

Speciation of iodine in soil-water system based on XANES and HPLC-ICP-MS

In 2011, the Fukushima Daiichi Nuclear Power Plant released radioactive iodine to wide areas in Japan (^{131}I and ^{129}I , half-lives = 8 days and 1.57×10^7 years, respectively). Since radioactive iodine can strongly affect human health, an urgent investigation of the distribution and behavior of radioactive iodine is required. However, the estimation of iodine behavior is difficult because of its different mobility among their possible species in the environment [1]. In soil-water systems, possible iodine species are iodide (I^-), iodate (IO_3^-), molecular iodine (I_2), and organic iodine species [1,2]. Iodine speciation in soils is occasionally investigated by sequential extraction. This method is practically an effective speciation method for a sample with low iodine concentration. However, the sequential extraction approach is associated with some uncertainties caused by readsorption in the remaining solid during the experimental procedure, cross-contamination, incomplete digestion and release of organic iodine, and transformation of chemical forms during the sequential extraction, especially in a strong acid/base solution [1]. In this study, we investigated iodine speciation in a natural soil-water system by nondestructive analysis, X-ray absorption near-edge structure (XANES) and high-performance liquid chromatography combined with inductively coupled plasma mass spectrometry (HPLC-ICP-MS).

Soil and pore water samples were collected around the Yoro hot springs, Chiba, Japan, at various depths (0, 3, 6, 9, and 12 cm). Brine water from the hot springs is associated with natural methane gas and contains a large amount of iodine. The sampling sites consisted of (i) soil under flooded conditions with the water layer several centimeters above soil surface and (ii) brine water from the tube well containing iodine as I^- at a concentration of 5.8 mg/L.

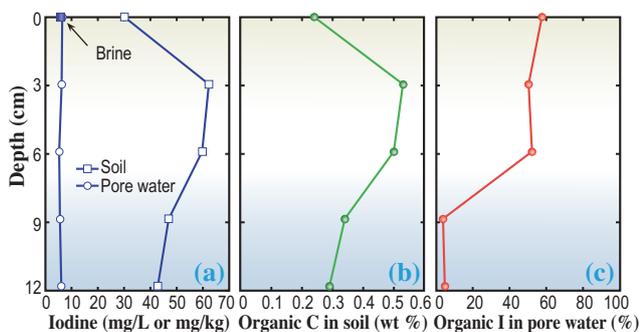


Fig. 1. Vertical profiles of (a) iodine concentrations in soil (\square), pore water (\circ) and brine water (\blacksquare); (b) organic carbon contents in soil; (c) organic iodine fraction in pore water.

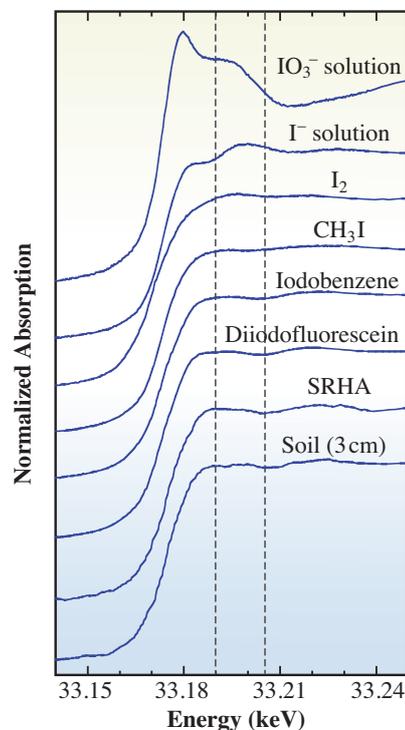


Fig. 2. XANES spectra of standard materials and soil sample collected at 3 cm depth (SRHA: Suwannee River humic acid).

Iodine concentration in soil (Fig. 1(a)) is highly correlated with the organic carbon content (Fig. 1(b)). The correlation coefficients (R^2) of iodine with iron, manganese, and organic carbon are 0.04, 0.01, and 0.95, respectively. Therefore, it is suggested that iodine immobilization in soil is strongly influenced by natural organic matter. Iodine species in soil were determined by iodine K -edge XANES, measured at beamline BL01B1 (Fig. 2) [3]. XANES spectra of iodobenzene, diiodofluorescein, and Suwannee River humic acid (SRHA) showed a concave curve around 33.205 keV and a moderate peak around 33.190 keV. These two structures are useful characteristic features for distinguishing organic iodine from its inorganic forms. According to the fitting of the spectra by the linear combination of organic iodine (humic substances, diiodofluorescein, or iodobenzene) and inorganic iodine (KI or I^- solution), iodine in soil was mainly found to be in organic iodine form.

To describe the host phase for iodine in soil, iodine mapping in soil particles on the micrometer scale was performed by micro-XRF analysis using the iodine $K\alpha$ -line (28.6 keV) irradiated at 35 keV, a high X-ray energy region that can be excited by the third-generation

synchrotron radiation facility (BL37XU). The air-dried soil sample collected at a 3 cm depth was embedded in a high-purity epoxy resin and polished to create a thin section of about 50 μm . X-rays from the undulator were monochromatized using a Si(111) double crystal and focused to $1.5 \times 1.5 \mu\text{m}^2$. Among the various soil particles examined, Fe-rich minerals coated with organic matter and clay minerals contained a large amount of iodine (Fig. 3). A comparison of iodine, Fe, Al, and C mapping results revealed that iodine concentration in organic matter rich areas is higher than that in Fe-rich and clay-rich areas. This result is consistent with the bulk speciation by XANES, illustrating the dominance of organic iodine species.

To determine the chemical reaction of iodine between soil and pore water, iodine speciation in pore water is also necessary. Iodine species in pore water were investigated by HPLC-ICP-MS with anion exchange and size exclusion columns for the separation of (i) I^- and IO_3^- , and (ii) inorganic and organic iodine species, respectively. Pore water collected at a 0–6 cm depth contained 50%–60% of organic iodine bound to dissolved organic matter, with I^- as the other species (Fig. 1(c)). At a 9–12 cm depth, 98% of iodine was in the form of dissolved I^- . According to soil incubation experiments using soil collected at a 3 cm depth, the dissociation of I^- from organic matter occurs under anoxic conditions (data not shown), which is consistent with the observation in the natural soil-water system.

In this study, species of iodine in both soil and pore water were determined. Using these results, the ratios of I^- and organic iodine concentration between soil

and pore water ($K_d = [\text{iodine in soil}]/[\text{iodine in pore water}]$) was calculated at various depths. Results show that iodide is distributed in the solution more than 10-fold greater than organic iodine species. The transformation of inorganic iodine to organic iodine plays an important role in iodine immobilization, especially in a surface soil-water system (Fig. 4).

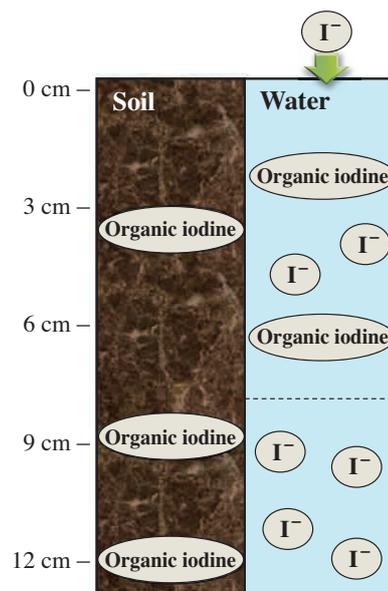


Fig. 4. Schematic of iodine species in soil-water system at Yoro area.

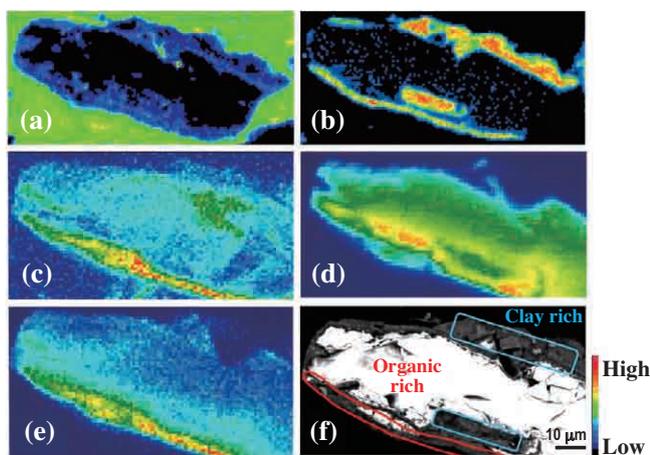


Fig. 3. (a) Carbon mapping, (b) aluminum mapping, (c) iodine mapping, (d) iron mapping, (e) zinc mapping, and (f) backscattered electron image for clay and organic matter-rich areas. (a), (b), (f): obtained by EPMA analysis. (c)–(e): obtained by micro-XRF analysis at BL37XU.

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