Geophysical Research Abstracts
Vol. 15, EGU2013-8368, 2013
EGU General Assembly 2013

Micro-Scale Distribution and Speciation of Arsenic in Peat

Peggy Langner-Hofmann, Christian Mikutta, and Ruben Kretzschmar
Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Zurich, Switzerland (christian.mikutta@env.ethz.ch)

Organic soils and peaty sediments frequently show arsenic (As) enrichments that suggest a direct association of As with natural organic matter (NOM). We have recently studied the speciation of As in a naturally As-enriched minerotrophic peatland (*Gola di Lago*) located in Southern Switzerland using bulk X-ray absorption spectroscopy (XAS) [1]. These analyses revealed that in deep peat layers, characterized by stable reducing redox conditions, the entire As was coordinated in its trivalent oxidation state to sulfhydryl groups of NOM. In shallow peat layers, however, the suite of As species comprised organically bound As, As sulfides, and As sorbed to Fe(III)-oxyhydroxides. Here we employed micro-X-ray fluorescence (μ-XRF) spectrometry combined with μ-XAS to explore the micrometer-scale distribution, speciation, and elemental correlations of As in the *Gola di Lago* peat. Undisturbed peat material (260-550 mg As/kg) was retrieved from depths $<$0.4 and 2.0-2.5 m, prepared as thin sections, and analyzed at beamline 10.3.2 of the Advanced Light Source (Berkeley, USA). We found marked differences in the distribution and speciation of As between both depth intervals. Whereas the surface-near peat was dominated by As hotspots of 10-100 μm size, As in the deep peat layers was for the most part evenly distributed on particulate NOM. Arsenic in the hotspots of the upper peat layer correlated with S, and μ-XAS measurements confirmed that realgar-type minerals (As_4S_4polymorphs) were the dominating As species. Despite that As sorbed to Fe(III)-oxyhydroxides was also identified by μ-XAS in the upper peat layer, no elemental correlation between As and Fe was observed. For the deep peat layer thin sections two spatial correlations between As and S were recognized. The first correlation comprised the homogenously distributed As, which was verified by μ-XAS to represent As(III) bound by organic S groups. The second As-S correlation was confined to rare but intense $<$20 μm As hotspots, where μ-XAS measurements indicated arsenian pyrite ($FeS_{2-x}As_x$) and arsenopyrite (FeAsS). In summary, the μ-XRF and μ-XAS analyses confirmed our earlier conclusions regarding the nature of As binding to NOM [1] but additionally revealed the presence of minor inorganic As species which have escaped detection by bulk XAS analyses. The fundamental differences in the micro-scale distribution and speciation of As as a function of depth imply a high spatial and temporal variability of As pore water concentrations in the peat.

[1] Langner, P.; Mikutta, C. and Kretzschmar, R. Arsenic sequestration by organic sulphur in peat. *Nature Geoscience* **2012,** 5 (1), 66-73.