Zn speciation in a soil contaminated by the deposition of a dredged sediment by synchrotron X-ray techniques

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Abstract: The nature and proportion of Zn species present in an agricultural soil overlaid by a dredged contaminated sediment have been untangled by the novel combination of three non-invasive synchrotron-based x-ray techniques: x-ray microfluorescence (μSXRF), microdiffraction (μXRD), and absorption spectroscopy (EXAFS). One primary (franklinite) and two secondary (phyllomanganate and phyllosilicate) Zn-containing minerals were identified in the initial soil, and another primary (ZnS) and a new secondary (Fe-(oxyhydr)oxide) Zn species in the covered soil. The quantitative analysis of EXAFS spectra recorded on bulk samples indicated that ZnS and Zn-Fe (oxyhydr)oxides amounted to 71±10% and 27±10%, respectively, and the other Zn species to less than 10%. The two new Zn species found in the covered soil result from the gravitational migration of ZnS particles initially present in the sediment, and from their further oxidative dissolution and fixation of leached Zn on Fe (oxyhydr)oxides.

1. INTRODUCTION

Dredging operations carried out to maintain the depth of navigational units worldwide generate high volume of sediments, which are generally deposited on soils along banks. In industrialized regions, these sediments are contaminated with heavy metals, and consequently, these deposits constitute an important source of pollutants for the surrounding environment, and specifically the underlying soil. Since metals solubility and mobility are predominantly controlled by their interactions with soil constituents, the knowledge of the molecular form of metals in solid phases is a key issue to assess the chemical risk and predict the effect of a variation of physico-chemical parameters on the fate of metals. Among the methods available to determine the speciation of metals in the solid phase of soils, x-ray absorption spectroscopy (EXAFS) is arguably the most efficient [1]. However, the existence of multiple species is a real limitation, and this drawback is generally overcome by fractionating the soil to reduce its heterogeneity in isolating or removing some metal species [2, 3]. Still, this approach is not fully satisfying because it has been found that chemical and physical treatments can cause artefacts in modifying the very chemistry one is trying to probe [4]. In this work, we used the new combination of three synchrotron-based x-ray techniques, i.e., x-ray microfluorescence (μSXRF), microdiffraction (μXRD), and absorption spectroscopy (μEXAFS and bulk EXAFS), as discussed by Manceau, et. al. [5], to speciate Zn in a soil impacted by the deposition of a dredged sediment. μSXRF was used to map the distribution of elements, μXRD enabled the identification of nanoscale particles, and μEXAFS allowed one to identify the mechanism of metal binding by the host phases (i.e., identify metal species). Then, the proportion of each metal species in the bulk was determined by analyzing the unknown multicomponent bulk EXAFS spectrum as a linear combination of component spectra corresponding to single metal species.

2. MATERIALS AND METHODS

Forty cubic meters of a sediment were dredged nearby a Zn smelter in Northern France ([Zn] = 6600 ppm), and deposited as a 40 cm thick layer on a non-polluted agricultural soil in July 1997. Originally, Zn was mainly speciated as ZnS and Zn-Fe (oxyhydr)oxides [2]. After 15 months of deposition, the Zn

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content amounted to 260 ppm in the < 50 μm fraction of the underlying soil compared to a geochemical background of 50 ppm. The < 50 μm fraction represented 90% of the mass of the soil and was considered as representative of the bulk soil. The < 0.2 μm fine fractions of the initial and affected soil were also extracted for powder and polarized-EXAFS (P-EXAFS) measurements. Finally, impregnated 30 μm-thick thin sections of the unperturbed soil before and after treatment were prepared for x-ray microscopic investigations.

μSXRF and μEXAFS measurements were performed on beamline 10.3.2 at the Advanced Light Source (ALS, Berkeley, USA), μXRD on beamline 7.3.3 at the ALS, and P-EXAFS and bulk EXAFS on beamline FAME at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Fe, Mn and Zn μSRXF maps were obtained by scanning thin-sections with a beam size of 16μm x 5μm while recording the x-ray fluorescence with a 7-element Ge solid-state detector. Zn-K edge μEXAFS spectra were then collected in fluorescence mode on various regions-of-interests. Point μXRD patterns were collected on the same thin-sections using a CCD camera [5]. Fluorescence-yield Zn K-edge P-EXAFS measurements were carried out on self-supporting films from the <0.2 μm fraction at incident angles between the electric field vector and the film plane of $\alpha = 0°$, 35° and 80° [6], and bulk EXAFS measurements were performed on pressed pellets from the <50 μm soil fraction. EXAFS spectra were compared to Zn-reference EXAFS spectra and least-squares fitted with linear combination of references. The fit criterion was estimated by $R= \Sigma|(k^3\chi_{exp}-k^3\chi_{model})| / \Sigma|k^3\chi_{exp}|$ and the addition of a new component was considered meaningful if the R decrease amounted to at least 20%.

3. RESULTS AND DISCUSSION

3.1 Speciation of Zn in the uncontaminated soil before the deposition of the sediment

3.1.1 μSXRF and μXRD

Several regions were examined by μSXRF and the mineralogy and crystal chemistry of Zn is completely represented by the region presented in Figure 1. This map shows that the soil is highly heterogeneous at the micrometer scale, containing distinct areas of concentrated Fe, Mn, and Zn. Three Zn species could be inferred from this analysis: Zn in association with Mn, Zn in grains ('hot spots'), and Zn in diffuse concentration throughout the fine matrix.

Figure 1. Gray-scale μSXRF maps in negative contrast showing the distribution of Fe, Mn and Zn in the uncontaminated soil. The Fe and Mn maps were collected at 10 keV, and the Zn map was obtained by subtracting the normalized fluorescence signal recorded 50 eV above and below the Zn K-edge to eliminate any noise. Beam size: 16μm x 5μm; step sized: 20μm x 20μm; dwell time: 400 ms/point.

In addition to minerals classically encountered in soils, such as quartz, calcite, microcline, albite, and dioctahedral phyllosilicates, μXRD identified vernadite (δMnO_2), a randomly-stacked phyllomanganate, in Mn-rich areas, and poorly-crystalline Fe (oxyhydr)oxides (likely feroxyhite, $\delta FeOOH$) in Fe-rich areas. No Zn precipitates were detected.

3.1.2 μEXAFS, P-EXAFS and bulk EXAFS spectroscopy

Zn-sorbed birnessite and franklinite ($ZnFe_2O_4$) were firmly identified by μEXAFS spectroscopy in Mn-rich areas and Zn hot spots (Fig. 2). The presence of Zn layered compounds in the fine matrix was established by P-EXAFS, which showed a strong angular dependence of the measured signal with α

angle. The $\alpha=35°$ P-EXAFS spectrum (i.e., powder spectrum) was correctly fitted with Zn-kerolite, a trioctraedral smectite used as proxy for Zn-containing phyllosilicate (Fig. 2c). The frequency and amplitude of the EXAFS spectrum for the <50 µm fraction resembles the <0.2 µm fraction (Fig. 2d), and the spectral simulation with two components (Zn-kerolite + Zn-sorbed birnessite or franklinite) did not result in a better spectral match. This analysis indicates that Zn is overwhelmingly speciated as phyllosilicate in the bulk uncontaminated soil and, hence, that franklinite and Zn-birnessite are minor species.
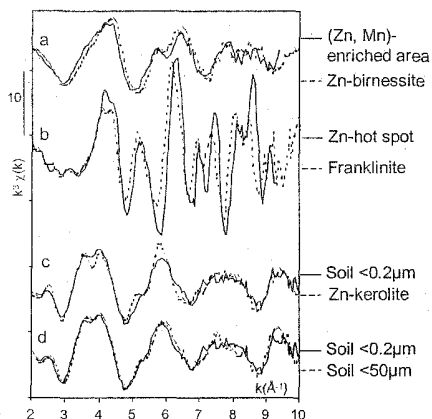

Figure 2: Uncontaminated soil before the deposition of the dredged sediment. (a,b) Zn K-edge µEXAFS spectra collected in selected points; (c) $\alpha=35°$P-EXAFS spectrum collected on the <0.2µm fraction compared to Zn-kerolite, (d) $\alpha=35°$P-EXAFS spectrum for the <0.2µm fraction compared to the EXAFS spectrum for the <50µm fraction.

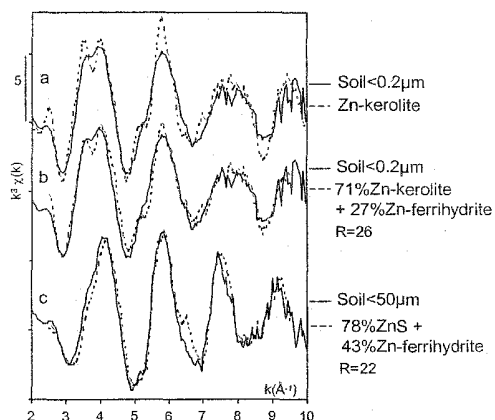**Figure 4**: Soil contaminated after the deposition of dredged sediment. (a) Zn K-edge $\alpha=35°$P-EXAFS spectrum collected on the <0.2µm fraction compared to Zn-kerolite, (b) two-component fit of the <0.2µm fraction, (c) two-component fit of the <50µm fraction.

3.2 Speciation of Zn in the soil contaminated after the deposition of sediment

3.2.1 µSXRF and µXRD

The element map presented in Figure 3 shows the occurrence of a Zn-containing slag (~1500 µm sized) in the upper left side of the mapped area. Similar coarse anthropogenic debris were observed in the sediment [2], and their presence in the underlying soil results from gravitational transfer. Four Zn forms or associations are visible on this map: Zn on the rim of the slag material, Zn bound to Mn in individual grains, Zn-rich grains, and Zn and Fe throughout the fine soil matrix.
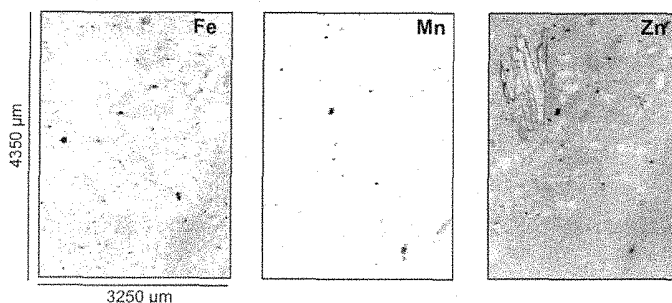

Figure 3. Gray-scale µSXRF maps in negative contrast showing the distribution of Fe, Mn and Zn in the soil contaminated after the deposition of the sediment. Elemental maps were collected at 10 keV. Since the concentration of Zn in this sample is high, the noise level of the Zn map is very low and all shaded areas indicate the presence of Zn. Beam size: 16µm x 5µm; step sized: 20µm x 15 µm; dwell time: 600 ms/point.

µXRD patterns recorded on the Mn grains identified vernadite. In the soil matrix, diffraction peaks from vernadite decreased while those of ferrihydrite and/or feroxyhite were detected systematically. No Zn precipitates or Zn-containing primary minerals were identified by this technique.

3.2.2 µEXAFS, P-EXAFS and bulk EXAFS spectroscopy

µEXAFS spectra collected on individual Fe and Mn grains allowed the identification of franklinite and Zn-phyllomanganate, as in the initial soil, and kerolite-like Zn-phyllosilicate was also detected by P-EXAFS spectroscopy (Fig. 4a). However, in contrast to the initial soil, a good match for the <0.2 µm spectrum required the addition of two-component spectra, Zn-kerolite and Zn-sorbed ferrihydrite in proportion of 71±10% and 27±10%, respectively (Fig. 4b). The EXAFS signal from the bulk soil was satisfactorily reconstructed by a mixture consisting of 78±10% ZnS and 43±10% Zn-sorbed ferrihydrite (Fig. 4c), indicating that the Zn-phyllosilicate and Zn-birnessite species are not quantitatively of paramount importance in the Zn-affected soil. This finding stands in strong contrast with results from the initial soil, and can be rationalized by the per descensum migration of ZnS slag material from the sediment and the sorption of Zn released by the oxidative dissolution of sphalerite on poorly crystallized Fe (oxyhydr)oxides.

4. CONCLUSION

Zn speciation in a soil contaminated by the deposition of a Zn-containing dredged sediment was successfully determined and quantified by collectively applying x-ray fluorescence, diffraction, and absorption. In the untreated soil, Zn is predominantly speciated as phyllosilicate, and secondarily as phyllomanganate and franklinite. In the treated soil, Zn is mainly present as sphalerite and Zn-Fe (oxyhydr)oxides, and to a lesser extent as Zn-phyllosilicate, Zn-phyllomanganate, and franklinite. ZnS grains originate from the sediment, and their oxidative weathering is responsible for the leaching and fixation of Zn on Fe (oxyhydr)oxides. This work illustrates the potential of the complementary use of µSXRF, µXRD and µEXAFS techniques as a quantitative analytical tool for speciation of dilute multi-component environmental materials not easily attainable with conventional methods.

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