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Monothioarsenate transformation kinetics determines arsenic mobility in sulfidic and organic-rich systems

J. BESOLD[1], A. BISWAS[1], E. SUESS[2], A. C. SCHEINOST[3], A. ROSSBERG[3], C. MIKUTTA[2], R. KRETZSCHMAR[2], J. P. GUSTAFSSON[4], B. PLANER-FRIEDRICH[1]*

[1] Environmental Geochemistry, Bayreuth Center for Ecology and Environmental Research, Bayreuth, Germany (*b.planer-friedrich@uni-bayreuth.de)
[2] Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Zurich, Switzerland
[3] The Rossendorf Beamline at ESRF, Grenoble, France, and Institute of Resource Ecology, HZDR, Dresden, Germany
[4] Department of Soil and Environment, Swedish University of Agricultural Sciences, Uppsala, Sweden

Peatlands play an important role in arsenic sequestration. In such carbon-rich and sulfidic environments the dominant species is generally assumed to be arsenite for which recent X-ray absorption spectroscopy (XAS)-based studies showed that it can strongly bind to natural organic matter (NOM) via reduced sulfur bridges [1]. However, in sulfidic solutions, arsenite can also react with sulfide or elemental sulfur to form thioarsenates. Thioarsenates are often overlooked due to a lack of suitable analytical methods [2] and their mobility in organic-rich systems is unknown. Porewater analysis of an arsenic-rich, minerotrophic peatland (Gola di Lago, Switzerland) showed that thioarsenates actually accounted for up to 70 % of total porewater arsenic, with monothioarsenate (MTA) being the dominant species. To investigate the extent, kinetics, and mechanisms of MTA binding to NOM, MTA was incubated with sulfurized peat at pH 4.5, 7.0, and 8.5. While MTA was stable for 41 days at pH 8.5, it was completely transformed to arsenite at pH 4.5, following acid-catalyzed and sulfide-dependent redox transformation kinetics. Total arsenic sorption was lowest at pH 8.5 and highest at pH 4.5 (7 and 32 µmol As/mol C, respectively). XAS revealed that in this sulfidic system, arsenic was bound to NOM as previously reported via reduced sulfur bridges as arsenite and additionally via oxygen as arsenite at low to neutral pH or as arsenate and low amounts of arsenite via oxygen at high pH. MTA did not bind to sulfurized NOM at all. The results demonstrate that the mobility of arsenic in sulfidic, organic-rich systems strongly depends on the pH, the sulfide-to-arsenic and the sulfide-to-carbon ratios which govern thioarsenate formation in solution, their transformation to arsenite and finally its sorption kinetics.

[1] Langner et al. (2012) *Nat. Geosci.* **5**, 66-73. [2] Planer-Friedrich et al. (2015) *Environ. Sci. Technol.* **49**, 6554-6563.