



Iodine speciation in the soil-water systems using XANES and HPLC-ICP-MS

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Introduction

Iodine is one of the essential elements for animal. The environmental behavior of iodine is of great importance especially related to the release of radioiodine from processing of nuclear fuel, nuclear accident, etc. In soil-water environment, possible iodine species are iodide (I^-), iodate (IO_3^-), molecular iodine (I_2), and organo-iodine species. To understand the fate of radioactive iodine in a soil-water system, it is necessary to establish speciation method of iodine in soil and water. X-ray absorption near-edge structure (XANES) has been recently used as an *in-situ* speciation method of iodine in solid materials. In this study, we comparatively measured K-edge and L_{III} -edge XANES using same samples to establish the direct speciation method for iodine in soil samples. In addition, XANES was applied to natural soil samples. Species of iodine in the soil water from the same site was also determined by high performance liquid chromatography connected to ICP-MS (HPLC- ICP-MS).

Experimental

Iodine K- and L_{III} -edge XANES was measured at beamline BL01B1 at SPring-8 (Hyogo, Japan) and beamline BL-9A at Photon Factory (Tsukuba, Japan), respectively. At both beamlines, XANES spectra were measured in fluorescence mode using a 19-elements Ge semiconductor detector except for reference materials at K-edge measured in transmission mode. Standard samples of KI, KIO_3 , I_2 , were diluted to 0.5wt.% and 5wt.% by addition of BN, pressed as pellet. The reference solutions, KI

aqueous solution (0.10 M), KIO_3 aqueous solution (0.10 M), and CH_3I in ethanol (1wt.%) were packed into airtight polyethylene bags. Suwannee River Humic Acid (SRHA) was received from International Humic Substances Society, which was used to obtain XANES spectrum of iodine in humic substances. Iodine was added up to 100 mg/kg to standard soil sample to examine the influence of major elements in soil in XANES measurements. Soil and soil water samples were collected at depths of 0, 3, 6, 9, and 12 cm from surface in Yoro area, Chiba, Japan. The soil profile was flooded with brine water from a tube well containing iodine (iodine concentration: 5.27 mg/kg). At each depth, Eh and pH were measured by a platinum electrode and a glass electrode, respectively. Species of iodine in the soil and soil water were determined by XANES and HPLC-ICP-MS, respectively.

Results and discussion

Comparison of XANES at K- and L_{III} -edges: The characteristic of L_{III} -edge XANES is more prominent than that of K-edge. Therefore, L_{III} -edge XANES is more effective to distinguish iodine species than K-edge. However, at L_{III} -edge measuring iodine L_{α} emission, the proximity of its energy to those of Ca K_{α} and $K_{\beta 1}$ causes a large contribution of background X-ray in the XANES spectra, since Ca is a major element in soil. Thus, it was concluded that K-edge XANES is more useful than L_{III} -edge for the speciation of iodine in natural soils owing to its lower detection limit.

Speciation of iodine in natural soil and water sample: The depth profile of iodine concentration in soil correlates quite well with that of organic carbon content. The XANES spectra of soil samples were well fitted by the spectrum of SRHA. Accordingly, most of the iodine in soil is combined with organic matter such as humic substances. In soil water, both iodide ion and organic iodine bound to dissolved humic substances were found. Since most of the iodine was bound to organic substances in the soil phase, it is suggested that iodine can be retained in soil mainly in the form of organic iodine species, especially associated with humic substances.

Reference: Y. S. Shimamoto and Y. Takahashi, Superiority of K-edge XANES against L_{III} -edge XANES in the speciation of iodine in natural soils, *Anal. Sci.*, 2008, in press.