

Arsenic and iron cycling in freshwater flocs under sulfate- reducing conditions

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Organic, Fe-rich flocs are common in surface waters of freshwater wetlands and are often found to be highly enriched in trace metal(loid)s.¹ Recently, flocs collected from streambeds of the naturally As-enriched peatland *Gola di Lago* (Switzerland) were shown to contain ferrihydrite and nanocrystalline lepidocrocite to which both As(III) and As(V) were bound in binuclear surface complexes.² Owing to their density, these flocs tend to settle under low-flow conditions and thus may become buried and subjected to reducing conditions over time. Speciation changes of floc As induced by sulfate-reducing conditions may either inhibit or enhance the mobility of As due to the formation of, for example, As sulfides or thioarsenic species. Here, we spiked As-rich flocs containing ≤ 35 wt.% C_{org} and ≤ 22 wt.% Fe with 5 mM bisulfide (molar S(-II)/As and S(-II)/Fe ratios = 290-720 and 0.73-1.55, respectively) at pH 7 and investigated changes in the solid- and aqueous-phase speciation of As, Fe, and S over one week using a combination of X-ray absorption spectroscopy, electron microscopy, as well as HPLC-UV and IC-ICP-MS analyses. Our results show that solid-phase Fe mineral transformations were dominated by mackinawite (FeS) formation, with a preferential transformation of ferrihydrite over lepidocrocite. Arsenic released from the solid phase was dependent on the molar S(-II)/Fe ratio, with highest As releases found for molar S(-II)/Fe ratios > 1 . Up to 34% of dissolved As was present as thioarsenates. Solid-phase As was primarily associated with mackinawite and lepidocrocite, with evidence of some As sulfide precipitation. Sulfur speciation analyses revealed that elemental S and polysulfides were almost exclusively associated with the solid phase, whilst oxidized S species detected in solution comprised thiosulfate and sulfate. In summary, our results imply an enhanced As mobility under sulfate-reducing conditions, despite the presence of residual Fe(III)-(oxyhydr)oxides and the formation of Fe and As sulfides.

[1] Plach *et al.* (2011) *Environ. Sci. Technol.* **45**, 2157-2164.

[2] ThomasArrigo *et al.* (2014) *Environ. Sci. Technol.* **48**, 13218-13228.