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Effect of Low Concentrations of Phosphate Ions on Extraction of Arsenic from Naturally Contaminated Soil

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Abstract The effect of low concentrations of phosphate ions on the extraction of arsenic (As) was tested on naturally contaminated soil (As 126 mg/kg) using batch experiments. Interaction entails the extraction of low concentrations of As (5.4–23.3 μg/L As). There are statistical differences in the contents of As, Ca, Cu, Ni, Pb and nitrate in the composition of the extracts. Three types of kinetic curves document that dissolution and precipitation reactions, adsorption, desorption and biological processes participate in determining the composition of the extracts. The elevated As contents in the phosphate extracts are probably caused by competition between phosphate and arsenate ions for soil adsorption sites.

Keywords Arsenic · Phosphates · Soil · Dissolution · Adsorption · Kinetics · Batch experiment

Arsenic (As) contained in the soil constitutes an environmental risk through potential entrance into further parts of the food chain (e.g., Chen et al. 1994; Száková et al. 2007). Sulphides containing As in mineral wastes, in tips and in the soil profile are weathered under the influence of oxidation conditions or microbial activity (e.g., Chatain et al. 2005; Mihaljevič et al. 2004). The composition of the solutions formed and secondary phases containing As are dependent mainly on the pH and Eh of the environment and the presence of other ions that react with As to form secondary arsenates (e.g., Juillot et al. 1999). Arsenates, e.g., weilite ($Ca[AsO_3OH]$), haidingerite ($Ca[AsO_3OH] \cdot H_2O$), pharmacolite ($CaH[AsO_4] \cdot 2H_2O$), picropharmacolite ($Ca_4\,Mg[(AsO_3OH)_2/(AsO_4)_2] \cdot 11H_2O$), pharmacosiderite ($KFe_4[(OH)_4/(AsO_4)_3]\ 6H_2O$), or hörnesite ($Mg_3[AsO_4]_2 \cdot 8H_2O$), have been described in soils with high As contents (Foster et al. 1998; Filippi et al. 2004; Juillot et al. 1999; Voigt et al. 1996). However, these minerals are formed in an environment with sufficient concentrations of Ca, Mg and Fe in soil solutions. While Fe arsenates are formed at pH 1–2, Ca arsenates are formed in the pH 3–4 interval (Filippi et al. 2004). On an increase in the pH, scorodite ($FeAsO_4 \cdot 2H_2O$) becomes unstable and is converted to goethite containing As (Juillot et al. 1999). Other soil components that affect the mobility of As include Mn and Al oxides, clay minerals and organic matter. The predominant form of As in oxidic soils is As(V), which is less toxic, less soluble and less mobile than As(III) (Matera et al. 2003). The bonding forms of arsenic in the soil are determined with instrumental surface analytical techniques or using extraction techniques (e.g., Goh and Lim 2005; Matera et al. 2003; Onken and Adriano 1997; Wenzel et al. 2001). Extraction techniques have limitations (e.g., Bacon and Davidson 2008) and their effectiveness can be compared on artificially prepared mixtures (Mihaljevič et al. 2003). Speciation analysis in solutions is most frequently performed by a combination of HPLC–ICP AES or HPLC ICP MS (Chausseau et al. 2000; Matera et al. 2003).

Arsenates are bonded in the soil particularly by specific adsorption on Fe, Al and Mn oxides via ligand exchange with surface hydroxyls or aqua groups (Lin et al. 2002; Manning and Goldberg 1997). Pentavalent oxyanions of

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arsenates and phosphates have a similar structure and chemical reactivity, reflected in the similar adsorption kinetics of the two ions (Luengo et al. 2007). Mobilization of As ions by phosphates probably occurs through the effect of the ligand exchange mechanism of PO_4 and AsO_4 (Goh and Lim 2005) and has practical applications in determination of the forms of As (e.g., Wenzel et al. 2001) and in remediation of As-contaminated soils (Alam et al. 2001).

Arsenic is an accompanying element in a number of Au deposits (Pokrovski et al. 2002; Zachariáš et al. 2004) and is reflected in high As contents in soils and mill tailings at these deposits (e.g., Bodénan et al. 2004; Filippi et al. 2004, 2007). Application of phosphate fertilizers or barnyard fertilizer can lead to mobilization of As ions. For example, up to 80% of the arsenate was released by phosphate ions in soils artificially contaminated with arsenates with subsequent 2.5 month stabilization (Wasay et al. 2000).

Experiments simulating the effect of PO_4 ions on mobilization of As were performed with high concentrations of PO_4 ions (Alam et al. 2001; Goh and Lim 2005; Violante and Pigna 2002). However, these concentrations are relatively high compared to the composition of soil solutions in agricultural soils. This work was performed in order to describe the behaviour of arsenic in soils under the influence of competition with PO_4 ions contained in soils in the low concentrations common for soil solutions, on the basis of laboratory batch experiments.

Materials and Methods

A sample of arable soil (~50 kg) was taken evenly over an area of ~1 ha in the cadaster of the municipality of Mokrsko (Czech Republic – for more information on the site, see Filippi et al. 2004, 2007; Mihaljevič et al. 2004; Sisr et al. 2007). The soil was dried to a constant weight in a dust-free environment and subsequently sieved using a 2-mm polyethylene sieve. Part of the under-sieve fraction (~1 kg) was ground to analytical fineness in an agate ring mill (Retsch, Germany). The contents of the main components were determined following complete mineralization of the sample by a mixture of acids ($HF–HClO_4$) or sintering of the sample and subsequent chemical analysis: Al_2O_3, Fe_2O_3, FeO, MgO and CaO were determined by volumetric analysis, SiO_2, CO_2 and H_2O were determined gravimetrically and P_2O_5 and TiO_2 were determined spectrophotometrically (CARY 50, Varian). The contents of Na_2O and K_2O were determined by flame emission spectrometry (Spectra AA 200 HT, Varian). The procedures for determinating the pH of H_2O, pH of KCl, specific surface area, cation exchange capacity, basic saturation, amount of extractable P_2O_5, total organic carbon and total inorganic carbon are given in the work by Sisr et al. (2007). The forms of As in the soil sample were determined by the extraction test according to Wenzel et al. (2001), with operationally defined nonspecifically adsorbed As(1), specifically adsorbed As(2), As bonded to amorphous and poorly crystalline oxides of Fe and Al(3), and As bonded to well-crystallized Fe and Al(4).

Extraction experiments were performed with deionized water (DIW) (Academic, Millipore) and a solution containing 28 μmol/L PO_4 (2.66 mg/L), which was prepared by dissolving the salt $Ca(H_2PO_4) \cdot H_2O$. The extraction experiments were performed in 125 mL PP vessels (Nalgene) into which 10 g of soil was weighed and 100 mL DIW or PO_4 solution was added. The samples were placed in a reciprocal shaker and shaken for periods of 1, 5, 10, 18, 24, 48 and 120 h. The extractions were performed in triplicate at a temperature of 23 ± 2°C. Immediately after taking the sample, the pH, Eh and conductivity were measured in the extracts using a Schott–Geräte Handylab 1. Subsequently, the samples were filtered through a 0.1-μm Millipore membrane filter. The Na, K, Mg, Ca and Fe contents were determined by flame AAS (Spectra AA 200 HT, Varian) and the As, Al and Pb contents were determined using ICP MS (PQ3 VG Elemental). The contents of F, NO_3, Cl, SO_4 and PO_4 were determined using HPLC (Dionex, ICS 2000). The amount of extractable As was determined according to the following relationship:

$$E_{As}(\%) = \frac{C_f \times V}{C_T \times M} \times 100\% \quad (1)$$

where E_{As} is the amount of extractable As (%), C_T is the total As content in the soil (mg/kg), C_f is the arsenic concentration in the extract (mg/L), V is the volume of extractant and M is the amount of extracted soil (kg).

Calculation of the speciation and saturation indices (SI) was performed using the PHREEQC program (Parkhurst and Appelo 1999). The calculation was performed using the wateq4f database, extended to include thermodynamic data contained in the work of Gaskova et al. (1999). The obtained results were compared statistically using the Statistica 5.1 program. Differences in the compositions of the individual extracts were tested using the Wilcox double-choice test at a significance level of $p = 0.05$.

Results and Discussion

Selected physical–chemical parameters of the studied soil are listed in Table 1. The soil was classified as light, loamy sandy, slightly acidic, brown soil (Cambisol) and contains crystalline phases of quartz, K-feldspar, chlorite, apatite, illite, kaolinite, chlorite and smectite. Arsenic extractable from the residual fraction in an amount of 69.2 mg/kg

Table 1 Selected physical chemical parameters of studied soil

Parameter (units)	Value	Parameter (units)	Value
SiO_2 (wt%)	64.94	pH H_2O	7.62
TiO_2 (wt%)	0.62	pH KCl	6.04
Al_2O_3 (wt%)	14.25	Specific surface (m^2/g)	8.3
Fe_2O_3 (wt%)	4.58	CEC (mmol+/kg)	160.4
FeO (wt%)	0.99	TOC (wt%)	1.12
MnO (wt%)	0.1	TIC (wt%)	<0.01
MgO (wt%)	1.47	As $(NH_4)_2SO_4$ soluble (mg/kg)	0.11
CaO (wt%)	2.24	As $NH_4H_2PO_4$ soluble (mg/kg)	3.72
Na_2O (wt%)	2.44	As NH_4 oxalate soluble (mg/kg)	16.3
K_2O (wt%)	2.13	As NH_4 oxalate ascorbate soluble (mg/kg)	36.6
P_2O_5 (wt%)	0.15	As residual (mg/kg)	69.2
CO_2 (wt%)	0.07	Ba (mg/kg)	511
H_2O+(wt%)	4.31	Pb (mg/kg)	241

predominates in soil with a total As content of 126 mg/kg, followed by As bonded to crystalline and amorphous Fe oxyhydroxides in an amount of 52.9 mg/kg. The content of specifically sorbed and nonspecifically sorbed As equals 3.83 mg/kg. The specific surface of the soil determined by the BET method equals 8.3 m^2/g. The cation exchange capacity (CEC) varies at the lower limit of the values for common soils (160.4 mmol(+)/kg) and consists mostly of Ca ions and less of Mg and K ions.

The compositions of the individual extracts during interaction of the soil with DIW and with the PO_4 solution are given in Table 2. The arsenic content in the extracts varies in the range 5.4–15.3 µg/L and 8.53–23.3 µg/L for DIW and PO_4 extracts. The amount of mobilizable As (E_{As}) in the soil in the Mokrsko area is very low according to Eq. (1) and varies in the range 0.04–0.18%. Extraction of the soil with DIW and with the PO_4 solution in the batch experiments differed statistically in the contents of As, Ca, Cu, Ni, NO_3 and Pb (Wilcox test, $p < 0.05$). The extracts differ in the Ca contents because Ca phosphate was used to prepare the PO_4 solution. The differences in the NO_3 contents between the compared extracts are probably

Table 2 Values of pH, Eh and concentration of extracted species by DIW and PO_4 solution (in parentheses)

Time (hours)	0.1	1	10	18	24	48	120
pH (std. units)	6.21 (6.0)	6.51 (6.34)	6.48 (6.31)	6.72 (6.87)	6.67 (6.54)	6.44 (6.75)	7.01 (6.53)
Eh (mV)	424 (428)	424 (421)	422 (422)	431 (424)	426 (422)	427 (424)	434 (431)
alk (meq/L)	0.52 (0.77)	0.50 (0.48)	0.57 (0.58)	0.62 (0.55)	0.67 (0.56)	0.71 (0.66)	0.71 (0.75)
Na (mg/L)	0.13 (0.33)	0.33 (0.40)	0.63 (0.48)	0.68 (0.54)	0.67 (0.55)	0.71 (0.56)	0.74 (0.64)
K (mg/L)	<DL (<DL)	<DL (<DL)	0.27 (0.20)	0.42 (0.41)	0.47 (0.43)	0.53 (0.50)	0.66 (0.60)
Ca (mg/L)	7.23 (3.47)	10.20 (7.46)	13.11 (11.63)	14.04 (13.08)	14.99 (13.75)	16.4 (15.68)	17.43 (16.73)
Mg (mg/L)	0.35 (0.29)	0.23 (0.31)	0.38 (0.28)	0.40 (0.35)	0.50 (0.33)	0.71 (0.62)	1.08 (1.32)
F (mg/L)	0.71 (0.76)	1.10 (1.05)	1.33 (1.34)	0.66 (1.15)	1.03 (1.13)	0.92 (1.02)	1.31 (1.00)
Cl (mg/L)	1.60 (0.62)	0.63 (0.19)	0.71 (0.16)	0.65 (0.15)	1.41 (0.35)	2.00 (0.49)	0.93 (1.64)
NO_3 (mg/L)	1.34 (2.86)	1.11 (1.82)	1.36 (1.82)	1.25 (1.48)	1.72 (2.11)	1.86 (2.32)	3.83 (5.68)
SO_4 (mg/L)	0.63 (1.08)	0.51 (0.45)	0.56 (0.46)	0.87 (1.11)	0.61 (0.68)	0.67 (0.86)	0.73 (1.17)
PO_4 (mg/L)	<DL (0.77)	<DL (0.58)	<DL (0.93)	<DL (0.65)	<DL (0.95)	<DL (0.84)	<DL (1.11)
Mn (µg/L)	3.87 (5.00)	5.12 (10.29)	11.05 (21.15)	13.19 (9.51)	8.43 (8.00)	2.07 (7.86)	0.99 (4.13)
Fe (µg/L)	<DL (<DL)	<DL (<DL)	<DL (<DL)	<DL (<DL)	<DL (<DL)	<DL (<DL)	<DL (<DL)
As (µg/L)	5.39 (8.53)	11.92 (18.96)	14.83 (23.3)	15.34 (23.07)	13.5 (20.16)	12.54 (19.31)	11.14 (17.59)
E_{As} (%)	0.04 (0.07)	0.09 (0.15)	0.12 (0.18)	0.12 (0.18)	0.11 (0.16)	0.10 (0.15)	0.09 (0.14)
Al (µg/L)	3.23 (5.00)	11.06 (10.29)	18.11 (21.15)	10.07 (9.51)	7.66 (8.00)	7.31 (7.86)	6.02 (4.13)
Ba (µg/L)	3.10 (5.55)	6.03 (7.23)	10.66 (12.54)	12.01 (13.59)	13.70 (15.78)	22.14 (19.80)	35.16 (28.39)
Cd (µg/L)	0.06 (0.08)	0.31 (0.57)	0.37 (0.42)	0.18 (0.11)	0.22 (0.12)	0.07 (0.10)	0.06 (0.07)
Pb (µg/L)	0.22 (0.32)	0.87 (1.11)	0.50 (1.01)	0.32 (0.52)	0.35 (0.51)	0.40 (0.34)	0.44 (0.69)

Detection limits (DL) of K, PO_4 and Fe determination are 0.01 mg/L, 0.1 mg/L and 0.009 mg/L, respectively connected with biological activity simulated by addition of PO_4 ions to the soil. Differences in the As, Cu, Ni and Pb contents can follow from the As, Cu, Ni and Pb phases, whose potential formation was confirmed by thermodynamic modelling of the chemical composition of the extracts. Following 120 h interaction, the soil-PO_4 solution extracts exhibit equilibrium with boehmite (α-AlOOH), pyromorphite $Pb_5(PO_4)Cl_3$, conichcalcite ($CaCu[OH/AsO_4]$), gibbsite (g-AlOOH), strengite ($FePO_4 \cdot 2H_2O$) and plumbogummite ($PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$) and are supersaturated with respect to the $Ba_3(AsO_4)_2$, diaspore (α-AlOOH) and apatite phases. As is present in the solutions as $H_2AsO_4^-$ and $HAsO_4^{2-}$, while *p* is present in the extract with PO_4 ions in the form of $H_2PO_4^-$, $FeH_2PO_4^+$, HPO_4^{2-}, $FeHPO_4$ and $CaHPO_4$. In contrast to the performed batch experiments, the extracts did not differ statistically in the column arrangement of interactions between DIW and PO_4 ions (Sisr et al. 2007). This is probably caused by the formation of preferential pathways for solutions in the column, a shorter time of interaction between the soil and the solutions and the impossibility of abrading the reaction surface during oxidation of sulphides (Sisr et al. 2007).

Clemente et al. (2008) analyzed the soil and soil solutions at locations with similar As content (18–143 mg/kg). In the soil solutions, the amount of dissolved As varied in the range 1–110 µg/L As and, in relation to the pseudototal concentration, attained a similarly low amount of dissolved metalloid 0.001–0.037% (Clemente et al. 2008). However, the studied soils were more acidic (pH 4.03–4.44) and contained larger amounts of As (up to 22%) in the more mobile fractions (extract in H_2O, 0.5 M $NaHCO_3$). Drahota et al. (2006) give an average As concentration in the surface water at Mokrsko of 150 µg/L, and in groundwater, of 761 µg/L; however, they simultaneously give higher As concentrations in the basement rock (1,401 mg/kg) and in the soil (496 mg/kg).

The shape of the soil-solution interaction can be seen from the kinetic curves, which follow three basic trends (Fig. 1). The first type of curve is typical for Na, K, Ca, Ba, Sr and SO_4 and is caused by dissolution of the solid phases. This type of curve exhibits a sharp increase in the rate at the beginning of the experiment, probably caused by dissolution of the fine fraction contained in the soil (the <44 µm fraction exceeds 30% of the total). In the second half of the experiment, the increase in the monitored substance occurred more slowly. The second type of kinetic curve (Fig. 1) depicts the variation in the concentrations of As, Al, Cd, Cu, Pb and Mn for DIW interaction and this group is supplemented by F, Zn and Ni for PO_4 interaction. This curve has a maximum close to the beginning of the experiment, followed by a decrease or only slight changes in concentration. This type of kinetic curve is controlled by a more complex system of dissolution and precipitation reactions and sorption–desorption reactions. At the beginning of the experiment, the monitored substances are released into the extractant solution, followed by their sorption on sorbents contained in the soil. The third type of kinetic curve is exhibited by the contents of NO_3, Mg and Cl (for PO_4 interaction), which initially have stable concentrations; in the next phase, they increase, probably in connection with decomposition of the organic matter. Following 120 h of interaction, the thermodynamic model (PHREEQC) of the chemical composition of the DIW extract exhibits equilibrium with gibbsite (γ-AlOOH) and boehmite (α-AlOOH) and is supersaturated with respect to conichcalcite ($CaCu[OH/AsO_4]$), the $Ba_3(AsO_4)_2$ phase and duftite ($PbCu[OH/AsO_4]$).

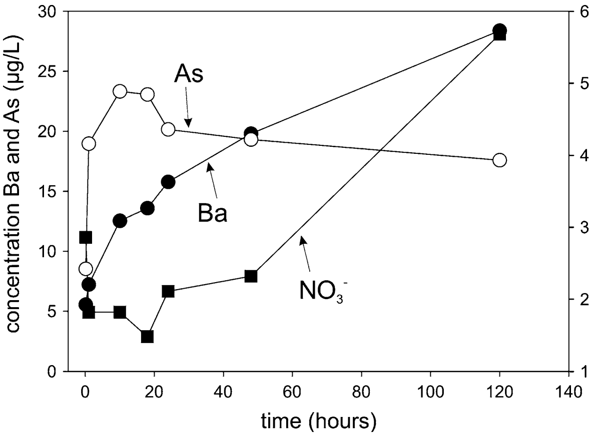

Fig. 1 Variations in the concentration of Ba (*curve type 1*), As (*curve type 2*) and NO_3 (*curve type 3*) in dependence on time in interaction of the soil with a PO_4 solution

Part of the arsenic in the studied soil is strongly bonded to sulphides (69.2 mg/kg) and part is present in crystalline and amorphous hydroxides (52.9 mg/kg). Oxidation of arsenopyrite and As-rich pyrites under these Eh and pH conditions (Eh ~420–430 mV; pH 6.0–7.0) produces $H_2AsO_4^-$, $HAsO_4^{2-}$ and hydrated Fe oxides. The isoelectric point of amorphous $Fe(OH)_3$, goethite (αFeO(OH) and hematite (α Fe_2O_3) is >7, i.e., As(V) is bonded as an inner surface complex to the functional groups of the Fe sorbent (Ladeira and Ciminelli 2004). Part of the As is coprecipitated in the structure of new Fe or AsO_4 phases. In the group of common anions (CO_3, SO_4, Cl and PO_4), especially PO_4 ions have the greatest ability to compete with and replace As(V) (Goh and Lim 2005). These authors applied 0.005–0.05 M PO_4 to soil containing 1,275 mg/kg As and found up to 50% extraction of the total As contained in the soil. However, the tested soil was artificially contaminated with As(V) and, following ageing, contained most of the As in the specifically adsorbed form (1 M NaH_2PO_4 leached) (Goh and Lim 2005). The amount of mobilizable As in the soil in the Mokrsko area is very much lower (0.04–0.18%) according to Eq. (1). However, this soil contains only 3% non-specifically and specifically bound As (Table 1) and a solution with a concentration of PO_4 ions two to three orders of magnitude lower was used for the interaction. The As (PO_4)/As DIW ratio is constant throughout the kinetic experiment (average = 1.55, SD = 0.04). This means that both release of As and also its sorption and desorption through the effect of PO_4 ions have similar kinetic parameters and affect the final amount of metalloids in solution.

To summarize, in batch experiments with DIW and a PO_4 solution, low concentrations of As (5.4–23.3 µg/L) are released from naturally contaminated soils at the Mokrsko gold deposit containing most of the As(97%) in the reducable, oxidizable and residual fractions. Laboratory batch experiments demonstrated greater amounts of mobilizable As when PO_4 ions are used. However, this mobilization is not the same as for high concentrations of weakly bonded As and high concentrations of applied competing PO_4 ions. Thus, soils with average As contents probably contribute to only a small degree to the contamination of surface and groundwaters at the Mokrsko location, even in the case of interaction with PO_4 ions.

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