Column leaching of arsenic in coal ash-impacted soils using citric acid (Zemianske Kostoľany, Slovakia)

Tomáš Faragó, Ľubomír Jurkovič, Katarína Peťková & Edgar Hiller

Department of Geochemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovak Republic; hiller@fns.uniba.sk

AGEOS

Abstract: This paper describes the mobilization of arsenic (As) in technosols (soils with high content of coal ashes) using 35–d experimental soil column studies. The two soil samples with high total concentrations of As (1100–1139 mg·kg⁻¹) were collected from an environmental burden near the village of Zemianske Kostoľany, which is one of the most As-contaminated areas in Slovakia. Amorphous solid phases, mainly glasses of variable chemical compositions, Fe oxy-hydroxides and un-burned coal residues, are the major components of the soil-ash samples. In this study, two different leaching agents (deionized water and 1 mM citric acid aqueous solution) were pumped through soil columns to assess the solubility of As. The results showed that citric acid was more efficient in the mobilization of As (> 14.5% of the total As content) than deionized water, confirming the assumption that organic acids produced by plants and soil microorganisms increase As leaching in soils. Soil column experiments with deionized water indicated lower extractabilities of As that ranged from 9.74% to 11.4%. In addition, water extractable As concentrations increased with increasing pH values of the leachates ($R^2 = 0.70$ at $p < 0.01$). It was also observed that extraction time was an important factor, affecting the release of As from the soil-ash samples.

Key words: contaminated soil, environmental burden, arsenic mobility, soil column, low molecular weight organic acid, coal ash

1. INTRODUCTION

An environmental burden located near the village of Zemianske Kostoľany is one of the most As-contaminated areas in Slovakia. The dam of the old coal ash pond was broken in 1965, and consequently, large volumes of liquefied coal ashes, containing high concentrations of As, were directly released into the surrounding soil environment and surface streams (Jurkovič et al., 2011; Veselská et al., 2013). However, no remediation measures were adopted after the accident, the spilled coal ashes were only covered by 30–100 cm thick layers of different soils imported from unknown sources. According to the World Reference Base for Soil Resources (WRB, 2006), the soil with a layer of coal ash derived from the Nováky power plant (ENO) could be classified as technosols. Due to severity of environmental contamination with As in wide surroundings of Zemianske Kostoľany, the whole area is considered to be an environmental burden of high priority. In addition, recently, these As-contaminated soils together with the several existing coal ash ponds are important sources of dissolved As to surface waters and sediments of local streams and the Nitra River, the main stream draining the study area, through its long-term leaching from the solid materials. Elevated concentrations of As in surface waters and stream sediments of the Nitra River can be observed even almost 80 km downstream from the environmental burden (Varga & Kolenčík, 2016). The detailed description of the investigated area can be found elsewhere (Keegan et al., 2006; Bolanz et al., 2012; Veselská et al., 2013).

Soil is a natural medium, through which As can be transported into the groundwater and surface waters. During its transport

in the soil environment, As undergoes the complex physico-chemical and biological processes, e.g. sorption, desorption, bio-volatilization, and bioaccumulation, that determine the mobility of As species. These complex processes are strongly dependent on the physico-biochemical and mineralogical properties of the solids involved in the transport of As (Manning & Goldberg, 1996, 1997; Goh & Lim, 2004; Hiller et al., 2009; Wang & Zhao, 2009). The rate and extent of the leaching of As and other metalloids from soils and coal combustion by-products are related to their total concentrations. The leaching behaviour of As is also affected by conditions during coal combustion, coal ash and soil properties, such as mineralogical and chemical composition, redox state that determine the valency of metalloids and stability of metalloid-bearing solid components, and more importantly, by pH conditions (Masscheleyn et al., 1991; Sadiq, 1997; Jankowski et al., 2006; Ward & French, 2006; Izquierdo & Querol, 2012; Neupane & Donahoe, 2013; Dousova et al., 2016). Another factor, having an effect on As leaching from natural solids, is the chemical composition of soil solution, mainly the presence of low molecular weight organic acids (LMWOAs), such as citric, acetic, aspartic, and oxalic acids (Wang & Mulligan, 2013; Ash et al., 2016). These organic acids are naturally produced in soils through plant metabolism, decomposition of soil organic matter and metabolic activity of soil microorganisms (Bolan et al., 1994; Strobel, 2001). Their concentrations in rhizosphere soil range from nM to mM, however, soil solution levels of some organic acids can reach up to tens of mM (Jones, 1998; Van Hees et al., 2002, 2005).

Because of their simplicity, reproducibility, and repeatability, static batch extraction experiments used for the

determination of chemical element mobilization from soils are attractive to potential users. However, the geochemical and eco-toxicological relevance of the information provided by batch experiments is questionable, since naturally occurring processes are always dynamic. Manual protocols, intended to simulate environmental scenarios, are based inherently upon attainment of single equilibrium between the solid and liquid phases (Miró et al., 2005). Column leaching experiments are regarded to be more realistic in simulating the leaching processes of chemical elements in the soil environment (Kumpiene et al., 2006; Parthasarathi & Sivakumaar, 2011). According to Banzhaf & Hebig (2016), column experiments are fast, flexible, and relatively easy to manage. Their boundary conditions can be controlled and they are cheap compared to extensive field experiments.

The main aim of this study was to investigate the release of As from soils that were affected by dam failure of one of the coal ash ponds in 1965 using 35–d soil column study in the water saturated regime. The saturated conditions represent the worst–case scenario of As release when contaminated soils are in continuous contact with leaching solution, i.e. flooded. Two different leaching solutions were used, specifically, deionized water and 1 mM citric acid solution in order to determine readily mobile As contents and the effect of rhizosphere soil solution on the release of As, respectively. Soil column experiments were complemented to mineralogical methods to provide information on mineralogy of these unique As-rich soil-coal ash mixtures. In addition, other relevant chemical parameters of the column leachates (pH, electrical conductivity, dissolved calcium (Ca), iron (Fe), and phosphate (PO_4^{3-}) concentrations) were measured to identify how they can affect the release of As from the ash-soil mixtures.

2. MATERIALS AND METHODS

2.1. Soil sampling and geochemical characterization

The soil samples were collected with a hand drill from two different depths near the village of Zemianske Kostoľany (48°41'18.5"N and 18°31'06.7"E) (Fig. 1). The soil profile was located in the flood plain of the Nitra River, in front of the active coal ash pond. The soil sample ZK30 was taken from a depth of 30 cm and represents a mixture of overlying soil with released coal ashes, while the sample from 60 cm depth (ZK60) is mostly weathered coal ash with traces of soil. The samples were air-dried at room temperature. Each sample was then gently crushed in an agate bowl and sieved to the size fraction < 2 mm.

The total concentrations of major chemical elements (Al, Ca, Fe, Mg, and P) and trace metals (Hg, Mn, Pb, and Zn) and As in the samples were analysed at ACME Analytical Laboratories, Ltd. (Vancouver, Canada) using inductively coupled plasma–mass spectrometry (ICP–MS) after strong multi–acid digestion with HNO_3, $HClO_4$, and HF. The particle size distribution (sand, silt and clay contents) was determined by the pipette method and calcium carbonate content ($CaCO_3$) was measured using a volumetric device (Jackson, 1958). The total organic carbon content (TOC) content was determined on C-MAT 5500 fy. Ströhlein instrument. The values of active (pHH_2O) and exchangeable (pHKCl) soil pH were measured in soil–water and soil–1 M KCl solution suspensions at a soil to water ratio of 1:2.5 (wt:wt), respectively (Fiala et al., 1999). Electrical conductivity (EC) was determined in a 1:2.5 (wt:wt) soil–water suspension.
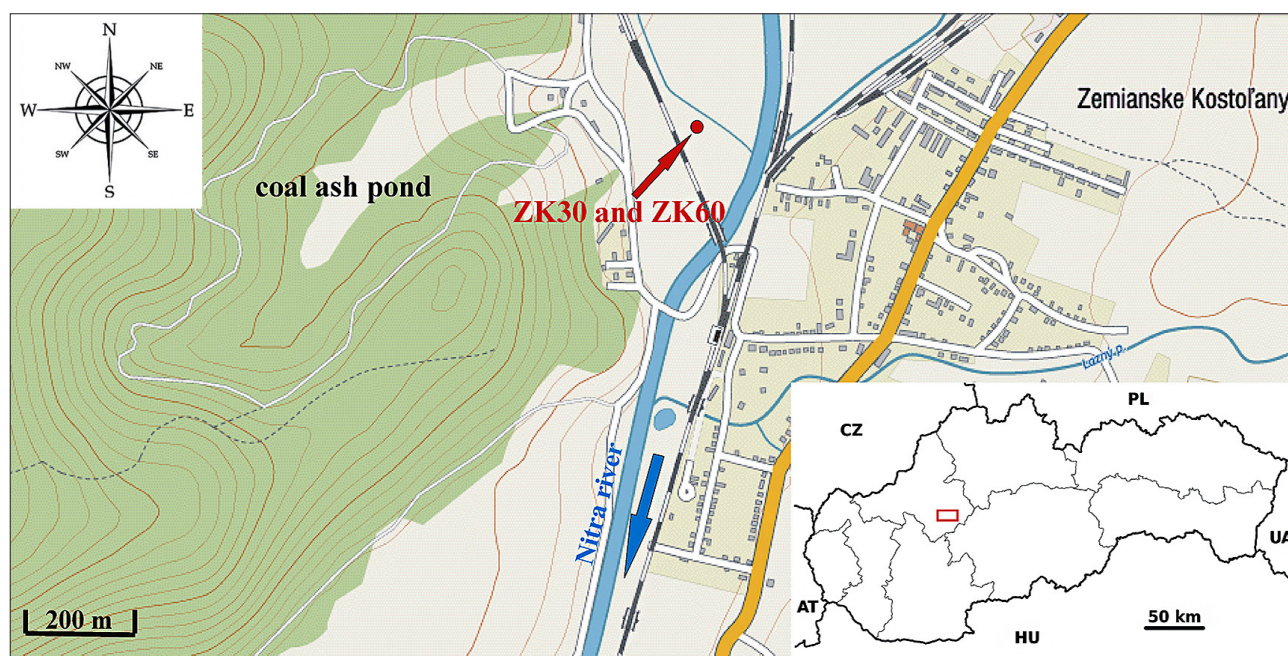

Fig. 1. Location of the study area and sampling site of the soils used in this study.

2.2. Laboratory soil column experiments

The aim of the soil column experiments was to assess the dynamic behaviour of As release from the soil samples. Soil column leaching experiments were performed in duplicate for each soil sample and solution. Glass columns (25 cm long and 2.5 cm internal diameter) were filled with 70 g of contaminated soil and leached with either deionized water (pH = 5.65) or 1 mM citric acid solution (pH = 3.22). Before filling the columns with dry sample, Whatman filters (pore size 1.5 μm) and 1 cm of pure silica sand were placed at the base and top of each column in order to prevent fine soil particles to escape into the polyethylene tubing material. The soils were leached upwards from the base of the column with a constant flow of leaching solution (1.00 cm^3·min^{-1}) maintained by a peristaltic pump (ISMATEC IPC 12). For better explanation of experimental setup, soil column leaching study is schematically shown in Fig. 2. Leachate samples were collected over a five-week period at weekly intervals. The leachates were filtered through Whatman membrane filters with a pore size of 0.45 mm and preserved at pH < 2 using HNO$_3$ for cation analyses. An aliquot of the leachates was left unacidified for PO$_4^{3-}$, EC, and pH measurements. In the leachates, the concentrations of As, Ca and Fe, and PO$_4^{3-}$ were analysed by hydride generation-atomic absorption spectrometry (HG–AAS), inductively coupled plasma-atomic emission spectrometry (ICP–AES), and ultraviolet-visible spectrophotometry (UV/VIS), respectively, at the accredited laboratories EL, Ltd., Spišská Nová Ves (Slovakia).

2.3. Mineralogical analyses

Bulk mineralogy of the soil samples was determined by X-ray diffraction (XRD) analysis with a Bruker AXS D8 Advance diffractometer equipped with a Cu K$_α$ radiation source and a diffracted-beam graphite monochromator. Main mineral phases were identified with the DIFFRACplus EVA software package
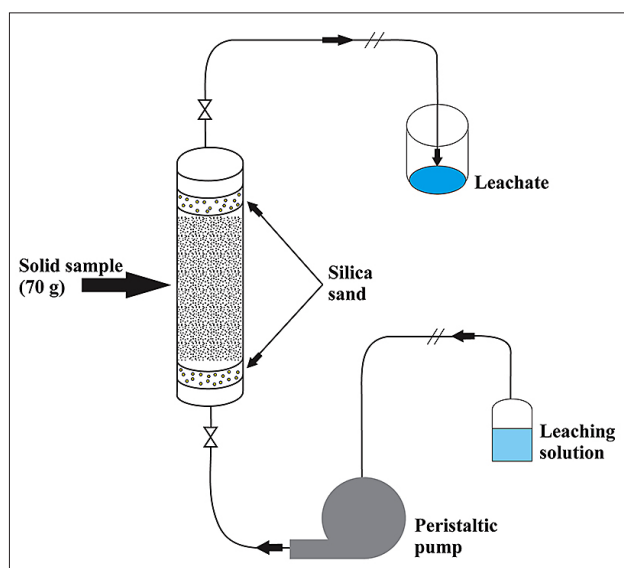

Fig. 2. Experimental design of soil column studies.

(Bruker, 2010^a). The abundance of the main mineral phases in the XRD patterns was quantified by the Rietveld refinement with the DIFFRACplus TOPAS program (Bruker, 2010^b) using fundamental parameters. α-Corundum powder was mixed into each sample as an internal standard.

Chemical compositions of the selected solid phases and back-scattered electron (BSE) images were obtained with a Cameca SX 100 electron microprobe (EMP) in the wavelength-dispersive mode (WDS) with an accelerating voltage of 20 kV, a constant current beam of 20 nA and a defocused beam size of 1–5 mm. Details of the EMP analyses are given in Veselská et al. (2013).

3. RESULTS AND DISCUSSION

3.1. Geochemical and mineralogical characterization of soil samples

The selected soil physico-chemical properties and total concentrations of selected major and trace chemical elements in the two soil-ash samples are shown in Tab. 1. The dominant soil size fractions were silt in ZK30 sample and sand in ZK60 sample, classifying them as loam and sandy loam soils, respectively. The soils were slightly alkaline (pH ~ 7.50) and poor in TOC but they had elevated content of calcium carbonates. Arsenic

Tab. 1 Physico–chemical properties of the soil–ash samples and total concentrations of selected trace and major chemical elements (arithmetic mean (standard deviation); $N = 2$)

	ZK30	ZK60
pH$_{H_2O}$	7.55 (0.01)	7.49 (0.01)
pH$_{KCl}$	7.47 (0.02)	7.42 (0.01)
EC (μS/cm)^a	68.2 (0.05)	73.3 (0.03)
TOC (%)^b	0.87 (0.05)	0.77 (0.08)
CaCO$_3$ (%)	9.63 (0.03)	5.21 (0.10)
Particle size distribution (%)		
Sand	40.5 (0.20)	54.7 (0.10)
Silt	49.1 (0.30)	40.2 (0.20)
Clay	10.4 (0.30)	5.10 (0.10)
Trace chemical elements (mg/kg)		
As	1139 (70.0)	1100 (55.0)
Hg	0.58 (0.05)	0.97 (0.09)
Pb	7.10 (0.32)	8.20 (0.51)
Zn	66.0 (3.78)	49.0 (2.65)
Mn	628 (22.0)	632 (28.0)
Major chemical elements (wt %)		
Fe	4.09 (0.27)	3.91 (0.23)
Al	3.70 (0.15)	3.66 (0.14)
Mg	3.45 (0.11)	3.18 (0.08)
Ca	3.70 (0.14)	3.66 (0.13)
P	0.08 (0.01)	0.07 (0.01)

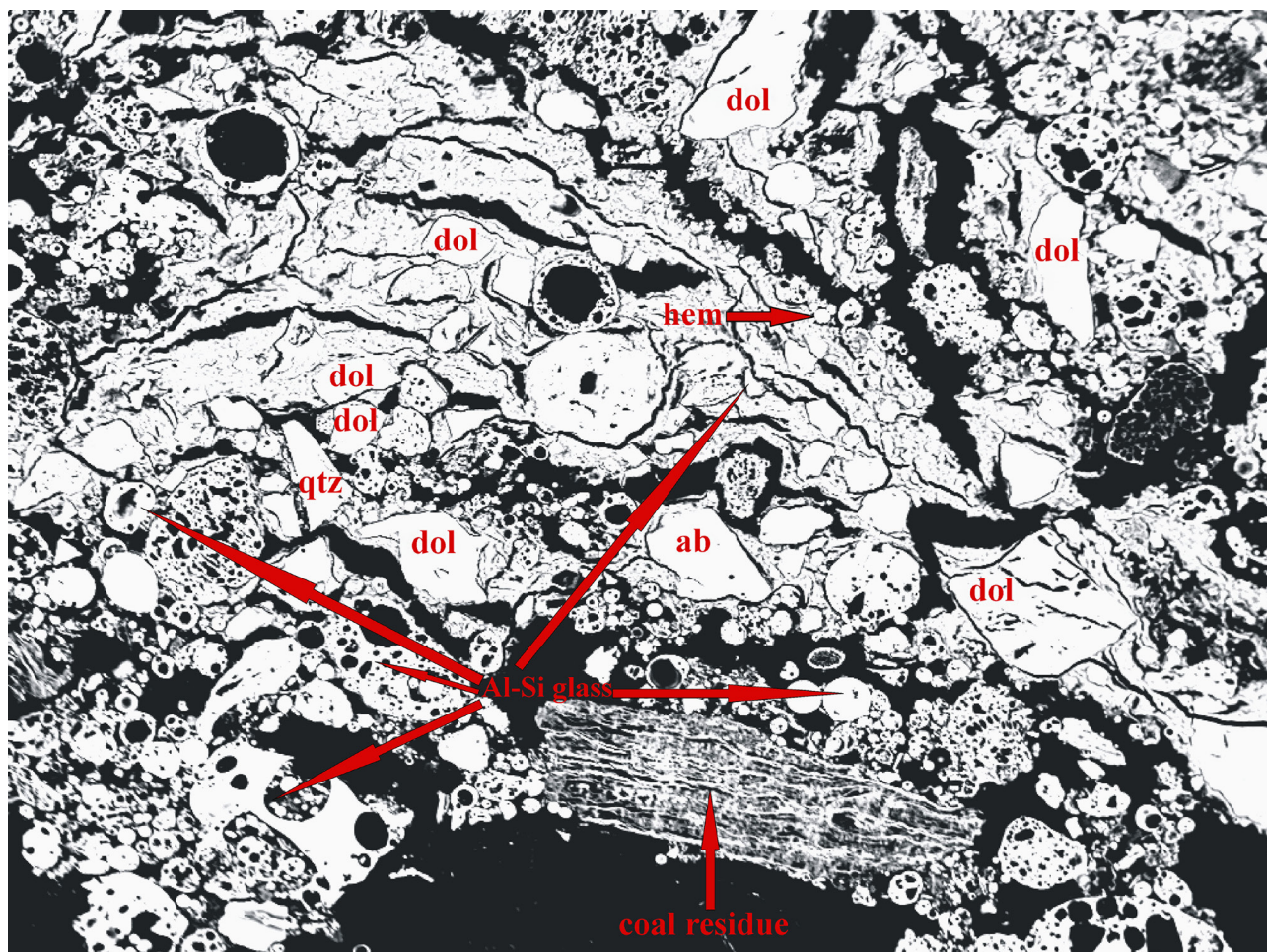^{a} electrical conductivity; ^{b} total organic carbon content

Fig. 3. Selected back-scattered electron (BSE) image; qtz – quartz, dol – dolomite, hem – hematite, ab – albite.

concentrations in the samples were high (> 1000 mg·kg^{-1}), confirming the severity of soil contamination with As in the whole area that was documented in previous studies by Keegan et al. (2002, 2006) and Jurkovič et al. (2011). These As concentrations exceeded almost 45–times its limit value for agricultural soils of sandy loam to loam textures (25.0 mg·kg^{-1}) (Anon, 2004). Although the distribution of As within individual operationally defined fractions of the soil-ash samples was not determined in this study, previous study of Bolanz et al. (2012) showed, using Tessier sequential extraction procedure and the same type of soil materials, that > 50% of the total As was bound in residual fraction, i.e. hardly soluble components of the soil-ash samples. Iron and Mn oxides accounted for ~ 35% of the total As, followed by As residing in organic matter (5.20%), carbonates (3.50%) and exchangeable As (~ 1.0%).

The quantitative XRD results showed that the major constituents of the samples were X-ray amorphous and poorly crystalline phases (Tab. 2). Based on EMP analyses and microscopy, these phases included mostly glass particles of variable chemical composition and morphology, unburned coal particles and traces of amorphous iron oxy–hydroxides (Fig. 3). The glasses were shown to consist mainly of Si, Al, Fe, and Ca, while the highest contents of As were in Ca-rich glass particles and vice-versa (see for details Peťková et al., 2011; Bolanz et

al., 2012; Veselská et al., 2013). The dominant occurrence of glass constituents in our samples, regardless of the fact that they are not pure coal ashes, is commonly described in the literature (e.g., Vassilev & Vassileva, 1996; Kukier et al., 2003; Ward & French, 2006; Dai et al., 2010). The most abundant minerals in both soil–ash samples were plagioclases, quartz, dolomite + calcite, micas, mullite, and cristobalite. Iron oxides, hematite and magnetite, were also identified. The majority

Tab. 2 Mineralogy of soil–ash samples from Zemianske Kostoľany area

	ZK30	ZK60		ZK30	ZK60
Albite	×××	××	**Cristobalite**	×××	×
Anorthite	××	××	**Kaolinite**	××	××
Dolomite	××	××	**Montmorillonite**	×	nd.
Calcite	××	×	**Rutile**	×	×
Quartz	××	××	**Muscovite**	××	××
Magnetite	×	××	**Biotite**	×	××
Mullite	××	××	**amorphous phases**	×××	×××
Hematite	×	××			

[a] ×××, abundant (~> 10 wt %); ××, present (~2–10 wt %); ×, less present (~< 2 wt%); nd. not detected
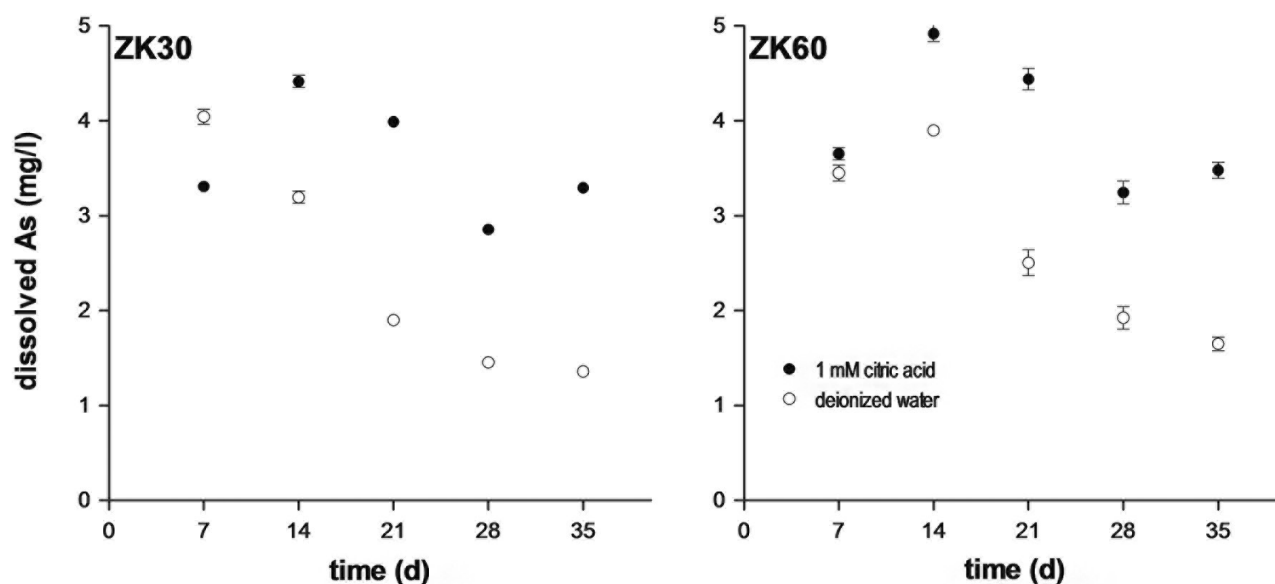
Fig. 4. Dissolved concentrations of As in the leachates recovered from soil–ash samples at the end of each leaching cycle over 35 d period.

of minerals are considered to be primary, since they occur in the source material of the ashes, i.e. brown coal from the Handlová-Nováky deposit (Verbich, 1998; Machajová et al., 2002) although these mineral constituents can also form during coal combustion (Vassileva & Vassilev, 2006). The exception is mullite, cristobalite and magnetite. Mullite is formed by the decomposition of clay minerals and other alumina-silicates under higher temperatures, while quartz in the power plant reactor can burst at higher temperatures (above 870 °C) to form cristobalite (Dai et al., 2010). Magnetite is not commonly present in coals, its occurrence in coal ashes is explained mainly by the thermal transformation and oxidation of iron sulphides, e.g. pyrite (Kukier et al., 2003).

3.2. Mobilization of As in column experiments

The chromatographic analysis of the leachates collected after 1st and 35th day of leaching showed that total dissolved As was exclusively present in its pentavalent form, i.e. as arsenate species (Tab. 3). This is in agreement with the finding that As in the solid components of the soil–ash mixtures is mostly pentavalent as shown by the analysis with X-ray absorption near-edge structure (XANES) spectroscopy (Bolanz et al., 2012; Veselská et al., 2013). The evolution of As concentrations in the leachates over 35–d period as well as the effect of the two different leaching solutions on As release from the soil–ash samples are illustrated in Fig. 4. The leaching pattern of As with deionized water over time differed from that using 1 mM citric acid solution. While As leaching with deionized water exhibited a decreasing tendency with time, citric acid solution showed an increased leaching at initial stages, followed by a decrease in As leaching, and then an increase at the end of the column experiments. Exact reasons of the differences in As leaching behaviour over time are unknown (Vítková et al., 2015; Ash et al., 2016) but the more reactive citric acid solution could begin to attack efficiently the more resistant solid

Tab. 3 Cumulative amount of As (in mg/kg), the corresponding fraction (in % of the total As content) and the oxidation state of As leached from the soil–ash samples during the whole time period of column leaching experiments

	ZK30	ZK60
deionized water		
As content	111 (0.63)	125 (3.39)
As fraction	9.74 (0.06)	11.4 (0.35)
As speciation	pentavalent	pentavalent
1 mM citric acid		
As content	166 (0.28)	183 (1.13)
As fraction	14.6 (0.07)	16.7 (0.10)
As speciation	pentavalent	pentavalent

phases at a later stage of the column study, thereby releasing As from the interior of phases into the solution. In general, the higher mobilization of As at early stages could be attributed to the dissolution of As that resides on the surface of coal ash particles and other constituents of the samples. The leachability of As on % basis, calculated as the ratio of the total As concentration mobilized during soil column experiments to its total content in soil-ash samples, is shown in Tab. 3. The mean values for ZK30 and ZK60 samples using deionized water were 9.74 % and 11.4 %, respectively. This relates well to the leachability of As from soil-ash samples collected in the same area but at different sampling sites during sequential $MgCl_2$ and acetic acid extraction that targets exchangeable As adsorbed on the surfaces of mineral constituents and its fraction bound to carbonates, respectively, accounting for 13 % of the total As content (Bolanz et al., 2012). Therefore, it seems that the sources of As mobilized during the column experiments are easily water-soluble, exchangeable and carbonate-bound As fractions, being supported by the results of other
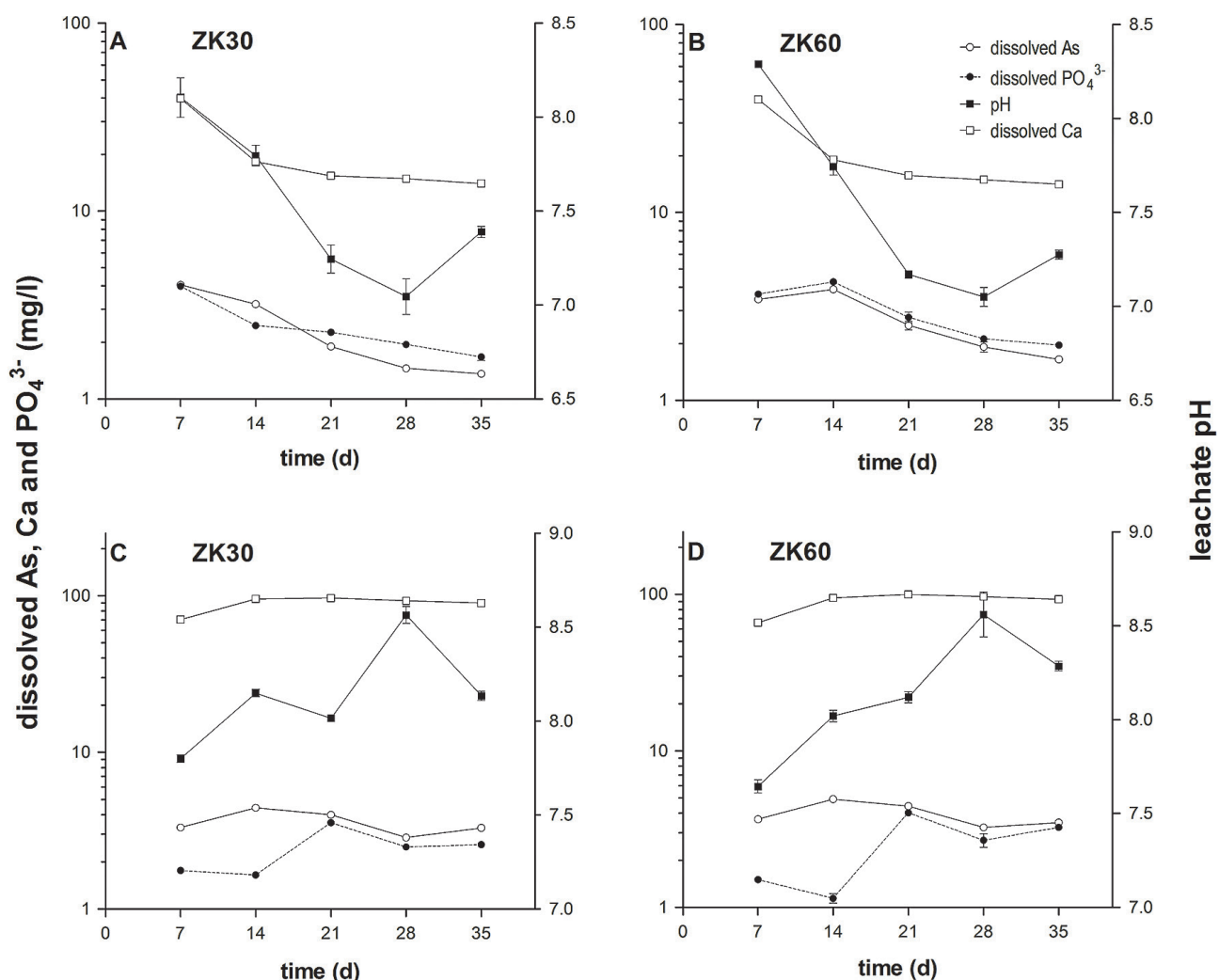
Fig. 5. Change in leachate pH and leaching of As, Ca and PO$_4^{3-}$ from soil–ash mixtures using **A), B)** deionized water and **C), D)** 1 mM citric acid solution.

studies (Neupane & Donahoe, 2013). As could be also seen from Tab. 3 and Fig. 4, citric acid solution consistently released more As and was approximately 1.5 times more efficient in the leaching of As than deionized water based on the calculated leachabilities, indicating an increase of the mobility of As in the presence of natural organic acids in the soil solution. As a product of metabolic activities of soil microorganisms and plants, LMWOAs are commonly present in the soil solution (Jones, 1998). Hence, these metabolic processes lead directly to the elevated mobilization of As from soils and its uptake by plants. The result is in agreement with the studies of Zhang et al. (2005), Wang & Mulligan (2013) or Ash et al. (2016) who have found a significant increase in the mobilization of As from solid samples in the presence of different LMWOAs. Although mechanisms of As release from solids involving LMWOAs have not been yet fully understood, direct ligand exchange, i.e. the replacement of As with organic acid anions on ligand exchange surfaces, ligand enhanced dissolution of As-bearing constituents and formation of stable soluble As-organic complexes are the most probable (Jones, 1998). It seems, however, that the complexation of As with citric acid to form stable, more soluble As species did not contribute to the increased leaching

of As from soil-ash mixtures, since as shown by Vítková et al. (2015) using geochemical modelling, As in the soil leachates was present only in the form of inorganic arsenate species.

Additionally, it was found that the evolution of pH and PO$_4^{3-}$ concentrations in the water leachates over time had the almost same pattern as the evolution of As concentrations (Fig. 5A,B). Leaching of As from coal ashes was shown in a number of studies to be strongly dependent on pH, displaying a plateau of its maximum solubility in the pH range between 7–10 (Izquierdo & Querol, 2012). In our study, a positive correlation between the leachate pH values and the leaching of As ($R^2 = 0.70$ at $p < 0.01$) using deionized water was likely caused by the concomitant release of Ca ions into the leachates that was highest at the start of the column experiment and decreased as the leaching progressed (Fig. 5A,B). Therefore, Ca concentrations in water leachates also correlated positively with the leachate pH ($R^2 = 0.77$ at $p < 0.001$). Querol et al. (2001) states that the pH of the ash-water slurries is controlled mainly by the leached amount of Ca and the conclusion is also supported by our findings although the leachability of Ca with deionized water was relatively low, with a mean of 2.57% and 2.63% for ZK30 and ZK60 samples, respectively. The low leachabilities of Ca were attributable to the

fact that the majority of Ca in the samples was bound to poorly water–soluble solid constituents, such as glasses, plagioclases and carbonates (Querol et al., 2001; Kukier et al., 2003; Veselská et al., 2013). Significant leaching of Ca is expected when coal ashes contain more water-soluble Ca-bearing phases, e.g. free lime, anhydrite or gypsum (Izquierdo & Querol, 2012 and references cited herein). Strongly positive relationship between the As and PO_4^{3-} concentrations in the leachates ($R^2 = 0.88$ at $p < 0.001$) from soil column study with deionized water was observed although extractable P fractions were lower (4.66 % and 6.40 % for ZK30 and ZK60, respectively) than As fractions but rather high compared with literature data (Izquierdo & Querol, 2012). Bolanz et al. (2012) have documented that P, most likely in the form of PO_4^{3-}, occupies the same surficial sites within the calcite veins of unburned coal particles as arsenic. Phosphorus geochemical behaviour is similar to that of As (Smith et al., 2002; Impellitteri, 2005; Wilson et al., 2010) and competes with As species for the same adsorption sites, since phosphates have almost identical physical properties and chemical reactivity as arsenates (Mohapatra et al., 2005). Therefore, mobilization of phosphate ions is controlled by the same factors that affect the leaching behaviour of As. However, no clear relationships between the As concentrations mobilized from the samples with citric acid and pH or PO_4^{3-} concentrations were observed (Fig. 5C–D). This may be due to several reasons: (i) different effect of citric acid on the formation of soluble P-organic complexes compared to As; (ii) different effect of citrate anions on the desorption of PO_4^{3-} through direct ligand exchange; and (iii) precipitation reactions between Ca and citrate anions or PO_4^{3-}, leading to formation of relatively insoluble calcium citrate or calcium phosphate, respectively.

4. CONCLUSIONS

The present study confirmed previous findings on the severe contamination of soils with As in the area of Zemianske Kostoľany that was affected by a release of As-rich coal ashes deposited in a pond. The total concentrations of As in the soil-ash samples were high, reaching more than 1000 mg·kg^{-1}. The water extractability of As from the samples, assessed using a 35–d soil column study was also high, and even higher in the presence of citric acid in the leaching solution, indicating a significant role of rhizosphere and soil microorganisms in the mobility of this toxic metalloid. In relative and absolute terms, deionized water mobilized 9.7–11.4% As of its total concentrations and 111–125 mg·kg^{-1}, while the values of 14.6–16.7% and 166–183 mg·kg^{-1} were obtained with 1 mM citric acid solution. Concomitant release of PO_4^{3-} from the soils into the water indicated that As and P could occupy the same surface sites of soil components that consisted mainly of X-ray amorphous constituents, such as glasses of variable major chemical composition (Si, Al, Fe, and Ca), unburned coal particles and Fe oxy–hydroxides. It was also found that pH was an important determinant of As leaching from the soils. The results of this study have implications towards the environmental impact of As-rich coal ashes and soils, since surface- and ground waters in the whole area contain elevated concentrations of As compared with its median national levels in waters. This means that As is releasing continuously from coal ashes deposited in ponds and covered by soils into natural waters.

References

Anon, 2004: Zákon č. 220/2004 Z.z. o ochrane a využívaní poľnohospodárskej pôdy [Law No. 220/2004 Z.z. on the protection and utilization of agricultural soil]. Ministry of Agriculture, Environment and Regional Development of the Slovak Republic. [in Slovak]

Ash C., Tejnecký V., Borůvka L. & Drábek O., 2016: Different low-molecular-mass organic acids specifically control leaching of arsenic and lead from contaminated soil. *Journal of Contaminant Hydrology*, 187, 18–30.

Banzhaf S. & Hebig K.H., 2016: Use of column experiments to investigate the fate of organic micropollutants – a review. *Hydrology Earth System Sciences*, 20, 3719–3737.

Bolan N.S., Naidu R., Mahimairaja S. & Baskaran S., 1994: Influence of low-molecular-weight organic acids on the solubilization of phosphates. *Biology and Fertility Soils*, 18, 4, 311–319.

Bolanz R.M., Majzlan J., Jurkovič Ľ. & Göttlicher J., 2012: Mineralogy, geochemistry, and arsenic speciation in coal combustion waste from Nováky, Slovakia. *Fuel*, 94, 125–136.

Bruker, 2010[a]: DIFFRACplus EVA. http://www.brukeraxs.com/eva.html.

Bruker, 2010[b]: DIFFRACplus TOPAS. http://www.bruker-axs.de/topas.html.

Dai S., Zhao L., Peng S., Chou C.L., Wang X., Zhang Y., Li D. & Sun Y., 2010: Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. *International Journal of Coal Geology*, 81, 4, 320–332.

Dousova B., Buzek F., Lhotka M., Krejcova S. & Boubinova R., 2016: Leaching effect on arsenic mobility in agricultural soils. *Journal of Hazardous Materials*, 307, 231–239.

Fiala K., Kobza J., Matúšková Ľ., Brečková V., Makovníková J., Barančíková G., Búrik V., Litavec T., Houšková B., Chromaničová A., Váradiová D. & Pechová B., 1999: Záväzné metódy rozborov pôd. Čiastkový monitorovací systém – pôda [Obligatory methods of soil analyses. Partial monitoring system – soil]. Soil Science and Conservation Research Institute, Bratislava, 139 p. [in Slovak]

Goh K.-H. & Lim T.-T., 2004: Geochemistry of inorganic arsenic and selenium in a tropical soil: effect of reaction time, pH, and competitive anions on arsenic and selenium adsorption. *Chemosphere*, 55, 6, 849–859.

Hiller E., Jurkovič Ľ., Kordík J., Slaninka I., Jankulár M., Majzlan J., Göttlicher J. & Steininger R., 2009: Arsenic mobility from anthropogenic impoundment sediments – Consequences of contamination to biota, water and sediments, Poša, Eastern Slovakia. *Applied Geochemistry*, 24, 11, 2175–2185.

Impellitteri C.A., 2005: Effects of pH and phosphate on metal distribution with emphasis on As speciation and mobilization in soils from a lead smelting site. *Science of the Total Environment*, 345, 1–3, 175–190.

Izquierdo M. & Querol X., 2012: Leaching behavior of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology*, 94, 54–66.

Jackson M.L., 1958: Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J., 498 p.

Jankowski J., Ward C.R., French D. & Groves S., 2006: Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems. *Fuel*, 85, 2, 243–256.

Jones D.L., 1998: Organic acids in the rhizosphere – a critical review. *Plant and Soil*, 205, 1, 25–44.

Jurkovič Ľ., Hiller E., Veselská V. & Peťková K., 2011: Arsenic concentrations in soils impacted by dam failure of coal-ash pond in Zemianske Kostolany, Slovakia. *Bulletin of Environmental Contamination and Toxicology*, 86, 4, 433–437.

Keegan T., Hong B., Thornton I., Farago M., Jakubis P., Jakubis M., Pesch B., Ranft U., Nieuwenhuijsen M.J. & The Expascan Study Group, 2002: Assessment of environmental arsenic levels in Prievidza district. *Journal of Exposure Analysis and Environmental Epidemiology*, 12, 3, 179–185.

Keegan T.J., Farago M.E., Thornton I., Hong B., Colvile R.N., Pesch B., Jakubis P. & Nieuwenhuijsen M.J., 2006: Dispersion of As and selected heavy metals around a coal-burning power station in central Slovakia. *Science of the Total Environment*, 358, 1–3, 61–71.

Kukier U., Ishak C.F., Sumner M.E. & Miller W.P., 2003: Composition and element solubility of magnetic and non-magnetic fly ash fractions. *Environmental Pollution*, 123, 2, 255–266.

Kumpiene J., Lagerkvist A. & Maurice C., 2006: Retention of metals leached from municipal solid waste incineration (MSWI) bottom ashes in soils. *Soil and Sediment Contamination*, 15, 4, 429–441.

Machajová Z., Verbich F. & Sýkorová I., 2002: The geology, petrography and mineralogy composition of coal from the Nováky deposit. *Acta Montanistica Slovaca*, 7, 1, 28–33.

Manning B.A. & Goldberg S., 1997: Arsenic(III) and arsenic(V) adsorption on three California soils. *Soil Science*, 162, 12, 886–895.

Manning B.A. & Goldberg S., 1996: Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Science Society of America Journal*, 60, 1, 121–131.

Masscheleyn P.H., Dlaune R.D. & Patrick Jr.W.H., 1991: Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environmental Science & Technology*, 25, 8, 1414–1419.

Miró M., Hansen E.H., Chomchoei R. & Frenzel W., 2005: Dynamic flow through approaches for metal fractionation in environmentally relevant solid samples. *Trends in Analytical Chemistry*, 24, 8, 759–771.

Mohapatra D., Singh P., Zhang W. & Pullammanappallil P., 2005: The effect of citrate, oxalate, acetate, silicate and phosphate on stability of synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite. *Journal of Hazardous Materials*, B124, 95–100.

Neupane G. & Donahoe R.J., 2013: Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. *Fuel*, 104, 758–770.

Parthasarathi R. & Sivakumaar P.K., 2011: Biosurfactant mediated remediation process evaluation on a mixture of heavy metal spiked topsoil using soil column and batch washing methods. *Soil and Sediment Contamination*, 20, 8, 892–907.

Peťková K., Lalinská-Voleková B., Jurkovič Ľ. & Veselská V., 2011: Chemical and mineralogical composition of the coal combustion waste (ashes) from the area of Zemianske Kostoľany. *Mineralia Slovaca*, 43, 4, 377–386. [in Slovak with English abstract and summary]

Querol X., Umaña J.C., Alastuey A., Ayora C., Lopez-Soler A. & Plana F., 2001: Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. *Fuel*, 80, 6, 801–813.

Sadiq M., 1997: Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. *Water Air & Soil Pollution*, 93, 1–4, 117–136.

Smith E., Naidu R. & Alston A.M., 2002: Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium and calcium on arsenic sorption. *Journal of Environmental Quality*, 31, 2, 557–563.

Strobel B.W., 2001: Influence of vegetation on low-molecular-weight carboxylic acids in soil solution – a review. *Geoderma*, 99, 3–4, 169–198.

Van Hees P.A.W., Jones D.L. & Godbold D.L., 2002: Biodegradation of low weight organic acids in coniferous forest podzolic soils. *Soil Biology Biochemistry*, 34, 9, 1261–1272.

Van Hees P.A.W., Jones D.L., Jentschke G. & Godbold D.L., 2005: Organic acid concentrations in soil solution: effects of young coniferous trees and ectomycorrhizal fungi. *Soil Biology Biochemistry*, 37, 4, 771–776.

Varga M. & Kolenčík M., 2016: Arsenic pollution study at Nitra-Krškany location as an example of line contamination. *Acta Regionalia et Environmentalica*, 13, 1, 6–11.

Vassilev S.V. & Vassileva C.G., 1996: Mineralogy of combustion wastes from coal-fired power stations. *Fuel Processing Technology*, 47, 3, 261–280.

Vassileva C.G. & Vassilev S.V., 2006: Behaviour of inorganic matter during heating of Bulgarian coals: 2. Subbituminous and bituminous coals. *Fuel Processing Technology*, 87, 12, 1095–1116.

Verbich F., 1998: Geochemistry and mineralization of Novaky coal seam. *Acta Montanistica Slovaca*, 3, 3, 378–383. [in Slovak with English abstract]

Veselská V., Majzlan J., Hiller E., Peťková K., Jurkovič Ľ., Ďurža O. & Voleková-Lalinská B., 2013: Geochemical characterization of arsenic-rich coal-combustion ashes buried under agricultural soils and the release of arsenic. *Applied Geochemistry*, 33, 153–164.

Vítková M., Komárek M., Tejnecký V & Šillerová H., 2015: Interactions of nano-oxides with low-molecular-weight organic acids in a contaminated soil. *Journal of Hazardous Materials*, 293, 7–14.

Wang S. & Mulligan C.N., 2013: Effects of three low-molecular-weight organic acids (LMWOAs) and pH on the mobilization of arsenic and heavy metals (Cu, Pb, and Zn) from mine tailings. *Environmental Geochemistry and Health*, 35, 1, 111–118.

Wang S. & Zhao X., 2009: On the potential of biological treatment for arsenic contaminated soils and groundwater. *Journal of Environmental Management*, 90, 8, 2367–2376.

Ward C.R. & French D., 2006: Determination of glass content and estimation of glass composition in fly ash using quantitative X-ray diffractometry. *Fuel*, 85, 16, 2268–2277.

Wilson S.C., Lockwood P.V., Ashley P.M. & Tighe M., 2010: The chemistry and behaviour of antimony in the soil environment with comparisons of arsenic: A critical review. *Environmental Pollution*, 158, 5, 1169–1181.

WRB, 2006: World Reference Base for Soil Resources – a framework for international classification, correlation and communication. FAO–ISRIC–ISSS, Rome, 128 p.

Zhang S., Li W., Shan X.Q., Lu A. & Zhou P., 2005: Effects of low molecular weight organic anions on the release of arsenite and arsenate from a contaminated soil. *Water Air & Soil Pollution*, 167, 1–4, 111–122.