

Molecular-scale pathways of contaminant arsenic cycling and bioavailability in climate-controlled weathered mine-tailings

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Legacy sulfide mine tailings pose serious risks to environmental and human health as point sources of arsenic and toxic metals. Upon deposition, these tailings undergo weathering transformations due to meteoric inputs (pO_2 , H_2O), leading to changes in the molecular form, or speciation, of contaminants and host minerals. The rate and nature of oxidative weathering depends on climate and tailings mineral composition, developing a range of ferric (sulf-oxy)hydroxide minerals with varying degrees of solubility and affinity for surface complexation reactions that results in site-specific differences in the lability and bioavailability of metal(loid)s. The objective of this research was to understand the geochemical grain-scale processes of tailings alteration as influenced by climate, particularly within fluid-filled pores, to better apply remediation strategies and predict risk. To investigate the mechanistic controls of arsenic mobility in tailings weathered in place, a hectare scale-field trial was established in a semi-arid Superfund site in Arizona, US. Additionally, >1 m soil pits and cores were collected from 13 sites across a climate gradient in the western US in similar arsenic-rich, sulfide-ore derived tailings and characterized for physical, mineralogical, and geochemical composition to evaluate weathering processes and bioaccessibility. The combined investigative strategy of a) field-scale, compost-assisted phytostabilization, b) laboratory-controlled batch experiments and flow-through columns, and c) *in vitro* bioassays of field and experimental products with synchrotron-based X-ray characterization, were undertaken to understand metal(loid) transformation pathways and mechanisms of release. Whereas field-scale phytostabilization was shown to reduce fugitive dust emissions, organic matter amendments hastened the oxidation of pyrite, enhancing acidification and increasing arsenic lability by destabilizing ferric hydroxides. Phytostabilization further altered the subsurface microbial community and compost addition reduced oxyanion arsenate to the neutral arsenite species, promoting partitioning to the aqueous phase and impeding re-adsorption. Similar biogeochemical dissolution reactions control *in vitro* bioaccessibility of arsenic-rich tailings in biofluid simulants. This work demonstrates that the release of arsenic to the environment and *in vitro* bioassay is controlled by contaminant and sorbate speciation, which alters as a function of sulfate, ferrous iron, and acid activity controlled by weathering reactions and parent material.

