Mineralogy of lead in a soil developed on a Pb-mineralized sandstone
(Largentière, France)

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ABSTRACT

Lead speciation was determined in a soil developed on a geochemical anomaly arising from a Pb-Zn stratabound deposit in Largentière (Ardèche, France). This geological setting offers the opportunity to determine the preferred form(s) of Pb following soil formation on this unique anomaly. In the soil profile studied, Pb concentrates in the B-horizon (2055 mg/kg Pb) relative to both the A- (1330 mg/kg Pb) and C- (1874 mg/kg Pb) horizons. Plumbogummite (PbAl3(PO4)2(OH)5·H2O) is the main host of Pb in the soil profile. Pb also appears to be associated with Mn-(hydr)oxides, as shown by micro-analyses (EMPA, SEM-EDS, and µ-SXRF), in the form of inner-sphere Pb2+ complexes, as suggested by Pb LIII-edge EXAFS spectroscopy. Linear least-squares fitting of background-subtracted, k3-weighted Pb LIII-edge EXAFS functions derived from bulk soil samples was carried out using Pb LIII-EXAFS spectra of 22 Pb-containing model compounds. Quantitative assessment of Pb speciation revealed that, whereas plumbogummite is the most abundant Pb phase in the soil profile, Pb2+-Mn-(hydr)oxide surface complexes are gradually replaced by Pb2+-surface complexes with other phases, possibly Pb2+-organic complexes, upward in the soil profile. The presence of large amounts of Pb-phosphate in the Largentière soil suggests that low solubility phosphates may be important long-term hosts of Pb in Pb-contaminated soils that have sufficiently high phosphorous activities to cause formation of these phases.

INTRODUCTION

Lead is a widespread pollutant often associated with airborne deposition from automobile exhaust and smelting operations. Once deposited in soils, this element can accumulate for hundreds of years and represents a potential environmental risk (Nriagu 1979; Fergusson 1991; Ross 1994). This accumulation in topsoil horizons can result either from surface reactions (adsorption or precipitation) with soil components (e.g., Fe-Mn-(hydr)oxides, organic matter, clay minerals) (see e.g., Morin et al. 1999) or precipitation of Pb-bearing secondary minerals such as pyromorphite (see e.g., Cotter-Howells et al. 1994). A knowledge of Pb speciation (i.e., its chemical form at the molecular level) in soils is key to understanding and predicting its behavior and fate at the Earth’s surface.

Many laboratory experiments involving batch uptake have demonstrated the strong affinity of Pb2+ for both Fe- and Mn-(hydr)oxides (Kinniburgh et al. 1976; McKenzie 1980; Roe et al. 1991; Manseau et al. 1992; Bargar et al. 1997, 1998) and organic matter (Schnitzer and Skinner 1967; Xia et al. 1997), but few of these experiments have focused on competitive effects between these two substrates. In contrast, in-situ studies using selective extractions (Bergkvist et al. 1989; Chlopecka 1996) or Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy have shown that Pb-organic matter complexes mainly control the mobility of this element in organic-rich Pb-contaminated topsoils, whereas Pb2+ sorption onto Fe- and Mn-(hydr)oxides dominates when the organic content is low (Manseau et al. 1996; Juillot 1998; Morin et al. 1999).

In-situ studies of Pb-contaminated soils (Davis et al. 1993; Cotter-Howells et al. 1994; Ruby et al. 1994; Juillot 1998) provide evidence that precipitation of secondary Pb phosphate minerals, mainly from the pyromorphite family (Pb,Ca)5(PO4)3(OH,Cl,F) is an important sequestration mechanism for Pb2+. In-situ immobilization of Pb in Pb-contaminated soils resulting from the formation of low solubility Pb-phosphates is supported by thermodynamic data (Nriagu 1979, 1984a; Lindsay 1979), and has been successfully demonstrated in laboratory experiments (Ma et al. 1993; Cotter-Howells and Caporn 1996; Laperche et al. 1996, 1997; Cotter-Howells et al. 1999). However, the question arises whether the mechanisms that control Pb mobility in laboratory experiments or in soils contaminated during historical times also describe the environmental behavior of Pb during the long-term evolution of a soil.

Here the molecular-level speciation of Pb has been investigated in a naturally enriched soil that exhibits Pb concentration similar to those encountered in smelter-impacted soils or...