

Rethinking Anaerobic Arsenic(III) Oxidation

Microorganisms play a key role in the redox transformation of arsenic (As) in aquifers. Under anaerobic conditions, more toxic As(III) species are typically predominant over As(V). X-ray absorption spectra show, however, that nitrate respirers can oxidize As(III) to As(V) using nitrate as an electron acceptor instead of oxygen within anaerobic landfills. This As(III) oxidation by nitrate respirers is beneficial for As immobilization in situ and to diminish the health risk of drinking elevated As groundwater.

During recent decades various treatment techniques have been extensively studied to remove As from groundwater.¹ As a consequence, As-bearing solid residuals in a significant amount are generated and disposed in landfills, in which the speciation and fate of As are generally determined by ubiquitous microbes in the aquifer. A series of bacteria have been isolated and employed to transform As(III) to As(V) for its remediation, because As(V) is much more strongly adsorbed on minerals than As(III). Considering the ubiquitous existence of As(III)-oxidizing bacteria in groundwater, these indigenous bacteria in groundwater could affect the speciation of adsorbed As in filters. In the subsurface under anoxic conditions, large nitrate concentrations generally restrain the release of As through the nitrate-dependent bacterial oxidation of As(III), but the impact of indigenous nitrate respirers in groundwater on the oxidation of As(III) in filters and of the subsequent landfill of the As-laden materials remains unclear.

Conceptually, the oxidation of As(III) is rooted at the microbe-arsenic-interface reaction. That situation is exactly what Chuan-Yong Jing (Chinese Academy

of Sciences) and his team studied to investigate the As(III) oxidation on granular TiO₂ (GTiO₂) with nitrate-dependent indigenous bacteria.² Collaborating with Ting-Shan Chan (NSRRC), Jing's team acquired As K-edge X-ray absorption near-edge-structure (XANES) spectra at **TLS 01C1** at cryogenic temperature (77 K) under ultra-high vacuum conditions, which precluded sample damage from X-ray-induced As(III) oxidation on TiO₂. NaAsO₂ and Na₂HAsO₄·7H₂O served as references for As(III) and As(V), respectively.

Figure 1 illustrates the As K-edge XANES spectra taken from samples of three treatments, including geogenic groundwater (GGW), GGW amended with 10 mg/L nitrate (GGW+NO₃⁻) and simulated groundwater (SGW) in GTiO₂ filters. The standards As(III) and As(V) exhibited disparate signals centred about 11,870 and 11,874 eV, respectively, which result from transitions from 1s states to 4p states. The transformation of As(III) to As(V) on TiO₂ under indigenous nitrate respirers in groundwater was identified by their signal shift. With linear-combination fitting (LCF), the results shown in **Fig. 1(a)** demonstrate that, at the beginning of anaerobic incubation after filtration

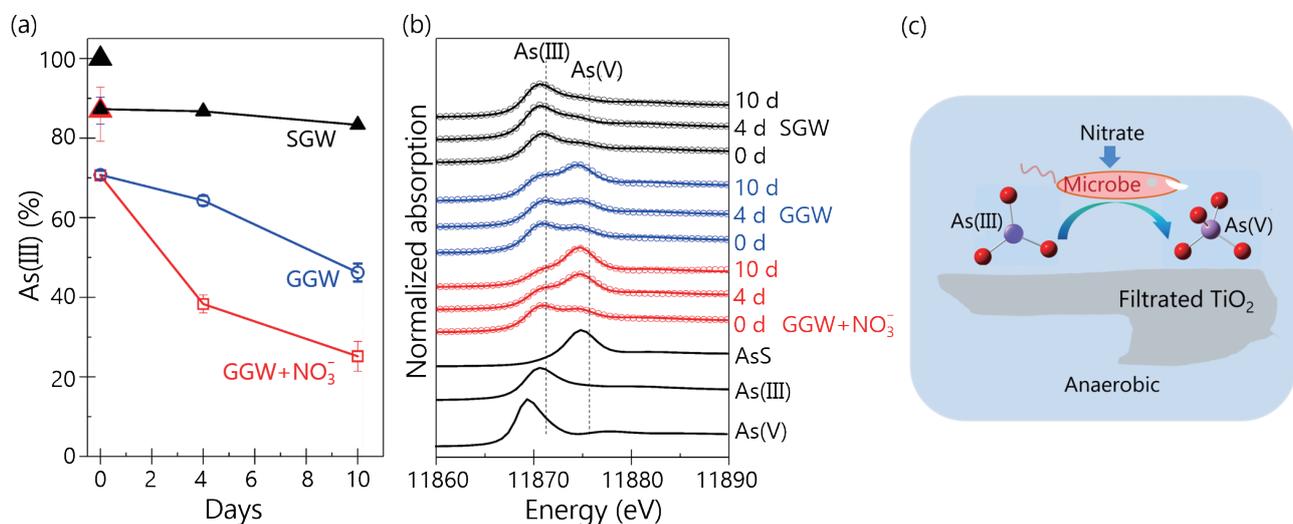


Fig. 1: (a) Variation of As(III) composition and (b) As K-edge XANES spectra on spent GTiO₂ during simulated anaerobic landfill using LCF analysis. Experimental spectra of XANES are displayed as dashed lines. (c) Schematic diagram showing that nitrate respirers anaerobically oxidized As(III) to As(V) using nitrate as a terminal electron acceptor. [Reproduced from Ref. 2]

($t = 0$ d), As(III) on spent GTiO_2 for SGW (black), GGW (blue) and $\text{GGW} + \text{NO}_3^-$ (red) were 87%, 71% and 71%, respectively. During the 10-d anaerobic landfill simulation, the As(III) content in SGW remained roughly constant from 87% at day 0 to 83% on day 10, showing no significant redox transformation of As species. In contrast, the content of As(III) in GGW decreased from 71% to 64% on day 4 and to 46% on day 10. Interestingly, the fraction of As(III) in $\text{GGW} + \text{O}_3^-$ showed a larger decrease from 71% to 38% on day 4, and to 25% on day 10. This observation indicates that some indigenous microbial species in the groundwater oxidized As(III) using nitrate as an electron acceptor in the absence of oxygen.

Iron species that are widely distributed in groundwater can impact As(III) oxidation. To identify their effect on As(III) oxidation, Jing's team also collected Fe K-edge XANES spectra at cryogenic temperature (77 K) at **TLS 01C1**. As **Fig. 2** shows, the retained Fe on GTiO_2 was dominated by amorphous iron(III) arsenate (amFeAsO_4) (67–69%), ferrihydrite (24–26%), and a small proportion of goethite (5–8%). The Fe phase showed no change during incubation for 10 d under anaerobic conditions, which indicates that oxidation of adsorbed As(III) was unrelated to Fe.

Arsenic biogeochemistry in groundwater aquifers is determined predominantly by ubiquitous microbes. The XAS results provided solid evidence that As(III)-oxidizing microorganisms depended on the reduction of nitrate rather than oxygen in the groundwater. In groundwater systems, a suitable electron acceptor for microbial As(III) oxidation is restrained by the redox chemistry of all terminal electron acceptors. The succession of the electron-accepting process for As(III) oxidation generally follows the order oxygen, nitrate, manganese, iron, sulfate and methanogenesis. In an oxygen-limited aquifer, nitrate therefore becomes first respired by microorganisms as the ecologically significant oxidant for anaerobic As(III) oxidation to As(V), which has a greater adsorption affinity for minerals in soil. The microbial-mediated As(III) oxidation by nitrate is beneficial for As immobilization *in situ* in groundwater and diminishes the health risk of As from groundwater to local residents.

In summary, Jing used XAS measurements to reveal that the As(III) adsorbed in spent filters is oxidized to As(V) in the presence of nitrate without oxygen. This work highlights that the presence of nitrate improves microbial As(III) oxidation in groundwater and facilitates immobilization of As *in situ* on spent adsorptive media under anaerobic conditions. (Reported by Ting-Shan Chan)

This report features the work of Chuan-Yong Jing and his collaborators published in Chemosphere 196, 223 (2018).

TLS 01C1 SWLS-X-ray Absorption Spectroscopy

- XANES
- Environmental Science, Chemistry, Surface

References

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2. J.-L. Cui, J.-J. Du, H.-X. Tian, T. S. Chan, C.-Y. Jing, Chemosphere. **196**, 223 (2018).

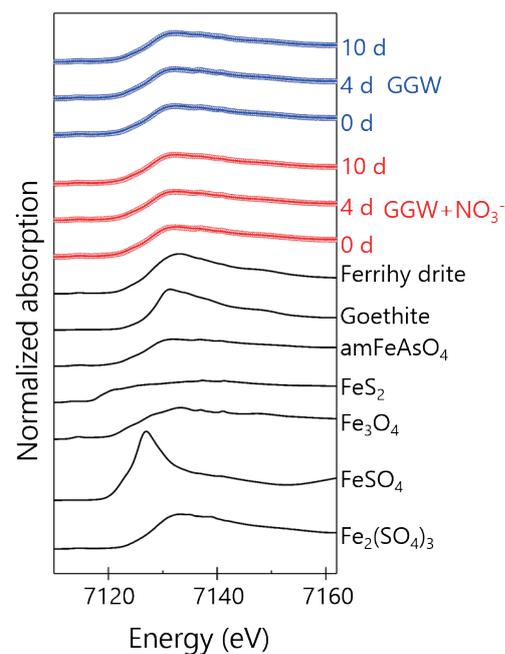


Fig. 2: Iron K-edge XANES spectra on spent GTiO_2 in columns during simulated anaerobic landfill. Experimental spectra are displayed as dashed lines. The solid lines are the LCF results. [Reproduced from Ref. 2]



The photo of the research team taken at **TLS 01C1** – (left to right) Ting-Shan Chan (NSRRC), Chuan-Yong Jing (RCEES, CAS), and Jin-Li Cui (RCEES, CAS).