XAFS analysis of Arsenic bound in holocellulose extracted from organic-rich contaminated sediments

Junko Hara[1,*], and *Susumu* Norota[2]

[1]Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Tsukuba, Ibaraki, 305-8567, Japan
[2]Geological Survey of Hokkaido, Environmental and Geological Research Department, Hokkaido Research Organization, Kita 19 Nishi11, Kita-ku, Sapporo, Hokkaido, 060-0819, Japan

Abstract. The arsenic bound in holocellulose, a precursor of humic substances extracted from organic contaminated sediments, was investigated using XANES (x-ray adsorption near-edge structure) and EXAFS (extended x-ray absorption fine structure) with fluorescence mode. The most abundant arsenic bound in holocellulose was As-O in the first coordination sphere. Sulphur and carbon were also found in a neighbouring coordination shell around arsenic. The arsenic oxidation state was judged to be As (III) by As K edge XANES spectra as a shift to higher absorption edge energy with the increasing formal oxidation state. This arsenic speciation and bounding were well matched with biochemical mechanisms of arsenic absorption into plants.

1 Introduction

Arsenic (As) contaminated water is a major environmental problem that occurs naturally in soils, sediments and groundwater as well as through anthropogenic activities. Arsenic can be present in combination with inorganic or organic substances due to the many different compounds it forms. High concentration of inorganic-bound arsenic is found mainly around mining, ore smelting and industrial areas, whereas organic-bound arsenic is prevalent in marine organisms. Arsenic accumulation in organic soils and sediments has also been observed in humic substances preceeding humification due to the influence of mining drainage or marine sediment [1, 2]. Holocellulose is the complex mixture of polysaccharides remaining after the removal of lignin from tree-wood by treatment with sodium chloride solution. This material is one of the precursors of humic substances, which consist of a heterogeneous mixture with no single structural formula. The arsenic in humic acid has been reported bound via inorganic elements such as iron, alumina, calcium, sulphur, or directly bound with amino, carboxyl, and phenolic functional group in humic substances [3-5]. The process whereby arsenic is incorporated into humic

---

*Corresponding author: j.hara@aist.go.jp

substances determines its stability in organic sediments and the evaluation of its toxicity. This research focused on how arsenic is bound in holocellulose in organic-rich contaminated sediments, with a discussion of arsenic accumulation in organic sediments.

2 Materials and Methods

2.1 Sediment samples

Organic-rich sediments were collected from five different depositional environments in Hokkaido, Japan. The sediments from a backshore marsh deposit (A) and flood plain deposit (B) were saturated with seawater, the river flood plain deposit (C) was saturated with blackish water, and the lacustrine deposit (D) and river terrace deposit (E) were saturated with fresh water at the time of sedimentation (Table 1). Total arsenic contents of these sediments are 65 to 277 mg/kg, which are higher than average arsenic contents of surrounding river sediments.

Table 1. Depositional environment and Arsenic contents of sampling sediments.

sample ID	organic phase	total As [mg/kg]	environment of deposition	porewater during sedimentation
A	humic clay	277	backshore marsh deposit	seawater
B	peat	174	flood plain deposit	seawater
C	peat	65	river flood plain deposit	blackish water
D	humic sandy silt	141	lacustrine deposit	fresh water
E	peat	126	river terrace	fresh water

2.2 Extraction of Holocellulose

Collected sediment samples were freeze-dried, and gravels ($\varphi \geqq 2$ mm) and roots were removed using a 200 mesh sieve, as well as careful picking with tweezers. Holocellulose was extracted as follows: (i) As a pre-treatment, samples were mixed with a benzene/ethanol (1:1) solvent for soxhlet extraction to remove bitumen and then dried for more than 24 hours; (ii) Lignin was extracted four times using a mixture of 83 mM $NaClO_2$ + 43.7 mM CH_3COOH at 80 °C for 1 hour in a nitrogen atmosphere; (iii) The holocellulose residue was rinsed using Milli Q water, dried and reduce to powder. Arsenic (As) concentrations were determined by XRF (EDX-720, Shimadzu Co. Japan) on powders mixed with boron nitride and pressed into disks.

2.3 Arsenic K-edge analysis

Arsenic K-edge absorption spectra (EXAFS and XANES) of organic substances and reference As materials were analysed at the BL-9A and BL-12C beamline of Photon Factory (PF) at the High-Energy Accelerator Research Organization (KEK), in Tsukuba, Japan. The rising K-edge energy of As was calibrated to 11865.0 eV. A Si(111) double-crystal monochromator was used at both beamlines with Ge filter, slit. The first ionization chamber was filled with N_2 and second with Ar. The XANES spectra of samples were collected in the fluorescence detection mode using a 19-element Ge semiconductor detector, whereas those of the reference materials were collected in the transmission mode.

3 Results and Discussion

3.1 Arsenic

The holocellulose extracted from lacustrine and river terrace deposit, which had been deposited in fresh water, had the As contents of 40-73 ppm, substantially higher than those deposited in blackish water and seawater with As contents of 11-19 ppm. The arsenic-rich terrestrial materials are also enriched in sulphur.

3.2 Chemical State of Arsenic in holocellulose

Although arsenic might be oxidized from As(III) to As(V) by the effect of X-ray irradiation heat due to long time exposure, As K-edge XANES spectra showed that As(III) is the major oxidation states of arsenic in holocellulose. Major arsenic binding in holocellulose as As-O, As-C and As-S was also detected in every depositional environment.

The As-S bond strength tends to be stronger in sulphur rich terrestrial sediments (Fig. 1). Low molecular thiol components in plants; cysteine, γ-glutamylcysteine glutathione, and phytokeratine, are reported as arsenic transporters and have the effect of arsenic detoxification [6,7]. As(V) is reduced to As(III) with the help of As reductase inside the plant cell, and As(III) is detoxified by the formation of complexes with thiol-rich peptides [8]. Arsenic speciation and binding with sulphur reflect the arsenic uptake into the plants. As-C bond strength in seawater affected sediments is greater than As-S bond strength. A recent study observes that plants cannot transform inorganic species into organic species [9]. The As-C bond is considered to reflect the arsenic methylation process in small animals and microorganisms. Organic arsenic compounds, such as DMA (dimethylarsinate) and MMA (monomethylarsinate), are generated as metabolic substances and are absorbable chemicals by plants. Although spectral strength is clear in terrestrial sediment due to higher arsenic concentration, the As-C bond in seawater-affected sediments is stronger than the As-S bond because the C/S ratio of holocellulose is greater than in terrestrial sediment due to enhanced biological activity in the former.
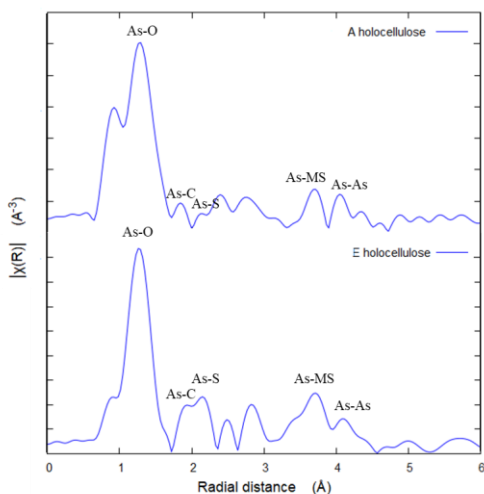

Fig. 1. Fourier transform of the k^3-weighted As EXAFS spectra of holocellulose in backshore marsh sediment (A) and terrestrial sediment (E), calculated in the k range 3-15 Å^{-1}.

4 Conclusions

EXAFS and XAFS analytical results for holocellulose from organic-rich various sediments shows that trivalent arsenic is prevalent and bound to oxygen in the first coordination sphere. The next neighbour coordination elements are carbon and sulphur. This result is consistent with arsenic transportation and detoxification in the plants.

Arsenic accumulation mechanisms of humic substances in sediments have not been clarified yet. This result shows that the arsenic trapping form at the early humification stage and stable arsenic bond in organic species remains the trace of soil organism activity.

References

1. L. Charlet, D.A. Polya, Elements, **2**, 91 (2006)

2. L. Winkel, M. Berg, M. Amini, S. J. Hug, C. A. Johnson, Nat. Geoc., **1,** 536 (2008)

3. P. Langner, C. Mikutta, R. Kretzschmar, Nat. Geoc., **5,** 66 (2012)

4. T. Lenoble, D.H. Dang, M. Loustau Cazalet, S. Mounier, H.R. Pfeifer, C. Garnier, Talanta, **134**, 530 (2015)

5. C. Catrouillet, M. Davranche, A. Dia, M. Bouhnik-Le Coz, M. Pédrot, R. Marsac, G. Gruau, Journ. of coll. Interf. Scien., **460**, 310 (2015)

6. W. Zhang, Y. Cai, K. R. Downum, L. Q. Ma, Environm. Poll.. **131(3)**, 337 (2004)

7. S. Misha, S. Srivastava, R. D. Tripathi, P. K. Trivedi, Aquat. Toxicol., **86(2)**, 205 (2008)

8. G. Abbas, B. Murthaza, I. Bibi, M. Shahid, N. K. Niazi, M. I. Khan, M. Amjad, M. Hussain, Natasha. Intern. Jour. of Environm. Res. and pub. Heal., **15(1)**, 59. (2018) https://doi.org/10.3390/ ijerph15010059

9. P. M. Finnegan, and W. Chen, Front. in Phys., **3**, 1 (2012)