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Arsenic Concentrations in Soils Impacted by Dam Failure of Coal-Ash Pond in Zemianske Kostolany, Slovakia

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Abstract In this study, the concentrations of arsenic were determined in the soils around old coal-ash pond. The soils in the study area were severely contaminated with arsenic after dam failure of the coal-ash pond. The mean concentrations of arsenic in soils collected from three sampling depths of 0–20, 20–40 and >40 cm were 173, 155 and 426 μg/g, respectively, exceeding greatly the Dutch intervention threshold for this element. Arsenic concentrations were positively correlated with total iron and aluminium contents in the soils ($r = 0.73$, $p < 0.001$ and $r = 0.72$, $p < 0.001$, respectively), indicating that oxyhydroxides of iron and aluminium may control the distribution of arsenic in these soils. Ammonium nitrate extractant was used to mimic availability of arsenic for plant uptake from the soils. Between 0.05 and 6.21% of the total soil arsenic were extracted using a single extraction test and a significant positive correlation between soil leachate pH and arsenic extractability ($r = 0.70$, $p < 0.01$) was observed. This suggested that soil pH might play a role in the bioavailability of arsenic.

Keywords Arsenic · Fly ash · Power plant · Coal · Soil

Arsenic is ubiquitous element in the environment and exhibits adverse health effects on living organisms, including human beings (Ferreccio et al. 2000; Milton et al. 2005). Coals are not only the main source of power used in thermal power plants to generate electricity, but also an important natural source of arsenic and other metals of environmental and health significance (Bouska and Pesek 1999; Ding et al. 2001). Once the coals are combusted, the metals in coals are liberated and concentrated in the fly and bottom ashes (Llorens et al. 2001; Goodarzi et al. 2008). These fly and bottom ashes comprise the bulk of the by-products of coal combustion which are impounded in the ash ponds of thermal power plants (Agrawal et al. 2010).

This study describes the soils enriched in arsenic (As) around coal-ash pond located near the village of Zemianske Kostolany (Fig. 1a) and 4 km south of the Elektrarne Novaky (ENO) thermal power plant at Novaky, Prievidza district in central Slovakia. These soils were seriously impacted by dam failure of the coal-ash pond in 1965, when approximately 3×10^6 tons of the ashes were released into the surrounding environment and the Nitra river. Up to 20 km^2 of the area was covered by the ash layers with the thickness of 50 cm. Later, the released ashes were covered by soils coming from different and often unknown sites of Slovakia. Therefore, the studied soils represent a heterogeneous mixture of the ash and the soil. Arsenic accumulated in soils cannot be considered to be totally isolated and unavailable for plant and animal uptake, depending on the strength of solid-As interactions and soil conditions. The main purpose of this work was to estimate the concentrations of arsenic in the soils and to assess the mobility of As in the selected soil samples using standardized short-term batch leaching test (norm DIN 19730) which determines the concentration of a metal available for plant uptake.

Materials and Methods

Soil samples were collected in September 2008 and April 2009. The sampling locations are shown in Fig. 1a. Soil

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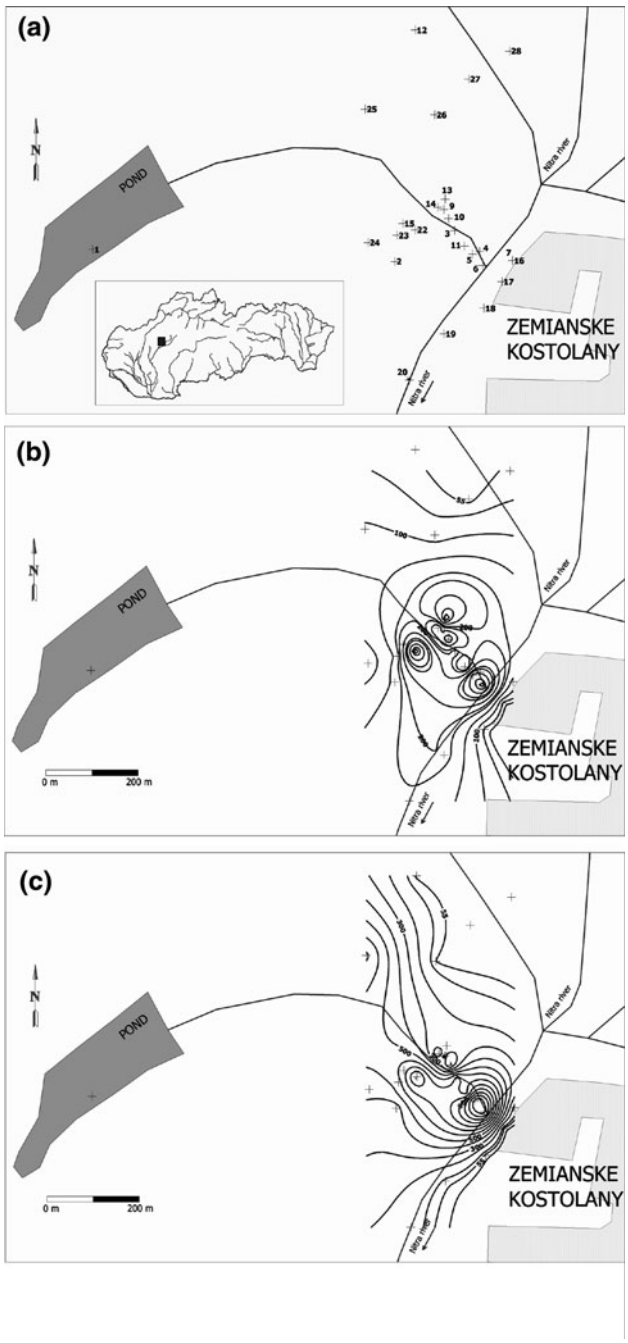

Fig. 1 **a** Study area and sampling locations of the soils and ash and spatial distribution of As concentrations in **b** topsoils and **c** subsoils

samples of about 2 kg were collected with a plastic scoop from manually excavated soil probes at each site. The collection of samples was done from three sampling depths of 0–20, 20–40 and >40 cm and all topsoil and subsoil samples were stored in polyethylene bags. Moreover, one ash sample (0–20 cm) was also taken from the coal-ash pond. Prior to analysis, soil samples were air dried at room temperature for 7 days, disaggregated using a pestle and mortar, homogenized, and then sieved to obtain the <1 mm fraction. All solid samples were analyzed by multi-elemental inductively coupled plasma-mass spectrometry (ICP-MS) at Acme Analytical Laboratories, Vancouver (Canada). Quality control was achieved by routine analyses of standards and duplicates. Analytical and method blanks, duplicates, and standard reference materials analyzed with the samples provide a measure of background noise, accuracy and precision, respectively.

To assess the mobility and bioavailability of arsenic, one standardized leaching test with 1 M NH_4NO_3 solution according to the norm DIN 19730 was performed on selected soil and ash samples. 12 g of dried sample was weighted into a 50-mL polyethylene centrifuge tube and then 30 mL of 1 M NH_4NO_3 solution was added. The suspension was shaken at 180 cycles/min for 2 h and then centrifuged at 2,800 rpm for 10 min. The obtained supernatant was filtered through a 0.45 μm membrane filter and one aliquot of the supernatant was diluted 10fold with 1% HNO_3 prior to analysis. The unacidified aliquot of the supernatant was used to measure pH and electrical conductivity (EC) using a WTW Multi 350i instrument equipped with SenTix^{R}41 and TetraCon^{R}325 electrodes, respectively. Leaching test was performed in duplicate. Concentrations of As in the supernatants were determined by atomic absorption spectrometry (Varian Spectr AA 220) equipped with a hydride generation system (VGA 76) at the accredited Environmental Laboratories (EL Ltd.) in Spisska Nova Ves. Limit of determination for As was 1.0 μg/L. Instrumental accuracy and precision were monitored using blind duplicates and found to be within the range of ±10% or better.

Results and Discussion

Concentrations of As, Fe, Al, and Mn in both topsoils and subsoils, and ash sample are presented in Table 1. Mean As topsoil concentration was 173 μg/g with a maximum of 434 μg/g. Subsoil samples with a mean As concentration of 426 μg/g taken from the depth of >40 cm were generally higher in As than topsoils and subsoils collected at 20–40 cm. This result was expected since the released ashes after the dam failure of coal-ash pond are the main solid material of these subsoils while the upper soil layers consist mainly of unknown soils used to cover the released ashes. Concentrations of As in >40 cm subsoils collected close to the coal-ash pond could be well compared with the As concentration of 714 μg/g measured in ash sample. Figure 1b, c show the spatial distribution of As concentrations in topsoils and subsoils taken from the depth of >40 cm. The highest As concentrations were detected either in the vicinity of the coal-ash pond or along a main dispersion of the released ashes. However, high

Table 1 Concentrations of arsenic, iron, aluminium and manganese in the ash and soil samples at different sampling depths

Sample	As (μg/g)			Fe (wt. %)			Al (wt%)			Mn (μg/g)		
	0–20	20–40	>40	0–20	20–40	>40	0–20	20–40	>40	0–20	20–40	>40
1 (ash)	714			3.88			2.89			707		
2	152	124	348	2.27	2.27	2.95	1.56	1.59	2.08	749	783	774
3	218		730	2.40		3.14	2.47		2.80	673		693
4			1,193			3.80			3.28			564
5	358		1,264	2.33		3.38	2.09		2.94	684		600
6	417		1,264	2.52		3.93	2.45		3.57	678		672
7	127		164	2.01		2.23	1.41		1.54	592		526
8	382		1,074	2.40		3.22	1.79		2.84	578		535
9	187		438	2.56		3.17	2.14		2.41	720		719
10	60		75	1.78		1.76	1.50		1.36	639		657
11	122		644	2.36		3.30	2.65		2.80	778		729
12			46			2.94			2.59			754
13	325	231	298	3.53	3.38	3.61	2.84	2.81	2.98	597	647	617
14	79	81	84	2.48	2.54	2.52	2.25	2.29	2.27	662	670	631
15	224	274	657	3.23	3.45	4.17	2.61	2.80	3.24	543	627	651
16	75	68	37	2.12	2.13	2.05	1.57	1.56	1.52	632	666	685
17	65	52	38	2.40	2.50	2.56	1.95	2.07	2.11	631	756	711
18	64	66	37	2.26	2.35	2.27	1.81	1.89	1.77	603	636	632
19	198	115	82	2.82	2.68	2.69	2.47	2.49	2.60	608	610	646
20	176	147	148	2.85	2.90	2.93	2.45	2.54	2.62	632	595	700
21	132	152	151	2.62	2.66	2.70	2.34	2.39	2.43	651	667	614
22	434	604	939	3.54	3.98	4.34	2.80	3.13	3.51	665	654	655
23	152	120	553	2.69	2.70	3.95	2.25	2.25	3.10	637	631	632
24	81			1.65			1.48			469		
25	105	58	724	3.04	3.04	4.39	2.46	2.48	3.41	669	701	653
26	84	72	51	2.42	2.54	2.61	1.91	2.01	2.11	634	606	677
27	51		18	2.16		2.07	1.71		1.53	671		662
28	58		25	2.42		2.48	1.97		1.99	671		745
Mean	173	155	426	2.51	2.79	3.04	2.12	2.31	2.52	643	661	659

concentration of As was found in sample 8 (Table 1) which is located 6 km southwest of the coal-ash pond, probably due to the riverine transport of the released ashes by Nitra river. The results of this study are consistent with those of Keegan et al. (2006) who showed that topsoils collected around the village of Bystricany sited south of the coal-ash pond contained more than 200 μg/g As. Previously Keegan et al. (2002), reported As concentrations in coals burnt at the Novaky power plant ranging from 292 to 1,540 μg/g with a mean level of 518 μg/g. This explaines high arsenic concentration measured in the ash and >40 cm subsoil samples and indicates that the main source of As in the study area are coals used by the Novaky thermal power plant to generate electricity. Figure 2a, b show that there were significant positive correlations between As concentrations and total Fe ($r = 0.68$, $p < 0.001$; 0.85, $p < 0.001$; and 0.75, $p < 0.001$ for topsoil, 20–40 cm subsoil, and >40 cm subsoil samples, respectively) and total Al ($r = 0.58$, $p < 0.01$; 0.72, $p < 0.01$; and 0.77, $p < 0.001$ for topsoil, 20–40 cm subsoil, and >40 cm subsoil samples, respectively). These results might indicate that hydrous Fe and Al oxides would play an important role in the retention of As in the natural solids, consistent with previous studies (Cai et al. 2002; Okonkwo 2007). The extent of soil contamination by As was evaluated using the Dutch target and intervention values of 29 and 55 μg/g for this element, respectively. Simple comparison between the As concentrations in soils and the intervention threshold shows that the soils can be considered seriously contaminated with As and pose a threat to the functional properties of human, plant and animal life (Visser 1995).

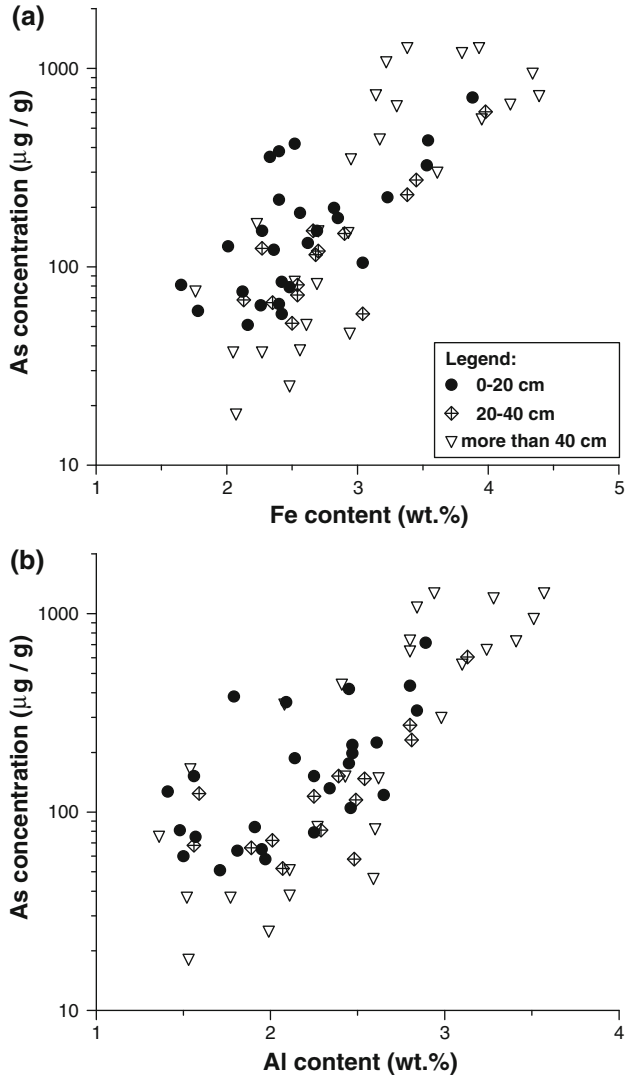

Fig. 2 Relationship between the As concentrations and **a** total Fe contents and **b** total Al contents in topsoil (0–20 cm) and subsoil (20–40 cm, >40 cm) samples

Levels of NH_4NO_3 extracted As in the samples ranged from 0.06 to 44.4 µg/g (Table 2). These concentrations, which indicate the mobile fraction accounted for between 0.05 and 6.21% of the total As concentrations in soil and ash samples. Although As concentrations extracted by NH_4NO_3 appeared to be low, they exceeded the limit of 0.40 µg/g for agricultural soil given by the Slovak legislation (Anon 2004) in 64% of the samples. This result is of an environmental importance since the NH_4NO_3 leachate is considered as the portion available for plant uptake (Hammel et al. 2000). Soil pH has a significant influence on As speciation, mobility and solubility (Wilson et al. 2010). A significant positive relationship was found between soil leachate pH and mobile As concentration ($r = 0.77$, $p < 0.001$) as well as for relative extractability of As expressed as percentage of the total concentrations ($r = 0.70$, $p < 0.01$). This study shows that only minor fractions of solid As are readily available for plant uptake and leaching, and therefore significant portions of this element should be associated with other phases which might represent long-term source of the mobile As by changing environmental conditions such as redox state and pH.

Table 2 Mean values of leachate pH, As concentrations extracted by NH_4NO_3, As extractabilities expressed as percentage of the total concentrations in samples and its concentrations in NH_4NO_3 leachates

Sample	Leachate pH	As extracted (µg/g)	Extractability (%)	As in NH_4NO_3 leachate (µg/L)
1 (ash)	7.51	44.4	6.21	17,800
2 (0–20 cm)	6.88	0.37	0.24	149
2 (20–40 cm)	7.05	0.06	0.05	23
2 (>40 cm)	7.08	0.35	0.10	138
3 (0–20 cm)	6.87	1.40	0.64	558
3 (>40 cm)	7.14	3.79	0.52	1,514
4 (>40 cm)	7.25	4.29	0.36	1,710
5 (0–20 cm)	6.98	1.12	0.31	447
5 (>40 cm)	7.15	4.63	0.37	1,850
6 (0–20 cm)	7.08	1.44	0.35	578
6 (>40 cm)	7.14	4.01	0.32	1,606
7 (0–20 cm)	6.88	0.26	0.20	103
7 (>40 cm)	6.86	0.25	0.15	102
8 (0–20 cm)	7.08	1.80	0.47	720
8 (>40 cm)	7.17	1.84	0.18	736

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