

Turning peatlands from arsenic sinks to sources – the pH-dependent role of reduced sulfur in controlling arsenic methylation, thiolation, and thereby net mobility

BRITTA PLANER-FRIEDRICH¹, ANNE EBERLE²,
JOHANNES BESOLD³, JOSÉ MIGUEL LEÓN-NININ⁴,
CAROLIN F. KERL⁵, KATHARINA KUJALA⁶, JUAN
SALVADOR LEZAMA-PACHECO⁷ AND SCOTT
FENDORF⁷

¹Environmental Geochemistry, Bayreuth Center for Ecology and Environmental Research, University of Bayreuth

²University of Bristol

³Bayreuth University

⁴University of Bayreuth

⁵Environmental Geochemistry, Bayreuth Center for Ecology and Environmental Research, University of Bayreuth

⁶Oulu University

⁷Stanford University

Presenting Author: b.planer-friedrich@uni-bayreuth.de

Peatlands are often reported being sinks for arsenic (As) due to efficient solid-phase sequestration of arsenate or arsenite by Fe(III) mineral phases at the surface and, with increasing depth, by O-, Fe-, or S-bearing groups of natural organic matter (NOM). However, it is overlooked that aqueous As speciation does not only comprise of oxyanions, but includes, in the presence of reduced sulfur, inorganic thioarsenates and, due to high microbial activity, methylated oxy- and thioarsenates. Lower sorption affinities for inorganic thioarsenates and methylated oxyarsenates have been reported before, explaining As remaining mobile, once released.

Here, we used batch experiments to study net desorption or retention of As presorbed on model peat when applying a 10fold excess of reduced sulfur in solution. Reduced sulfur caused substantial As retention at acidic conditions but actively remobilized solid-phase-bound As at neutral to alkaline pH. In these sterilized batch experiments, inorganic thioarsenates dominated As speciation and they remained in solution without (re)sorption to peat. X-ray absorption spectroscopy confirmed As(III)-S-C binding but no binding of thioarsenates to NOM.

Potential implications of S-induced As mobilization from peat were then investigated in a mine water impacted peatland which has received pre-treated process effluent waters containing As since 2010. In comparison to pristine acidic peatlands in the vicinity, that treatment peatland showed a neutral to slightly alkaline pore water pH and, at the surface, about 10-fold higher solid-phase-As concentrations as a result of a documented efficient As removal over the past years. Despite continued overall efficient As retention, our study now revealed one hotspot of substantial As re-mobilization where pore water concentrations exceeded mine water input concentrations by a factor of 20. At the same spot, a peak of reduced S species was detected. Arsenic speciation comprised besides arsenite up to

26% methylated oxyarsenates, 15% methylated, and 7.9% inorganic thioarsenates.

Mimicking different potential future scenarios for this treatment peatland acting as net As sink or source, incubation experiments revealed the highest risk of As re-mobilization when oxic, Fe-rich near-surface layers of high water flow were subjected to stagnant anoxic conditions promoting sulfate reduction and thereby As methylation and thiolation.