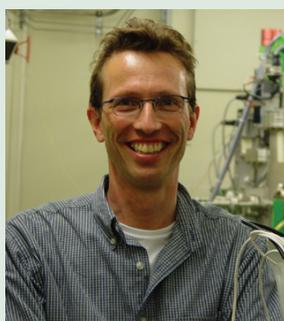


Chemical Forms of Zinc in a Smelter-Contaminated Soil

A.C. Scheinost¹, R. Kretzschmar², S. Pfister², D.R. Roberts³, and D.L. Sparks⁴

¹ROBL, European Synchrotron Radiation Facility, France; ²Institute of Terrestrial Ecology, ETH Zurich, Switzerland; ³Department of Physics, University of Ottawa, Canada; ⁴Department of Plant and Soil Sciences, University of Delaware

Zinc is contained in many objects of our daily life, from baby care products to anti-corrosive coatings of cars. Concomitant of its frequent use, zinc is released into the environment and accumulates in soils. While zinc is benign to human health, it is phytotoxic at relatively modest concentrations, thereby reducing plant growth. In spite of its importance, relatively little is known on the chemistry of zinc in soils. We have used a combination of microscopic, spectroscopic, wet chemistry, and chemometric tools to investigate the chemical forms of zinc in a strongly acidic soil near the historic zinc smelter at Palmerton, Pennsylvania.



Andreas Scheinost

Due to the burning of coal and other fossil fuels, zinc ore smelting and processing, and the application of sewage sludge and agrochemicals, soils are increasingly contaminated with zinc. In Switzerland, and most likely also in other industrialized countries, zinc concentrations in soils may soon reach levels which could significantly reduce the production of food, fiber, and renewable energy sources. The problem of such predictions is, however, that the toxicity of plants for zinc, called phytotoxicity, in a given soil cannot be simply predicted from its concentration. For instance, aqueous zinc cations in soil solution are readily taken up by plant roots and are therefore very phytotoxic, while the incorporation of zinc into the crystal structure of recalcitrant (i.e. very insoluble) soil minerals may drastically reduce its solubility and hence phytotoxicity. Knowing the chemical forms of zinc is therefore a prerequisite for risk assessments and the development of effective remediation strategies.

Previous investigations have shown that Zn-bearing soil clay minerals, called phyllosilicates, may form after raising the soil pH to neutral values. Consequently, the bare soils in the vicinity of a zinc smelter in France could be re-vegetated by applications of lime and fly ash. On the other hand, a similar approach to remediate the Palmerton Superfund Site in Pennsylvania largely failed (**Figure 1**). The intention of our work was to determine the specific problems of this site by determining the chemical forms of zinc in a soil profile.

The zinc speciation was based on extended x-ray fine-structure absorption (EXAFS) spectroscopy performed at beamline X11A. While EXAFS is perhaps the only tool capable of identifying the various species possibly present in soils, it was complemented by additional methods to achieve unequivocal results. First, we made use of the non-homogeneous distribution of species at the micrometer scale, employing micro-focused x-rays for elemental mapping and microspectroscopy. Second, we made use of the different solubilities of species with respect to various solvents. We employed a sequence of six wet-chemical extraction procedures for a step-wise removal of increasingly recalcitrant species, while monitoring the remaining species with EXAFS spectroscopy. Third, we used statistical methods like principal component

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Contact information

Andreas Scheinost, ROBL, European Synchrotron Radiation Facility, France

Email: scheinost@esrf.fr

analysis to extract the single components hidden in the experimental spectra of species mixtures.

Our results are summarized in **Figures 2** and **3**. In the topsoil with an extremely acidic pH of 3.1, most zinc atoms occur in franklinite, a zinc-iron oxide spinel-type mineral (**Figure 2**). Zinc sulfide (the mineral sphalerite) constitutes the second largest fraction. Divalent zinc cations dissolved in the soil water or exchangeably bound to clay minerals are the smallest fraction. The topsoil contains 6200 mg kg^{-1} zinc, however, this easily plant-available fraction still constitutes 620 mg kg^{-1} , a definitively phytotoxic concentration.

Both franklinite and sphalerite were part of the zinc ores smelted in the Palmerton furnaces. The deposition of these minerals by smelter-emitted dust initiated the geochemical cycle of zinc in the surrounding soils. While franklinite has a low solubility, sphalerite dissolves in the presence of oxygen releasing sulfuric acid. This ongoing release of protons explains the difficulty of raising the soil pH for longer than just a few years by applying lime and fly ash.

In the subsoil, the zinc concentration is lower (900 mg kg^{-1}). Due to the protective cover of the topsoil, no smelter-emitted minerals are present. Since the pH is still quite acidic (3.9), relatively stable inner-sphere sorption complexes and known zinc-bearing soil minerals cannot form. Therefore, we would have expected that all zinc is dissolved or easily exchangeable. Surprisingly, however, we found that 45% of zinc was bound by Al-hydroxide interlayers sandwiched between phyllosilicate layers (**Figure 3**). This clay mineral (HIM) is quite common in acidic soils, and may effectively scavenge a range of transition metals at low pH, thereby reducing their ecotoxicity.

Additional Publication:

D.R. Roberts et al., "Zn Speciation in a Smelter-Contaminated Soil Profile using Bulk and Micro-Spectroscopic Techniques," *Environ. Sci. Technol.*, 36, 1742 (2002).



Figure 1. Blue Ridge Mountains near Palmerton PA. What looks like a desert now was a lush green deciduous forest before the smelter operation began. Although the emissions were drastically reduced several decades ago, soil infertility still prevents re-vegetation.

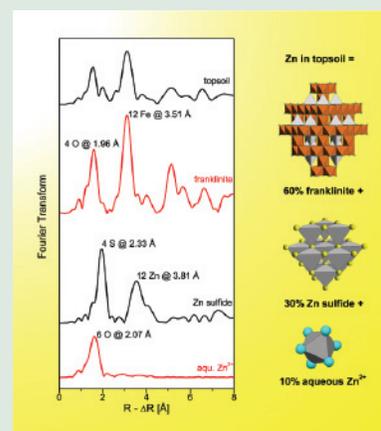


Figure 2. Zn speciation of topsoil sample. The graph on the left shows the Zn K-edge EXAFS spectra of the soil sample together with the spectra of the identified zinc species. The structure of the species and their quantity is given at the right.

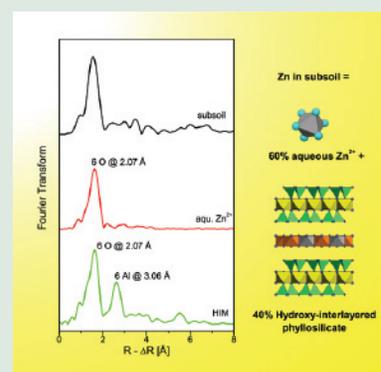


Figure 3. Zn speciation of subsoil sample (see Figure 2 for further explanations).