Sulfur-Induced Arsenic Mobilization in Peat

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Arsenic (As) can be sequestered in deep, anoxic peat layers under slightly acidic pH via As(III)-thiol bonds [1]. At more shallow layers and circumneutral pH, however, thioarsenates can form and dominate As speciation in pore waters of peat deposits [2]. The most abundant As species, monothioarsenate, showed no affinity for binding to peat natural organic matter, demonstrating its high mobility. Further, first sulfidization experiments with organic iron flocs at pH 7 documented sulfur-induced mobilization of As through thioarsenate formation [3]. A clear pH-dependent reaction pathway, however, was unknown to date. To investigate potential As mobilization, we conducted laboratory experiments with As-loaded purified model peat at pH 4.5, 7.0 and 8.5, where As was bound to peat via thiol- and O-bearing groups. We subsequently sulfurized the As-loaded peat with an excess of aqueous polysulfide (PS) or sulfide (HS^-), and followed total As in the solid phase and As speciation in the aqueous phase over 180 h. At pH 4.5, total solid As after 180 h increased with sulfurization; whereas at pH 7.0 and 8.5, solid As decreased compared to controls without sulfur addition. Total aqueous As analyses showed the same trend with highest mobilization based on solid-phase As at pH 7.0 and 8.5. Aqueous concentrations of As were slightly higher in PS than in HS^- treatments. Aqueous As speciation revealed that thioarsenates accounted for up to 80% of dissolved As at pH 7.0 as well as at pH 8.5 and only for ~20% at pH 4.5. The slightly higher release of As to porewater in the PS treatment at pH 7.0 and 8.5 may be explained by reaction of zero-valent sulfur (ZVS) with solid-phase released arsenite, forming thioarsenates, which is underlined by lower required (aqueous) ZVS concentrations in the HS^- treatment. Our results demonstrate that peat-bound As can be released under changing peat conditions through sulfurization, with reduced sulfur species forming thioarsenates that are known to be highly mobile at neutral to slightly alkaline pH.

[1] Langner et al. (2012) *Nat. Geosci*., 5, 66-73. [2] Besold et al. (2018) *Environ. Sci. Technol.*, 52, 7317-7326. [3] ThomasArrigo et al. (2016) *Environ. Sci. Technol.*, 48 ,13218–13228.