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Discerning the Interplay Between Biotic and Abiotic Mechanisms for Arsenite Oxidation in a Photosynthetic Microbial Mat

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Arsenic is a ubiquitous and naturally occurring contaminant whose speciation, fate and transport is influenced by complex biogeochemical interactions. Oxidation of arsenite (As(III)) to arsenate (As(V)) lowers toxicity and mobility and thus has implications relating to natural arsenic cycling and remediation. Oxidation can be achieved by a variety of abiotic and biotic processes, and recent findings from our laboratory showed that benthic photosynthetic biomat within the novel, unit process open water constructed wetland (UPOW) accelerates arsenite oxidation rates [1]. Here we combine laboratory batch experiments and geochemical modeling to investigate intertwined biotic and abiotic mechanisms involved in oxidizing As(III). Aerobic-light, aerobic-dark, and anaerobic-dark biomat microcosms were established with gradients of initial arsenite and nitrate. These kinetic experiments showed modest adsorption but fast homogeneous microbial oxidation of As(III) under all investigated conditions. RT-qPCR backed by metagenomic sequencing confirmed that this process engaged a canonical arsenite oxidase AioA. Active expression of *arxA* gene was also observed from field metatranscriptomics, suggesting the presence of arsenite-based anoxygenic photosynthesis. Autoclaved biomat controls also exhibited oxidation at approximately 1/10 the rate of biologically active incubations whereas no oxidation was observed in the absence of biomat. Subsequent quenching experiments with Fe-chelating agents and sequesters of reactive oxygen species suggested Fe-containing minerals within the biomat were a major contributor to abiotic oxidation. Rate constants mined from literature were used to calibrate a system-specific kinetic model for arsenic speciation and adsorption, which can be incorporated into transport models to decipher the cycling of arsenic and guide the design of nature-based treatment systems.

[1] Wang, Weishi, et al. "Photosynthetic pretreatment increases membrane-based rejection of boron and arsenic." Water Research 252 (2024): 121200.