

**THE RISK ELEMENTS BIOMONITORING
IN THE AMBIENT AIR OF AN UNDERGROUND
PARKING LOT***

***Lenka Demková*¹, *Július Árvay*², *Lenka Bobul'ská*¹,
*Jozef Oboňa*¹**

¹ Department of Ecology
University of Prešov in Prešov, Slovakia

² Department of Chemistry
Slovak University of Agriculture in Nitra, Slovakia

Key words: moss and lichen bags, RAF value, traffic pollution, air pollution, vehicles.

Abstract

Moss and lichen bag technique with use of three mosses (*Pleurosium* spp., *Rhytidiadelphus* spp., *Polytrichum* spp.) and one lichen *Pseudevernia furfuracea* taxon was used to monitor air quality in underground parking lot in the city of Prešov, Slovakia. Moss and lichen bags were exposed for 6 weeks at different distances from the entrances/exits. Accumulation ability was expressed by relative accumulation factor. The study aims to detect the level of pollution by the risk elements using relative accumulation factor (RAF) and compare accumulation abilities of different moss and lichen taxa. Accumulation ability of exposed taxa decreased in order: *Pleurosium* spp. > *Rhytidiadelphus* spp. > *Pseudevernia furfuracea* > *Polytrichum* spp. Comparing the evaluated elements, Zn and Ni reached the highest RAF values. The distance from the entrance/exit did not affect the level of elements. It is not being given much attention to the air quality assessment in enclosed parking lots in the world, and this is the first such kind of research in Slovakia.

Address: Lenka Demková, University of Prešov, 17. Novembra 1, 081 16 Prešov, Slovak Republic, phone: e-mail: lenka.demkova@unipo.sk

* This work was supported by the project of Ministry of Education, Science, Research and Sport of the Slovak Republic, VEGA 1/0326/18 and by the project of Grand Agency of Prešov University, Grant no. GaPU 27/2018.

BIOMONITORING SZKODLIWYCH ZWIĄZKÓW W WENTYLOWANYM POWIETRZU PARKINGU PODZIEMNEGO

Lenka Demková¹, Július Árvay², Lenka Bobuľská¹, Jozef Oboňa¹

¹ Katedra Ekologii

Uniwersytet Preszowski w Preszowie, Słowacja

² Katedra Chemii

Słowacki Uniwersytet Rolniczy w Nitrze, Słowacja

Słowa kluczowe: pakiety mchów i porostów, wartość RAF, zanieczyszczenie powietrza, pojazdy mechaniczne.

Abstrakt

Do monitorowania jakości powietrza na podziemnym parkingu w Preszowie na Słowacji użyto techniki biomonitoringu za pomocą tzw. pakietów mchów i porostów z wykorzystaniem trzech mchów (*Pleurosium* spp., *Rhytidiadelphus* spp., *Polytrichum* spp.) i jednego taksonu porostów *Pseudevernia furfuracea*. Pakiety mchów i porostów były eksponowane przez 6 tygodni w różnych odległościach od wejść/wyjść. Zdolność akumulacji wyrażono względnym współczynnikiem akumulacji. Celem badania było wykrycie poziomu zanieczyszczenia szkodliwymi związkami za pomocą względnego współczynnika akumulacji (RAF) i porównanie zdolności akumulacyjnych różnych taksonów mchów i porostów. Zdolność akumulacji narażonych taksonów zmniejszyła się w kolejności: *Pleurosium* spp. > *Rhytidiadelphus* spp. > *Pseudevernia furfuracea* > *Polytrichum* spp. Porównując oceniane zanieczyszczenia, Zn i Ni osiągnęły najwyższe wartości RAF. Odległość od wejścia na parking i od wyjścia z niego nie miała wpływu na poziom zanieczyszczeń.

Ocenie jakości powietrza w zamkniętych parkingach na świecie nie poświęcono do tej pory wiele uwagi. Jest to pierwsze tego rodzaju badanie również na Słowacji.

Introduction

The urbanisation and continuous increase in the number of vehicles cause a great pressure to the environment. Industrial activities, domestic fuel burning, agricultural activities, natural dust, and salt, are together with the traffic the most involved in air pollution in urban areas. Traffic related emission originates predominantly from exhaust fumes, tyre wear, asphalt erosion, wear of braked and engines, rusting of the car body, as well as sand and silt transported by wind and other means (THROPE and HARRISON 2008). Numerous studies have confirmed significant relationship between car intensity and the trace metals concentrations (LUILO and OTHMAN 2008, WEI et al. 2015). There has been found that the biggest

volume of risk elements is released from the cars during cold-starts (CHEN et al. 2011, REITER and KOCKELMAN 2016) and at lower speeds typical for driving into or out of car parking lots (ZIELINSKA et al. 2012). Underground parking lots hold a lot of cars and additionally, they are partially closed what causes accumulation of emissions. Ventilation systems to remove contaminated air out of the parking lot is usually inadequate or irregularly controlled (CHITHRA and NEGENDRA 2012). Accumulation of the risk elements leads to the cancer risk (VUKOVIĆ et al. 2015), respiratory or cardiovascular diseases (POPE 2000) and nervous system and reproductive systems defects (PAPANIKOLAOU et al. 2005). VUKOVIĆ et al. (2015), who evaluated the concentration of heavy metals in the underground parking areas in Belgrade have found, concentrations lower than acceptable limits set by the US environmental Protection Agency (EPA). The higher values of Zn and Cr at the exits comparing entrances were found in the underground garages in Wuhan (China) (LI and XIANG 2013).

There are many traditional methods for air pollution monitoring, but they are limited by the high costs or difficulties of carrying out extensive sampling (SZCZEPANIAK and BIZIUK 2003). Mosses and lichens, naturally occurred or transplanted, are very often used for air biomonitoring purposes in various types of the environment such as forest areas (KŁOS et al. 2018), indoor environment of the buildings (TONG et al. 2016), environment along roads and/or urban areas (VUKOVIĆ et al. 2013), or near the mines (BALABOVA et al. 2014) or tailing ponds (DEMKOVÁ et al. 2017). The high accumulation capacity makes mosses and lichens suitable organisms for biomonitoring studies (VUKOVIĆ et al. 2013).

The aim of the study was i) to assess the level of risk elements at underground parking lot in the city of Prešov (Slovakia) using relative accumulation factor (RAF), ii) compare the accumulation ability of mosses and lichen (M/L) taxa and iii) evaluate the influence of the presence/absence of the daylight on the accumulation ability of selected taxon.

Research activities devoted to the assessment of the content of hazardous elements in the air due to transport are still insufficient. Moreover, this is the first research focused on air quality in underground parking lots in Slovakia.

In this study, we hypothesise high volumes of the risk elements in the underground parking lot, due to combustion of fossil fuels and car body corrosion. Additionally, we hypothesise increasing volumes of the risk elements from outside to the inside of the parking lot. We also suppose that different mosses/lichens show different ability to accumulate different elements, that's why is suitable to use them together.

Material and Methods

Three mosses (*Pleurosium* spp., *Polytrichum* spp., *Rhytidiadelphus* spp.) and one lichen taxon (*Pseudevernia furfuracea*) were sampled in June 2016 in Slanske vrchy hills (the Eastern Slovakia). Sampling locations were selected at least 1 km from main road and 500 m from the forest road. Around 500 g of each taxon was sampled, stored in plastic bags, and transported to the laboratory. The samples were manually cleaned from needle, parts of the bars and residues of other plants. Moss/lichen (M/L) taxa were washed three times, lasting 20, 15 and 10 minutes (with 10 L of distilled water per 100 g M/L dry weight), hand squeezed and dry out (60°C for 24 h) according to the procedures described in ADAMO et al. (2007). 5 g of each taxon was wrapped into the nylon mosquito net cut at pieces 10 x 10 cm. Underground parking lot (Figure 1), with an area 10.148 m² and 356 parking spots, containing two similar parts with the entrance/exit localized at opposite (Figure 2).



Fig. 1. Localization of the underground parking lot in the Prešov city (Slovakia)

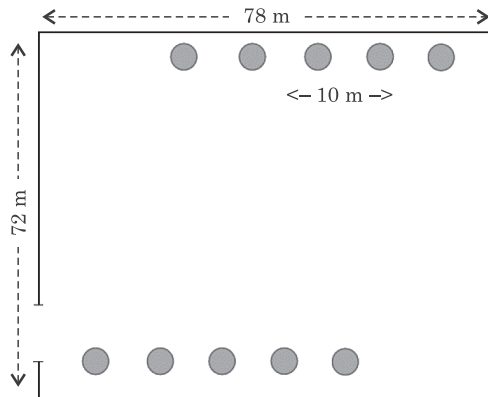


Fig. 2. Exposure position of the M/L taxa bags in underground parking lot

Ten exposition positions (EP), five at each side of the parking area, directed from the main entrance/exit inside the parking lot (48°59'59,71"N; 21°16'14,34"E) were selected. At each EP (approximately 3 m height), two samples of each taxa (a total 80 samples) were exposed for 6 weeks. The experiment was carried out twice, in May 2017 and again in October 2017. After exposure, the M/L samples were stored in closed plastic bags (-18°C) prior to analysis.

The homogenized M/L samples were prepared by milling in a laboratory grinder IKA A10 basic (IKA Works, Wilmington, USA). The homogenized samples were stored in closed plastic bags until the next treatment step. For pressure microwave digestion, approximately ~0.20 g (with a precision to 4 decimal places) of samples was weighed into PTFE digestion tubes. Consequently, 5 mL of HNO₃ and 1 mL of H₂O₂ (trace purity) were purchased from Lambda Life spol. s r.o., Bratislava, Slovakia (producer: Sigma-Aldrich Chemie GmbH, Steiheim, Germany), was added directly to the PTFE vessels. The digestion procedure was carried out using pressure microwave digestion system ETHOS-One (Milestone, Srl., Italy). Elemental analysis was carried out on an Agilent ICP-OES spectrometer 725 (Agilent Technologies Inc., Santa Clara, CA, USA) with axial plasma configuration and with an auto-sampler SPS-3 (Agilent Technologies, GmbH, Germany). Detailed experimental conditions were set as follows: RF power 1.45 kW; plasma gas flow 16.0 L min⁻¹; auxiliary gas flow 1.50 L min⁻¹ and nebulizer gas flow 0.85 L min⁻¹ and CCD detector temperature -35°C. Signal accumulation time 3 s for 3 replicates. In total, 80 M/L samples were analysed for concentration of 14 elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb and Zn). Calibration of the analytical method ICP-OES was realized using mixed standard TraceCert ICP 5 (Sigma Aldrich, GmbH, Steiheim, Nemecko), which was diluted to the three calibration levels (I – 0.0475 mg kg⁻¹; II – 0.950 mg kg⁻¹; III – 0.190 mg kg⁻¹). Argon and carbon were used as internal standard elements. ERM[®]-CE278k (mussel tissue; IRMM, Belgium) was used for quality measurements control. Following spectral lines were used for quantitative and qualitative elements determination: Al – 167,019 nm; As – 188,980 nm; Ba – 455,403 nm; Cd – 226,502 nm; Co – 228,615 nm; Cr – 267,716 nm; Cu – 324,754 nm; Fe – 234,350 nm; Li – 670,783 nm; Mn – 257,610 nm; Ni – 231,604 nm; Pb – 220,353 nm; Sb – 206,834 nm and Zn – 206,200 nm. All risk elements data were calculated to the mg kg⁻¹ DW. Total content of the risk elements was determined also in the reference material – M/L samples not exposed. The final values of risk elements in M/L bags were computed as the measured (exposed) valued minus reference values. The same procedure was used in both experimental seasons. The final values

of risk elements content were computed as the average values of both (May, October) measurements.

Relative accumulation factor - RAF (Equation 1) was calculated, to assess the risk element accumulation in the evaluated M/L taxa, as follows:

$$\text{RAF} = (C_{\text{exposed}} - C_{\text{initial}}) / C_{\text{initial}} \quad (1)$$

The differences in risk elements RAF values between taxa were analysed using One-way ANOVA test, followed by the Tukey's multiple comparison test. Cluster analysis (CA)Wards method was used to find out the similarities between taxa to accumulate evaluated risk elements. Spearman's correlation coefficient was used to determine significant correlation of risk elements RAF and the EP in the underground parking lot. One-way ANOVA test the same as Spearman's correlation coefficient were considered statistically significant if P-value was less than 0.05 and/or 0.01. Principal Component Analysis (PCA) was used to distinguished taxa based on the risk elements concentrations. All statistical analyses were performed using R studio (R Studio Team, Boston). All data were log-transformed prior to analysis.

Results and Discussion

The descriptive statistics of the risk elements RAF in M/L taxa in the underground parking lot is shown in the Table 1. The average RAF concentrations decreased in the following order: Zn > Ni > Mn > Fe > Cr > Cd > Co > Pb > Sb > Li > Al > As > Cd > Cu (Table 2). High RAF values of Zn

Table 1

The descriptive statistics of the risk elements RAF values in the different M/L taxa

		<i>Pleurosimium</i> spp.	<i>Polytrichum</i> spp.	<i>Pseudevernia furfuracea</i>	<i>Rhytidiadelphus</i> spp.
Al	min.–max	1.21–1.83	0.98–1.42	2.04–2.95	0.68–1.03
	median±std	0.24±1.57	0.20±1.20	0.39±2.25	0.15±0.86
As	min.–max	1.16–2.22	0.00–4.23	0.00–2.61	0.27–1.97
	median±std	0.48±1.22	1.69±0.99	0.97±0.77	0.61±1.04
Ba	min.–max	0.42–1.56	1.00–1.14	0.37–0.63	1.27–1.49
	median±std	0.46±0.61	1.12±0.07	0.46±0.11	1.38±0.09
Cd	min.–max	0.88–1.84	0.72–1.14	1.01–1.83	5.69–9.00
	median±std	1.53±0.36	0.81±0.16	1.31±0.31	6.7–1.31

Co	min.–max	0.19–1.00	0.24–1.05	0.05–0.46	3.98–14.9
	median±std	0.62±0.33	0.85±0.31	0.26±0.15	7.69±4.00
Cr	min.–max	1.39–7.17	1.16–2.05	2.44–4.72	2.17–4.28
	median±std	3.19–2.39	1.74±0.34	3.66±0.86	2.50±0.68
Cu	min.–max	0.22–0.27	0.57–0.66	0.66–0.96	0.99–1.48
	median±std	0.27±0.02	0.59±0.04	0.86±0.12	1.23±0.21
Fe	min.–max	2.02–3.93	1.97–2.48	2.81–5.32	2.76–3.59
	median±std	3.49±0.82	2.30±0.19	4.36±0.96	1.18±0.31
Li	min.–max	1.29–2.50	1.71–2.24	1.01–1.37	0.87–1.42
	median±std	1.82±0.54	2.08±0.23	1.20±0.13	1.01±0.22
Mn	min.–max	2.47–6.57	1.83–2.37	2.54–4.10	8.25–9.64
	median±std	4.62±1.45	2.10±0.20	3.77±0.61	8.96±0.55
Ni	min.–max	3.80–9.43	3.80–5.01	6.19–12.1	5.17–5.90
	median±std	5.43±2.31	4.06±0.51	7.96±2.25	5.62±0.30
Pb	min.–max	1.37–13.3	1.35–1.76	0.96–1.68	1.46–2.03
	median±std	2.08±5.15	1.68±0.16	1.48±0.28	1.83–0.24
Sb	min.–max	0.75–1.62	2.30–3.20.39	1.11–1.8	1.31–2422
	median±std	1.36±0.32	2.87±0.39	1.24±0.29	1.86±0.42
Zn	min.–max	32.9–157	9.57–12.6	16.3–24.3	45.6–51.0
	median±std	47.1±51.9	11.7±1.13	21.4±2.96	47.4±2.2

Table 2

RAF values of risk elements in M/L samples after the 6 weeks of exposure in underground parking lot

RAF	Element
≤0	–
0–1	Al, As Ba, Cu
1–5	Cd, Co, Cr, Fe, Li, Mn, Pb, As, Sb
<5	Zn, Ni

were confirmed in several studies focused on the traffic pollution or urban air pollution (VUKOVIĆ et al. 2015). Except zinc, in the surrounding of the heavy traffic places serious concentrations of Cd, Cu, Ni and Pb were found (ALSOUBOU and AL-KHASHMAN 2018, BUDAI and CLEMENT 2018). In our case, the pollution by Cd and Cu wasn't as serious. Comparing taxa, the highest RAF values of Cr, Pb and Zn were found for *Pleurosiium* spp.; As, Li and Sb for *Polytrichum* spp., Ba, Cd, Co, Cu and Mn for *Rhytidiadelphus* spp., and Al, Fe and Ni for *Pseudevernia furfuracea*. *Pleurosiium* spp. was found as the best accumulator of Zn in a study focused on ambient air quality assessment around petrol stations (DEMKOVA' et al. 2017). One-way ANOVA followed by Tukey post-hoc test was used to detect significant differences in accumula-

tion abilities between taxa. Significantly highest ability to accumulate Sb was found for *Polytrichum* spp. *Rhytidiadelphus* spp. was statistically confirmed as the best accumulator of Co, Cd and Mn ($p < 0.01$) – Table 3.

Table 3

The results of one-way ANOVA for the comparison the risk elements RAF values between different taxa and between EP

Risk element	Factor	Df	F-value	p	Factor	Df	F-value	p
Al	between taxa	3	34.59	3.18e-07**	between EP	4	0.155	0.958
As		3	0.361	0.782		4	3.884	0.023*
Ba		3	14.46	8.09e-05**		4	0.218	0.924
Cd		3	120.8	3.35e-11**		4	0.08	0.987
Co		3	59.18	7.01e-09**		4	0.073	0.989
Cr		3	3.58	0.0376*		4	1.754	0.191
Cu		3	79.87	7.65e-10**		4	0.081	0.987
Fe		3	8.56	0.00123**		4	0.106	0.978
Li		3	2.74	0.000164		4	0.100	0.981
Mn		3	44.19	5.75e-08**		4	0.145	0.962
Ni		3	6.63	0.00406**		4	1.488	0.255
Pb		3	1.488	0.256		4	0.398	0.807
Sb		3	14.38	8.36e-05**		4	0.374	0.823
Zn		3	25.62	2.39e-06**		4	0.083	0.986

* $P < 0.05$; ** $P < 0.01$

Highest Cd and Mn accumulation ability of *Rhytidiadelphus* spp. was confirmed in the study focused to the air pollution monitoring around tailing pond (DEMKOVA et al. 2017). *Pseudevernia furfuracea* and *Polytrichum* spp. were significantly different in their ability to accumulate Cr and Ni. All evaluated taxa significantly differ in their ability to accumulate Cu. No differences in Pb, Zn and As RAF values were confirmed between taxa. Comparing taxa (average risk element RAF value for each taxon), the decrease in order *Pleurosium* spp. > *Rhytidiadelphus* spp. > *Pseudevernia furfuracea* > *Polytrichum* spp. was detected. *Pleurosium schreberi* is very often used for bioaccumulation studies in Europe, because of its wide spread distribution (HARMENS et al. 2015) and excellent ability to accumulate not only heavy metals but also organic pollutants (KOSIOR et al. 2017). VINGIANI et al. (2015) have found, that in the same exposure conditions, the element accumulation in moss-bags was higher than in lichen-bags. Because moss and lichen taxa differ in accumulation ability of various risk elements, it is suitable to use them together to obtain more thorough results (LOPPI and BONINI 2000). In our case, *P. furfuracea* did not stand

out in accumulation capacities compared to the mosses. M/L bags were deployed in different distances from the main entrance/exit (Figure 2). Reduction of the daily light in the inward direction could disrupt the lichen taxon accumulation because they need sunlight and humidity for their good functionality (SHUKLA et al. 2014). On the other hand, bright sunlight and high temperature have an inhibiting effect on the lichen growth (SHUKLA et al. 2014).

Mean RAF values (average value for each taxon at each EP), the same as partial RAF values (RAF values of individual risk element for each taxon at each EP) were computed to determine correlation between EP and the average RAF value of the individual taxon. EP has no influence on the risk element accumulation in case of *P. furfuracea*, *Rhytidiadelphus* spp., and *Pleurosium* spp. Significant negative correlation ($p < 0.05$) was found between average RAF value and EP in case of *Polytrichum* sp.

Specifically, Mn and Zn gave significant negative correlation ($p < 0.01$) and Al significant positive ($p < 0.05$) correlation with the EP in case of *Polytrichum* spp. The average RAF (regardless the taxon) are listed in the Figure 3.

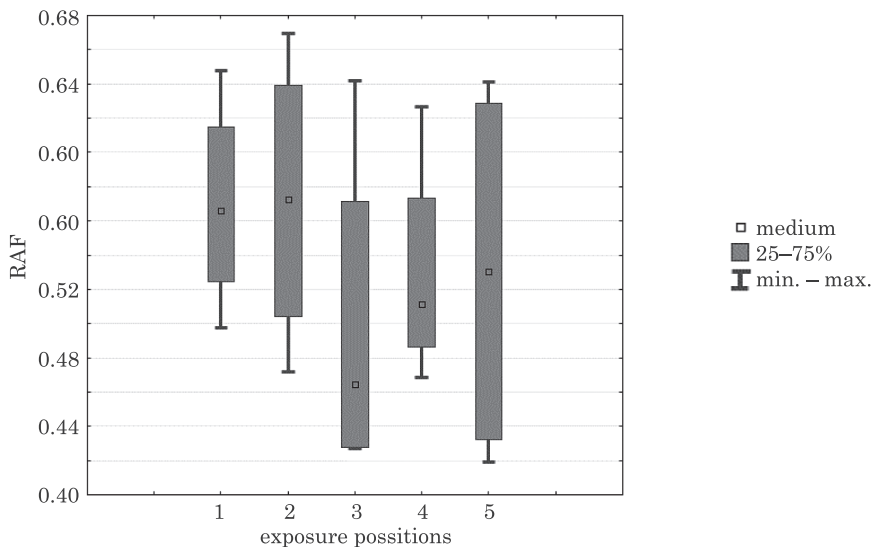


Fig. 3. The median values of RAF at the various EP regardless the M/L taxa

The highest average RAF value was determined at the second EP, then fell slightly. The highest RAF variation was confirmed for the last (5th) EP. Air flow, car movement, and ventilation system affected the distribution of metals within the parking lot (YAN et al. 2017, ZHAO AND ZHAO 2016). One-way ANOVA test (Table 3) was used to determine the

differences in the taxa's risk elements accumulation ability between EP. In our case, no significant differences were found for all evaluated risk elements RAF values except As. The As values were significantly highest in the EP located next to the entrances/exits. Some studies confirmed that fuels, oils, brake pads and tyres have traces of As (LUILO et al. 2014). But, on the other hand, the main As pollution comes from industrial activities or agricultural activities (herbicides or insecticides using), what could affect their accumulation in the EP located next to the entrance (KABATA-PENDIAS 2011).

It has been found that the risk elements originating from the same source correlate with each other (LI et al. 2008). Spearman's correlation coefficient was used to find out correlation relationships between RAF values of evaluated risk elements. Based the Spearman's correlation coefficient, no significant correlation between risk elements RAF values and the EP were found (Table 4). Only arsenic RAF gave significant negative correlation with the EP. The values of arsenic increase towards the exists/entrances. Zinc gave significant positive correlation ($p < 0.01$) with the Cd, Mn, Pb and significant negative correlation with Sb ($p < 0.05$).

Table 4
The Spearman's correlation analysis, between risk elements RAF values themselves, and between risk elements RAF values and the EP

	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	Sb	Zn
EP	0.18	-0.57**	0.11	-0.08	-0.09	-0.36	-0.06	-0.12	-0.02	-0.07	-0.37	0.12	-0.18	0.04
Al		-0.2	-0.7	-0.55*	-0.72	0.44*	-0.25	0.63**	0.13	-0.36	0.52*	0.03	-0.4	-0.13
As			0.03	-0.02	-0.06	0.04	-0.25	-0.04	0.17	0.07	0.12	0.09	0.03	0.10
Ba				0.58**	0.72**	-0.49*	0.35	-0.28	-0.04	0.44*	-0.50*	0.41	0.48*	0.29
Cd					0.92**	0.16	0.67**	0.18	-0.55*	0.91**	0.09	0.03	-0.03	0.56**
Co						-0.01	0.66**	-0.02	-0.46*	0.77**	-0.11	0.05	0.22	-0.06
Cr							0.01	0.64**	-0.01	0.36	0.84**	-0.18	-0.3	0.24
Cu								0.24	-0.71**	0.44*	0.18	-0.29	0.23	-0.26
Fe									-0.22	0.33	0.75**	0.14	-0.39	0.33
Li										-0.45*	-0.20	0.12	0.26	-0.23
Mn											0.29	0.12	-0.26	0.73**
Ni												-0.19	0.26	0.11
Pb													-0.08	0.65**
Sb														-0.48*

* $P < 0.05$; ** $P < 0.01$

Arsenic gave significant negative correlation with Cd, Co and Fe. As mentioned above, arsenic originates predominantly from anthropogenic activities related to agricultural (the use of pesticides and fungicides)

(CHUNG et al. 2014). Large quantities of As are released into the environment through industrial activities, what causing its increased concentrations, especially in the urban areas (BHATTACHARYA et al. 2007).

Significant positive correlation was found between Al, Fe, Ni and Cr themselves. Additionally, all of them gave negative (significant for Ni and Cr) correlation with Ba. The presence of these elements in the underground parking lot could be attributed to the vehicle bodywork corrosion. Chromium is very often used in refractory steels (FURINI 2012), Ni in alloys and metal processing industries, and Al as corrosion inhibitor (KABATA-PENDIAS 2011). Close relationship was found between Cd, Ba, Co, Cu, Mn and Zn, which gave positive correlation (almost significant) between themselves, except Cu-Zn and Co-Zn. Cu, Cd and Zn are attributed to tyre abrasion (LI and XIANG 2013), lubrication oils (CHRISTOFODIS and STAMATIS 2009), and galvanized automotive parts (BLOK 2005). Ba and Mn are mainly released from fuel combustion (KABATA-PENDIAS 2011). Significant but negative correlation gave Li with Cd, Co, Cu and Mn. Lithium is usually used in batteries. Significant positive correlation was confirmed between Pb-Zn ($p < 0.01$) and Sb-Ba ($p < 0.05$). The presence of lead in gasolines has been banned in many countries for its toxicological effects, but it is still used in some types of fuel additives (SANTOS et al. 2015).

The results of the cluster analysis (Figure 4), based on the RAF risk element contents, indicate two clusters: (1): Zn and (2): Al, As, Ba, Cd, Cu, Co, Cr, Fe, Li, Ni, Mn, Pb, Sb. Inside the group 2, we can differentiate two smaller groups a) Al, Fe, Cr, Ni and b) As, Ba, Co, Cd, Cu, Li, Mn, Pb, Sb.

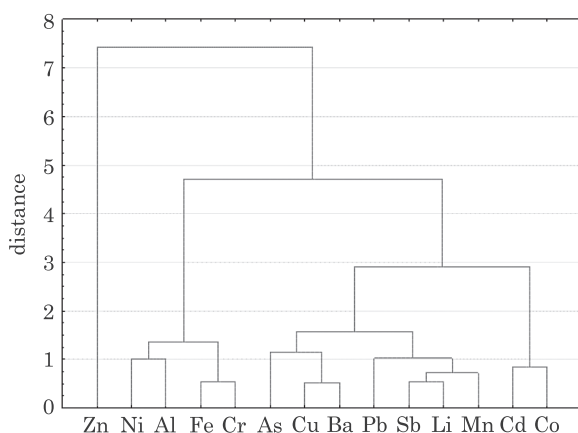


Fig. 4. Dendrogram of the RAF risk elements values determined in the M/L bag samples

Compared to the other risk elements, zinc reached the highest RAF values in moss and lichen insoles, what explain their separate position in cluster. Close relationship between Fe, Ni, Cr and Al was identically determined by Spearman's correlation. PCA distinguished evaluated taxa based on risk elements (Figure 5). The total variance explained by PCA was 74.51% (component 1: 55.79%; component 2: 18.72). The position and the direction of the risk elements towards the evaluated taxa, reflect the accumulation capacities of individual taxon values determined in the M/L bag samples.

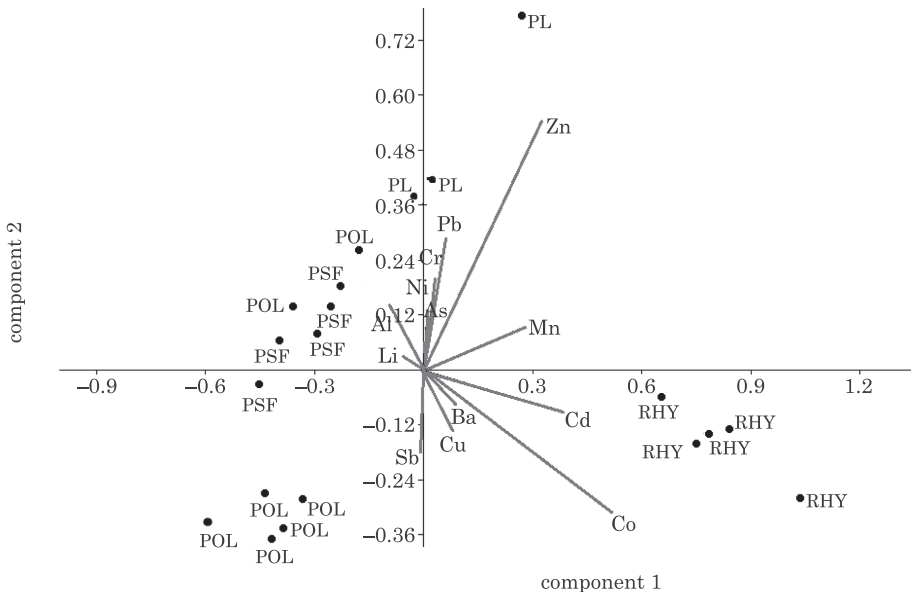


Fig. 5. The PCA biplot showing separation of different risk elements based on various taxa

As we hypothesised, serious pollution was determined in the underground parking lot, and more detailed statistical analysis pointed to the origin of the individual elements. The distance from the entrance/exit did not influence the concentrations of individual elements (with exception of arsenic), what is probably caused by a ventilation system that influences the airflow. As we supposed, mosses/lichens differ in their ability to accumulate different risk elements, what supports the theory of using them together to obtain complex results.

Conclusion

Zn, Ni, Mn and Fe were found as the most serious pollutants in underground parking lot. Accumulation abilities of individual taxa decreased in

order *Pleurosium* spp. > *Rhytidiadelphus* spp. > *Pseudevernia furfuracea* > *Polytrichum* spp. *Rhytidiadelphus* spp. was found to be the best accumulator of Co, Cd and Mn, *Polytrichum* spp. as the best accumulator of Sb. Close relationship between Al, Fe, Ni and Cr, which originate from car body corrosion, was confirmed by cluster analysis as well as Spearman's correlation relationship. Fuel combustion, releasing of the lubricate oils, or tyre abrasion are the main sources of risk elements such as Cd, Ba, Co, Cu, Mn and Zn. M/L bags were found as the suitable bioindicator of the air pollution conditions in underground parking lot. Because M/L taxa differ in accumulation ability of various risk elements, it is suitable to use them together to obtain more thorough results. No comprehensive work was until now focused on the risk elements evaluation in the underground parking lots in Slovakia. Based on the obtained results we can conclude, there is a serious accumulation of the toxic substances in underground parking lots, but regular maintenance could improve the air quality.

Accepted for print 25.08.2018

References

- ADAMO P., CRISAFULLI P., GIORDANO S., MINGANTI V., MODENESI P., MONACI F., PITTAO E., TRETIACH M., BARGAGLI R. 2007. *Lichen and moss bags as monitoring devices in urban areas. Part II: Trace element content in living and dead biomonitors and comparison with synthetic materials*. Environ. Pollut., 146: 392–399.
- ALSBOU E.M.E., AL-KHASHMAN O.A. 2018. *Heavy metal concentrations in roadside soil and street dust from Petra region, Jordan*. Environ. Monit. Assess., 190(1): 48.
- BALABOVA B., STAFINOV T., ŠAJN R., BAČEVA K. 2014. *Comparison of response of moss, lichens and attic dust to geology and atmospheric pollution from copper mine*. Int. J. Environ. Sc. Te., 11(2): 517–528.
- BHATTACHARYA P., WELCH A.H., STOLLENWERK K.G., MCLAUGHLIN M.J., BUNDSCHUH J., PANAU-LAH G. 2007. *Arsenic in the environment. Biology and Chemistry*. Sci. Total Environ., 379: 109–1020.
- BLOK J. 2005. *Environmental exposure of road borders to zinc*. Sci. Total Environ., 348(1–3): 173–190.
- BUDAI P., CLEMENT A. 2018. *Spatial distribution patterns of four traffic-emitted heavy metals in urban road dust and the resuspension of brake-emitted particles. Findings of a field study*. Transp. Res. D. Transp. Environ., 62: 179–185.
- HARMES H., NORRIS D.A., SCHARPS K., MILLS G., ALBER R., ALEKSIAYENAK Y., BLUM O., CUCU-MAN S.M., DAM M., DE TEMMERMAN L., ENE A., FERNÁNDEZ J.A., MARTINEZ-ABAIGAR J., FRONTASYEVA M., GODZIK B., JERAN Z., LAZO P., LEBLOND A., ZECHMEISTER H.G. 2015. *Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hot-spots" remain in 2010*. Environ. Pollut., 200: 93–104.
- CHEN R.H., CHIANG L.B., CHEN CH.N., LIN T.H. 2011. *Cold-start emissions of an SI engine using ethanol gasoline blended fuel*. Appl. Therm. Eng., 31(8–9): 1463–1467.
- CHITHRA V., NEGENDRA S. 2012. *Indoor air quality investigations in a naturally ventilated school building located close to an urban roadway in Chennai, India*. Build. Environ., 54: 159–167.

- CHRISTOFORDIS A., STAMATIS N. V. 2009. *Heavy metal contamination in Street dust and roadside soil along the major national road in Kavallas Region, Greece*. Geoderma, 151(3–4): 257–263.
- CHUNG J. Y., YU S.D., HONG Y.S. 2014. *Environmental source of arsenic exposure*. J. Prev. Med. Public Health, 47: 253–257.
- DEMKOVÁ L., BOBULSKÁ L., ÁRVAY J., JEZNY T., DUSCAY L. 2017. *Biomonitoring of heavy metals contamination by mosses and lichens around Slovinky tailing pond (Slovakia)*. J. Environ. Sci. Health. Part B, 52(1): 30–36.
- FURINI A. 2012. *Plants and heavy metals*. Springer Dordrecht Heidelberg New York, London.
- KABATA-PENDIAS A. 2011. *Trace elements in soil and plants*. Taylor & Francis Group, London–New York.
- KOSIOR G., PŘIBYLOVÁ P., VAŇKOVÁ L., KUKUČKA P., AUDY O., KLÁNOVÁ J., SAMEČKA-CYMERMAN A., MRÓZ L., KEMPERS A.J. 2017. *Bioindication of PBDEs and PCBs by native and transplanted moss Pleurozium schreberi*. Ecotoxicol. Environ. Saf., 143: 136–142.
- KŁOS A., ZIEMBIK Z., RAJFUR M., DOŁHAŃCZUK-ŚRÓDKA A., BOCHENEK Z., BJERKE J.W., TØM-MERVIK H., ZAGAJEWSKI B., ZIÓŁKOWSKI D., JERZ D., ZIELIŃSKA M., KREMS P., GODYŃ P., MARCINIAK M., ŚWISŁOWSKI P. 2018. *Using moss and lichens in biomonitoring of heavy-metal contamination of forest areas in southern and north-eastern Poland*. Sci. Total Environ., 625: 438–449.
- LI W., ZHANG X., WU B., SUN S., CHEN Y., PAN W., ZHAO D., CHENG S. 2008. *A comparative analysis of environmental quality assessment methods for heavy metal contaminated soils*. Pedosphere, 18(3): 344–352.
- LI Y., XIANG R. 2013. *Particulate pollution in and underground car park in Wuhan, China*. Particuology, 11(1): 94–98.
- LOPPI S., BONINI I. 2000. *Lichens and mosses as biomonitors of trace elements in areas with thermal springs and fumarole activity (Mt. Amiata, central Italy)*. Chemosphere, 41: 1333–1336.
- LUILO G.B., OTHMAN O.C. 2008. *Lead pollution in roadside urban environments*. Tanzan. J. Sci., 32: 61–68.
- LUILO G.B., OTHMAN O.C., MRUTU A. 2014. *Arsenic. A toxic trace element of public health concern in urban roadside soils in Dar es Salaam City*. Journal of Material and Environmental Sciences, 5(6): 1742–1749.
- PAPANIKOLAOU N.C., HATZIDAKI E.G., BELIVANIS S., TZANAKAKIS G.N., TSATSAKIS A.M. 2005. *Lead toxicity update. A brief review*. Med. Sci. Monit., 11(10): 329–336.
- POPE C.A. 2000. *Review: epidemiological basis for particulate air pollution health standards*. Aerosol Sci. Technol., 32: 4–14.
- REITER M.S., KOCKELMAN K.M. 2017. *The problem of cold starts. A closer look at mobile source emissions levels*. Transp. Res. D. Transp. Environ., 43: 123–132.
- SANTOS A.P.M., SEGURA-MUNOS S.I., NADAL M., SCHUMACHER M., DOMINIGO J., MARTINEZ C.A., MAGOSSO TAKAYANAGUI A.M. 2015. *Traffic-related air pollution biomonitoring with Tredescantia pallida (Rose) Hunt. cv. Purpurea Boom in Brasil*. Environ. Monit. Assess., 187(2): 39.
- SHUKLA B., BAJPAI R., UPRETI D.K. 2014. *Lichens to biomonitor the environment*. Springer, India.
- SZCZEPANIAK K., BIZIUK M. 2003. *Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution*. Ecotoxicology, 93(3): 221–230.
- THROPE A., HARRISON R.M. 2008. *Source and properties of non-exhaust particulate matter from road traffic: a review*. Sci. Total. Environ., 1(1–3): 270–282.
- TONG Z., CHEN Y., MALKAWI A., ADAMKIEWICZ G., SPENGLER J.D. 2016. *Quantifying the impact of traffic-related air pollution on the indoor air quality of naturally ventilated building*. Environ Int., 89–90: 138–146.
- VINGIANI S., DE NICOLA F., PURVIS W. O., CONCHA-GRANA E., MUNIATEGUI-LORENZO S., MAHÍA-LÓPEZ P., GIODANO S., ADAMO P. 2015. *Active Biomonitoring of Heavy Metals and PAHs with Mosses and Lichens: a Case Study in the Cities of Naples and London*. Water Air Soil Pollut., (226): 240.
- VUKOVIĆ G., UROŠEVIĆ M.A., RAZUMENIĆ I., GORYAINOVA Z., FRONTASYEVA M., TOMAŠEVIĆ M., POPOVIĆ A. 2013. *Active moss biomonitoring of small-scale spatial distribution of airborne major and trace elements in the Belegrade urban area*. Environ. Sci. Pollut Res., 20(8): 5491–5470.

- VUKOVIĆ G., UROŠEVIĆ M.A., GORYAINOVA Z., PERGAL M., ŠKRIVANJ S., SAMSON R., POPOVIĆ A. 2015. *Active moss biomonitoring for extensive screening of urban air pollution. Magnetic and chemical analyses.* Sci. Total Environ., 521–522: 200–210.
- WEI X., GAO B., WANG P., ZHOU H.D., LU J. 2015. *Pollution characteristics and health risk assessment of heavy metals in street dusts from different functional areas in Beijing, China.* Ecotoxicol. Environ. Saf., 112: 186–192.
- YAN Y., HE Q., SONG Q., GUO L., HE Q., WANG X. 2017. *Exposure to hazardous air pollutants in underground car parks in Guangzhou, China.* Air Qual Atmos. Hlth., 10(5): 555–563.
- ZHAO Y., ZHAO J. 2016. *Numerical assessment of particle dispersion and exposure risk in an underground parking lot.* Energ. Buildings, 133: 96–103.
- ZIELINSKA B., FUJITA E., OLLISON W., CAMPBELL D., SAGEBIEL J., MERRITT P., SMITH L. 2012. *Relationship of attached garage and home exposures to fuel type and emission levels of garage sources.* Air Qual Atmos. Hlth., 5:89–100.

