

Remediation Strategies for Redox-Active Elements Using Combined Experimental, Spectroscopic, and Computational Approaches

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Contaminants such as arsenic (As), mercury (Hg), and other redox-active elements pose particular challenges to remediation because of their ability to readily change oxidation state and speciation at surface conditions from coupled microbial-abiotic processes that are spatially and temporally dynamic. A variety of *in situ* sediment or soil amendment treatments, whether added directly to geomedium or emplaced within barriers or caps, can sequester and stabilize contaminants in place in order to reduce their ability to partition to water or biota, their toxicity, and their potential for transport. Computational approaches such as thermodynamic-kinetic reaction path and reaction transport models capable of simulating biogeochemical, speciation, partitioning, and transport processes are valuable tools for assessing remediation effectiveness when constrained by spectroscopic and experimental investigations of laboratory and field systems. The contrasting chemical behavior and exposure pathways of As and Hg illustrate how remediation approaches using amendments or sediment caps can be optimized by minimizing the concentration of specific chemical species associated with maximum health risk. For As, inorganic arsenite (As^{III}(OH)₃) is the most toxic form and human exposure is typically through drinking water. Combined field, laboratory, and modeling studies show that sorption or amendment sequestration of arsenate (As(V)) under oxic conditions, or precipitation of solid As sulfides under anaerobic conditions, are most effective for limiting concentrations of dissolved arsenite. For Hg, remediation should target reduction of net methylation of inorganic Hg to methylmercury, which results primarily from bacterial sulfate reduction in anaerobic environments and is the first step in Hg bioaccumulation. Approaches such as sediment chemical amendments or caps can reduce methylation by limiting bioaccessibility of inorganic Hg through solid encapsulation or irreversible sorption, reducing the total concentration of dissolved sulfide species, buffering system oxidation potential above sulfate reduction, and/or buffering pH at circumneutral or above.

Biogenic Influence on Sea-Spray Aerosol and its Impacts

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Marine aerosol, whether primary or secondary, comprises both inorganic and biogenic organic components. Although primary sea-spray mass is dominated by super-micron sea-salt, the sub-micron sizes dominate the sea-spray number concentration leading to important contributions to both direct and indirect radiative effects [1,2]. The relative contributions of sea-salt and primary organic matter to sub-micron sea-spray has been shown to be influenced by biogenic productivity in oceanic waters, with the organic mass fraction ranging from 10% under low biological activity, to 90% under high activity [3, 4]. The organic enrichment reduces the spray's hygroscopicity [4]; however, there is a dual-state effect leading to hygroscopicity flipping between a high hygroscopicity to low hygroscopicity as the organic matter volume fraction exceeds ~50%. The effect leads to a ~3-fold reduction in scattering enhancement as a function of increasing relative humidity and potentially a reduction in the radiative impact of sea-spray from -6.5 Wm⁻² to -1 Wm⁻² under wind speeds of 20 m s⁻¹.

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