XAFS study on the behaviors of Antimony and Arsenic in soil-water system under various redox conditions

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Antimony (Sb) is a toxic element and belongs to group 15 of the periodic table, under arsenic (As). The geochemical behavior of Sb in environment is still largely unknown. Since the behavior of Sb in the environment depends on its oxidation state, Sb analysis in environmental samples requires quantitative measurement of Sb(III) and Sb(V). The aim of this study is the speciation of Sb and As in both solid and water phases to understand the reaction of Sb in soil-water environment and to compare the Sb behavior with As examined in mine tailing (Ichinokawa mine, Ehime, Japan) in a natural system and in a soil-water system synthesized in laboratory [1]. The oxidation states and host phases of Sb and As in soil samples of mine tailing (Ichinokawa mine, Ehime, Japan) and in laboratory systems were determined by X-ray absorption fine structure (XAFS) spectroscopy. HPLC-ICP-MS was used for speciation of Sb and As in soil water.

In the natural soil-water system, Sb was present exclusively as the oxidized form, Sb(V), over a wide redox range (from Eh = 360 to -140 mV, pH 8), while As was present as a mixture of As(III) and As(V). This finding was confirmed in the laboratory experiments. EXAFS analyses of Sb and As suggest that the host phases of Sb and As in soil were Fe(III) hydroxides under all redox conditions in this study. Under reducing condition, Sb abundance in soil water decreased in both the natural laboratory systems opposite to the findings of As. Microscopic observation of Ichinokawa soil grains using μ-XAFS shows that significant Sb(III) was locally observed at the rim of the Fe hydroxides particles, while Sb(III) was not observed at the core of the particle. It is reported that the solubility of Sb(III) is much lower than that of Sb(V). Therefore, the findings obtained by the microscopic analysis suggest that Sb reduced to Sb(III) was precipitated on the mineral surface due to its low solubility and that the precipitates containing Sb(III) like Sb_2O_3 may cause the fixation of Sb to the solid phase under reducing condition.

[1] Mitsunobu *et al*. (2006) *Environ. Sci. Technol.* **40,** 7270-7276.

Distribution of Rare Earth Elements in riceplant (*Oryza stiva var. japonica*)

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The concentrations of 15 rare earth elements (REEs: Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in riceplant (*Oryza stiva var. japonica*) were determined. Pot experiments were performed by planting three seedlings in each pot (30 cm of diameter and 30 cm of height) containing soil from the farm in Kyusyu University. The pots were kept outside and water was supplied if necessary. Three pots were prepared to harvest at three different stages of the plants' growth; one month after planting the seedlings, and one week and one month after the appearance of ears. Riceplant shoots were cut off with a plastic knife near the soil surface and washed. The roots were separated from soil by washing carefully with de-ionized water. The plant materials were dried at 80 °C for 48 hours and the dried plant tissue was weighed and finely ground with agate mortar and pestle before REEs determination.

The concentrations of REEs in riceplant shoots and roots were determined by ICP-MS(Agilent 7500). Sample solutions for ICP-MS measurement were prepared by a series of pretreatment consisted of 3 main stages: dissolution of samples, removal of Fe and Al, and REEs concentration with calcium oxalate. In this method, the recovery of REEs was confirmed to be more than 90%.

The observed concentration of REEs in riceplant mostly ranged from 0.05 to 10 ppm. There was not observed clear difference among the samples harvested at different stage of growth. All samples showed similar REE pattern, i.e., light REEs enriched REE patterns. However, concentrations determined in roots were almost 10 times higher than those in shoots. These results suggest that REEs have strong tendency to be retained in/on roots of riceplant.