Assessment of Zn bioavailability: XAFS study on speciation of zinc-particulate organic matter associations in polluted soils

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Abstract. We present a study about the behavior of Zn in agricultural soils polluted 100-50 years ago by metallurgical fallout and used nowadays for corn production. Such type of soil concerns an area of several km² around former metallurgical complex in Northern France. Despite the moderated metal amounts of these soils, the metals deposited over the agricultural area still indirectly expose nowadays populations through the food chain. In contrast to the most contaminated industrial site, these more distant agricultural areas have been less studied. The study was focused on Zn, a relative mobile metal element, since its predominant occurrence in the surface horizon of sandy textured soils, fifty years after cessation of metallurgical activity suggests its immobilization due to specific soil mechanisms. To evaluate how Zn is associated to POM, Zn K-edge XAFS spectra were collected at 293 K at the SLS on beamlines superXAS and microXAS, using Si(111) monochromators and solid state Ge detectors. Energetic resolution is ca. 2 eV at 9 KeV. Lateral resolution varied from ca. 1 mm² to 15 micron². Spectra were normalized with the XAFS 3.0 software. We studied different POM size fractions isolated from soils. The largest POM particles correspond to recent leaves or roots fragments. The finest POM particles correspond to decomposition by-products. The results revealed a multiple and heterogeneous speciation of Zn with POM. We observed that little interactions from next-nearest neighbors around Zn. We concluded that most of the Zn tends to be located in the POM matrix as a Zn-organic speciation. We also collected macroscopic EXAFS data on selected intact POM particles probed at the micron scale. The results show that the remaining Zn-distribution related to inorganic (hot-spots), possibly franklinite-type, is minor compared to the Zn-organic speciation. Such observations will help to better understand the mechanisms that regulate the bioavailability and immobilization of Zn in polluted soils.

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1. Introduction
At the beginning of the 20th century, a number of metal smelters were active in northern France, generating broad atmospheric metalliferous fallout. Emitted dust particles sized from a few to several tenth of micrometers [1]. Nowadays, pollution generated by metallurgical activity widely decreased but soils are effective sinks for heavy metals released by industrial pollution, leading to their predominant accumulation in surface horizons, but also their migration toward depth. In contrast to many studies on highly polluted industrial sites, the fate of metal pollution in less contaminated soils of agrosystems surrounding metal smelters remains poorly documented. Studies on interactions between soil constituents and heavy metals at different study scales are essential for an increased understanding of the fate and impacts of metal pollutants in these soils. Physical fractionation experiments on soil samples collected in the vicinity of a former metal smelter highlighted the particular affinity of particulate organic matter (POM) for heavy metals [2]. This organic matter pool has a rapid turnover in soils and knowledge on metal speciation in POM particles is important for assessing environmental risk regarding metal mobility and bioavailability. Labanowski et al. [3] observed that metals on finer POM were little leachable by chemical treatment (e.g. extraction with EDTA), suggesting different mechanisms for POM-metal associations that control bioavailability.

This work aimed at understanding and giving direct evidence for the association of metals and POM by using synchrotron light source radiation techniques. For this, we selected undisturbed samples from the surface horizon of an agricultural soil under arable land use, near a former industrial complex. POM particles were isolated from the soil samples by physical fractionation in water and then studied at micro and macro scale with the X05 and superXAFS beamlines, respectively, at Swiss Light Source (SLS).

![Figure 1](image1.png)

**Figure 1:** Zn Kα μXRF mapping (10 keV; beam size was 20x20 μm; X05; X and Y scale in 10⁻¹ mm) of several POM particles (A, B, C and D samples above) selected from the horizon soil contaminated

![Figure 2](image2.png)

**Figure 2:** Zn K-edge μ-XANES spectra (X05) for various spots collected in the map shown on Figure 1

2. Samples and methods
We studied Zn speciation in several samples of crushed POM representative of 4 size fractions: 2000-200 μm (991 ppm Zn), 200-100 μm (1338 ppm Zn), 100-50 μm (1330 ppm Zn), and 50-20 μm (1483 ppm Zn). Theses fractions are called V200, V100, V50, and V20 respectively. The largest POM particles correspond to recent leaves or roots fragments, whereas the finest POM corresponds to decomposition by-products from microbiological activity. The soil clay fraction was also isolated. Non-crushed POM fragments 200-100-μm size fraction (POM100) was also studied. The V20 fraction was also analyzed after treatment by EDTA (0.05 M; pH=6). Because of the complexity of Zn speciation in the studied soils, EXAFS data from several synthetic and natural model compounds were used to help interpret EXAFS data. We used bulk and micro-XAFS techniques to evaluate whether the metals are associated to POM. XAFS experiments were conducted at 293 K at the SLS on beamlines.
Such clay fractions. They reported 56-65% Zn-kerolite [Si
4
(\text{Zn}^\text{wurtzite (not shown).}

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POM-100 (Figure 3k) has a CCWT close to that for sphalerite and on the speciation of Zn for the V20 fraction. If POM-200 is close to that for polymerized organics finely divided Zn/Fe spinel minerals. Also, EDTA treatment (see Figures 3h and i) has a small effect reporting the presence of Zn-bearing clays, Zn/Al-hydrotalcite acting as precursors for clay minerals and 0.008 molar ratio or Zn-substituted goethite, or Zn-sorbed ferrihydrite. In contrast, Juillot sorbed birnessite Zn/Mn = 0.126 molar ratio and 14-18% of either Zn-sorbed birnessite with Zn/Mn = 0.008 molar ratio or Zn-substituted goethite, or Zn-sorbed ferrihydrite. In contrast, Juillot et al. [10] previously characterized such clay fractions. They reported 56-65% Zn-kerolite [Si₄(Mg₁₉Zn₁₉)O₁₇(OH)₂nH₂O], 21-26% Zn-sorbed birnessite Zn/Mn = 0.126 molar ratio and 14-18% of either Zn-sorbed birnessite with Zn/Mn = 0.008 molar ratio or Zn-substituted goethite, or Zn-sorbed ferrihydrite. In contrast, Juillot et al. [10] report the presence of Zn-bearing clays, Zn/Al-hydrotalcite acting as precursors for clay minerals and finely divided Zn/Fe spinel minerals. Also, EDTA treatment (see Figures 3h and i) has a small effect on the speciation of Zn for the V20 fraction. If POM-200 is close to that for polymerized organics (stearate) (Figures 3j and b), POM-100 (Figure 3k) has a CCWT close to that for sphalerite and wurtzite (not shown).

3. Results

Exhaustive mineralogical and geochemical study on the industrial site [6] showed that the dominant forms of emitted metals were sulphides (sphalerite, ZnS; galena, PbS), highly unstable in alternating wet and dry soil conditions. Other minerals have been identified in dense soil fractions using XRD and powder EXAFS [7], such as franklinite (ZnFe₂O₄), willemite (Zn₂SiO₄), hemimorphite (Zn₅Si₄O₁₁(OH)₂H₂O). Zn seems to be also associated with secondary zinc minerals (i.e., hydrozincite, scholzite; that was not produced by the atmospheric fall-out from the factory). A possible explanation is Zn precipitation by inorganic ligands (hydroxyl and carbonate) at the surface of the POM particles.

Figure 1 shows a typical µXRF map collected at 10 keV on various isolated POM particles fractions; whereas Figure 2 shows typical Zn K-edge μXANES collected for different samples. They all are rather similar and only the XANES region shows weak but noticeable differences. Hence, a thorough XANES analysis is needed, based on trends imposed by a large corpus of XANES spectra collected for model compounds of Zn and ab-initio Zn K-edge XANES calculations (FEFF 8.4) [8] of those models, to unravel the respective importance of (single-scattering) SS and multiple-scattering (MS) contributions to the XANES region and their structural origins. For instance, the CCWT diagrams for Zn-organic model compounds show well-distinct features while their FT’s are nearly identical. Those structural differences, only visible in the XANES region, are related to the polymerization of organic carbon molecules around Zn visible on the CCWT (see Figures 3a,b). On the other hand, zincsilite (a Zn-smectite from its type locality in Russia) and aqueous Zn also show distinct CCWT diagrams, with a more ordered-, and a less ordered medium range environment, respectively. Ab-initio XANES calculations for those models show that MS signals arising from ZnO₆ structure are not negligible but they are not dominant at low k-values as compared to SS signals arising from the medium range environment of Zn (as in smectite or Zn-organics).

Performing the CCWT analysis of the XANES spectra collected on V200, V100, V50, V20 and V20EDTA samples, suggests that the samples are loosing SS signals related to signals ascribed to organic ligands (lesser polymerized on the average, as in Zn-acetate) with a decreasing average size of POM particles. By contrast, the contributions arising from the medium range environment of Zn around structures are not negligible but they are not dominant at low k-values as compared to SS signals arising from the medium range environment of Zn (as in smectite or Zn-organics).

SUPERXAFS and X05, using Si(111) monochromators and solid State Ge detectors. Energetic resolution is ~2 eV at 9 KeV. Lateral resolution varied from ~1 mm² to 15 μm². Spectra were normalized from k=0 using standard methods (XAFS 3 package) [4].

X-ray absorption fine structure (XAFS) spectroscopy (including XANES and EXAFS regions) is a powerful tool for investigating the short-, and medium-range environment around a selected absorbing atom. Usually, Fourier transform (FT) methods are used to obtain a frequency decomposition of the normalized EXAFS signal. However, FT analyses only provide a one-dimensional decomposition in the direct space (interatomic distances uncorrected for phase-shifts) of the EXAFS data, highly affected by the low-k cutoff, which removes a lot of important structural information, particularly that arising from weakly backscattering next-nearest neighbors in disordered systems as is the case with our samples. To compensate for both limitations, we present Cauchy Continuous Wavelet Transform (CCWT) analyses of the XANES spectra [5], providing a more accurate 3D description of the local structure around Zn (figures automatically generated by computation using Matlab).
4. Discussion

Some impacts of coating of POM with granulometric soil clay fraction (<2 μm) can be suspected. Complementary micromorphological work in the studied soils showed a particle distribution pattern with fine material covering coarse quartz and POM particles. Such information is consistent with our findings on the presence of clays on POM surfaces. Such fine matrix coatings often are composed of a mixture of very fine quartz, clays, and organic matter. Previous XAFS experiments carried out on a soil in the same area [7] have also shown that coatings on quartz grains contained large amount of heavy metals. The present study highlights the diversity of the Zn-POM associations pointing to different Zn speciation with POM, such as Zn-organic, and ZnS. But, POM particles isolated by fractionation procedure may contain some impurities. Hence, the study of Zn speciation on POM particles may reveal association of Zn with others particles (e.g. clay minerals) intimately stacked on POM particles. That variation in speciation probably controls the bioavailability of Zn in soils.

![CCWT diagrams for Zn K-edge XANES spectra](image)

**Figure 3:** CCWT diagrams for Zn K-edge XANES spectra of (a) zinc acetate, (b) zinc stearate, (c) zincsilite (Zn-smectite), (d) aqueous zinc, (e) V200, (f) V100, (g) V50, (h) V20, (i) V20, EDTA treated, (j) POM 200, (k) POM 100 (identical to ZnS) and (l) the soil clay fraction (<2 μm). Colormap ranges from dark blue (0) to red (max. of CCWT modulus for each normalized XANES spectrum).

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