



	Experiment title: Arsenic speciation and mobility in sulfidic sediments: Role of oxythioarsenates	Experiment number: EC- 831
Beamline:	Date of experiment: from: 28 April 2011 to: 04 May 2011	Date of report: 4 October 2013
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Report:

This beam-time lead to the following 2 peer-reviewed articles:

1. Couture R-M, Rose J, Kumar N, Mitchell K, Wallschläger D, Van Cappellen P. (2013) Sorption of arsenite, arsenate and thioarsenates to iron oxides and iron sulfides: a kinetic and spectroscopic investigation. Environmental Science & Technology (47) 5652-5659.

<http://pubs.acs.org/doi/abs/10.1021/es3049724>

Abstract: Sorption to iron (Fe) minerals determines the fate of the toxic metalloid arsenic (As) in many subsurface environments. Recently, thiolated As species have been shown to dominate aqueous As speciation under a range of environmentally relevant conditions, thus highlighting the need for a quantitative understanding of their sorption behavior. We conducted batch experiments to measure the time-dependent sorption of two S-substituted arsenate species, mono- and tetrathioarsenate, and compared it to the sorption of arsenite and arsenate, in suspensions containing 2-line ferrihydrite, goethite, mackinawite, or pyrite. All four As species strongly sorbed to ferrihydrite. For the other sorbents, binding of the thiolated As species was generally lower compared to arsenate and arsenite, with the exception of the near instantaneous and complete sorption of monothioarsenate to pyrite. Analysis of the X-ray absorption spectroscopy (XAS) spectra of sorbed complexes implied that monothioarsenate binds to Fe oxides as a monodentate, inner-sphere complex. In the presence of Fe sulfides, mono- and tetrathioarsenate were both unstable and partially reduced to arsenite. Adsorption of the thiolated As species to the Fe sulfide minerals also caused the substitution of surface sulfur (S) atoms by As and the formation of As–Fe bonds.

2. Couture R-M, Wallschläger D, Rose J, Van Cappellen P (2013) Arsenic binding to organic and inorganic sulfur species during microbial sulfate reduction: a sediment flow-through reactor experiment. *Environmental Chemistry* (10) 285-294. [open access]

<http://dx.doi.org/10.1071/EN13010>

Abstract: Flow-through reactors (FTRs) were used to assess the mobility of arsenic under sulfate reducing conditions in natural, undisturbed lake sediments. The sediment slices in the FTRs were supplied continuously with inflow solutions containing sulfate and soluble AsIII or As V and, after 3 weeks, also lactate. The experiment ran for a total of 8 weeks. The dissolved iron concentration, pH, redox potential (Eh), as well as aqueous As and sulfur speciation were monitored in the outflow solutions. In FTRs containing surface sediment enriched in labile organic matter (OM), microbial sulfate reduction led to an accumulation of organically bound S, as evidenced by X-ray absorption spectroscopy. For these FTRs, the inflowing dissolved As concentration of 20mM was lowered by two orders of magnitude, producing outflow concentrations of 0.2mM monothioarsenate and 0.1mM arsenite. In FTRs containing sediment collected at greater depth, sulfide and zero-valent S precipitated as pyrite and elemental S, while steady-state outflow arsenite concentrations remained near 5mM. The observations thus suggest that As sequestration is enhanced when sediment OM buffers the free sulfide and zero-valent S concentrations. An updated conceptual model for the fate of As in the anoxic As–C–S–Fe system is presented based on the results of this study.