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# Thiolated arsenic in mine tailings: a new consideration for mine waste management

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The biogeochemical cycling of arsenic (As) in wetlands, groundwater, and hydrothermal systems can be significantly affected by the formation of thiolated As species (thio-As). Numerous mine sites across the globe have challenges with high As levels in seepage and waste systems (tailings impoundments, waste rock piles). These mine waste storage systems commonly harbor the same neutral-to-alkaline and sub-oxic conditions that favour the occurrence of thio-As in other environments, however, quantitative data on the existence and mobility of thio-As in mine waste environments is lacking. Notably, thio-As behaves differently from their oxyanionic counterparts; thio-As have a lesser tendency to adsorb or co-precipitate with secondary minerals and may therefore explain anomalous As loading rates observed in the field.

Building upon recent experimental work demonstrating the production of thio-As from weathering mine waste rock, we conducted a field investigation to identify and characterize thio-As at As-rich legacy mine tailings sites in Cobalt, Ontario, and Nova Scotia, Canada. Dissolved thio-As were ubiquitous across these legacy tailings, mostly in the form of monothioarsenate, with some minor di- and tri-thioarsenate as well as methylated thio-As. Higher thio-As abundances were observed in the Nova Scotia tailings (up to 17.3% of total dissolved As), where As was hosted in As-sulfide minerals (arsenopyrite and realgar) compared to the Cobalt tailings (up to 5.9% of total dissolved As), where As was mostly contained in oxidized arsenates (erythrite-annabergite or yukonite) and to a lesser extent in As-sulfide minerals such as cobaltite/gersdorffite. Dissolved thio-As were most abundant in sub-oxic porewaters and inundated tailings samples across the studied sites, and thio-As concentrations were strongly related to the prevailing redox conditions and porewater hydrochemistry, and to a lesser extent, the As-bearing mineralogy.

Overall, this study demonstrates that thio-As occurs in widely different tailings systems and geochemical conditions, at concentrations (up to 4.7 mg/L in our studied tailings) that can be above permissible As limits. Thus, thio-As, as well as other elements that are prone to thiolation (e.g., selenium, antimony, molybdenum, tungsten) should be carefully considered in mine wastewater management and monitoring programs, particularly in high-As environments with strong redox gradients.