

Changes in Zn speciation in the rhizosphere of graminaceous plants induced by phytostabilization of a contaminated sediment

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The maintenance of waterways generates large amounts of dredged sediments, which are often rich in metal contaminants. Understanding how the metals are speciated at the molecular level is critical for formulating effective metal containment strategies, such as phytoremediation. The mineralogical transformations of Zn-containing phases induced by the graminaceous plants, *Agrostis tenuis* and *Festuca rubra*, in a contaminated sediment ($[Zn] = 4700 \text{ mg kg}^{-1}$, $[P_2O_5] = 7000 \text{ mg kg}^{-1}$, $pH = 7.8$), untreated or amended with hydroxylapatite (AP) or Thomas basic slag (TS), were investigated after two years of pot experiment by SEM-EDS, μ -SXRF, and powder- and μ -EXAFS.

Seven Zn species were identified at the micrometer-scale: sphalerite, gahnite, franklinite, Zn-containing ferrihydrite and phosphate, (Zn,Al)-hydrotalcite, and Zn-substituted, kerolite-like, trioctahedral phyllosilicate. Bulk fractions of each species were quantified by least-squares fitting of the powder EXAFS spectra to linear combinations of the identified Zn species spectra. In the untreated and unvegetated sediment, Zn was distributed as ~50 % sphalerite, ~40 % Zn-ferrihydrite, and ~10-20 % (Zn,Al)-hydrotalcite plus Zn-phyllosilicate. In unvegetated but amended sediments (AP and TS), ZnS and Zn-ferrihydrite each decreased by 10 to 20 % and were replaced by Zn-phosphate (~30-40 %). In the presence of plants, ZnS was almost completely dissolved and the released Zn bound to phosphate (~40-60 %) and to Zn phyllosilicate plus (Zn,Al)-hydrotalcite (~20-40 %). Neither the plant species nor the co-addition of mineral amendment affected the Zn speciation in the vegetated sediment. The sediment pore waters were supersaturated with respect to Zn-containing trioctahedral phyllosilicate, near-saturation with respect to Zn-phosphate, and strongly undersaturated with respect to (Zn,Al)-hydrotalcite. Therefore, the formation of (Zn,Al)-hydrotalcite in slightly alkaline conditions ought to result from heterogeneous precipitation on mineral surface.

Coprecipitation of As(III) with synthesized phyllosilicates and hydrotalcite-like phases

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We have previously reported the existence of As(III)-bearing smectites from the geothermal environment. Synthesis experiments were conducted to understand the possible mechanisms how trace metals are incorporated into the layered structure of smectites and hydrotalcite-like phases. In all experiments, arsenic uptake was observed through initial uptake by precursory phases. Further uptake occurred by ageing the precursory phases into their final mineral forms. The mechanism of uptake involves complexation of As(III) with dissolved species (e.g. Al) prior to the formation of the solid precursory phase (i.e. X-ray amorphous solids). The stabilization of the As(III) in the final mineral phase (e.g. phyllosilicate or hydrotalcite-like phases) occurs during ageing. The observed uptake of As(III) depends on the initial complexation reactions and timing of the precursory phase precipitation. If these synthesized materials show the stabilization of As(III) similar to the natural sample previously reported, they can be effectively used in demobilizing dissolved As(III) in contaminated natural waters.