12C/2002G243

XANES study on the arsenic behavior in paddy field during the cycle of flooded and non-flooded periods

Yoshio TAKAHASHI, Reiko MINAMIKAWA, and Satoshi MITSUNOBU
Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

Introduction

Recently, naturally high concentrations of As in groundwater in the Ganges delta plain (Bangladesh and West Bengal in India) have received significant concerns. Groundwater is used not only for drinking, but also for irrigation of paddy fields, which produces the staple food in the region. Therefore, it is important to understand the behavior of As in paddy fields, but there is few systematic study including the application of in-situ spectroscopic method about the behavior of As in actual paddy fields. This study presents the behavior of As in a well-controlled experimental paddy field in NIAES (National Institute for Agro-Environmental Sciences) in Tsukuba, Japan. Few studies have been conducted on the speciation of these elements in actual paddy soils. We measured the oxidation states of Fe, Mn and As in-situ in soil using XANES (X-ray absorption near-edge structure) analysis.

Experimental

The K-edge XANES spectra of Fe, Mn, and As were measured at BL-12C in Photon Factory, KEK, Tsukuba, Japan. All spectra were collected in the fluorescence mode using a 19-element Ge semiconductor detector (SSD). The energy step was typically 0.25 eV in XANES region. The energy of the peak did not shift more than 0.25 eV throughout all measurements.

Results and Discussion

The Eh values in various depths in the paddy field have been monitored between 1998 and 2001. The Eh values are constantly high around 600 mV during the non-flooded period and decrease after the introduction of water at the beginning of May. The Eh values continue decreasing until the end of August probably because of increased bacterial activity during summer months. The Eh variation is profound at the depth of 0.10 to 0.20 m compared to the depth of 1.0 m.

The depth profiles of dissolved Fe, Mn, and As concentrations in soil water and groundwater were measured, showing that little Fe, Mn, and As were dissolved in water under oxic condition during non-flooded period. In contrast, the reducing water carries high concentrations of these ions during the flooded period. The difference is profound at the depth of 0.20 - 0.50 m, where the soil becomes most reducing condition compared with other depths. This is consistent with the fact that Fe, Mn, and As accumulate in the soil below the depth, i.e. between 0.60 - 1.50 m depth. The data suggests reductive didssolution of Fe, Mn, and As from soil during the flooded period.

To understand the different behaviors of Fe and Mn, XANES technique was applied to soil samples collected under flooded and non-flooded conditions. Comparison of the spectra between the soil samples and references suggests that Mn in soil is Mn(IV) during non-flooded period and that it is reduced to Mn(II) and Mn(III) during the flooded period. On the other hand, the Fe species in the two periods are present as ferrihydrite, which exhibits little change during the flooding and non-flooding cycle. Sequential extraction study showed that As is sorbed on the Fe phase both in the flooded and non-flooded period.

The comparison of the spectra from the soil sample with the reference material ($NaAs(III)O_2$ and $NaH_2As(V)O_4$) shows that 30 % of As is As(III) under non-flooded condition and that up to 70% under the flooded condition. Preferential partition of As(III) into aqueous phase compared with As(V) suggests that this reduction of As in soil explains the increased As concentration in the soil water. This interpretation was supported by our laboratory experiment, where the temporal change of As concentrations and As(III)/As(V) ratios of soil water and submerged soil were determined under various Eh conditions.

This study showed that the dissolution of As in the paddy field is controlled by the reductive dissolution of Fe (hydr)oxide and reduction of As(V) to As(III). It was suggested that As in water is incorporated as As(V) in the soil of paddy fields during the non-flooded period and that it is released to water as As(III) during the flooded period. This implies that rice plants likely incorporate the mobile As(III) from soil water because rice plants grow during the flooded period.

References

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* takahasi@geol.sci.hiroshima-u.ac.jp