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Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy

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Abstract

The concentration trends and chemical fractionation of Pb was studied in eight tilled and forest soil profiles heavily polluted by Pb metallurgy in the Příbram district, Czech Republic. The highest Pb concentrations were observed in surface and subsurface horizons attaining 35 300 mg kg^{-1} in forest soils and 1233 mg kg^{-1} in tilled soils. Total Pb concentrations were one order of magnitude lower in tilled soil due to intensive ploughing and annual crop off-take. The results of the Tessier sequential extraction procedure showed the preferential binding of Pb in forest soils to operationally-defined exchangeable positions and soil organic matter (oxidisable fraction). The Pb exchangeable fraction is thought to correspond to weak electrostatic binding on the functional groups of organic matter. In tilled soil, Pb is predominantly bound to operationally-defined Fe and Mn oxides (reducible fraction). A comparison with the background Pb concentration values showed a strong contamination even in mineral horizons IIC and confirmed a strong vertical mobility of Pb within the soil profiles. The calculated mobility factors (MF) showed that up to 72% of Pb is mobile and bioavailable in forest soils. In contrast, the bioavailability of Pb in tilled soils was significantly lower as the MF accounted for up to 30%. In the most polluted horizon of forest soil profile, the X-ray powder diffraction (XRPD) analysis confirmed the presence of anglesite ($PbSO_4$), derived likely from the smelter emissions.

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1. Introduction

Lead metallurgy is one of the most important sources of Pb pollution in the environment. The impact of base metal smelting on soil contamination is a well-known phenomenon on numerous smelting sites (e.g., Morin et al., 1999; Rieuwerts et al., 1999; Dumat et al., 2001; Kabala and Singh, 2001). The knowledge of bulk concentrations and bioavailability of metals and other inorganic contaminants is essential for an assessment of the risk for the ecosystem, including humans. Lead contamination in the vicinity of primary and secondary smelters is mainly airborne and represents the longest-term pollution effect of metallurgy, especially in agriculturally developed zones.

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Metal ions bound to the solid phase can be mobilised into the solution phase by changes in soil pH, temperature, redox potential, soil organic matter decomposition, leaching and ion exchange and by microbial activity (Kennedy et al., 1997). The nature of metal bonding on individual soil solid phases is commonly studied by sequential extractions although the interpretations of the data obtained are often difficult. Nevertheless, a combination of sequential extraction results with the knowledge of other chemical properties of soil (pH, organic carbon content, sulphur and phosphorus content) helps to determine potential "mobile" fractions of metals in soil, corresponding to forms available for uptake by plants.

This study follows up numerous research projects focused on metal contamination in the vicinity of the secondary Pb smelter in Příbram, Czech Republic (Rieuwerts et al., 1999; Ettler et al., 2001, 2004). The intent of this paper is (i) to determine the differences in Pb concentration profiles in forest and tilled soils according to the prevailing wind directions and subsequent direction of emission movement from the smelter stack, (ii) to understand the effect of tilling, soil type and geological background on Pb concentration and its speciation in soil profiles, and (iii) to estimate possible vertical Pb mobility in soil profiles and bioavailability in individual soil horizons.

These data are the first evidence of detailed chemical fractionation of lead in such extremely contaminated soils and complete previous diagnostics of bulk metal contamination of topsoil layers (Rieuwerts et al., 1999). Together with the Pb isotope approach (Ettler et al., 2004), this study helps to clarify the vertical mobility of Pb in these smelter-impacted soil environments.

2. Materials and methods

2.1. Description of the study area

The district of Příbram located approximately 60 km SW of Prague, the capital of the Czech Republic, has a long history of Ag and Pb mining and smelting. The secondary Pb smelter (49°42.318′ N, 13°58.690′ E) located 4 km NW from the center of Příbram has been in operation for over two centuries. Detailed information on the smelter activity and smelter stack emissions are given elsewhere (Rieuwerts et al., 1999; Ettler et al., 2001). The prevailing winds in the area are mainly NW according to the wind frequency diagrams for years 1971–2000 (Czech Hydrometeorological Institute, 2003). This is in agreement with the highest Pb concentrations in topsoils located SE from the smelter as evidenced by Rieuwerts et al. (1999). The Pb isotopic data showed that the prevailing source of soil contamination in the area has been airborne Pb from smelting emissions (Ettler et al., 2004). Agricultural soils in the studied area are used for cultivation of wheat (*Triticum aestivum* L.), maize (*Zea mays* L.), barley (*Hordeum sativum* L.), rye (*Secale cereale* L.), rape (*Brassica napus oleifera* L.) and horse bean (*Faba vulgaris* Moench.). In the last decade, only nitrogen fertilisers are regularly applied on tilled soils (between 85–115 kg ha^{-1}) without any liming. Wooded areas are mainly afforested by Norway spruce (*Picea abies* (L.) Karst.).

2.2. Soil sampling

Eight soil profiles were sampled on four sampling sites as a function of geological background, distance from the smelter and the prevailing wind directions in the area. The localisation of the profiles is given in Fig. 1. At each sampling site, one forest soil profile and one tilled soil profile were sampled. The distance between two soil profiles on each sampling site was 40 m maximum, both corresponding to the soils developed on the same geological unit. Cambrian geological units (greywackes and conglomerates) corresponded to the geological background of sampling sites 1 and 4 with low Pb concentrations of 6.01 and 2.50 mg kg^{-1}, respectively. Proterozoic volcano-sedimentary complex (metalliferous basalt veins in clastic sediments) corresponded to the geological background of sampling sites 2 and 3 with significantly higher background concentrations of 96.7 and 85.0 mg Pb kg^{-1}, respectively.

Soils were sampled in a 1 × 1-m-wide pit according to the natural development of soil horizons, down to the mineral horizon IIC. The top surface horizon composed of fresh grass cover and fresh litter was removed. The underlying bedrock was sampled under each profile (up to 5 kg of solid rock material). Soil and bedrock samples were stored in polyethylene (PE) bags and treated immediately on returning to the laboratory. According to Soil Taxonomy (Soil Survey Staff, 1999), the studied soils were classified as Inceptisols of soil types Typic or Aquic Dystrudepts.

2.3. Analytical procedure

2.3.1. Sample preparation

A total of 30 soil samples were air-dried in the laboratory to constant weight and sieved through an acid-cleaned polyethylene 2-mm sieve and homogenised by mixing. No other treatment of sample for sequential extraction was applied in order to maintain the field properties of the soil as much as possible (Kennedy et al., 1997). A 20-g aliquot part obtained by quartation on a sample splitter and finely ground in an agate mortar was used for subsequent bulk Pb, organic carbon, S and P analyses. The underlying bedrock was finely ground in an agate mortar and prepared for acid dissolution and subsequent Pb analysis.

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