

Characterization of Fe(III) (hydr)oxides in arsenic contaminated soil under various redox conditions by XAFS

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Fe(III) (hydr)oxides are ubiquitous components of soils and sediments, where they occur in a variety of phases ranging from poorly crystalline ferrihydrite to well-crystallized minerals such as goethite and hematite. Fe(III) (hydr)oxides play an important role in the natural environment, since they can be a sorbent of various trace elements due to their high adsorptive capacity and large abundance. For example, it is reported that Fe(III) (hydr)oxides as host-phases for As play an important role in As mobility in the Ganges delta plain, where As concentrations in groundwater are often high. For a particular Fe(III) (hydr)oxides phase, a range of crystallinities can exist; these correlate with particle size, surface area, and solubility of the mineral. Such variations lead to various reactivities of Fe(III) (hydr)oxides toward chemical dissolution for diverse assemblages of Fe(III) oxides present in environmental samples. There are many examples for the dynamic change of Fe oxides and their influence on the behaviors of trace elements in the environment. For example, when the structural order of ferrihydrite decreases, Fe(III) (hydr)oxides have a larger specific surface area and hence a greater potential for As removal.

Our recent study showed that the host-phase of As in a mine tailing impacted soil-water system was Fe (hydr)oxides, and that As concentrations increase with Fe under reducing conditions within the deeper part of the soil profile. This finding suggests that the dissolution of As can be controlled by (1) the reductive dissolution of Fe (hydr)oxides and/or (2) the reduction of As(V) to As(III). Similar explanations for the As release under reducing condition have been provided previously. However, determining the relative importance of these two factors on As mobility is still not clear, since the dependence of the sorptive potential of Fe(III) (hydr)oxides for As species on particle size and crystallinity has not been evaluated in many cases. In addition, since Fe(III) (hydr)oxides can be the host phase in soils and sediments of many toxic elements, it is

important to characterize Fe species and their crystallinities to understand the fate and distribution of trace elements in soil/sediment-water systems under various redox conditions. However, few studies have examined the effect of the changes of redox condition on the particle size, crystallinity, and specific surface area of Fe(III) (hydr)oxides.

Thus, characterization of Fe(III) (hydr)oxides in soils near the Ichinokawa mine was conducted in this study using X-ray absorption fine structure (XAFS) and Mössbauer spectroscopies, and the structural changes were correlated with the release of As into pore-water. The Eh values decreased monotonically with depth. Iron is mainly present as poorly-ordered Fe(III) (hydr)oxides, such as ferrihydrite, over a wide redox range (from Eh = 360 to -140 mV). Structural details of the short-range order of these Fe(III) (hydr)oxides were examined using Mössbauer spectroscopy by comparing the soil phases with synthesized ferrihydrite samples having varying crystallinities. The crystallinity of the soil iron (hydr)oxides decreased slightly with depth and Eh. Thus, within the redox range of this soil profile, ferrihydrite dominated, even under very reducing conditions, but the crystalline domain size, and, potentially, particle size, changed with the variation in Eh. In the soil-water system examined here, where As concentration and As(III)/As(V) ratio in soil water increased with the depth, ferrihydrite persisted and maintained or even enhanced its capacity for As retention with increased reducing conditions. Therefore, we conclude that As release from these soils largely depends on the transformation of As(V) to As(III) rather than reductive dissolution of Fe(III) (hydr)oxides.

References

[1] S. Mitsunobu, Y. Sakai, and Y. Takahashi, *Applied Geochem.*, 23 (2008) 3236-3243.

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