

Formation of hydrozincite, Zn layered double hydroxide and Zn phyllosilicates in contaminated calcareous soils

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The incorporation of Zn into layered mineral structures such as layered double hydroxides (LDH) or phyllosilicates may reduce its mobility and bioavailability in soils. The quantity and structure of Zn bearing layered phases forming in soils depend on soil physicochemical properties and contamination level. To date, most spectroscopic studies on the speciation of Zn considered neutral to acidic non-calcareous soils. In this study, we investigate the reactivity and speciation of Zn in contaminated soils developed from calcareous and dolomitic parent material.

Five soils developed from limestone and one developed from dolomite were sampled below power line towers made from galvanized steel that had been constructed 30 to 50 years ago. All soils have been contaminated by input of runoff water containing dissolved Zn from corrosion. The soils cover a wide range in clay content (90-450 g/kg), inorganic carbon content (10-89 g/kg), and Zn concentration (1'300 - 30'000 mg/kg). They have pH values between 6.1 and 7.5. The molecular scale speciation of Zn in the soil matrix was investigated by Zn K-edge EXAFS spectroscopy on powdered soil samples. Thin sections from two calcareous soils (1'300 and 30'000 mg kg⁻¹ Zn) and the dolomitic soil (1'400 mg kg⁻¹ Zn) were further studied by μ -X-ray fluorescence (μ -XRF) and μ -EXAFS spectroscopy. Principal component analysis and target testing indicated that octahedrally coordinated Zn in layered minerals and tetrahedrally or octahedrally coordinated sorbed Zn are likely candidate species. In the dolomitic soil, pure Zn-phyllosilicate was identified in Zn-rich spots. In the calcareous soil containing 30'000 mg kg⁻¹ Zn, the Zn was diffusely distributed in the soil matrix with a spectrum similar to Zn-LDH. Crusts on calcite particles from the same soil were identified as hydrozincite using powder X-ray diffraction and EXAFS spectroscopy. Linear combination fits to the bulk EXAFS spectra indicate that LDH- and phyllosilicate-type precipitates account for a considerable fraction (17-53%) of the total Zn in all soils. To quantify the reactivity of Zn, the soils as well as synthetic references were fractionated using a 7-step sequential extraction procedure (SEP). Between 32-65% of the total Zn in the soils was extracted in the first two fractions (1M NH₄NO₃ and 1M NH₄-acetate at pH 6.0, respectively), suggesting that most Zn occurred in labile species. Zn-LDH, Zn-phyllosilicates and hydrozincite showed similar chemical reactivity with 46 to 84% of the total Zn mobilized in the first two fractions.