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Heavy metals compounds from tailing pond sludge and their distribution to the tissues of the selected common *Poaceae* species and crop plants

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Abstract. This study deals with the issue of contaminant transfer from a tailings pond (Rosina-Žilina, Slovakia) to the surrounding environment. More than one hundred samples of soil and plant tissues were taken. Analysis focused to two species of the *Poaceae* family (*Phragmites australis* and *Calamagrostis* sp.) as well as common crops (corn, apple, cherry) in the vicinity of the tailings pond. All samples were analysed by x-ray spectrometry for rapid and accurate measurements in situ as well as in laboratory conditions. We assessed the risk of ash-waste contamination to the ecosystem during transfer and the related potential threat to human health long term. Arsenic content in soil samples of ash material ranged from 41 to 91 ppm, but these values did not confirm the transfer of this element into the tissues of monitored plants. Mercury levels were only detected in samples from the tailings pond where mean values in soil and stems and blooms were equal. The presence of lead in soil samples and plant tissues was also detected. The data obtained indicates possible bioaccumulation of lead, especially in *Calamagrostis* sp.. Soil samples from tailings pond contained a mean of 36 ppm of lead and individual measured tissues of *Calamagrostis* sp. contained lead levels of 13 to 18 ppm. These findings support the hypothesis that heavy metals are bio-avalible via the food chain, especially for herbivores. Heavy metals in investigated crops did not differ between sample sites. Corn leaves were more polluted than kernels, while fruit seeds were more polluted than pulp or leaves.

Key words: crop plants, *Phragmites australis, Calamagrostis* sp., contamination, heavy metals

Introduction

The processing and storage of waste material from anthropogenic activities is the subject of much research as many deposited substances in landfills or in sludge disposal sites can become a long-term risk to human health and the local ecosystem (Jacob and Otte 2004; Liang *et al.* 2017; Gabbarón *et al.* 2018).

Power and thermal plants that use coal produce various forms of ash. These by-products from the combustion of coal are usually transported by water in the form of sludge and deposited in landfills called tailings ponds. These ponds are generally to be the main source of pollution in regions where they occur (Demková *et al.* 2019), because they could affect environmental components such as air, water and soil (Ettler *et al.* 2009; Hiller *et al.* 2009; Petrilean *et al.* 2014). Several studies confirm the content of arsenic and lead in the deposited ash material (Scherer *et al.* 2015). In addition to heavy metals (HM), the sludge was found to contain various organic and inorganic compounds (Ruhl *et al.* 2009; Lam *et al.* 2010). After sedimentation of the sludge, the surface of the sludge bed is formed out of small particles that could be transferred to the surrounding area, as well as over longer distances (Razo *et al.* 2004). Wind erosion plays a significant role in this process, particularly in warm weather. Generally, these small dust particles in the air reach the surface through a dry or wet deposition process and contaminate the environment with possible consequences to human health (Zanuzzi *et al.* 2009; Desouki and Feng 2012). Different heavy metals (HM) may be associated with different particle sizes (Yoo *et al.* 2002; Demková *et al.* 2017), and can be transported over greater distances. Water discharge from drainage systems may also have dangerous impacts, mainly during periods of increased precipitation (Mayes *et al.* 2011), as excess water in tailings ponds discharge to the nearest water source. Accidents caused by the rupture of a dam are particularly serious (Majerník *et al.* 2012).

Bioindicators are widely used for assessment of pollution load in environments (Fränzle 2003). Various risk assessment studies (e.g., Shahid *et al.* 2020) provide valuable information about possible pathways into the food chain for trace elements with potential health risks. It is well known that the HM accumulation capacity of plants depends on various conditions (Kabata-Pendias 2011), including type, morphology and physiology of plants, type of metal, soil conditions (Barman *et al.* 2001), as well as multiple stress factors (Vighi and Villa 2013). These differences were also found in individual parts of plants (Chaplygin *et al.* 2018). If we compare the levels of HM in one species at several localities (polluted and reference), we can achieve satisfactory estimates of environmental pollution.

Approximately 56 tailings ponds exist in Slovakia (Masarovičová *et al.* 2008). Fifteen of these are used for storage of ash and slag materials that are a byproduct of coal generated heating and power plants (Bosák 2017). Reclamation of these sites will be a major milestone in Slovakia's transition to a low carbon economy. Many published studies deal with old mining sites (e.g., Angelovičová and Fazekašová 2014; Angelovičová *et al.* 2014; Demková *et al.* 2017, 2019; Jurkovič *et al.* 2019) but studies regarding the current impacts of active tailings ponds on the environment is lacking. At this time only basic operational monitoring is conducted. This research focuses on a biomonitoring study at one of the tailings ponds in Žilina – Rosina, which is close to a populated area.

The main aim of our study is the determination, using x-ray, of selected heavy metal content (Pb, Hg, As and Cd) in plant substrates and tissues, including an emphasis on the *Poaceae* family. These analyses may help indicate which parts of plants are most polluted and help estimate the potential heavy metals pose to the trophic chain, particularly for herbivores living and feeding close to tailings ponds. In addition, we analysed three crops to estimate the pollution load that may be present in the human food chain.

Material and Methods

The study area encompassed a tailings pond in Rosina – Žilina (Slovakia), where deposited waste ash material from the local heating plant (Žilinská teplárenská, a.s.) has been present since 1985. This company uses brown coal to produce heat. The pond is located in an agricultural area characterised by a slightly undulating flat landscape with an average altitude of 400 m. asl., where quaternary fluvial and eluvio-deluvial sediments comprised of mostly with clays and gravels are dominant. The tailings pond consists of a valley dam system with a height of 22 meters. The length of the dam crown is 420 m. Waste ash (with waste from desulphurisation) is transported by water circulation through the drainage system of the tailings pond where seepage water is repeatedly used. The rest of the seepage water flows into the Bytčický potok stream. The potential accumulation volume is more than 2 milion m^3, and covers an area of 25 ha. This tailings pond represents an environmental burden with a high priority placed on monitoring and future remediation and reclamation (Masarovičová *et al.* 2008; EIA 2019).

For purpose of the study we selected two species of the *Poaceae* familly *Phragmites australis* and *Calamagrostis* sp. that were well represented in proximity to the tailings pond as well as within selected reference areas. Reference areas were carefully chosen based on similarity of habitats and a minimum distance of 2 km from the tailings pond. Additionally, crop samples of corn (*Zea mays*), apples (*Malus domestica*) and cherries (*Prunus avium*), were harvested from the areas immediatly surrounding the tailings pond and reference areas. Together with the *Poaceae* species, soil samples were collected from the top soil layer down to 10 cm in the place where individual plants grew up (without plant residue). All samples of selected plants were collected during 2018, between April and July, and their site distribution is shown in Fig. 1. The *Poaceae* species samples were collected directly from the tailings pond from the desimented ash layer. At the reference sites,

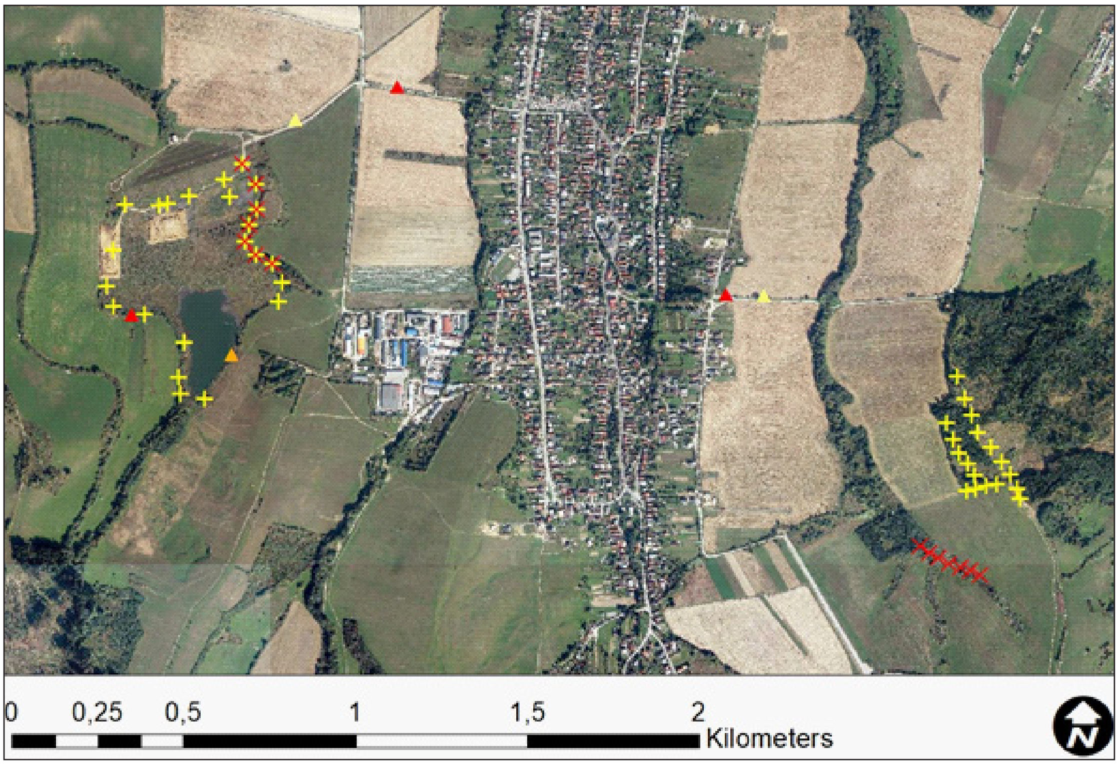

Fig. 1. Sampling sites (Tailing pond at left side, reference areas at right side; red x – *Phragmites australis*; yellow cross + – *Calamagrostis sp.*; yellow triangle – corn; red triangle – apple; orange triangle – cherries).

these species were collected from their natural habitats. Samples were divided into underground (roots), ground floor (sheats) and above ground (stems with blooms) parts. Crop samples (apples and cherries) were divided into leaves and fruits, and the fruits were further divided into seeds and flesh. In the case of corn, leaves and kernels were separated from the cob. Samples were not washed in order to better estimate the total potential amount of metals that may enter the organisms through the food chain.

All divided samples were dried using the Memmert IF 160 laboratory Plus dryer (Memmert, Germany) for 12 hours at 60 degrees °C and subsequently mechanically homogenized using a cryomill (Cryomill, Retsch, Germany). In the study we focused on heavy metal concentrations such as lead (Pb), mercury (Hg), arsenic (As) and cadmium (Cd). For analysis we used the ED-XRF spectrometer DELTA Premium with Portable WorkStation (Olympus, Innov-x Systems, USA), which is also used as an suitable, effective and convenient tool for determination of metal concentrations in various kinds of materials (Nganvongpanit *et al.* 2016; Buddhachat *et al.* 2018; Kompišová *et al.* 2020). Homogenized samples were measured in a plastic vial (minimum 15 mm layer). Multiple-beam measurement was used, in which every measurement consisted of 3 beams for 80 seconds, repeated three times, and then averaged. The results were given in ppm (parts per million) units. The detection limits were individual for each measured element. Pb (2-4 ppm), As (1-3 ppm), Hg (2-4 ppm) and Cd (6-8 ppm) (Innov-X Systems 2018). Standards used for basic calibration of the device were in a clean homogenous SiO_2 matrix without interfering elements. An additional calibration matrix was used for plant material analysis (certified plant standards INCT-PVTL-6 (ICHTI, Poland) and BCR-191), to ensure accurate measurement. NIST 1575a was used as the standard for soil measurements. Samples were randomly measured repeatedly and relative standard deviation was below 10 %. Samples with values too low or close to detectable levels were excluded.

The measured data were statistically evaluated by Statistica 12 (StatSoft, USA). The data had a normal distribution according to the Shapiro-Wilk test, but in the case of this small dataset ($N < 30$) we used nonparemetric statistical methods. Therefore, for differences between groups, One-way ANOVA or the Kruskal Wallis test (KW) was used with a significance level of $p < 0.05$.

Results

In the case of the *Poaceae* family, 30 samples were analysed near the tailings pond, and an additional 30 were sampled in the reference area. The same number of idividuals, 23 *Calamagrostis* sp. and seven *Phragmites australis*, were collected at each site. Preliminary results show that levels of Hg and

Samples	**N**	**Mean Pb**	**N**	**Mean Hg**	**N**	**Mean As**	**N**	**Mean Cd**
Reference site	30	51	-	-	27	15	1	10
Calamagrostis sp.	23	58	-	-	21	16	1	10
Soil	23	58	-	-	21	16	-	-
Roots	-	-	-	-	-	-	1	10
Sheats tissues	-	-	-	-	-	-	-	-
Stems and blooms	-	-	-	-	-	-	-	-
Phragmites australis	7	27	-	-	6	9	-	-
Soil	7	27	-	-	6	9	-	-
Roots	-	-	-	-	-	-	-	-
Sheats tissues	-	-	-	-	-	-	-	-
Stems and blooms	-	-	-	-	-	-	-	-
Tailing pond	**93**	**22**	**28**	**12**	**34**	**52**	**3**	**13**
Calamagrostis sp.	86	21	19	13	27	41	1	10
Soil	23	36	10	13	21	48	-	-
Roots	21	15	3	12	6	20	1	10
Sheats tissues	21	13	2	10	-	-	-	-
Stems and blooms	21	18	4	15	-	-	-	-
Phragmites australis	7	38	9	11	7	91	2	15
Soil	7	38	7	11	7	91	-	-
Roots	-	-	-	-	-	-	1	8
Sheats tissues	-	-	-	-	-	-	1	21
Stems and blooms	-	-	2	11	-	-	-	-
Sum ∑	**123**	**29**	**28**	**12**	**61**	**35**	**4**	**12**

Table 1. Measured levels of heavy metals (Pb, Hg, As and Cd; in ppm) by x-ray method in samples of *Poaceae* family collected in tailings pond and reference areas.

Cd were not detected in the reference area, with the exception of one root sample of *Calamagrostis* sp. that exhibited Cd content (Table 1). Cd levels were detected in three samples from tailings pond; *Calamagrostis* sp. root, and two samples of roots and tissues of *P. australis*, sampled from different places in the vicinity of the pond. Seventeen of the soil samples from the tailings pond location had detactble Hg levels, including all soil samples of *P. australis* (mean 10.9 ppm) and ten soil samples of *Calamagrostis* sp. (13.4 ppm) without significant differences between these groups (KW: H (1, 17) = 0.292, p = 0.589). In the reference area, Pb and As levels were observed only in soil samples and surprisingly, Pb levels were significantly higher than in soil samples from the tailings pond (Fig. 2a). This could be due to the location of the reference site, and its proximity to other sources of pollution. However, soil samples taken from the reference area near *P. australis* were less polluted by Pb (KW: H (1, 14) = 9.887, p = 0.001) than at the pond (Fig. 2b). Generally, the levels of As were significantly higher in soil samples collected from the tailings pond (Fig. 3a, b (F (1, 53) = 22.741, p = 0.001). While soil samples of *P. australis* from the reference area had significantly lower As levels (9.3 ppm) (Fig. 3a), the opposite was true at the tailings pond site, where this species had significantly higher levels of As (Fig. 3b, 91.3 ppm) when compared to samples of *Calamagrostis* sp. (47.5 ppm). It must also be considered that the reference areas for both species were different. Reference samples of *P. australis* were taken from a terrain depression where small a stream springs, and reference samples of *Calamagrostis* sp. were taken from a forested area (sparse canopy) a top a small hill.

Reliable and detectable levels of Pb in species of *Poaceae* family, measured by x-ray, were detected only in the samples of genus *Calamagrostis* sp. (N = 21), which were taken at the tailings pond. Hg levels were detected in less than half of the samples (N = 9). It is clear that grasses of the genus *Calamagrostis* sp. accumulated much more lead at the tailings pond, although there were lower lead values found in the soil than at the reference site. We observed significant differences in Pb accumulation among investigated tissue groups of this species (F (2, 60) = 16.451, p = 0.001). Higher levels of Pb were found in samples of stems with blooms (Fig. 5a, b). There was not a significant difference in Hg levels between tissue groups of *Calamagrostis* sp. (KW: H (2, 9) = 1.625 p = 0.444) and we observed only slight mean differences with higher values in stems with blooms. Since the samples have not been washed, these results point to the total amount of metals that may be introduced to organisms through the food chain. The biggest impact is to herbivores feeding in the vicinity of the tailings pond that may consume vegetation covered in ash - dust. *P. australis* is at tall grass occurring in humid environments. Thus, in terms of biomass, this species may not demonstrate a great ability to accumulate metals.

In addition, crop samples of corn, apple, and cherry were also collected and analysed from the area by the tailings pond and the reference areas (10 samples for each crop and each site). We were able to reliably measure and detect Pb

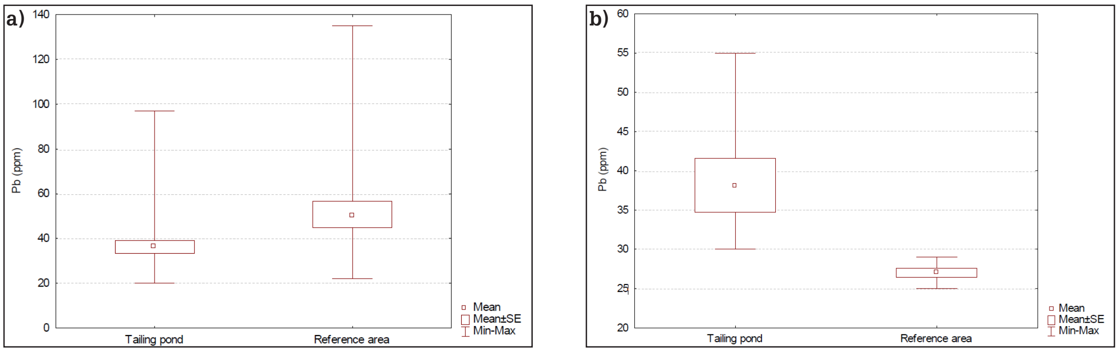

Fig. 2. Levels of Pb (in ppm) in soil samples. **a)** all sites (F (1, 58) = 4.796, p = 0.033); **b)** sites of *Phragmites australis* (KW: H (1, 14) = 9.887, p = 0.001).

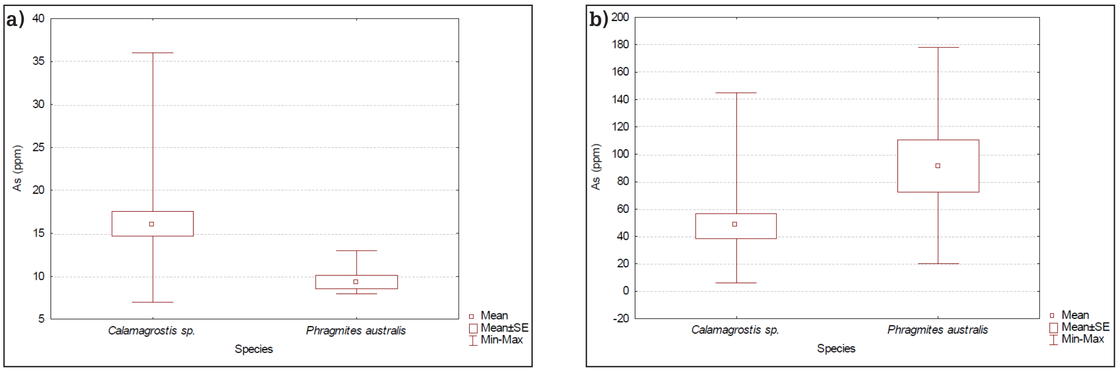

Fig. 3. Levels of As (in ppm) in soil samples of investigated species of *Poaceae* family. **a)** reference area (KW: H (1, 27) = 6.763, p = 0.009); **b)** tailings pond (KW: H (1, 28) = 4.398, p = 0.036).

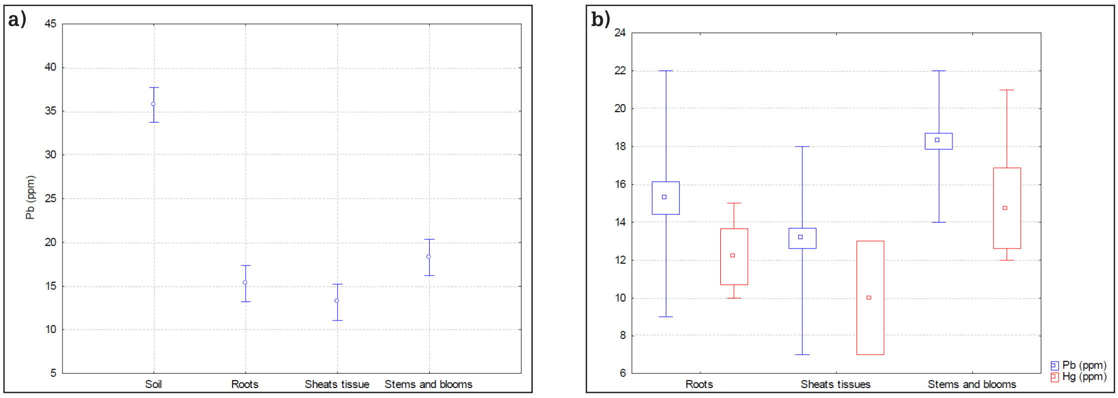

Fig. 4. a) – Levels of Pb (in ppm) in divided samples of *Calamagrostis sp.* (Least squares, Vertical bars denote +/- standard errors); **b)** – Comparison of Pb (F (3, 82) = 26.152, p = 0.001) and Hg (KW: H (2, 9) = 1.625, p = 0.444) levels in divided plant samples of *Calamagrostis sp.* (Mean; Box: Mean ± SE; Whisker: Min-Max).

levels using the x-ray method, as levels of As and Hg were below the detection limit and Cd levels were only detected in four samples of apple. Two of these were taken close to tailings pond (one leaf sample and one fruit sample) and the other two (one leaf sample and one fruit sample) were taken from the reference area. General tendencies were observed based on levels of Pb. Corn had significantly more polluted leaves (mean 12 ppm) than kernels (4 ppm; F = 273; p = 0.001), but a significant difference was not found between localities (Fig. 5a; p = 0.780). Apple seeds had significantly higher Pb levels than both apple pulp and leaves (Fig. 5b; F = 66; p = 0.001). However, when comparing sites, apples to the east of the tailings pond had significantly higher lead concentrations than those found near the western part of the tailings pond (F = 6.14; p = 0.003). To the east there are prevailing winds and thus increased dust levels. There is a significant interaction between factors such as site and tissue type (F = 4.7, p = 0.002). Apple samples taken along the road on the way to the east side of the tailings pond had a higher level of lead in pulp and leaves but lower levels in seeds. Samples taken from the western side of the tailings were the opposite. In the case of cherries, Pb levels were only detected in leaves. Mean lead values did not differ between sites (F (1.16) = 0.32, p = 0.570) close to the tailings pond and the reference area (Tatra region specially for this case).

Discussion

Tailings ponds, which are generally used for the storage of power plant waste ash, sediments from chemical factories, or sludge from mining operations, can pose a burden on the environment. Sedimented sludge eroded by wind can be carried as dust into the environment (Ettler *et al.* 2009; Hiller *et al.* 2009). Increased precipitation can lead to the dangerous discharge of excess water from the tailings pond into the nearest water source. The environmental impact is mainly related to the composition of the ash and the potential for the transfer of hazardous substances into the ecosystem. Biota contamination may not be visible at first sight (Feketeová *et al.* 2016). One of the risk processes is the leaching of individual components of the sludge, which may increase concentrations of hazardous substances in water (Ugurlu 2004), including arsenic, selenium, boron, strontium, and barium (Ruhl 2010). In their study, Lokeshappa and Dikshit (2012) pointed out that the concentration of elements such as arsenic and chromium accumulates over time. In this study, the substrate analysis taken directly from the sludge sedimentation of the tailing pond had the highest level of arsenic content, at 178 mg/kg. The average arsenic concentration of all samples of sludge substrate was 55 mg/kg. In comparison, the highest arsenic measured in the substrate of the reference

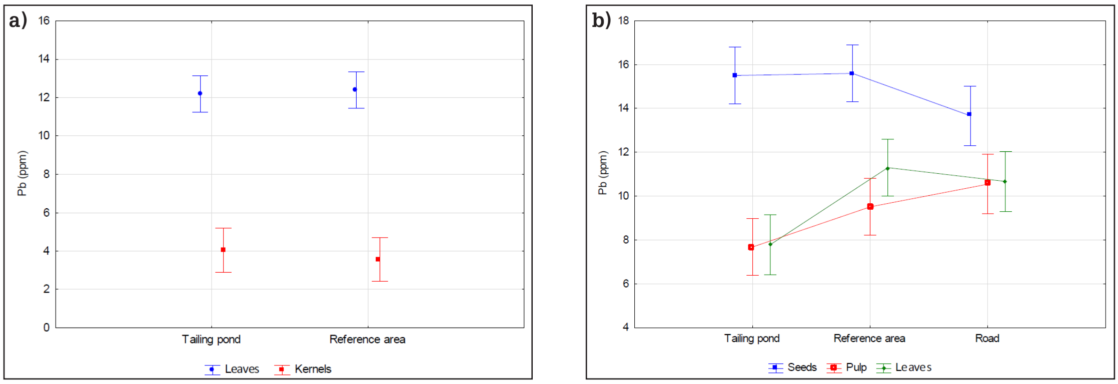

Fig. 5. a) Levels of Pb in divided samples of corn; **b)** Levels of Pb in divided samples of apples. (Averages with 0.95 % confidence interval).

site reached 36 mg/kg and the mean value of this element was 15 mg/kg. Comparatively, ash content from the Kingston coal-burning power plant exhibited As values averaging 75 mg/kg (Ruhl *et al.* 2009).

Plants represent a path to wider contamination of the ecosystem. Because they are the food source for herbivores, even low concentrations of pollutants in individual plant tissues are systematically accumulated in animal organs at the top of the trophic chain, where levels can reach harmfull concentrations (Peralta-Videa *et al.* 2009; Gall *et al.* 2015). For comparison, Sychra *et al.* (2011) measured cadmium, lead, and mercury concentrations in *Phragmites australis* and sediments in 21 ponds in Moravia, in the Czech Republic. They found that in the sediments of these ponds the values (in mg/l) of cadmium ranged between 0.63 - 1.42 mg/l for lead 2.52 - 46.3 mg/kg and for mercury 0.014 - 0.236 mg/kg. Values in the tissues of common reeds were much lower, e.g. cadmium ranged from 0.007 - 0.037 mg/kg, lead 0.04 - 1.19 mg/kg, and mercury 0.003 - 0.026 mg/kg. In this study, the cadmium, lead, and mercury in the *Phragmites australis* were not measured either in the tailings ponds or at the reference site. This may point to the fact that common reeds are not a good accumulator of these metals compared to other plant species (Drbal 1991; Svobodová *et al.* 1996). Cadmium was not detected in any soil samples. Mercury was detected in the 17 soil samples from the tailings pond. The highest value of mercury detected in the sample from the sludge deposit reached 28 mg/kg, while average values reached 12 mg/kg.

Calamagrostis grasses, which contained more lead in the tailings pond than at the reference site, offer a different perspective. Lead content in the soil at the tailings pond was found to be lower than the soil at the reference site. Higher lead concentrations in the soil at the reference site may be due to the deposition of lead from transmissions, as the reference site was situated on a windward crest. A similar windward effect of lead deposition was also shown by Klamárova and Solár (2017) in a study of the spatial distribution of trace elements near Ružomberok, as well as in many other studies (Grigoras *et al.* 2012; Da Silva 2019). The phenomenon of higher lead concentrations in grasses of the genus *Calamagrostis* in the tailings pond, may be related to plant physiology, soil moisture, pH or temperature (Lone *et al.* 2004; Suchá 2010). Translocation of heavy metals from soil to plant tissues is also significantly affected by the presence of chelating agents (Kaduková *et al.* 2006) and soil salinity (Otte 1991; Fitzgerald *et al.* 2003).

Measurable values of Pb were detected in the plant tissues of crop plants, while measurable values of As were detected in sludge deposits from the tailings pond. While it is positive that the crops did not demonstrate high levels of arsenic, this may speak more to the low bioavailability of this element that to their potential to accumulate it (Khan *et al.* 2015). Lead is usually strongly bonded to soil particles, and when absorbed, generally accumulates in the roots (Kaduková *et al.* 2006). Because lead transport from root to aerial plant parts is limited (Pourrut *et al.* 2011), it is likely that aerial plant parts accumulate high levels of heavy metals as a result of wind-born particles (Styk 2001; Suhadiyah *et al.* 2011). Wind direction, distance from the source of pollution and precipitation, and anatomical and physiological characteristics of each species affect the potential for absorption of hazardous substances. Different plant species have vastly varying tendencies to accumulate lead and heavy metals overall, as well as differing thresholds constituting toxicity, which may vary depending on both the element and plant in question (Tripathi 2009). For example, Tripathi (2009) shows that heavy metals are more likely to accumulate in vegetables than in fruits. In further scientific literature it is also mentioned that leafy crop plants (*Lactuca sativa* L., *Spinacia oleracea* L.) have the greatest capacity to accumulate heavy metals (Li *et al.* 2014). Out of the three crop plants studied, lead was detected in the leaves, seeds and pulp of both corn and apples. The highest values of lead were detected in the seeds of apples from both the tailings pond area and the reference area. Lead values in the seeds of apples were higher than in the leaves. This does not correspond with Svičeková and Havránek's study (1993), which states the highest values of heavy metals elements are found in the leaves. Primary accumulation of heavy metals in leaves (after roots) is mentioned in a number of studies (Bi *et al.* 2009; Roba *et al.* 2015), but this does not account for variations between species.

Finally, this study did not directly confirm the path of tissue contamination through the roots from contaminated soil substrate, but based on measured data it is expected that there is possible additional contamination by wind transfer of small ash particles. This phenomenon was also observed in urban and industrial areas, where pollutant concentrations correlate with the distance from the source of pollution (Simon *et al.* 2010) and wind flow (Oztas and Ata 2002). In this study, the focus was on surface distribution of hazardous elements from deposited material, but in the monitored area there is also a risk of groundwater contamination, as confirmed by Scherer *et al.* (2015). Older and deeper deposited layers of ash material may contain higher concentrations of arsenic and other heavy metals, and also due to the redox potential of eH and pH, may be transformed by heavy metal compounds into more toxic forms (Jašová *et al.* 2009). Therefore, we consider it appropriate to subject this area of research to longer-term monitoring in order to enhance the protection of human health and the health of the living ecosystem in general.

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