Determination of $\mathrm{As^{III}/As^{V}}$ Ratio in Alluvial Sediments of the Bengal Basin Using X-ray Absorption Near-edge Structure

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In this study, we applied X-ray absorption near-edge structure spectroscopy (XANES) to the determination of the $\mathrm{As^{III}}$/$\mathrm{As^{V}}$ ratios in sediments in the Bengal Basin, where groundwater contamination of As causes serious health hazard. The depth profile of oxidation state of As in sediment shows that $\mathrm{As^{III}}$ is dominant species in the depth where As concentration of groundwater is high. This result is consistent with the general understanding about mobility of inorganic As species in various field observations.

Arsenic in natural occurrences has attracted world-wide attention because of its high toxicity and complex geochemical behavior.[1] The major public concern arises from the use of naturally As-contaminated groundwater. The mechanism of the As contamination has to be clarified to construct effective mitigation strategies. Although many researchers have paid attention to the formation mechanism of As-contaminated groundwater in the worst polluted area in Bangladesh, its detailed mechanism is still under debate.

Arsenic is easily soluble into groundwater as inorganic arsenate and arsenite species. Their mobility is regulated by adsorption–desorption equilibrium between water and various solid phases, particularly amorphous Fe oxyhydroxide and Mn oxide[1] in the aquifer. One of plausible trigger for As release from sediment is reduction of arsenate to arsenite, because the mobility of arsenite is generally higher than that of arsenate.[1,2] Thus, speciation of As in sediment is essential to examine the reaction occurring in contaminated aquifer.

X-ray absorption fine structure (XAFS) is the most useful method applicable to direct determination of oxidation state of As in the sediment samples without any pretreatment which would cause change of the valence of As in the sediment sample. However, Smedly and Kinniburgh mentioned that As concentration in the sediments in the Bengal Basin is too low (<2–20 mg/kg) to speciate As in the samples by XAFS,[1] and few XAFS studies have been done for the sediments in this area.[3–5] In this study, we successfully measured X-ray absorption near-edge structure (XANES) of drilled core sediments by the detection of fluorescence X-ray using 19-element Ge semiconductor detector, which enables us to specify the oxidation state of As in bulk sediment.

Sediment cores (3.5 cm in diameter) were taken by penetration drilling from the As-polluted groundwater in Sonargaon area, central Bangladesh. The sediment cores were recovered using a 60-cm long split barrel sampler. Since the sediment was tightly filled in barrel sampler during drilling and recovery, that was not contacted with air and should be preserved As oxidation state. The recovered sediment was immediately packed under vacuum in an oxygen impermeable film bag (Escal film, Mitsubishi Gas Chemical Co., Inc.) with a deoxidizer to avoid oxidation. The samples were brought back to the Institute for Study of the Earth's Interior, Okayama University, Japan, within two weeks after sampling and have been kept in a freezer at −18 °C.

The As K-edge XANES spectroscopic measurements were carried out at BL-12C, Photon Factory, Japan. Emitted X-ray was monochromized by Si(111) double crystal monochromator and then focused using a bent cylindrical mirror. The spectra were detected in the fluorescence mode using a 19-element Ge semiconductor detector. The XANES spectra were recorded in

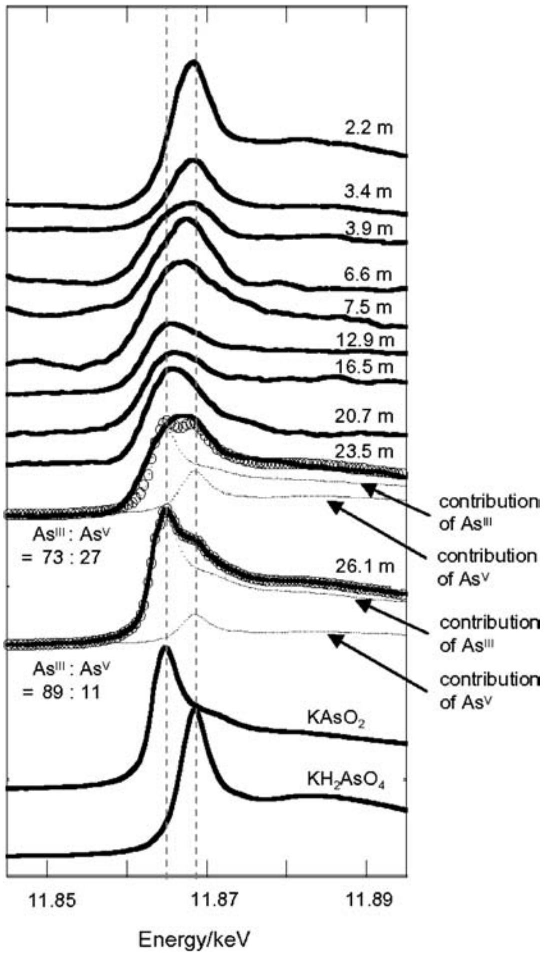

Figure 1. XANES spectra of As in sediment samples and reference compounds: Solid lines, measured spectrum; circles, simulation results by the reference compounds; dotted lines, deconvoluted spectra of $\mathrm{As^{III}}$ and $\mathrm{As^{V}}$ species.

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the energy range between 11.535 and 12.100 keV. Dead time correction of the fluorescence signal was conducted.[6]

Freeze-dried sediment was used for the analysis of total As concentration. The sediments were fused with alkaline reagent, and decomposed into diluted HCl solution, then quantified by hydride generation atomic absorption spectrophotometry (HG-AAS).[7]

The XANES spectra of two reference materials and twelve sediments sampled from 2.2–26.1-m depth from the surface are shown in Figure 1. The peak energy in XANES for $KH_2As^VO_2$ (11.868 keV) was clearly higher than that of $KAs^{III}O_2$ (11.865 keV). Takahashi et al. confirmed that As^{III}/As^V ratio in natural solid samples could be determined by a simulation using normalized spectra of arsenite and arsenate used as the references above, when arsenite and arsenate are the dominant As species.[8] The spectra of the sediments were deconvoluted by least-squares fitting within the energy range between 11.850 to 11.875 keV by a XAFS software package REX 2000 (Rigaku) as shown in Figure 1. XANES spectrum of each sediment sample is used for estimating the As^{III}/As^V ratio based on those of the two reference materials. The quality of the fit was given by the goodness-of-fit parameter R, defined by

$$R = \frac{\sum\{\chi_{\mathrm{obs}}(E) - \chi_{\mathrm{cal}}(E)\}^2}{\sum\{\chi_{\mathrm{obs}}(E)\}^2}, \qquad (1)$$

where $\chi(E)_{\mathrm{obs}}$ and $\chi(E)_{\mathrm{cal}}$ are experimental and calculated data points, respectively. Mean R value of the spectra of 10 samples is 0.08, suggesting that it is reasonable to estimate arsenate and arsenite as the dominant As species in the studied sediments. According to the duplicate measurements for 3 samples (collected from 6.6, 23.5, and 26.1 m), average standard deviation of $As^{III}/(As^{III} + As^V)$ is ±0.09.

The $As^{III}/(As^{III} + As^V)$ ratios (Figure 2) show that the As in the studied sediments from 2.2 to 3.4-m depth is mostly arsenate. A drastic reduction of arsenate occurs around the 3.9-m depth from the surface, where the water table was present at the surveyed period, suggesting that the reduction of arsenate to arsenite occurs at the depth of water table where the redox condition changes drastically associated with the seasonal fluctuation of air intrusion. Below the water table, arsenite increases with the depth and becomes dominant at the depth below 13 m. Recently, Polizzotto et al. indicated that arsenate reduction is marked within surface soil collected from Munshiganj district, Bangladesh, from microanalysis using μ-XAFS measurements of As.[5] Our results based on the bulk analysis of As oxidation state agree well with their results in a different area in Bangladesh, suggesting that the occurrence of As reduction near the surface is generally found in Bangladesh.

Total As concentration of the sediments, which may be regulated by the several factors, i.e., grain size, mineral composition, etc., varies from 1.7 to 8.2 mg/kg (average = 3.6 mg/kg, $n = 12$) concordantly with the $As^{III}/(As^{III} + As^V)$ ratio. This result indicates that the reduction of arsenate to arsenite may induce the release of As from sediments.

Dixit and Hering claimed that the general understanding, which means arsenite is more mobile than arsenate, is not always correct. According to their laboratory experiments, higher proportion of arsenite adsorbed on Fe oxyhydroxide rather than arsenate within near neutral pH.[9] Similar trends were also exhibited by the other reports.[10,11] Our XANES results clearly show that arsenite is dominant species of As in sediments contacted with contaminated groundwater. This is consistent with the previous field observations showing that arsenite is dominant in contaminated groundwater.[1,12]

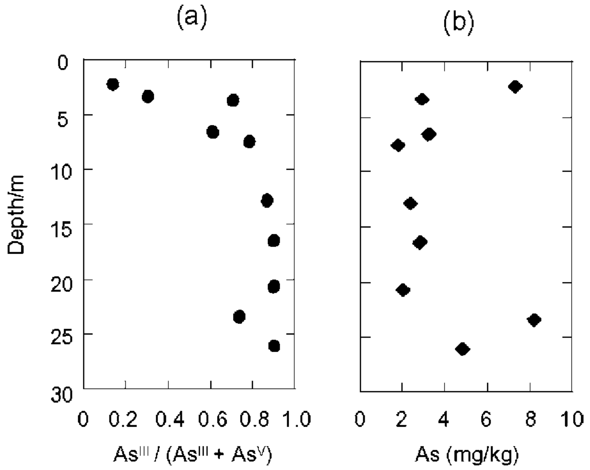

Figure 2. Depth profile of (a) $As^{III}/(As^{III} + As^V)$ and (b) As concentration in sediments.

As shown in this study, despite many laboratory experiments have been focused on the difference of adsorption behavior between arsenite and arsenate on Fe oxyhydroxide, they are still not enough to explain the phenomenon occurring in the Bengal Basin. Further XAFS study for As and also for Fe is being progressed in our laboratory to clarify the factors which make the discrepancy between the field observation and laboratory based experiments.

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