EXAFS analysis of reactive nanoscale iron oxidation in water

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Nanoscale zerovalent iron particles rapidly degrade chlorinated solvent groundwater contaminants into non-toxic products *in situ*. The efficacy of this approach is partially dependent on the reactivity and longevity of the zerovalent iron, which is readily oxidized in groundwater. Oxidation on the surface of the nanoscale iron particle can passivate the particle, potentially resulting in lowered reactivity toward target contaminants. A fundamental understanding of the chemical and structural changes that occur as a result of oxidation at the nanoiron surface in aqueous systems is necessary to assess the related impacts on reactivity and to determine the ultimate utility of the particles towards remediative goals.

Nanoscale zerovalent iron particles (initially 70% Fe^0/30% Fe_3O_4 core/shell particles) were allowed to oxidize in anaerobic water for various times ranging from a few days up to 1 year. The resulting iron particles with varying degrees of oxidation were studied using high intensity synchrotron radiation methods at Stanford Synchrotron Radiation Laboratory, beamline 11-2. Iron K-edge extended X-ray absorption fine structure (EXAFS) spectra provided element-specific information regarding the short-range structural order around iron in the nanoparticles. Fitting of the iron EXAFS spectra using model phase and amplitude functions allowed quantification of the direct relationship between oxidation time and relative amount of oxygen present in the atomic structure. Specifically, over the range of samples analyzed the average Fe-Fe coordination number declined from 8.2 ± 0.4 to 2.5 ± 0.3 while the average Fe-O coordination number increased from 1.2 ± 0.8 to 3.1 ± 0.9. The Fe-O and Fe-Fe interatomic distances and coordination numbers determined from the EXAFS fitting process were then compared to those of known crystalline iron oxides/oxyhydroxide phases in order to characterize the progressive structural transformation of the nanoparticles during their oxidation in water.

Metals from agriculture in oxic fluvial sediments: A case study in Western Iberia

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The transport of fine fluvial sediments and associated pollutants in mountainous rivers is very dynamic, in response to precipitation episodes. The present study highlights the impact of human activities, mainly farming, in a “natural” mountainous catchment in Northern Portugal, underlain by crystalline rocks, in a temperate climate. Some inferences regarding Cu, Pb, Zn and Ca concentrations, their spatial and temporal variability, and potential bioavailability in oxic fluvial sediment samples are presented.

The study was performed on the <63µm sediment fractions. The modified BCR sequential extraction procedure (Rauret *et al.*, 1999) was used to assess metal contents in geochemical phases. The residual phase was decomposed by *aqua regia*. The element concentrations were obtained by ICP-AES.

The studied metals had contents in the ranges (ppm) Cu (1-99), Pb (5-154), Zn (29-448) and Ca (362-40860), showing higher contents in sampling stations located at those points draining areas with intense agriculture. These elements are common components of fertilizers, pesticides and animal manures (cow, horse, rabbit), the last widely used in the studied area. In these sites, the metals' relative contents present in the soluble, oxidisable, and organic fractions are considerably higher. However, differences in the distribution of the potential bioavailable fraction are observed, with marked increases in different phases: Cu in the organics, Zn in the soluble and oxidisable, and Pb in the oxidisable.

Calcium was also considered in this study. Although ubiquitous in natural water systems, its concentrations in the sediment samples are relatively high, considering the local geology (granites and schists). Calcium is a major component in the chemical fertilizers used in the studied area. Calcium is low in the residual fraction, owing to its geochemical behaviour, but is present in considerable amounts in the soluble fraction. The correlations between Ca and Cu, Pb and Zn are highest at the end of the dry period. The first autumn rain leads to increased transport of these elements, either by runoff or leaching of agricultural lands.

Reference

Rauret, G.; Lopéz-Sánchez, J.F.; Sahuquillo, A.; Rubiu, R. ; Davison, C.; Ure, A.; Quevauviller, Ph. (1999), *J. Environ. Monit.* **1**, 57-61.