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Different low-molecular-mass organic acids specifically control leaching of arsenic and lead from contaminated soil

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ABSTRACT

Low-molecular-mass organic acids (LMMOA) are of key importance for mobilisation and fate of metals in soil, by functioning as ligands that increase the amount of dissolved metal in solution or by dissociation of metal binding minerals. Column leaching experiments were performed on soil polluted with As and Pb, in order to determine the specificity of LMMOA related release for individual elements, at varying organic acid concentrations. Acetic, citric and oxalic acids were applied in 12 h leaching experiments over a concentration range (0.5–25 mM) to soil samples that represent organic and mineral horizons. The leaching of As followed the order: oxalic > citric > acetic acid in both soils. Arsenic leaching was attributed primarily to ligand-enhanced dissolution of mineral oxides followed by As released into solution, as shown by significant correlation between oxalic and citric acids and content of Al and Fe in leaching solutions. Results suggest that subsurface mineral soil layers are more vulnerable to As toxicity. Leaching of Pb from both soils followed the order: citric > oxalic > acetic acid. Mineral soil samples were shown to be more susceptible to leaching of Pb than samples characterised by a high content of organic matter. The leaching efficiency of citric acid was attributed to formation of stable complexes with Pb ions, which other acids are not capable of. Results obtained in the study are evidence that the extent of As and Pb leaching in contaminated surface and subsurface soil depends significantly on the types of carboxylic acid involved. The implications of the type of acid and the specific element that can be mobilised become increasingly significant where LMMOA concentrations are highest, such as in rhizosphere soil.

1. Introduction

Particulate depositions from fossil fuel combustion and the pyrometallurgical industry are major contributors to the high anthropogenic loads of potentially toxic elements (PTE) in soil, which are still largely detectable in many areas of northern Czech Republic (Sucharová et al., 2011). Although metals are natural components of many soils, toxicity is expressed when the metal is labile and present in concentrations that are deemed excessive for a given land use or soil type. A metal's lability can be assessed by means of continuous leaching in laboratory column experiments. Column leaching experiments are commonly used for the simulation of a solution percolating through a contaminated soil, as the mobilisation mechanisms are suggested to be close to those found in the field (Jean-Soro et al., 2012). The experiment allows the researcher to determine the level of binding and mobility of metals through applied leaching of the solution of interest; metals dissolved in the extract represent an environmental hazard, while metals left in the soil following leaching are likely to be present in chemically-stable mineral forms and bound to non-labile soil fractions (Leštan et al., 2008). Low-molecular-mass organic acids (LMMOA) are simple carboxylic acids of low molecular weight. Their occurrence in the environment and in organisms is extensive; in soils, the conditions of release are largely provided by the slow decomposition of abundant soil organic matter and are usually confined to the upper portion of

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weathering profiles. LMMOA in soils function as ligands increasing the total amount of dissolved cations in soil solutions by chelation/complexation (Hue et al., 1986; Fox, 1995). Therefore, complexes of LMMOA with metals are readily transported in pores through the soil profile (Strobel, 2001). It has been suggested that LMMOA also promote desorption of metals by dissolving the minerals that adsorb the metal (Collins, 2004). In general, a complex metal ion is more soluble in water, less retained on the solid phase, and more easily transported through the porous medium (Berkowitz et al., 2008). Extractability of PTE in rhizosphere soil is influenced by the ionic species, which are dependent on the pH, and chemical compositions of root exudates, such as LMMOA (Chiang et al., 2006). The importance of organic acid exudates in the transport of metals is particularly evident in hyper-accumulating plant species, which contain high endogenous levels of organic acids (Boominathan and Doran, 2003). Levels reported for different LMMOA vary between nM to mM, and soil solution concentrations of the dominant organic acids can range from 1 to 100 mM (Van Hees et al., 2002, 2005). However, in common soil solutions, concentrations of LMMOA are suggested to be usually up to 1 mM (Ettler et al., 2004). Due to the potential of LMMOA to form soluble metal complexes, a number of researchers have focused on their application in soil leaching experiments (e.g., Qin et al., 2004; Ettler et al., 2009; Ash et al., 2013). However, the impact of rhizospheric processes on metal speciation and extractability is not well understood, and the impacts of rhizosphere chemistry on the behaviour of individual elements in soils require further attention.

The aim of this study was to describe trends of As and Pb release from soil by continuous leaching using different LMMOA (acetic, oxalic, and citric acid). Using the leaching data, it was possible to identify the most effective LMMOA (type and concentration) for the extraction of As and Pb in organic and mineral soil samples. The resulting data bring new insight into the roles that are played by LMMOA in polluted soils, with respect to the availability, mobility, and consequent toxicity of As and Pb. We test the hypotheses:

i. Cumulative amounts of As and Pb released from soil samples by LMMOA of differing molar concentration will not be linear but will plateau in the upper concentration range (up to 25 mM);
ii. Differences in the extent of As and Pb leaching will reflect the carboxylic structure of LMMOA; an organic acid with a greater number of carboxyl groups is a more effective extracting agent than an acid of simpler carboxylic structure (citric > oxalic > acetic);
iii. The major leaching mechanism for As and Pb from soil is similar for each of the studied LMMOA.

2. Material and methods

2.1. Sample collection and treatment

Soil samples were collected from a wooded area (approximately 0.4 km^2) to the north of Příbram in the Czech Republic (average annual temperature 7 °C, rainfall 651 mm). The sampling area is to the east of an adjacent lead smelter (downwind) that presently functions as a part of a lead battery processing plant. Due to the smelting activities, the land has been heavily contaminated with As, Cd, Pb, Sb and Zn, as identified in previous studies (Ettler et al., 2010; Rieuwerts and Farago, 1996). Particularly high concentrations of PTE are expected in forest soils downwind of smelting facilities due to interception of emissions by the canopy (Ettler et al., 2010). The tree stand is composed predominantly of spruce (*Picea abies*), with the occasional presence of oak (*Quercus* sp.). Because of the abundance of spruce trees, the litter layer consists almost exclusively of needles. The sampled region overlies a Cambrian sandstone and arkose sequence. Deep mineral ore veins (As, Pb, Zn) occur in dykes that intersect the Příbram bedrock (Cathro, 2006). Arsenic bearing minerals of the district are mainly arsenopyrite (FeAsS) and admixtures of common sulphides (galena PbS, sphalerite ZnS, and chalcopyrite $CuFeS_2$) (Ettler et al., 2010). Other PTE bearing minerals that were mined and smelted in Příbram, mainly for their silver content, include freibergite, pyrargyrite, and stephanite.

A trench approximately 50 cm deep and 1 m wide was excavated to reveal horizons for taxonomic description. Soil type was identified as toxic (Tx) Cambisol (Inceptisol), having in some layer within 50 cm of the soil surface toxic concentrations of organic or inorganic substances other than ions of Al, Fe, Na, Ca and Mg. A number of composite samples were collected by trowel along the trench from the two following soil layers: soil O (3–11.5 cm); mixture of F and H horizons (after litter layer removed), and soil AB (11.5–25 cm); mixture of A and B horizons. Samples were air dried at 21 °C to constant weight. A sample of the litter layer was collected for analysis of LMMOA content in a fresh state; soil solution was separated from samples by centrifuging (1509 *g* at 10,000 rpm) for 5 min in Maxi-Spin filter tubes. Soil solution was then measured immediately for content of anions by means of ion chromatography, ICS 1600 equipped with IonPac AS11-HC. After drying, soil samples were sieved (<2 mm). Prior to analysis, bulk soil was sterilised by gamma ray treatment to mitigate the possibility of microbial decomposition of LMMOA during the experiment. The procedure was performed according to the standard outlined by the Ministry of Health of the Czech Republic (Ministerstvo Zdravotnictví, 2009).

2.2. Determination of soil properties

Active (pHH2O) and exchangeable (pHKCl) soil pH were measured by preparing a 1:5 soil:liquid (w:v) ratio using deionised water (DI_{H2O}) or 1 M KCl solution respectively, then measuring the mixture using a calibrated Denver Instrument UB-5 pH meter after agitation. Salinity of soil DI_{H2O} leachate was measured using a conductivity probe (inoLab WTW). Content of soil organic matter (SOM) was measured by the loss on ignition method. Quality of humic substances was calculated from spectrophotometric analysis (HP Agilent 8453 UV–visible spectroscopy system), taken as the ratio of a pyrophosphate soil extract absorbance at wavelengths 400 and 600 nm (A_{400}/A_{600}), according to Podlešáková et al. (1992). Amounts of amorphous Al and Fe were determined by an acid ammonium oxalate extraction method performed in the dark (Carter and Gregorich, 2008). Cation exchange capacity (CEC) was determined according to the Bower method as described by Hesse (1998). Concentration of Na in the final