Sb sorption complexes on Fe oxide surfaces: An EXAFS study

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Antimony, an increasingly investigated pollutant, occurs in various crustal and surficial environments. Soils polluted by Sb can be found in the vicinity of smelters, mining sites, and in areas contaminated by shooting activities, among others. Studies on these contaminated soils showed that Sb is often associated with Fe oxides and oxyhydroxides, suggesting that these phases may act as a natural barrier for the released Sb. Understanding the geometry of Sb adsorption complexes formed on different Fe oxide surfaces can help to assess the role of these phases as scavengers of Sb. Therefore, we synthesised goethite, lepidocrocite, and ferrihydrite with adsorbed Sb ranging in concentration from 0.01 to 0.6 mol% Sb_2O_5. Characterisation of the samples showed that the synthesis resulted in 2 μm long goethite needles with an BET surface area of 33 m^2/g. The 1 μm long lepidocrocite platelets and the ferrihydrite samples revealed a surface area of 84 and 200-300 m^2/g, respectively. Sb K-edge EXAFS spectra were collected and processed to model the immediate surrounding of the Sb atoms.

The first coordination shell in all samples could be described well by an Sb-O path representing six oxygen atoms at an equal distance of 1.99 Å. Modelling of the second coordination shell allowed us to distinguish three different types of Sb neighbors on the various Fe oxide surfaces. These are Sb-Fe edge- and corner-sharing, and Sb-Sb edge-sharing octahedra. The backscattering peak of a Fe atom at a distance of 3.06, 3.12, and 3.09 Å on the goethite, lepidocrocite and ferrihydrite surfaces, respectively, is attributed to the Sb-Fe edge sharing octahedra. Sb-Sb neighbours on the surface of samples with high surface Sb loading reveal their presence by a Sb backscattering peak at a distance of 3.16 Å. The formation of Sb-Sb neighbours with increasing Sb concentrations indicates surface precipitation and formation of a separate Sb phase. The distance between the Sb and Fe atoms in the corner-sharing octahedra is 3.6 Å, showing the same distance on all three Fe oxide surfaces. The abundant Sb-Fe neighbors represent inner-sphere complexes, indicating high affinity of Sb for the surfaces of the studied iron oxides. As with other metals and metalloids (e.g., As), iron oxides appear to be very efficient sorbents of Sb.

Assessing natural attenuation of a PCE-contaminated aquifer using a combined CSIA and groundwater dating approach

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The combination of compound-specific stable isotope analysis (CSIA) with groundwater dating provides *in situ* determination of degradation rates. This information is essential for assessing the natural attenuation (NA) potential of contaminated aquifers. To test this approach, a former dry cleaning site, originally contaminated by tetrachloroethene (PCE), was investigated. Due to almost stagnant hydrogeological conditions and considerable aquifer heterogeneity, it was not possible to clearly define contamination plumes and flow pathways. Therefore, groundwater dating (^{3}H-^{3}He method) was necessary to assess this site.

The presence of degradation products, active PCE-degrading microcosms and the results of biomolecular analysis of field sediments provided clear evidence for occurring NA. Carbon isotopic signatures of PCE were used to quantify biodegradation using the Rayleigh model. Together with groundwater residence times, a first-order degradation rate of PCE-transformation of k = 0.2 y^{-1} was estimated (Fig. 1).

The evaluation of the total isotopic signature of PCE and its degradation products furthermore allowed assessing the total PCE-detoxification potential. A simple 1D-reactive transport model was used to support these results.
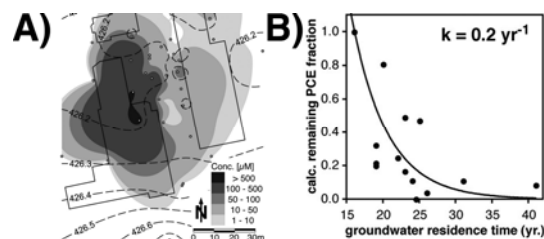

Figure 1: A) Field site location with contamination plume and hydraulic heads. B) Estimation of *in situ* first-order PCE degradation rate using isotopic signatures (to calculate degraded PCE-fraction) and groundwater residence times.