

## Oxidant identity determines the As(III) removal pathway during treatment of groundwater rich in As(III), Fe(II) and Mn(II)

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Effective methods to remove arsenic (As) from groundwater are needed in view of increasingly stringent As drinking water limits around the world. The oxidation of anoxic As(III)-rich groundwater, which often contains co-occurring Fe(II) and Mn(II), is one of the simplest groundwater treatment methods. In this method, an oxidant is introduced to convert aqueous Fe(II) to insoluble Fe(III) (oxyhydr)oxides that bind As and can be removed by filtration. While aeration is inexpensive, dosing O<sub>2</sub> to As(III)-rich groundwater often cannot achieve low As levels because O<sub>2</sub> alone cannot rapidly oxidize As(III) to the readily-sorbed As(V) oxyanion. Therefore, water providers have proposed switching to strong oxidants to meet lower As limits.

This presentation will compare the addition of weak (O<sub>2</sub>), intermediate (NaOCl) and strong (KMnO<sub>4</sub>) groundwater oxidants on the fate of As during As(III), Fe(II) and Mn(II) co-oxidation. Experiments were performed by dosing the oxidants with automated reactors to initially anoxic solutions containing 50 µg/L As(III), 5 mg/L Fe(II) and 0.5 mg/L Mn(II) and relevant groundwater ions. The removal of As was quantified by ICP-MS and the solid reaction products were characterized by As, Fe and Mn K-edge X-ray absorption spectroscopy.

Our results showed that the oxidizing agent largely determined the pathways and efficiency of As removal. Adding O<sub>2</sub> removed Fe(II), yielding Mn(III)-incorporated lepidocrocite, but was unable to decrease As to <10 µg/L, which was attributed to inefficient As(III) oxidation. Dosing NaOCl consistently decreased As to <10 µg/L (and often <5 µg/L), and removed As(III) via oxidation and As(V) sorption to co-precipitated Mn(III)-rich hydrous ferric oxide (HFO) in the binuclear, bridging (<sup>2</sup>C) complex. The addition of KMnO<sub>4</sub> removed As(III) most effectively, yielding lower residual As concentrations (by as much as 50%) than the NaOCl experiments. The enhanced As removal with KMnO<sub>4</sub> coincided with a systematically shorter As-metal bond length in the solids ( $R_{As-Fe/Mn}=3.24\pm 0.02$  Å) compared to NaOCl addition ( $R_{As-Fe/Mn}=3.29\pm 0.02$  Å), consistent with As(V) sorption to both HFO and MnO<sub>2</sub> produced from KMnO<sub>4</sub> reduction. The implications of these results will be discussed in the context of optimizing groundwater treatment to meet stringent As limits while also considering particle suspension characteristics (i.e. colloidal stability).

