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# Seasonal arsenic mobilization in a minerotrophic peatland as a response to formation of methylated thioarsenates and their low sorption

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Peatlands contribute substantially to retention, transformation, and mobilization of trace metals and metalloids, such as Arsenic (As). Retention and (re)mobilization are affected by the speciation of As and interaction with sorption sites such as natural organic matter (NOM) and Fe(III)-oxyhydroxides. Both speciation of As and the abundance of these sites are affected by (microbially catalyzed) redox transformations, which change through seasonal variations in temperature and redox regimes.

Under oxic conditions, arsenate is sequestered by Fe(III)-oxyhydroxides. With enhanced microbial activity, redox regimes transition to suboxic conditions, which triggers dissimilatory Fe(III)-oxyhydroxides reduction and releases previously adsorbed arsenate, which is further reduced to arsenite. Once anoxia develops, sulfate-reducing bacteria (SRB) mediate arsenite methylation to form methylated oxyarsenates and further produce sulfide as a product of sulfate reduction. On the one hand, NOM can complex sulfide (NOM-S), which forms a sorption site for arsenite; on the other hand, free sulfide can thiolate arsenite and methylated oxyarsenates to inorganic or methylated thioarsenates, respectively. Inorganic arsenic thiolation was shown to increase the As mobility in peatlands because of low affinity to NOM-S functional groups of inorganic thioarsenates[1], and recent research from a peatland used for process-water purification showed that methylated thioarsenates contributed to up to 15 % of all dissolved As species[2]. While arsenite is efficiently retained in peatlands under anoxic and sulfidic conditions, inorganic and methylated thioarsenates emerge.

How and to which extent methylated thioarsenate formation contributes to As mobilization in natural peatlands is currently unknown. Seasonal depth-resolved porewater sampling in a natural minerotrophic peatland showed that methylated thioarsenates dominated As speciation (60 % of all As species) in summer. Sorption experiments with model peat and peat from the sampling site confirmed low affinity of methylated thioarsenates to peat under anoxic and sulfidic conditions, suggesting high mobility in peatlands, especially in summer.

1. Besold, J. *et al.* Monothioarsenate Transformation Kinetics Determining Arsenic Sequestration by Sulfhydryl Groups of Peat. *Environ. Sci. Technol.* **52**, 7317–7326 (2018).

2. Eberle, A. *et al.* Potential of high pH and reduced sulfur for arsenic mobilization – Insights from a Finnish peatland treating mining waste water. *Sci. Total Environ.* **758**, 143689 (2021).