Binding of arsenic to natural organic matter in a minerotrophic peatland

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In soils and sediments, arsenic (As) is known to be effectively immobilized by metal-(hydr)oxides under oxidizing, and sulfide minerals under strongly reducing conditions. Recently, the binding of As to natural organic matter (NOM) has been proposed for organic soils depleted in metal-(hydr)oxides. However, direct spectroscopic evidence for this sequestration mechanism is still lacking. In order to investigate the role of NOM for As sequestration, we studied the speciation of As and iron (Fe) in a natural As-enriched peatland in southern Switzerland.

Sampled peat cores were shock-frozen in the field and kept anoxic in order to prevent speciation changes of redox-sensitive elements. The peat contained up to 950 g kg^{-1} NOM and 1.8 g kg^{-1} As (dry weight basis). Iron and sulfur (S) concentrations ranged between 3 to 60 and 0.03 to 40 g kg^{-1}, respectively. Enrichments of As were found either within the top 0.2 m, or at depths between 1.5 and 2.8 m. The speciation of As and Fe was investigated by bulk As and Fe K-edge X-ray absorption spectroscopy at 77-80 K.

Based on linear combination fitting, we found significant differences in Fe and As speciation as a function of sampling depth. While in the upper parts Fe(III)-(hydr)oxides represented the major Fe species, the deeper peat layers were dominated by pyrite. Speciation analyses of As indicated that close to the peat surface, As was mainly present in the form of realgar, whereas in the lower part of the peat profiles, As(III) was predominantly coordinated to S atoms of NOM. The extended X-ray absorption fine structure of As in these samples closely resembled that of As(III) bound to cysteine residues in which As is coordinated to three S atoms at a distance of 2.20 to 2.25 Å [1-3]. This S-bound As fraction accounted for up to 88% of the total As in the peat.

Our results document that the sorption of As by particulate NOM can be regarded as a potent sequestration mechanism under sulfate reducing conditions. These observations represent a great step forward in our understandings of the potential mobility and toxicity of As in waterlogged environments enriched in NOM.

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Prospects for nanoscale, hard x-ray studies of extraterrestrial materials

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Analyses of the many primitive extraterrestrial materials available are challenged by extreme heterogeneity at the smallest observable scales and limited sample masses. These materials include interplanetary dust particles (IDPs) harvested from the stratosphere and microparticles collected by the Stardust spacecraft during flyby of the Wild-2 comet. These particles range in size from a few tens of micrometers down to a few hundred nanometers and below. In the case of the Stardust cometary particles, the particles were largely aggregates of sub-micron components which gradually disintegrated upon penetrating the aerogel collection substrate.

Spatially-resolved x-ray analyses, such as x-ray fluorescence (XRF), x-ray absorption fine structure (XAFS), x-ray diffraction (XRD) and computed microtomography (CMT), are extremely valuable in studying such materials, providing chemical and physical state information in a largely non-destructive manner, leaving the samples available for additional study by complementary methods, such as spatially-resolved mass spectrometry (e.g. SIMS). Hard x-rays can also allow analyses with the samples still within their collection media, for example, in the case of the aerogel collected comet dust.

One challenge has been achieving appropriate spatial resolution with these x-ray methods. Soft x-ray (<1 keV) approaches, such as scanning transmission x-ray microscopy (STXM), routinely achieves tens of nanometers resolution allowing, for example, carbon speciation mapping. But, hard x-ray (>4 keV) approaches have generally been limited to the micrometer resolution. That situation is improving with more use being made of the few, currently existing higher resolution hard x-ray microprobes for this purpose. In addition, the advent of new x-ray sources and advances in x-ray optics will allow the spatial resolution of these hard x-ray instruments to be pushed to below the 100 nm regime. Higher spatial resolution is also advantageous for research on fine-grained, poly-mineralogic matrices that occur in larger meteorites.