Values of average concentration (C), chronic daily intake (CDI), slope factor (SF) and calculated incremental cancer risk (ILCR) for different heavy metals and PAHs in PM_{10} samples collected in two parking garages

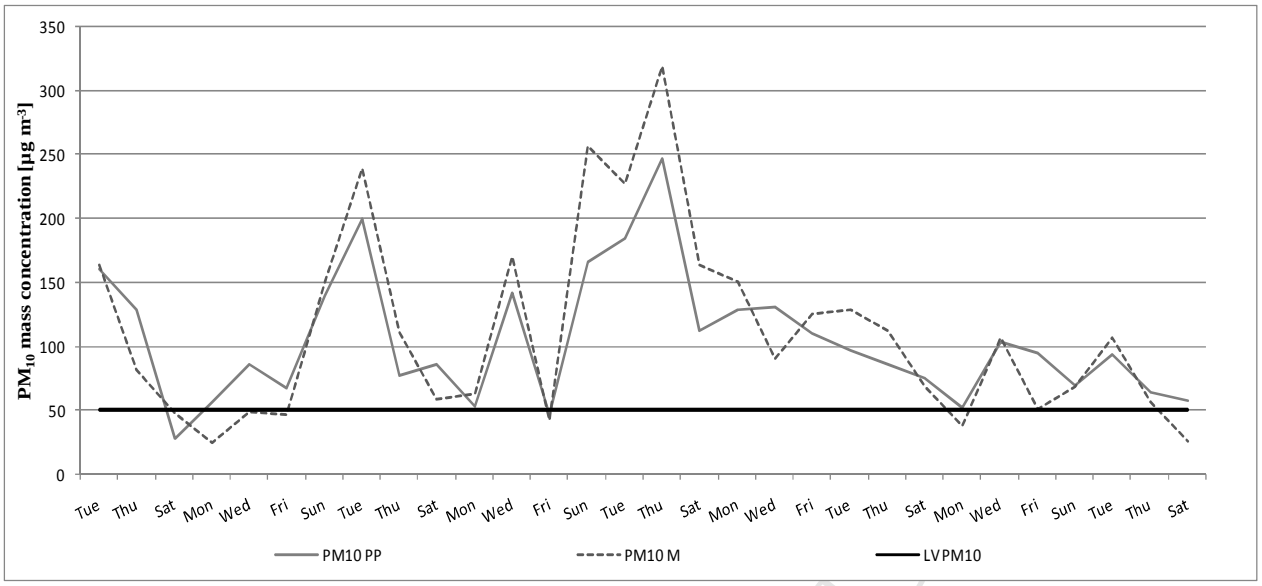
	Masarikova			Pionirski park				
	C ($\mu g\ m^{-3}$)	**CDI ($\mu g\ kg^{-1}\ day^{-1}$)**	**ILCR**	**C ($\mu g\ m^{-3}$)**	**CDI ($\mu g\ kg^{-1}\ day^{-1}$)**	**ILCR**	**Unit Risk ($\mu g\ m^{-3}$)$^{-1}$**	**SF ($\mu g\ kg^{-1}\ day^{-1}$)$^{-1}$**
Cd	$3.70\cdot10^{-3}$	$9.75\cdot10^{-5}$	$6.13\cdot10^{-7}$	$4.60\cdot10^{-3}$	$1.21\cdot10^{-4}$	$7.62\cdot10^{-7}$	$1.80\cdot10^{-3}$ [a]	$6.30\cdot10^{-3}$ [a]
Cr	$3.66\cdot10^{-2}$	$9.62\cdot10^{-4}$	$4.04\cdot10^{-5}$	$3.00\cdot10^{-2}$	$7.88\cdot10^{-4}$	$3.31\cdot10^{-5}$	$8.40\cdot10^{-2}$ [b]	$1.20\cdot10^{-2}$ [b]
Ni	$7.25\cdot10^{-2}$	$1.95\cdot10^{-3}$	$3.27\cdot10^{-6}$	$6.28\cdot10^{-2}$	$1.69\cdot10^{-3}$	$2.83\cdot10^{-6}$	$4.80\cdot10^{-4}$ [a]	$1.68\cdot10^{-3}$ [a]
Pb	$4.51\cdot10^{-2}$	$1.21\cdot10^{-3}$	$5.09\cdot10^{-8}$	$1.13\cdot10^{-1}$	$3.04\cdot10^{-3}$	$1.28\cdot10^{-7}$	$1.20\cdot10^{-5}$ [a]	$4.20\cdot10^{-5}$ [a]
B[a]P	$1.30\cdot10^{-3}$	$3.42\cdot10^{-5}$	$1.32\cdot10^{-7}$	$1.60\cdot10^{-3}$	$4.20\cdot10^{-5}$	$1.62\cdot10^{-7}$	$1.10\cdot10^{-3}$ [a]	$3.85\cdot10^{-3}$ [a]
B[a]A	$2.40\cdot10^{-3}$	$6.31\cdot10^{-5}$	$2.43\cdot10^{-8}$	$3.10\cdot10^{-3}$	$8.15\cdot10^{-5}$	$3.14\cdot10^{-8}$	$1.10\cdot10^{-4}$ [a]	$3.85\cdot10^{-4}$[a]
Cry	$1.10\cdot10^{-3}$	$2.89\cdot10^{-5}$	$1.11\cdot10^{-9}$	$1.40\cdot10^{-3}$	$3.68\cdot10^{-5}$	$1.42\cdot10^{-9}$	$1.10\cdot10^{-5}$ [a]	$3.85\cdot10^{-4}$ [a]
B[b]F	$2.50\cdot10^{-3}$	$6.57\cdot10^{-5}$	$2.53\cdot10^{-8}$	$3.10\cdot10^{-3}$	$8.15\cdot10^{-5}$	$3.14\cdot10^{-8}$	$1.10\cdot10^{-4}$ [a]	$3.85\cdot10^{-4}$[a]
B[k]F	$2.30\cdot10^{-2}$	$6.04\cdot10^{-4}$	$2.33\cdot10^{-7}$	$2.90\cdot10^{-3}$	$7.62\cdot10^{-5}$	$2.93\cdot10^{-8}$	$1.10\cdot10^{-4}$ [a]	$3.85\cdot10^{-4}$ [a]
DB[a,h]A	$2.80\cdot10^{-3}$	$7.36\cdot10^{-5}$	$3.09\cdot10^{-7}$	$3.40\cdot10^{-3}$	$8.93\cdot10^{-5}$	$3.75\cdot10^{-7}$	$1.20\cdot10^{-3}$[a]	$4.20\cdot10^{-3}$ [a]
Cumulative cancer risk			$4.51\cdot10^{-5}$			$3.75\cdot10^{-5}$		

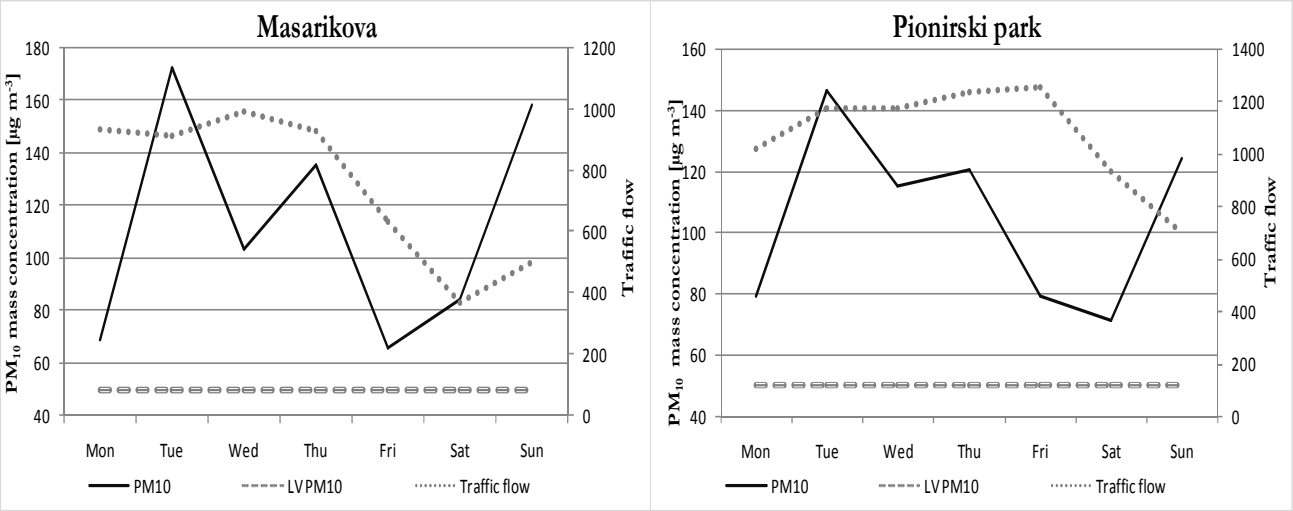
[a]RAIS
[b]IRIS

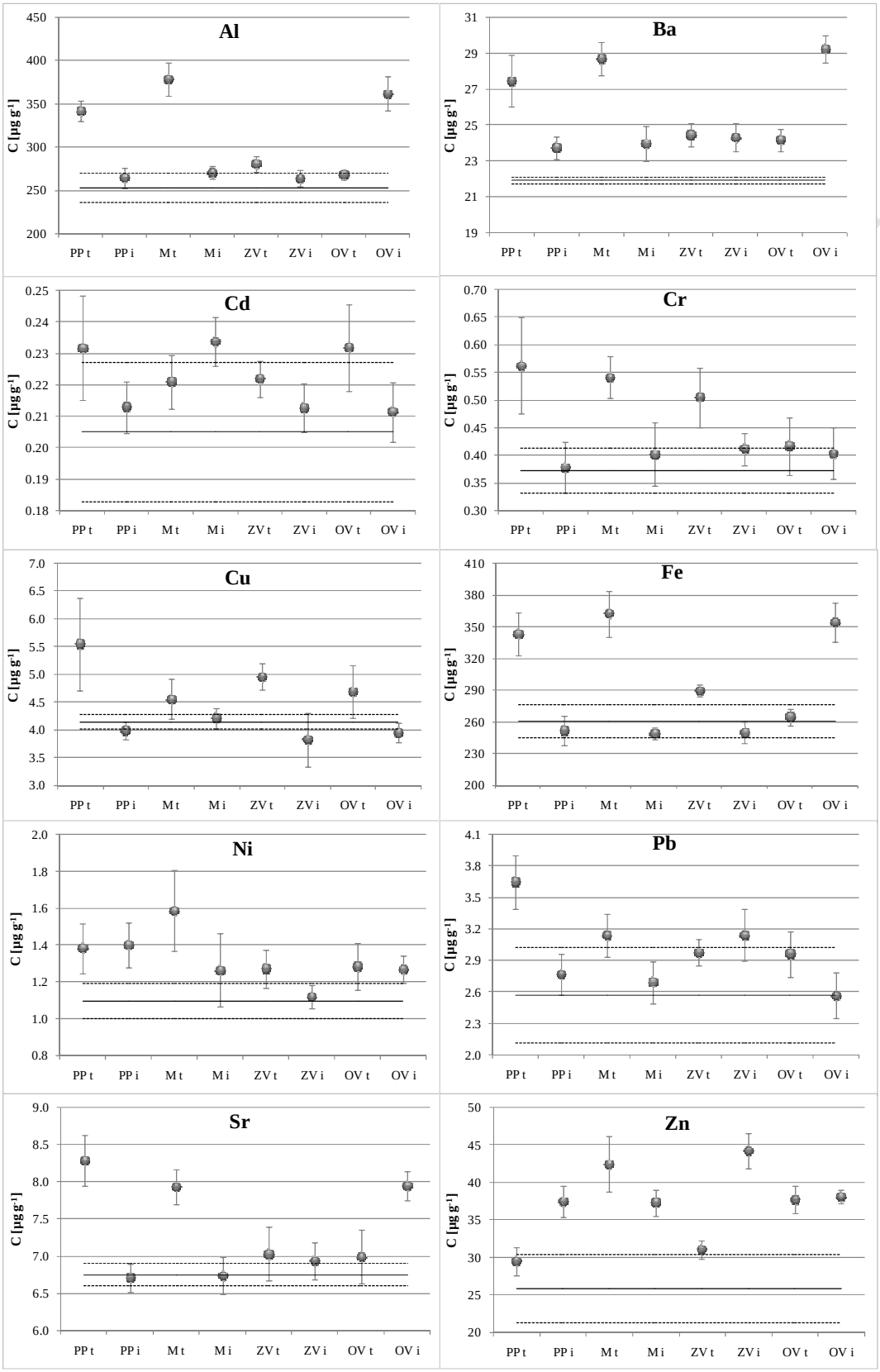




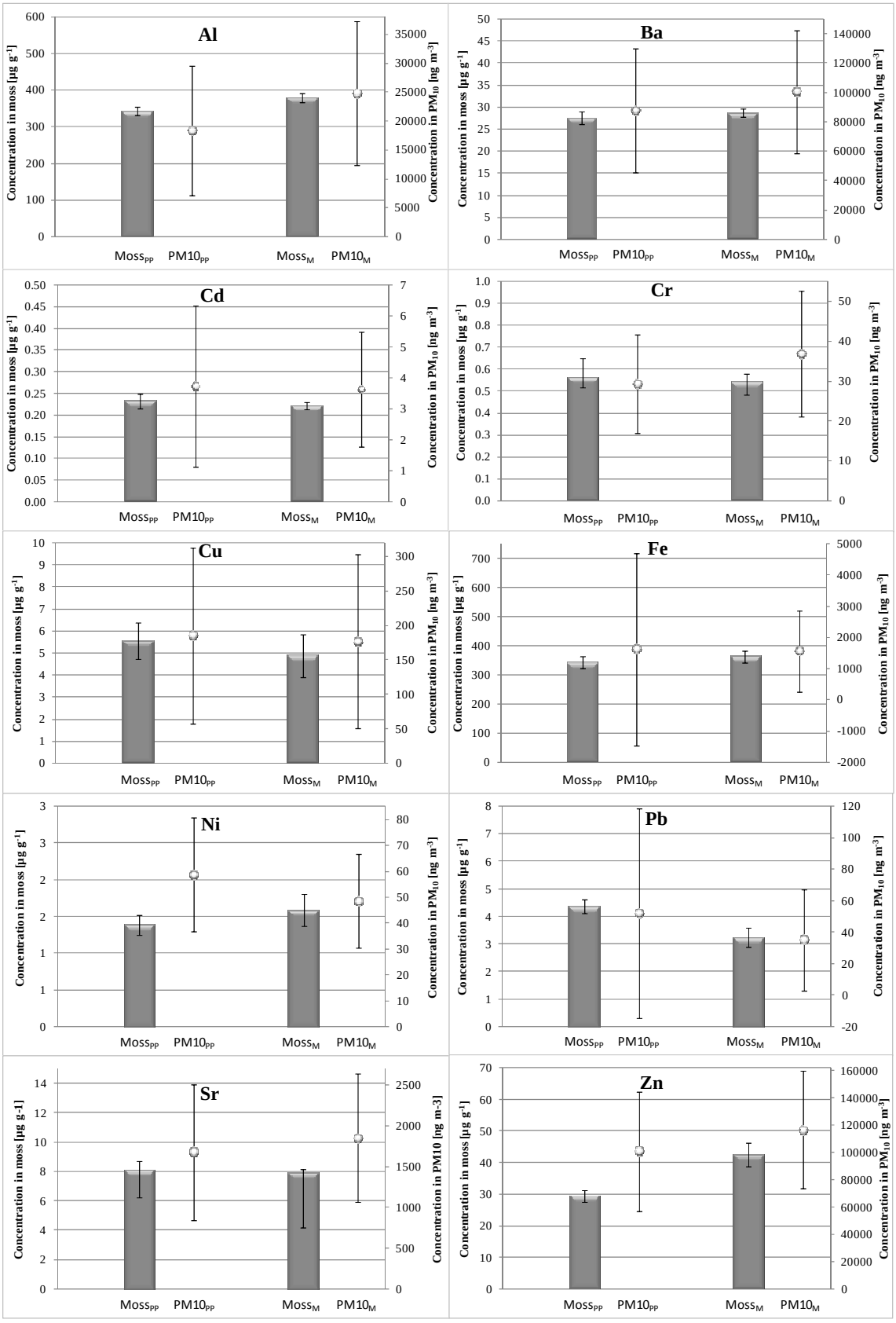








PP- Pionirski park M - Masarikova OV - Obilićev venac ZV - Zeleni venac
t - toll gate i - interior — back ---- back ± σ


Al
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Ba
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Cd
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Cr
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Cu
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Fe
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Ni
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Pb
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Sr
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M
Zn
Concentration in moss [µg g-1]
Concentration in PM10 [ng m-3]
Moss_PP PM10_PP Moss_M PM10_M

Highlights

- In garages, average PM_{10} level was about 110 μg m^{-3}, exceeded the EU set value.
- Zn, Ba and Cu were two orders of magnitude higher than those at urban sites in Europe.
- Average B[a]P concentrations was 1.5 ng m^{-3} exceeded the EU set value-1 ng m^{-3}.
- Heavy metals, in comparison with PAHs, are dominant contributors to the cancer risk.
- Moss bags application for indoor air quality assessment needs further evaluation.