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Lead migration in smelter-impacted deciduous and coniferous organic soil horizons based on a long-term *in-situ* implantation and laboratory column experiments

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ABSTRACT

Lead (Pb) contamination of forest soils constitute a serious threat against soil organisms and wildlife and the transport of previously deposited Pb from surface soils is of high environmental relevance. We studied the migration of Pb in highly contaminated deciduous and coniferous soils in a smelting area. A mixture of fermented/humified (*F* + *H*) deciduous and coniferous soil horizons highly contaminated by Pb smelting operations were implanted to the same horizon types in an area of low Pb atmospheric input for 6 months. The implantation was accompanied with mechanical turbation, which caused changes in the soil parameters, i.e., CEC (cation exchange capacity), $C_{org.}$ (organic carbon) or pH. The target soil horizons *F* + *H* (and partly *A*) were enriched with Pb, compared to background concentrations. The retention of Pb in smelter-impacted coniferous forest soil horizons *L* (raw litter), *F* + *H*, *A* (organo-mineral) and *C* (mineral) was studied using a column experiment.

As a result of the Pb addition with a specific isotope composition (American galena) it was found that with the exception of the *L* horizon, all of the added Pb was completely retained in soil horizons. The isotope composition of Pb in eluate from the *L* horizon was represented by linear mixing between the original and added Pb sources. The majority of Pb would be eluted from the *L* horizon after less than 5 years (using linear approximation).

1. Introduction

The mining and smelting area Příbram is situated approximately 60 km South West from Prague, Czech Republic. The history of metallurgy in the area of Příbram dates back 700 years (the first written document is from 21st of April 1311). According to the press release of the company Kovohutě Příbram (Anonymous, 2011), the smelter has been located at its current location since 1786. The estimated Pb smelter production, from the beginning of operations to the present time, has reached more than 1.5 million tons (Anonymous, 2011). Since 1972, the smelter has been processing secondary material (i.e., lead accumulators, solder, dust and sludge from metallurgy, etc.) (Dostál et al., 2007). After Kovohutě Příbram became part of the German company Varta in 1994 a new furnace with modern after-burning technology was installed. The smelter is now capable of processing all of the lead waste produced in the Czech Republic in a more environmentally-friendly manner.

However, researchers have detected high levels of toxic metals in soils (Ettler et al., 2004, 2005; Rieuwerts et al., 1999) and stream sediments (Ettler et al., 2006) in the area, as a consequence of the rich mining and smelting history of the Příbram district. Ettler et al. (2005) studied Pb speciation in forested and tilled soils, adjacent to the Příbram smelter; the concentration of Pb in tilled soils was lower than in the forest soils. Accordingly, the mobility factor calculated by Kabala and Singh (2001), was much lower in tilled soils compared to forest ones, reaching 30% and 72%, respectively. Based on Pb isotope evidence, pollution caused by the smelter in the organic soil horizon has shifted towards the mineral soil horizon, with a penetration rate between 0.3 and 0.4 cm year^{-1}. The velocity of Pb vertical migration was obtained by dividing the depth of the organic soil horizon by the exposition time (30 years of car battery processing in the Příbram smelter) (Ettler et al., 2004). High Pb concentration was observed in surface and subsurface horizons, attaining 35.3 g kg^{-1} (Ettler et al., 2004, 2005). The highest value

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of 58.5 g kg^{-1} was found downwind from the smelter furnace (Rieuwerts et al., 1999).

Due to the installation of advanced smelter technology, the current Pb emissions are only a fraction of the maximum values measured in the 1960s, as observed in peat cores and spruce tree rings (Mihaljevič et al., 2008). Highly contaminated forest soils in smelter areas present a serious environmental risk, due to downward penetration of Pb in deeper soil horizons. The plants may have contributed to an upward flux of Pb through root uptake (litter fall pump). In non-contaminated boreal forest soils, the upward flux from the mor layer and the mineral soil was estimated to be about 0.05 mg Pb m^{-2} $year^{-1}$ (Klaminder et al., 2005). In the case of highly contaminated soils the upward flux by plant pumps should be very small in comparison to annual atmospheric deposition and migration losses.

Despite to the fact that current Pb emissions have decreased, the "older" Pb accumulated in the upper soil horizons may have affected the ecosystems for decades. For example, Berglund et al. (2009) demonstrated that insectivorous birds living around smelters are permanently exposed to Pb via their prey. The concentrations of Pb in birds' livers and feces have decreased since the 1980s (by 9–15% and 18–40% for liver and feces, respectively) while the bulk emissions were reduced by 98% Berglund et al. (2009).

Semlali et al. (2001) studied the origin and migration of exogenous and endogenous Pb related to Sc. They found exogenous Pb in all particle-size fractions, however the concentrations increased with decreasing particle diameter. The concentrations of exogenous Pb continuously decreased with soil depth where endogenous Pb represented the bulk amount in the mineral soil horizon. Colloidal transport of metals through the soil profile was published by van Oort et al. (2006). The authors detected Pb-bearing iron coatings in mineral horizon related to the precipitation of its colloid forms.

The aim of this study was to test the stability of Pb in soils originally derived from the smelting operations, when introduced into an uncontaminated organic forest soil system. The deciduous and coniferous organic forest soil horizons (fermented and humified, *F* + *H*) from the Příbram smelter area were implanted in horizons which were situated in an area with a low atmospheric Pb input.

Additionally, a laboratory column experiment simulating precipitations enriched with Pb from an American galena with a distinct and different isotope composition was set up to evaluate whether the newly added dissolved Pb will be retained or released in the highly contaminated organic soil horizons. We were able to describe the retention of Pb in forest soil in the horizons, on the basis of mixing the two sources.

2. Material and methods

2.1. Soil sampling, sample preparation and basic soil characteristics

Two localities (with different Pb concentration in soils) were chosen for the implantation experiment (Table 1). The mixed soil samples of partially (*F*) and completely (*H*) decomposed organic humified horizons, which developed under conifers (predominantly Norway spruce, *Picea abies* L.) and deciduous trees (beech, *Fagus sylvatica* L.), were taken from the vicinity of the secondary Pb-smelter (Příbram, Czech Republic, sampling coordinates of N49°42.310′ and E13°59.440′). The smelter has been operational for more than 200 years for primary Pb/Zn ore. The soil profile is developed on a Proterozoic volcano-sedimentary rock complex (basalt veins in clastic sediments) belonging to the Příbram ore district. The soil is classified as a Gleyic Cambisol. The atmospheric Pb fluxes decreased rapidly in the last century due to the installation of modern smelting and filtration technologies. According to Mihaljevič et al. (2006), Pb atmospheric fluxes culminated in the 1970s around 320 mg m^{-2} $year^{-1}$, while in 2003, they varied between 5 and 89 mg m^{-2} $year^{-1}$.

The area with low Pb input from the atmosphere selected for the implantation experiment is located in South Bohemia (Czech Republic). Due to the absence of major industrial zones it may be considered as an unpolluted site. In this area we found both deciduous and coniferous sites with the same prevailing tree species as in the polluted area. The area is situated near the Czech–Austrian border. The relatively shallow soil profile is developed on Proterozoic porphyric granodiorites and has been classified as a Haplic Cambisol. More information about the area of low Pb atmospheric input can be found in our earlier work (Chrastný et al., 2012a). The annual precipitations on both localities were similar and ranged between 600 and 700 mm in 2012, with an average temperature of 6–7 °C.

Appropriate sub-samples (both from the polluted area and from the area with a low atmospheric Pb input) were taken to the laboratory in order to determine the basic soil characteristics. Samples were air-dried to constant weight and homogenized. Prior to decomposition, the samples were finely ground in an agate mortar.

The soil pH was measured using a 1:5 (v/v) ratio of soil and water and 1 M KCl solution using an inoLab Level 1 pH meter. We determined total organic carbon (TOC) and dissolved organic carbon (DOC) content by catalytic oxidation (1350 °C) using ELTRA Metalyt CS 500 analyser. Cation exchange capacity (CEC) was computed after saturation of soil samples with 0.1 M $BaCl_2$ and Ba^{2+} release using $MgSO_4$ (ISO 11260:1994). Excess Mg present in the solution was determined using Varian SpectrAA 280FS flame atomic absorption spectrophotometer (FAAS).

The total decomposition of soil samples was achieved under higher temperature and pressure in a mixture of strong acids (HNO_3, HCl, HF) in a microwave unit (MARS5, CEM, USA). In order to obtain the operationally defined fractionation forms of Pb in all soil samples we used the modified BCR sequential extraction procedure (BCR SE) by Quevauviller (2002).

2.2. In-situ experiment

The different Pb migration in highly smelter-impacted soils was studied under natural and laboratory conditions related to different Pb forms (smelter-derived Pb in an *in-situ* experiment and using a Pb-salt in a laboratory column experiment). We implanted the smelter impacted soil horizons *F* + *H* from deciduous and coniferous trees into the same forest soil types in the area of low Pb atmospheric input (coordinates: N48°57.925′; E14°14.568′ and N48°59.732′; E14°10.922′ for the coniferous and deciduous forests, respectively). The experimental field was vertically isolated from the surroundings using polyethylene foil. After isolation, we removed carefully the upper soil horizon *L* from the experimental field. A filtration membrane on the original soil horizons (Table 1) was installed in both deciduous and coniferous forest sites. Both implanted and original soil horizons were then separated using a filtration membrane with a defined porosity (40 μm, polyamide). Well mixed soil horizons with specified amounts were evenly spread (*F* + *H* from the polluted area) on the membrane. The experimental site was then compacted. A map of soil profiles and the implantation procedure is presented in Fig. 1.

We performed the implantation experiment for a period of 6 months. We sampled the implanted (smelter-derived *F* + *H*) and incubated (low Pb atmospheric input *F*, *H*, *A*) soil horizons. All horizons were sampled before and after the incubation period. Soil samples were decomposed to obtain the total Pb concentration and the BCR SE was carried out to describe changes in operationally-defined Pb fractions, before and after the incubation.