MINERAL/WATER INTERFACE USING MOLECULAR SCALE TECHNIQUES

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An understanding of the kinetics and mechanisms of metal sorption on soil minerals and soils is fundamental in assessing the speciation, mobility, and bioavailability of metals in natural systems. Traditionally, sorption has been studied using macroscopic, equilibrium approaches. It is now well recognized that the kinetics of metal sorption/release must be understood if accurate predictions are to be made about metal fate/mobility and soil remediation. With some metals (e.g., Co, Ni, Zn) residence time affects the rate of metal release from soil minerals while with other metals such as Pb, there is little effect on residence time. To definitively understand the dynamics of metal sorption mechanisms, one must employ molecular scale approaches.

In this paper, recent advances in elucidating the dynamics and mechanisms of metal sorption and precipitate transformation on soil minerals and soils and speciation of metals in contaminated soils via macroscopic and molecular approaches (x-ray absorption fine structure and diffuse reflectance spectroscopies and scanning probe microscopy) will be discussed. It will be shown that with metals such as Ni and Zn, metal hydroxide precipitates form on an array of mineral surfaces that are common in the soil environment and in laboratory and field-contaminated soils. The precipitates form on rapid time scales, at metal surface loadings far below a theoretical monolayer coverage, and in a pH range well below that at which metal hydroxide precipitates would be expected to form according to the thermodynamic solubility product. XAFS and DRS studies indicate that mixed metal-Al hydroxide precipitates (layered double hydroxides, LDH) form when a metal such as Ni(II), Co(II), and Zn(II) is introduced into an environment in which there is a source of hydrolyzed species of Al(III). Formation of metal hydroxide phases, particularly LDH phases, significantly stabilize the metal, as revealed from dissolution studies. Recent use of micro-XAFS and micro-XRF techniques to speciate metal-contaminated field soils will also be discussed. The advances that have occurred in understanding metal sorption/release in soils have major impacts on the long-term evaluation of toxic metal speciation and remediation.