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Incorporation of arsenic and other contaminants into secondary iron mineral products of ferrihydrite transformation in a contaminated soil

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In surface environments, the iron mineral ferrihydrite (Fh) is an efficient scavenger of dissolved contaminants and nutrients and as such plays an important role in controlling their mobility. However, under reducing conditions, Fh is prone to reductive dissolution and/or to mineral transformation into secondary Fe minerals. During these processes, dissolved or Fh-bound elements such as arsenic (As) can be (re)incorporated into the mineral products of the Fh transformation, depending on their composition and mineral structure. Although these mechanisms have been well studied in laboratory model studies, little is known about the relative importance of Fh transformation products for scavenging As and other contaminants in complex soil systems.

To better understand these processes, we incubated ferrihydrite in a multi-metal-contaminated soil (containing high levels of As, Zn, Pb), both as pure mineral in porous mesh bags [1] and as ^{57}Fe-labelled Fh diluted in the soil matrix [1,2]. The slightly alkaline soil (pH ≈ 7.5) was maintained under permanent flooding, and reducing conditions were quickly established (Eh < −200 mV), resulting in elevated pore water concentrations of dissolved Fe(II) and other metal(loid)s, particularly As(III). X-ray diffraction and ^{57}Fe Mössbauer spectroscopy on Fh samples incubated for up to 16 weeks showed progressive transformation to a mix of siderite $FeCO_3$, goethite α−FeO(OH) and a poorly ordered Fe(II) phase, which relative proportions strongly depend on the initial Fh conditioning (pure mineral or ^{57}Fe-labelled Fh mixed with soil). This underlines the impact of soil complexity and mineral dilution as compared to model laboratory studies [1]. Elemental analysis of the incubated pure mineral samples showed significant incorporation of major and trace elements, particularly of Ca, Mn and As. Preliminary micro-X−ray fluorescence data suggests that the identity of the mineral products of Fh transformation determines their ability to scavenge contaminants, as we observe a differential element incorporation into the various Fe mineral products, with As preferentially accumulating in the goethite grains, and Ca favoring siderite.

[1] Schulz et al 2024, *Environ. Sci. Technol.* 58 (24), pp 10601-10610.

[2] Notini et al 2023, *Environ. Sci. Technol.* 57 (27), pp 10008-10018.