

## Photochemistry of arsenite on ferrihydrite and goethite

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The photochemistry of arsenite (As(III)) in the presence of the iron oxyhydroxides, ferrihydrite and goethite, has been investigated. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray absorption near edge structure (XANES), and solution phase analysis have been used to characterize the surface bound and aqueous phase species. Both ATR-FTIR and XANES show that the exposure of ferrihydrite or goethite to As(III) for up to 24 h in the dark leads to no change in the oxidation state of the adsorbed or aqueous phase As species. Exposure of either the As(III)/ferrihydrite or As(III)/goethite system to simulated solar radiation results in the majority of the surface bound As(III) becoming oxidized to arsenate (As(V)). At a solution pH of 5, this conversion of As(III) to As(V) on ferrihydrite results in the partitioning of a stoichiometric amount of Fe(II) into the aqueous phase. The majority of the As(V) product remains bound to the ferrihydrite surface. This chemistry on ferrihydrite is relatively similar in the absence or presence of dissolved oxygen. Also, in the ferrihydrite circumstance, the As(III) to As(V) conversion shows the characteristics of a self-terminating reaction in that there is a significant suppression of this redox chemistry before 10% of the total iron making up the ferrihydrite partitions into solution as ferrous iron. The self-terminating behavior exhibited by this photochemical As(III)/ferrihydrite system is likely due to the passivation of the ferrihydrite surface by the strongly bound As(V) product. In contrast, the As(III)/goethite system shows a different photochemical behavior in the absence or presence of dissolved oxygen. In the presence of dissolved oxygen at a solution pH of 5, results suggest that in contrast to ferrihydrite the majority of the As(V) product is in the aqueous phase and the relative amount of aqueous Fe(II) is significantly less than in the ferrihydrite circumstance. A possible reason for this experimental observation is that in the oxic environment Fe(II) on the goethite, which forms via the photoinduced oxidation of As(III), is oxidized to Fe(III) by dissolved oxygen resulting in the formation of reactive oxygen species that can lead to the further oxidation of As(III) in solution. Additional experiments suggest that this behavior is not observed on ferrihydrite at pH 5, due to the lower affinity of the surface for Fe(II), compared to goethite. Overall, the research has brought forward how differences in the surface properties of iron oxyhydroxides can result in changes in redox chemistry.

## Characterisation of arsenic and trace metals in acid sulfate environments

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### Contaminant mobilisation in acid sulfate environments

Disturbed acid sulfate environments pose a serious threat to water quality, ecosystem health and commercial activities. The interaction between hydro-biogeochemical factors leads to the discharge of sulfuric acid and toxic concentrations of dissolved contaminants including iron and aluminium to adjacent water bodies. Comparatively little is known about trace metals and arsenic mobilisation in these environments.

We evaluated the mobilisation of trace metals and arsenic in groundwater and adjacent drain waters during a 10-day rainfall event at our Tweed Valley field site, NSW, Australia. This site has previously been identified as a metal mobilisation hotspot. We used multi-piezometers, drain water autosamplers and Diffusive Gradients in Thin films (DGT) devices to monitor the temporal changes in contaminant mobilisation. Metal and metalloid concentrations were determined using ICP-MS, and arsenic speciation (As(III), As(V), DMA and MMA) was analysed using HPLC-ICP-MS. Changes in contaminant concentrations were compared to concomitant changes in redox potential, pH, anions and dissolved organic carbon concentrations in order to characterise mobilisation processes. Elevated concentrations of cadmium, zinc and arsenic (arsenate and arsenite) were detected, suggesting that trace metals and arsenic also contribute to the poor water quality in these environments. DGT devices were effective in metal and metalloid assessments, and we were able to measure the fluctuations in contaminant concentrations downstream from the metal mobilisation hotspot.

### Outcomes

These results will help us to understand the mobilisation and transport processes of trace metals and metalloids in these environments and better predict their risk to water quality.