



Arsenic and zinc in a contaminated wetland soil: Chemical speciation and distribution between soil matrix and rhizosphere

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Riparian wetland soils throughout Europe have been contaminated from the emissions of mining and smelting, industry, and sewage runoff. Soil flooding and fluctuations in the water table cause regular changes between oxidizing and reducing conditions. However, even under reducing conditions, plants may transport air into their roots, thereby causing locally oxic conditions in the rhizosphere. Gradients in the redox status between the rhizosphere and the surrounding soil matrix lead to the enrichment of Fe-oxides around roots and may also strongly influence the sequestration of contaminants and consequently their mobility and bioavailability in wetland soils.

In this study, the distribution of As and Zn between the rhizosphere and the soil matrix of a highly contaminated wetland soil from the Mulde river (Bitterfeld, Saxony-Anhalt, Germany) has been studied by μ -X-ray fluorescence spectroscopy (μ -XRF) on soil thin sections. Microspectroscopic results and additional data on manually separated rhizosphere and matrix soil indicate that the major fraction of total As in the soil is sequestered into the oxidized rhizosphere, where also Fe-oxides are markedly enriched (2500 mg/kg As and 77 g/kg Fe in rhizosphere, 100 mg/kg As and 22 g/kg Fe in matrix, 270 mg/kg As and 27 g/kg Fe in total soil). As K-edge extended X-ray absorption fine structure (EXAFS) spectra collected on soil thin sections and on powdered bulk soil samples confirm that most As in the soil is bound to amorphous Fe-oxides in the rhizosphere as oxidized As(V). Reducing conditions in the soil matrix during soil flooding are expected to cause the dissolution of iron oxides and the reduction of As(V) to the more mobile As(III). Oxidation of Fe(II) and As(III) in the oxygenated rhizosphere then may lead to the observed As enrichment in the vicinity of roots. Zn

is found to be less enriched in the soil rhizosphere than As (740 mg/kg Zn in rhizosphere, 470 mg/kg Zn in matrix and total soil). Zn K-edge EXAFS spectra suggest that the major fraction of Zn is contained in layered Zn-bearing phases (Zn-phyllsilicate, Zn in the gibbsitic sheets of Al-hydroxy interlayered clay minerals or lithiophorite). Thus, only a minor fraction of the total Zn is susceptible to spatial redistribution due to redox gradients in the soil. Our results show that in the studied wetland soil, As was mostly contained in Fe(hydr)oxides in the rhizosphere. The effects of As enrichment in the rhizosphere on the leaching of As from flooded wetland soils and on the availability of As for uptake by plants need to be addressed in more detail.