Determination of the As(III)/As(V) Ratio in Soil by X-ray Absorption Near-edge Structure (XANES) and Its Application to the Arsenic Distribution between Soil and Water

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The details of a method used to determine the As(III)/As(V) ratio in soil by arsenic K-edge XANES spectroscopy are described. The spectra of mixtures of NaAs(III)O₂ and NaH₂As(V)O₄, conducted for an As(III)/As(V) calibration, were well-fitted by combining normalized spectra of NaAsO₂ and Na₂HAsO₄, where the coefficients multiplied by the normalized spectra were identical to the molar ratio of As(III) and As(V) in the mixtures. XANES spectra of arsenic in soil samples could also be fitted by a linear combination of the spectra of NaAsO₂ and Na₂HAsO₄, which enabled us to estimate the As(III)/As(V) in a soil containing 10.2 mg/kg arsenic. The As(III)/As(V) ratio in the soil was compared with that of a soil solution contacted with the soil determined by HPLC-ICP-MS, showing that As(III) is distributed to water more readily than As(V). The application of the XANES method is important for a better understanding of the behavior of As(III) and As(V) independently in a natural aquifer.

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Introduction

Arsenic is one of the most toxic elements in the environment, and has been of great interest in environmental studies.^{1,2} In particular, naturally occurring arsenic contamination in groundwater in the Ganges delta plain has been a great issue, and has received significant attention.¹⁻³ It has often been discussed that the dissolution of an iron (hydr)oxide phase containing a large amount of arsenic is an important process for the contamination of arsenic in a reductive condition, such as in ground water.¹ In addition, it has also been indicated that the high mobility of As(III) compared with As(V) is another essential factor concerning the high concentration of arsenic in ground water. However, a quantitative comparison of these two factors is not easy, partly because there have not been many studies on the speciation of arsenic in the solid phase, whereas speciation in the aqueous phase has been conducted more readily by HPLC-ICP-MS or the hydride generation method coupled with atomic absorption spectroscopy or ICP-AES.^{1,4-6} In this study, we employed XANES (X-ray absorption near-edge structure) to determine the As(III)/As(V) ratio in the solid phase, and applied it to arsenic distribution experiments between the soil and water phases. Although there have been some papers on the speciation of arsenic by XANES,⁷⁻¹⁰ most of them do not include details of the quantitative analysis of the As(III)/As(V) ratio for solid media. For example, the difference in the X-ray absorption cross section of white line peaks for the

As(III) and As(V) species must be assessed, since this factor can alter the ratio of different species as can be seen in the case of sulfur when XANES is employed for speciation work.^{11,12}

In this study, the As(III)/As(V) ratio in the aqueous phase was also determined by HPLC-ICP-MS. The determinations of As(III) and As(V) in both the aqueous and solid phases enable us to compare the soil-water distribution coefficients independently for As(III) and As(V), which will produce important information to understand the behavior of arsenic in the environment.

Experimental

Reagents and minerals

Four arsenic compounds were used as standard materials for XANES: oxides (As₂O₃ and As₂O₅) and sodium salts (NaAs(III)O₂ and Na₂HAs(V)O₄·7H₂O). The purity of the starting reagents, purchased from Sigma-Aldrich, Inc. (oxides) and Wako Chem. Ind. (sodium salts), were more than 99%, except for NaAsO₂. The purity of NaAsO₂ measured in this study was 93.1%, determined by ICP-MS, which was taken into account to determine the As(III)/As(V) ratio in the calibration. In order to compare arsenic species sorbed on soil with naturally occurring arsenic minerals, four minerals were received from Hori Mineralogy (Tokyo, Japan), which were confirmed by XRD. The minerals were arsenopyrite (FeAsS), realger (AsS), adamite (Zn₂(AsO₄)(OH)), and erythrite ((Co,Ni)₃(AsO₄)₂·8H₂O). The As(III) standard solution (1000 mg/dm³) received from Spex Certi Prep, Inc. was also included in the reference materials.

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XANES spectroscopy

Arsenic K-edge XANES spectroscopy was employed to determine the As(III)/As(V) ratio in soil samples. XANES spectra were measured at BL-12C of Photon Factory (PF) under the condition of 2.5 GeV, 450–300 mA.¹³ X-rays were monochromatized with an Si(111) double-crystal monochromator and then focused to $1 \times 0.5 \text{ mm}^2$ with a bent cylindrical mirror, which also reduced the higher orders. For all experiments, As_2O_3 was used as an energy reference material, where we set the energy of the white line peak maximum of As_2O_3 at 11.866 keV. The relative energy to this peak was employed to display the XANES spectra in this paper. Arsenic K-edge XANES spectra were recorded in the energy range between 11.830 and 11.920 keV, except for NaAsO_2 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, for which we measured EXAFS. The energy step was typically 0.25 eV at the XANES region. The energy of the peak top did not shift by more than 0.25 eV throughout all of the measurements. All spectra were collected in the fluorescence mode with the sample positioned at 45° with respect to the beam. The fluorescence yield was measured using a 19-element Ge semiconductor detector (SSD). The detection system of the SSD was reported elsewhere.^{14,15} A shaping time of 0.25 μs was adopted for the counting system in this study. Windows of SCAs were tuned to count the arsenic K-line fluorescence selectively. The total count entering the detector (ICR: incoming count rate) was kept lower than 200 kcps by adjusting the distance between the SSD and the sample. It was necessary to correct the SCA windowed signal due to the increase in the dead time when the ICR was increased by large intensities of the fluorescence and scattering X-rays. The correction was made by the code CORDT3U.^{14,15}

HPLC-ICP-MS

The As(III)/As(V) ratio in a soil solution was determined by HPLC connected to ICP-MS (VG PQ-3). The pump and oven used were a Pu-2089 Plus (JASCO) and a Co-2065 Plus (JASCO), respectively. The experimental condition was similar to that described by Donais.⁵ An ODS column (CrestPak C18T-5; inner diameter 4.6 mm; length 250 mm) was used at 40°C . The mobile phase optimized in our laboratory was pH 8 water, containing 0.050% methanol, 0.20 mM Tris buffer, and 0.30 mM tetrabutylammonium phosphate as an ion-pair reagent. The flow rate was 1.0 ml/min. The As(III) peak was observed at around 3.5 min, while As(V) was at 5.8 min. Organoarsenic species were not observed in the soil solution examined in this study.

Soil incubation experiments

Soil incubation experiments were conducted based on a method described by Yuita *et al.*¹⁶ The soil sample used in this study was surface soil (plowed horizon) of a paddy field of the National Institute for Agro-Environmental Sciences (NIAES) at Tsukuba, Japan. The sample was air-dried and sieved (2 mm). Some characteristics of the soil sample are tabulated in Table 1. The concentration of arsenic in the soil was 10.2 mg/kg.¹⁹ The free water content involved in an air-dried soil sample was 4.90%, determined by drying soil sample at 110°C . A 10.0 g portion of the soil sample, 9.51 g as dried weight (110°C), was mixed with various amounts of Milli-Q water in a plastic cylindrical bottle. The water content was defined by the sum of the free water content and the amount of water added to the sample. The degree of water saturation (W_s) is defined as

$$W_s(\%) = 100V_w/V_s, \quad (1)$$

Table 1 Some characteristics of the soil used in the dissolution experiment

Soil classification ^a	Fine textured Gray lawland soil
Soil horizon ^a	Ap _g (0–18 cm)
Soil texture	Light clay (LiC)
pH (H ₂ O)	5.7
True specific gravity	2.64
Major element composition (wt. %, air-dried basis) ^b	
SiO ₂	59.5
TiO ₂	0.85
Al ₂ O ₃	17.8
Fe ₂ O ₃ ^c	7.19
MnO	0.10
MgO	1.05
CaO	1.19
Na ₂ O	1.37
K ₂ O	1.76
P ₂ O ₅	0.20
LOI ^d	9.05
Organic carbon (wt. %) ^e	1.86
Moisture content (wt. %) ^f	4.90

a. Reported by Yuita *et al.*¹⁷

b. Measured by X-ray fluorescence spectroscopy (Rigaku ZSX-101e).

c. Total iron as Fe₂O₃.

d. Loss on ignition at 980°C for 3 h.

e. Measured according to a method developed by Froelich.¹⁸

f. Obtained from weight loss by drying at 110°C overnight.

where V_w is the total volume of water in the soil and V_s is the volume of soil. The degree of water saturation was varied by the amount of Milli-Q water added to the soil. The total water amount mixed with the soil was 3.10 g, 4.55 g, 5.99 g, and 7.44 g to prepare 100%, 140%, 180%, and 220% of W_s , respectively. The sample names used in this study were W-100, W-140, *etc.* Above 140%, the water was flooded on the soil surface. These samples were incubated at 25°C for 21 days. Eh and pH were measured by a platinum electrode and a glass electrode (Fujiwara Sci. Com., EHS-120), respectively, inserted at a depth of a few cm from the surface of the soil. Before sampling the soil solution, Milli-Q water was added and shaken for every sample to keep the water-soil ratio identical to the sample of W-220. For example, 4.34 g of water (= 7.44 g – 3.10 g) was added to the W-100 sample just before sampling. After being centrifuged for 20 min at 3000 rpm, the soil solution was immediately recovered by filtration (0.45 μm membrane filter). The As(III)/As(V) ratio in the extracted soil solution was immediately measured by HPLC-ICP-MS. The soil sample after recovering the soil solution was kept frozen until the XANES measurement at PF. XANES measurements could be conducted directly to frozen samples in plastic bottles. It is considered that the signal from arsenic in the aqueous phase is negligible in the XANES spectra, since the arsenic concentration in water is less than $10 \mu\text{g}/\text{dm}^3$, which is much smaller than the arsenic concentration in soil ($\geq 10 \text{ mg}/\text{kg}$).

Abundances of arsenic, Fe, and Mn

The total amount of arsenic in the extracted soil solution was determined by ICP-MS (VG PQ-3) after adjusting the solution to a 2% HNO₃ solution. The internal standard was Ge-73 and In-115. The contribution of $^{40}\text{Ar}^{35}\text{Cl}$ to mass number 75 was negligible for all samples measured in this study. The manganese concentration in the soil solution was also measured by ICP-MS using Ge-73 as an internal standard, while the iron

Fig. 1 Arsenic K-edge XANES spectra of reference materials (H_3AsO_3 , NaAsO_2 , As_2O_3 , Na_2HASO_4 , As_2O_5), natural minerals (arsenopyrite, realger, adamite, erythrite), and a soil sample (W-180). The horizontal axis is the energy of the incident X-rays relative to the energy at the peak maximum of the white line of As_2O_3 (11.866 keV).

concentration was determined by atomic absorption spectroscopy using the graphite-furnace method (GF-AAS; Jarrell Ash AA-8200).

Results and Discussion

XANES spectra of various arsenic species

Arsenic K-edge XANES spectra of some reference materials and arsenic minerals are shown in Fig. 1. The arsenic concentrations were adjusted below 1% for every sample by diluting with SiO_2 powder. It is obvious that the absorption edge shifts to a higher energy when the oxidation state of arsenic is larger. This can be qualitatively explained by the larger attraction force between an electron and a nucleus for the ion at a larger oxidation state. This suggests that the position of the XANES peak can be used to distinguish As(III) bonding to O, As(V) bonding to O, and other arsenic minerals bonding to S and Fe (arsenopyrite and realger) shown in Fig. 1.

An example of the spectrum of a soil sample (W-180) is also included in Fig. 1. It must be noted that the spectrum was obtained for 10.2 mg/kg arsenic, showing that the fluorescence XANES using 19-element SSD is quite sensitive for arsenic in soil. The sample was the most reductive one ($E_h = 154$ mV, pH 5.53) among those which we studied (Fig. 6). The peak maximum of the sample exists between those of As(III) and As(V) species. This suggests that the sample W-180 contains both the As(III) and As(V) species. The feature at around 11–12 eV in the As_2O_3 spectrum was not found in the sample. A similar structure also observed in As_2S_3 was interpreted theoretically.²⁰ Hence, we employed sodium salts (NaAsO_2 and Na_2HASO_4) to prepare a calibration line to estimate the oxidation state of arsenic in soil samples. The As(III) standard solution (Spex CentriPrep, Inc.) can also be a reference material for As(III), the chemical form of which is presumably H_3AsO_3 in a solution based on the Eh-pH diagram of arsenic.^{10,21}

Fig. 2 First derivative of the XANES spectra of NaAsO_2 , Na_2HASO_4 , arsenopyrite, and a soil sample (W-180).

However, we did not use the solution to prepare reference materials, since (1) the As(III)/As(V) ratio may change during the mixing of As(III) and As(V) solutions and (2) the determination of the As(III)/As(V) ratio in solid media is the purpose of this study. Thus, we employed NaAsO_2 and Na_2HASO_4 as reference materials for As(III) and As(V) species. The energy of the peak maximum of the white line was similar among NaAsO_2 , H_3AsO_3 , and As_2O_3 , suggesting that the As(III)/As(V) ratio determined by XANES analysis would be similar by employing any three of the materials used as As(III) species. In the soil sample (W-180), the contribution of arsenopyrite, the most abundant arsenic mineral in ores, is not important, as can be seen from the spectra. This fact was also supported by the first derivative of the spectra (Fig. 2), where the contributions of As(III) and As(V) were indicated by the soil spectrum, while that of arsenopyrite was slight. This is consistent with previous studies showing that the major arsenic species are the As(III) and As(V) species contained in the metal oxides, particularly those of Fe, Al, and Mn, in soils in the environment.^{1,2}

Determination of the As(III)/As(V) ratio in the solid phase

We can estimate the As(III)/As(V) ratio from the XANES spectrum based on a proper analysis of the spectrum. In this study, the As(III)/As(V) ratio in the solid phase was determined by fitting the sample spectrum by the reference materials, NaAsO_2 and Na_2HASO_4 . Mixtures of reference materials containing 0%, 18.9%, 38.2%, 58.2%, 78.9%, and 100% of As(III) among the total arsenic species, As(III) + As(V), were prepared and diluted by SiO_2 powder. The total concentration of arsenic was adjusted to 1.0%. The mixed sample was kept in a plastic bag, where the oxygen content was regulated at $\text{O}_2 < 0.1\%$ by oxygen absorbers.

The variation in the XANES spectra for mixtures of NaAsO_2 and Na_2HASO_4 are shown in Fig. 3. These spectra were fitted by the spectra of the end members, NaAsO_2 and Na_2HASO_4 . Before the fitting procedure, each spectrum of NaAsO_2 and Na_2HASO_4 was normalized based on the EXAFS spectra by defining the absorption between 500 and 900 eV as one. The spectra of the mixtures ($\mu(\text{mixtures})$) were simulated by a linear combination of the normalized spectra of NaAsO_2 and

Fig. 3 Arsenic K-edge XANES spectra of a soil sample (W-100) and mixtures of NaAsO_2 and Na_2HAsO_4 . The mixing ratios for the mixtures are indicated in the figure. Least-squares fittings by the spectra of NaAsO_2 and Na_2HAsO_4 are shown for a sample and a mixture containing 38.2% of As(III). The solid curves indicate the spectra obtained by the simulation, while dashed curves show the contributions of As(III) and As(V). The results show that these spectra can be well fitted by those of NaAsO_2 and Na_2HAsO_4 . The deconvolutions of NaAsO_2 and Na_2HAsO_4 spectra conducted by the combination of a Lorentzian and an arctangent functions were also shown.

Fig. 4 Relationship between the molar ratio of As(III) ($= x_{\text{III}}/(x_{\text{III}} + x_{\text{V}})$) and the ratio of coefficients multiplied to the spectra of NaAsO_2 and Na_2HAsO_4 to simulate those of mixtures ($= r_{\text{III}}/(r_{\text{III}} + r_{\text{V}})$) as indicated in Eq. (2). A line obtained by a least-squares analysis was indicated with the correlation coefficient (r).

Na_2HAsO_4 ($\mu_{\text{N}}(\text{NaAsO}_2)$ and $\mu_{\text{N}}(\text{Na}_2\text{HAsO}_4)$, respectively):

$$\mu(\text{mixtures}) = r^{\text{III}}\mu_{\text{N}}(\text{NaAsO}_2) + r^{\text{V}}\mu_{\text{N}}(\text{Na}_2\text{HAsO}_4), \quad (2)$$

where r^{III} and r^{V} are coefficients showing the contributions of

Fig. 5 Concentrations of As(III) and As(V) in (a) soil solution and (b) soil at different degrees of water saturation. The definition of the degree of water saturation is given in the text.

As(III) and As(V). A simulation was conducted by a least-squares fitting in the -15 eV and 20 eV region using a routine, Solver, supplied with Microsoft Excel. The spectra of the mixtures were well-fitted by the model (Fig. 3). The $r^{\text{III}}/(r^{\text{III}} + r^{\text{V}})$ values were identical to the molar ratio of As(III) and As(V), $x^{\text{III}}/(x^{\text{III}} + x^{\text{V}})$, as shown in Fig. 4. This shows that the As(III)/As(V) ratio can be determined by a simulation using normalized spectra of NaAsO_2 and Na_2HAsO_4 , if we can consider that As(III) and As(V) are the main species in soil. The error defined as the square root of the unbiased variance obtained from the difference between the measured value and the estimated value given by the regression line in Fig. 4 was 0.04 for $x^{\text{III}}/(x^{\text{III}} + x^{\text{V}})$.

Deconvolutions of the normalized spectra of NaAsO_2 and Na_2HAsO_4 were conducted by combining a Lorentzian and an arctangent functions. The area of the white line expressed by the Lorentzian function was 5.13 and 5.08 (eV $\times$ absorption intensity in normalized spectra) for NaAsO_2 and Na_2HAsO_4 , respectively, showing that the two peak areas are quite similar to each other. This implies that the absorption cross section for the electron transition which produces the white line is similar between the As(III) and As(V) species, though the absorption cross section can vary among different oxidation states, as observed in the case of sulfur.^{11,12} This suggests that the As(III)/As(V) ratio can also be determined by the deconvolution of an unknown spectrum by two pairs of a Lorentzian and an arctangent functions, where the As(III)/As(V) ratio can be directly obtained from the peak area of two Lorentzian functions.

The application of XANES to soil samples in soil incubation experiments

The arsenic K-edge XANES spectra of a soil sample (W-100) prepared in this study are shown in Fig. 3 along with the fitting result, suggesting that the simulation using the model compounds employed in the fitting can give a good agreement with the spectrum of the soil sample. This suggests that the As(III) and As(V) ratio in soil can be estimated by XANES, as conducted in this study. Coupled with HPLC-ICP-MS used for the arsenic species in solution, the As(III) and As(V) concentrations in both the aqueous and solid phases were determined (Fig. 5). It is clear that the As(III)/As(V) ratio in soil is rather similar for every sample, while the contribution of As(III) increases with an increase in the degree of water saturation (Ws) in a soil solution. The Eh value decreases with an increase in Ws, which is consistent with the larger

Fig. 6 Concentrations of dissolved Fe, Mn, and total arsenic in (a) soil solution with (b) Eh and pH condition in water at different degrees of water saturation.

As(III)/As(V) ratio in a soil solution (Fig. 6b). The total concentration of arsenic dissolved in the aqueous phase increased with an increase of W_s . The behavior of arsenic in the aqueous phase is quite similar to those of Fe and Mn (Fig. 6a). This strongly suggests that arsenic is dissolved in a soil solution by the dissolution of Fe and Mn (hydr)oxides containing a large amount of arsenic, as reported in many studies.^{1,6,8,9} In addition, the high mobility of As(III) has been thought to be another factor to cause a high concentration of arsenic in water under a reductive condition.^{1,6,8,9} The distribution coefficients, K_d (ml/g), independently determined for As(III) and As(V) based on the present methods suggest that As(III) is distributed in soil more readily than As(V) (Fig. 7). This supports that As(III) is more mobile in the soil-water system, as has been inferred in many studies.^{1,2} The establishment of appropriate methods to independently determine the distribution coefficients for As(III) and As(V) is a prerequisite to comparing these two factors. XANES is a powerful technique that enables us to determine As(III) and As(V) species quantitatively in soil and other solid media.

Conclusions

This paper describes the details of a method used to determine the As(III)/As(V) ratio by XANES in solid media like soil. The K-edge XANES of arsenic in soil can be well simulated by a linear combination of NaAsO_2 and Na_2HAsO_4 used as reference materials of the As(III) and As(V) species, respectively. The ratio of the coefficients multiplied by the normalized spectra of NaAsO_2 and Na_2HAsO_4 to simulate the spectra of mixtures of NaAsO_2 and Na_2HAsO_4 was identical to the molar ratio of As(III) and As(V), suggesting that the As(III)/As(V) ratio can be directly determined by the mixing ratio of the normalized spectra. The method was successfully employed to determine

Fig. 7 Distribution ratios, K_d (ml/g), of As(III) and As(V) between soil and soil solution at different degrees of water saturation.

the As(III)/As(V) ratio in soil, where the arsenic content was 10.2 mg/kg, showing that the fluorescence XANES using 19-element SSD is sensitive enough to conduct arsenic speciation in natural solid media. The XANES coupled with the speciation method in water (HPLC-ICP-MS or atomic absorption spectroscopy with hydride generation) can be a powerful tool to estimate the behavior of arsenic in a natural aquifer based on the independent information of As(III) and As(V).

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