

Occurrence of Zn/Al hydrotalcite in smelter-impacted soils from northern France: Evidence from EXAFS spectroscopy and chemical extractions

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ABSTRACT

Zinc speciation was studied by EXAFS spectroscopy, μ -SXRF elemental mapping, XRD, and chemical extraction methods in two smelter-impacted soils sampled near one of the largest Pb and Zn processing plants in Europe, which is located in northern France about 50 km south of Lille. The tilled and wooded soils chosen for study differ in Zn concentration (\approx 600 and 1400 mg/kg, respectively), soil pH (7.5 and 5.5, respectively), and organic matter content (1.5 and 6.4 wt% TOC, respectively). In both soils, the occurrence of Fe- and Zn-rich (up to 10 wt% Zn) slag particles ranging in size from a few micrometers to a few millimeters, was shown by μ -SXRF elemental mapping of soil thin sections as well as by SEM and chemical analysis of different soil size fractions. For both soils, XRD analysis of the dense coarse fraction, which contains up to 10 wt% Zn, revealed the presence of a minor amount (1–1.5 wt%) of crystalline ZnS (sphalerite and wurtzite). In this fraction, EXAFS data show that Zn is mainly incorporated in the tetrahedral sites of a magnetite-franklinite solid solution.

The clay fraction ($<2 \mu\text{m}$) represents the largest pool of Zn in both soils, with 77 and 62% of the total Zn in the tilled and wooded soils, respectively. However, XRD was not able to detect any Zn-bearing phases in this fraction. Comparison of Zn *K*-EXAFS data of untreated and chemically treated samples from the bulk ($<2 \text{mm}$) and the clay ($<2 \mu\text{m}$) soil fractions with Zn *K*-EXAFS data from more than 30 model compounds suggests that Zn is present in the following chemical forms: (1) Zn outer-sphere complexes, (2) Zn-organic matter inner-sphere complexes, (3) Zn/Al-hydrotalcite (Zn/Al-HTLC), (4) phyllosilicates in which Zn is present in the dioctahedral layer at dilute levels, and (5) magnetite-franklinite solid solutions inherited from the smelting process. The presence of exchangeable Zn outer-sphere complexes and of Zn inner-sphere complexes on organic matter is indicated by the relative increase of second-neighbor contributions in the EXAFS RDFs after chemical treatments with 0.01 *M* CaCl₂ and 0.1 *M* Na₄P₂O₇. The occurrence of Zn/Al-HTLC is demonstrated by the persistence of a Zn-Zn pair correlation at $3.10 \pm 0.04 \text{ \AA}$ (i.e., edge sharing ZnO₆ octahedra in the trioctahedral layer structure) in EXAFS data of Na₄P₂O₇ treated soil samples and its disappearance after treatment with 0.45 *M* HNO₃. This latter treatment also revealed the occurrence of Zn-bearing phyllosilicate minerals, as shown by two Zn-Mg/Al/Si pair correlations at $3.05 \pm 0.04 \text{ \AA}$ and $3.26 \pm 0.04 \text{ \AA}$, and of magnetite-franklinite solid solutions, as indicated by a Zn-Mn/Fe/Zn pair correlation at $3.50 \pm 0.04 \text{ \AA}$. Significant changes in the relative proportions of the different forms of Zn between the two soils explain their different responses to chemical treatments and emphasizes the relationships between solid state speciation and mobility of Zn in soils.