Role of Fe speciation on arsenic solubility in flooded paddy soil

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Introduction
Health risks associated with the chronic, low-dose uptake of arsenic (As) have been of great concern. In paddy soil, mobility of As is controlled by soil redox condition [1]. In addition, Fe speciation in soil is a determining factor in controlling As mobility. Fe (hydr)oxide undergoes reductive dissolution with the development of anaerobic conditions and the adsorbed As is concomitantly released to solution due to loss of the adsorption phase. Nonetheless, Fe speciation in soil solid phase and its relation with As mobility has not been well understood. The purpose of this study was to evaluate the role of Fe speciation on As mobility.

Methods
Two kinds of paddy soils (Soil A and B) were incubated under flooded condition. After incubation, Eh and pH were determined then soil and solution phases were separated by centrifugation. The supernatant was filtered and analyzed for As by ICP-MS.

To reveal whether the Fe-bearing solid phase was changed after flooded incubation, the Fe K-edge EXAFS of wet soil paste were acquired at BL12C. A variety of Fe-bearing phases exist in soil, and it is difficult to identify all of the Fe-bearing phases by EXAFS. Therefore, we attempted to determine which mineral phase was increased after the flooded incubation. The $k^3$-weighted $\chi(k)$ spectra of soil samples after flooded incubation (Soil A-red and Soil B-red) were fitted with those before incubation (Soil A-ox and Soil B-ox) as well as with model compounds: ferrihydrite, goethite, lepidocrocite, siderite, and magnetite.

Results and discussion
The physicochemical properties relevant to the behavior and concentrations of As did not differ much between the two soils used in this study. However, the amounts of As released from soil after the flooded incubation differed almost threefold between the two soils; 173 and 468 µg L$^{-1}$ for soil A and B, respectively. More than 80% of As in the soil solid phase was in the form of As(III) after the flooded incubation [2]. Larger amount of Fe was dissolved from soil B than from soil A, suggesting that the dissolution of As was related with the behavior of Fe.

Figure 1 shows Fe K-edge EXAFS spectra of soil samples before and after incubation and those of ferrihydrite and siderite. The Fe K-edge EXAFS spectra of soils A and B were similar before incubation, and ferrihydrite was the major component in the soils. The changes in EXAFS spectra after flooded incubation indicated the formation of a secondary mineral phase. The LCFs of $k^3$-weighted $\chi(k)$ spectra of soil A after flooded incubation indicated that the secondary mineral phase formed was siderite, FeCO$_3$. The proportion of siderite was estimated as 20% of the total Fe-bearing phase.

Figure 1  Fe K-edge EXAFS spectra of soil samples before and after flooded incubation.

Regarding to the As(III) adsorption on siderite [3], it is possible that secondary formation of siderite prevented the dissolution of Fe as well as of As(III). Our results indicated that the soil-to-solution partitioning of As was controlled by speciation and dissolved amounts of Fe-bearing phase in addition to the Eh and pH. As a strategy to regulate As dissolution from paddy soils, it is important to consider the transformation of Fe minerals under anaerobic conditions, despite the fact that, when soil properties are evaluated, most minerals formed under anaerobic conditions are usually unstable under aerobic conditions.

References

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