

Formation of Organic Iodine Supplied as Iodide in a Soil–Water System in Chiba, Japan

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 Supporting Information

ABSTRACT: Speciation of iodine in a soil–water system was investigated to understand the mechanism of iodine mobility in surface environments. Iodine speciation in soil and pore water was determined by K-edge XANES and HPLC–ICP-MS, respectively, for samples collected at a depth of 0–12 cm in the Yoro area, Chiba, Japan. Pore water collected at a 0–6 cm depth contained 50%–60% of organic iodine bound to dissolved organic matter, with the other portion being I^- . At a 9–12 cm depth, 98% of iodine was in the form of dissolved I^- . In contrast, XANES analysis revealed that iodine in soil exists as organic iodine at all depths. Iodine mapping of soil grains was obtained using micro-XRF analysis, which also indicated that iodine is bound to organic matter. The activity of laccase, which has the ability to oxidize I^- to I_2 , was high at the surface of the soil–water layer, suggesting that iodide oxidizing enzymes can promote iodine organification. The distribution coefficient of organic iodine in the soil–water system was more than 10-fold greater than that of iodide. Transformation of inorganic iodine to organic iodine plays an important role in iodine immobilization, especially in a surface soil–water system.

INTRODUCTION

Radioactive iodine, ^{131}I and ^{129}I , is produced by the fission of uranium and can be released by nuclear testing, processing of nuclear fuel, and nuclear accidents.^{1,2} Since the half-lives of ^{131}I and ^{129}I are 8 days and 1.57×10^7 years, respectively, the assessment of iodine behavior is very important in both the short and long term. Speciation of iodine is essential to determine iodine mobility in the environment. In soil–water systems, possible iodine species are iodide (I^-), iodate (IO_3^-), molecular iodine (I_2), and organic iodine species.^{2–4} Among them, IO_3^- has much greater affinity for solid media than I^- .^{5–7} Conversion of IO_3^- to I^- has been reported in previous studies.^{7–9} On the other hand, organic iodine is one of the major chemical forms in surface soil.^{3,10–12} The influence of microbial activity on the accumulation of iodine in soil has been investigated in many studies.^{12–15}

Iodine speciation in soils and sediments is occasionally investigated by sequential extraction.^{2,3,16} This method is practically an exclusive 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 procedure, cross-contamination, incomplete digestion and release of organic iodine, and transformation of chemical forms during sequential extraction, especially in a strong acid/base solution.² When iodine concentration is high enough, direct measurement of iodine speciation can be performed using X-ray absorption fine structure (XAFS).^{6,7,10,12,17} Shimamoto and Takahashi¹⁰ compared the performance of K-edge and L_{III} -edge X-ray absorption near-edge structure (XANES) and found that the detection limit of K-edge XANES is lower

than that of L_{III} -edge XANES, although L_{III} -edge XANES is more informative than K-edge XANES.

Iodine speciation in solution samples including I^- , IO_3^- , and organic iodine bound to naturally occurring high molecular weight organic matter such as dissolved humic substances is easily determined by high-performance liquid chromatography connected to inductively coupled plasma mass spectrometry (HPLC–ICP-MS). Identification of organically bound iodine in humic substances can be achieved using size exclusion chromatography (SEC).¹⁸

In this study, we investigated iodine speciation in a natural soil–water system in the Yoro area, Chiba, Japan, where soil and pore water samples were collected at various depths. Iodine species in soil were determined by K-edge XANES. To describe the host phase for iodine in soil, iodine mapping for soil particles on the micrometer scale was performed by micro-XRF analysis using iodine K-line (28.6 keV) irradiated at 35 keV, a high X-ray energy region that can be excited by a third-generation synchrotron radiation facility (SPRING-8). Iodine species in pore water were also investigated by HPLC–ICP-MS equipped with anion exchange and size exclusion columns for the separation of (i) I^- and IO_3^- and (ii) inorganic and organic iodine, respectively. The novel speciation data obtained using these direct methods allowed for a discussion of the formation of organic iodine and its importance in iodine immobilization in the natural

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soil–water system, where iodine is initially supplied as inorganic iodine.

MATERIALS AND METHODS

Yoro Soil and Pore Water Samples. Yoro soil and pore water samples were collected around the Yoro hot springs (35°15'N, 14°09'E), Chiba, Japan. The temperature of these hot springs, which are of nonvolcanic origin, is generally less than 25 °C.¹⁹ Brine water from the hot springs is associated with natural methane gas and contains a large amount of iodine. The Kazusa Group, which is a possible origin of the brine water, is composed of marine sandstone and mudstone turbidite sequences.¹⁹

The sampling site 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 at a concentration of 5.8 mg/L, as reported for other brine waters found in this area.^{19,20} The brine water upwelled from a depth of 450 m through a tube installed in the area. In this soil–water system, downward water flow is not predominant, and the water is more stagnant. Before sample collection, E_h and pH were measured using a platinum electrode (Fujiwara Sci., EHS-120) and a glass electrode (Horiba, D-51), respectively, by inserting the electrodes into selected depths in the flooded soil layer. Pore water and soil samples were collected at five depths: 0, 3, 6, 9, and 12 cm. Pore water samples were extracted using soil–water samplers (Fujiwara Sci., FV-448), which is equipped with a suction lysimeter with borosilicate glass filter connected to a Teflon tube and syringe. Subsequently, samples were filtered through 0.45 μ m membrane filters. On the other hand, soil samples were scooped up from the soil surface with a spatula. Collected soil samples were packed into polyethylene bags and frozen until XANES analysis to avoid any change in the chemical state of the iodine. Pore water samples were stored at 4 °C until measurement.

Pore Water Analyses. Iodine concentrations in pore water samples were determined by ICP-MS (Thermo Fisher Science PQ-3 or Agilent 7500). Pore water samples were diluted with 1.25 wt % tetramethylammonium hydroxide (TMAH) and spiked with Re as an internal standard. The I^-/IO_3^- ratio in pore water was determined by HPLC–ICP-MS using an anion exchange column (TSKgel super IC-AP, Tosoh). However, dissolved organic iodine was trapped in the column packing material and did not elute from the column. Hence, SEC was performed to detect the fraction of large molecular weight (MW) organic iodine using TSKgel G3000 PWXL (Tosoh). Relative amounts of dissolved humic substances were also measured by UV absorbance at 260 nm. In the Supporting Information, (i) the correction method of different sensitivity between I^- and organic iodine and (ii) the conditions of the HPLC system are described (Figure S1 and page S2, Supporting Information).

Soil Analyses. Soil samples were dried in an oven at 50 °C for more than 24 h. Iodine in the soil was extracted with 5 wt % TMAH at 70 °C for 3 h, according to the method described by Yamada et al.,²¹ and the iodine concentration in the extract was determined by ICP-MS. Concentrations of major elements in the soil were measured by X-ray fluorescence spectrometry (XRF; Rigaku ZSX-101e) using the glass bead method.²² Mineral compositions were analyzed using an X-ray diffractometer (XRD; MAC Sci., M18XHF). Organic carbon (OC) content of the soil was measured using a CHNS analyzer (Perkin-Elmer, 2400 II). Inorganic carbon was removed by the addition of 2 mL of 1 M

HCl to a 20 mg soil sample, followed by sonication for 1 h prior to drying at 50 °C.

XANES and Micro-XRF Analyses. The analytical method for iodine K-edge XANES spectra is described by Shimamoto and Takahashi.¹⁰ Preparation of reference materials is shown in the Supporting Information. Iodine K-edge XANES was measured at beamline 01B1 using a bending magnet at SPring-8 (Hyogo, Japan). A Si(311) double-crystal monochromator with two mirrors was used to obtain the incident X-rays. Standard samples and Yoro soil samples were measured in transmission and fluorescence modes, respectively. A 19-element Ge semiconductor detector was used in the fluorescence mode. Data analyses, such as background subtraction, normalization, and linear combination fitting of XANES spectra, were performed with REX2000 Ver. 2.5 software (Rigaku).

An air-dried soil sample from a 3 cm depth was embedded in a high-purity epoxy resin (Eposet, Maruto Co., Ltd.) and polished to create a thin section. Details of the preparation of the thin section were described in Takahashi et al.²³ To determine the distribution of Fe oxides, organic matter, and clay minerals in the soil particles, Fe, C, and Al mapping and backscattered electron (BSE) images were obtained using electron probe microanalysis (EPMA) (JEOL JXA-8200). Iodine mapping was obtained at beamline 37XU (SPring-8) by a micro-XRF technique.²⁴ X-rays from the undulator were monochromatized by a Si(111) double-crystal and were focused to $1.5 \times 1.5 \mu\text{m}^2$ (beam size at sample) by the Kirkpatrick–Baez (K–B) mirror system.²⁵ The X-ray energy was fixed at 35 keV. A two-dimensional (2D) analysis was made by an X–Y axis stepping-motor-driven stage. The sample was fixed on a sample holder oriented at 10° to the orthogonal direction of the beam. The X-ray fluorescence intensities were measured by Si(Li)-SSD (SEIKO EG&G). The step size of the stage was set to 1 μ m and exposure time at each step was 0.5 s. Measurements were carried out in air and at room temperature.

Activity of Laccase. The relative activity of laccase was determined after extraction of enzymes from soil by Milli-Q (MQ) water. The procedure is described in detail in the Supporting Information.

Soil Incubation Experiments. Soil incubation experiments were performed using soil collected at 3 cm depth. Soil and MQ water were mixed 1:1 by weight and incubated for 293 h under oxic and anoxic conditions. After 26 h, samples for the anoxic condition were moved to an anoxic chamber, while the oxic sample was kept under oxic conditions. We collected a portion of water from the anoxic samples after 26, 131, and 293 h and determined concentrations of inorganic and organic iodine (see the Supporting Information).

RESULTS AND DISCUSSION

Concentrations of Iodine in Soil and Pore Water Samples from Yoro. As the depth of the Yoro soil samples increased, the E_h values decreased from 299 to 58 mV, while the pH values remained almost constant (Figure 1a). Ionic strength and composition of pore water at the 0 cm depth are given in Table S1 (Supporting Information). Iodine content of pore water was similar to that of brine water (5.8 mg/L) at all depths (Figure 1b). On the other hand, the iodine concentration in the soil was highest at the 3 cm depth and decreased at greater depths. The soil was a sandy soil, consisting mainly of quartz and feldspars. The depth profile of iodine did not correlate with the profiles of Fe or Mn but positively correlated with the OC content (Figure 1b,c). The correlation

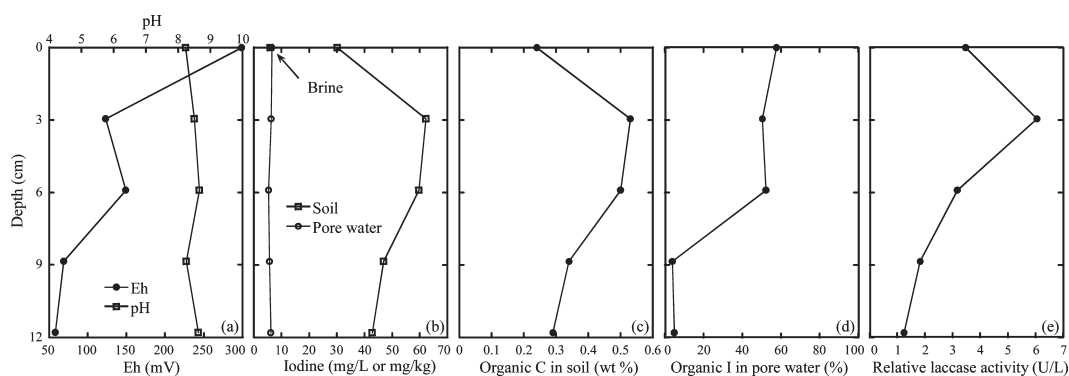


Figure 1. Vertical profiles of (a) pH and E_h ; (b) iodine concentration in soil (\square), pore water (\circ), and brine water (\blacktriangle); (c) organic carbon contents in soil; (d) organic iodine fraction in pore water; and (e) relative laccase activity.

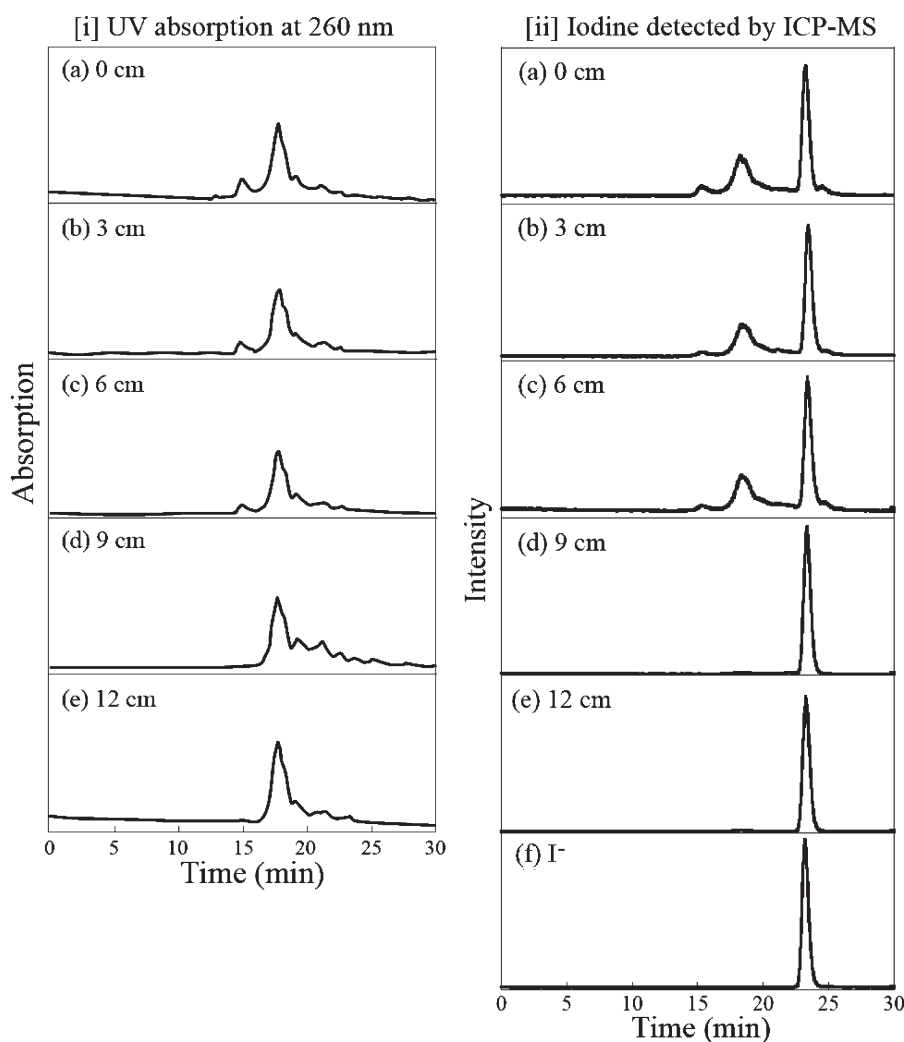


Figure 2. (i) Chromatograms of UV absorption at 260 nm of pore water samples. The vertical range is constant among the samples. (ii) (a–e) Chromatograms of iodine in pore water samples from various depths separated by SEC-ICP-MS. (f) Chromatogram of standard KI solution.

coefficients (R^2) of iodine with Fe, Mn, and OC 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 (NOM).

Speciation of Iodine in Pore Water. The species of iodine in pore water were determined by HPLC–ICP-MS. An anion exchange column was used to determine the I^-/IO_3^- ratio in pore

water and original brine water, and only I^- was detected (Figure S2, Supporting Information).

Brine water contained a lot of dissolved organic matter; the concentration of dissolved OC was 45 mg/L, which suggested that organic iodine can be present in the aqueous phase. To separate organic and inorganic iodine, SEC was employed in the HPLC

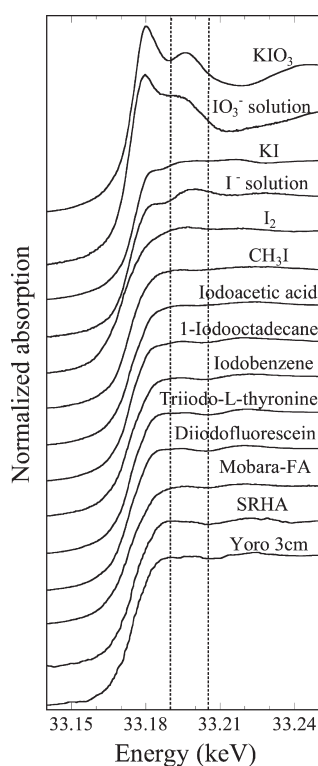


Figure 3. XANES spectra of standard materials and soil sample collected from 3 cm depth (Mobara-FA, Mobara fulvic acid; SRHA, Suwannee River humic acid).

system. With a SEC column, smaller molecules elute later than larger molecules. The separation ability of SEC is shown in Figure S3 (Supporting Information). To evaluate the MW distribution of dissolved organic matter in Yoro samples, the UV absorption at 260 nm was selected. Although UV absorption by organic matter is greater at shorter wavelengths, I^- absorbs UV around 220–230 nm, with a contribution that was not negligible below 260 nm.

In the chromatogram (Figure 2i), the peak of the highest MW fraction at 15 min became weaker as the sample depth increased, and the peak was not observed for samples taken at 9–12 cm. In contrast, the peak of a lower MW fraction became stronger as sample depth increased. This can be attributed to the preferential removal of higher MW fractions in shallower regions due to their larger affinity to solid surfaces.²⁶ The chromatograms of UV absorption at 260 nm and ^{127}I intensity in ICP-MS were well-matched for all MW fractions, except for the peak of free I^- observed at 23 min (Figure 2j,ii). This indicates that iodine is not enriched in a specific MW fraction of dissolved organic matter but is uniformly distributed among the different molecular sizes. The ratio of organic to inorganic iodine was calculated using the peak areas (Figure 1d). Fifty to sixty percent of iodine was dissolved in the organic form at 0–6 cm depth, while 98% of iodine was in the form of I^- at 9–12 cm depth, showing that iodine organification is dominant in the surface pore water. Schwehr et al.¹³ investigated organic iodine formation under oxic conditions by batch sorption (incubation) experiments using soil and aquifer sediments. They demonstrated that the OC content is the limiting factor in organic iodine formation and also suggested dissociation of iodine from organic matter. In the samples in the present study, the amount of dissolved organic matter is almost

constant at the various depths (Figure 2i), suggesting that some factors other than OC content inhibit the formation of organic iodine at 9–12 cm and/or low microbial activities. It is also possible that dissociation of iodine from organic matter is enhanced under suboxic conditions at 9–12 cm.

Speciation of Iodine in Soil by K-edge XANES. XANES spectra of iodobenzene, 3,3',5-triiodo-L-thyronine, diiodofluorescein, Mobara-FA, and SRHA showed a concave curve around 33.205 keV (Figure 3). Three reference materials (iodobenzene, 3,3',5-triiodo-L-thyronine, and diiodofluorescein) were selected because Schlegel et al.¹⁷ found that iodine in natural humic substances is covalently bound to the aromatic ring of humic substances. This characteristic feature around 33.205 keV in iodine K-edge XANES is useful for distinguishing organic iodine from its inorganic forms. XANES spectra of Yoro soil samples at depth of 3, 9, and 12 cm also exhibit a concave curve around 33.205 keV (Figures 3 and S3, Supporting Information). In addition, a moderate peak around 33.190 keV is also unique to organic iodine species including the Yoro soil samples. According to the fitting of the spectra by linear combination of organic iodine (humic substances, diiodofluorescein, or iodobenzene) and inorganic iodine (KI or I^- solution), it was estimated that more than 87% ($\pm 5\%$) of iodine is in the form of organic iodine at any depth (more details are found in the Supporting Information).

We also determined the organic iodine content in soil collected at 3 cm depth using a sequential extraction method.³ Here, it is assumed that all iodine species can be initially extracted by 5 wt % TMAH solution at room temperature. The humic acid fraction was determined after acidification to pH 1.5, while the fulvic acid fraction was determined by incorporation into calcium oxalate precipitate in solution. Following this method, organic iodine bound to humic and fulvic acids in our samples was determined to be 63% ($\pm 2\%$, $n = 4$). The value is less than 87% of the total organic fraction of iodine determined by K-edge XANES. To explain this difference, the organic iodine fraction in the extract was determined by SEC-ICP-MS, and it was 46% after extraction by TMAH at room temperature. This shows that organic iodine can be transformed into inorganic iodine in alkaline solution due to the substitution of iodine in organic matter by abundant OH^- in alkaline solution.²⁷ In addition, a considerable amount of iodine should be bound to the humin fraction, which cannot be extracted by the method. Because of the dissociation of inorganic iodine from organic iodine in the alkaline solution and the presence of unextractable humin fraction that can contain iodine, the sequential extraction method can give organic iodine content lower than that given by XANES. Considering these two effects, we can conclude that (i) the organic iodine fraction determined by XANES (=87%) here is consistent with the value indicated by the sequential extraction method (=63%) and that (ii) XANES is a better method to determine directly the organic iodine content in soil samples.

Micro-XRF. Sampling depths of EPMA and micro-XRF analysis of iodine using $I\ K\alpha$ are about 1 μm and >50 μm (=thickness of the thin section), respectively. Among the various soil particles examined, Fe-rich minerals coated with organic matter and clay minerals contained a large amount of iodine (Figure 4). BSE images gave important information for characterization of soil particles (Figure 4a). The area comprising organic matter and clay minerals, which have a smaller average atomic number, appears gray in the BSE image. According to carbon mapping, most organic matter surrounded mineral surfaces. The thickness of the carbon coating for the BSE analysis was adequately homogeneous

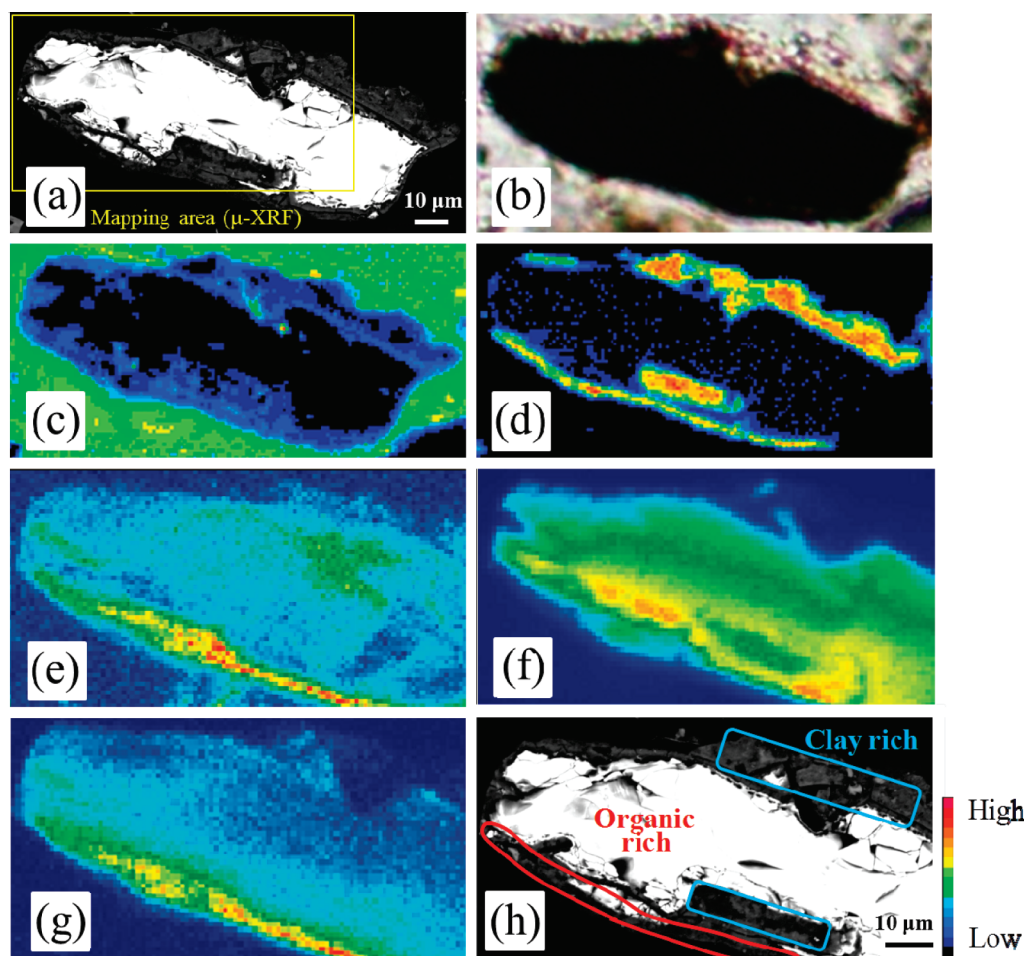


Figure 4. (a) Backscattered electron image, (b) transmission microscope photograph, (c) carbon mapping, (d) aluminum mapping, (e) iodine mapping, (f) iron mapping, (g) zinc mapping, and (h) backscattered electron image, depicting clay and organic matter rich area. Images a, c, and d were obtained by EPMA. Images e–g were obtained by micro-XRF analysis at SPring-8, beamline37XU.

and did not create contrast in the carbon image. Since the carbon content in the resin was 67%, the highest carbon content area (green color; Figure 4c) can be attributed to the resin itself. Carbon content in the area surrounding the mineral (blue) is higher than that in the Fe-rich area (black). The blue area is considered to be composed of NOM in the sample. Aluminum is also rich in the gray-colored area in the BSE image (Figure 4d). This area can also be rich in clay minerals (Figure 4h). These findings suggest that NOM is present as an organic–inorganic (=clay) complex in the soil.

Comparison of iodine, Fe, Al, and C mapping revealed that iodine concentration is higher in areas rich in organic matter than in Fe-rich and clay-rich areas. This result is consistent with the bulk speciation analysis by XANES, illustrating the dominance of organic species for iodine. One may think that the iodine-rich area does not overlap strictly to C-rich area, which is possibly due to the different probing depths of iodine and C in our analyses. Zinc was also distributed in areas rich in organic matter, indicating that Zn is also present as an organic complex in the soil. This is consistent with the fact that Zn favors organic complexes.²⁸

Activity of Laccase. The vertical profile of laccase was similar to the variation of iodine in soil (Figure 1e). Laccase activity was highest at 3 cm and decreased at deeper levels. Laccase, produced by plants, fungi, and bacteria,^{29,30} is one of the copper-containing

oxidases and can function as an enzyme for iodide oxidation to I_2 .²⁹ Warner et al.³¹ evaluated the rate of reaction of $I_2(aq)$ with humic substances and the formation of iodine-substituted phenols. In this reaction, $I_2(aq)$ is more reactive as an electrophilic species than I^- . One possible pathway of iodine uptake by soil, as proposed by Amachi,³² involves the oxidation of iodide in soil and sediments to I_2 by microbial enzymes and incorporation into organic compounds. Schwehr et al.¹³ also suggest that organic iodine formation in the surface sediment is related to bacterial enzymatic activity, according to the kinetics of organic iodine formation. Our study shows a strong correlation between depth profiles of the organic iodine content and the activity of laccase and is consistent with these previously proposed mechanisms of iodide organification. Findings revealed that there is a relatively greater ability for organification at the surface under oxic conditions, where the laccase activity is relatively greater.

Soil Incubation Experiment. In pore water samples from 9 to 12 cm depth under suboxic conditions, most of the iodine exists as I^- . To demonstrate the effect of redox conditions on the dissociation of organic iodine, soil incubation experiments were performed. Variations of E_h , pH, and concentrations of organic iodine and I^- with the elapsed time during the incubation experiment are shown in Figure S5 (Supporting Information). Only I^- was detected after using an anion exchange column in

both systems (i.e., IO_3^- was not detected). During the incubation period, organic iodine concentration decreased with time as the anoxic condition developed. At 293 h, organic iodine concentration under anoxic condition is less than that under oxic condition. On the other hand, concentration of I^- in the anoxic sample increased with decreasing E_h and became much higher than that of the oxic sample. According to Francois,²⁷ iodine in organic matter can be substituted by nucleophiles such as sulfide ions and thiosulfate. Although it is difficult to show the specific pathway of dissociation of I^- from organic matter, the incubation experiments clearly demonstrated that dissociation of I^- occurs under anoxic conditions.

Comparison of Soil–water Distributions of Organic Iodine and Iodide. The ratios of I^- and organic iodine concentration between soil and pore water ($K_d = [\text{iodine in soil}]/[\text{iodine in pore water}]$) were calculated at various depths. It was assumed that 87% of iodine in soil is in the organic form (Figure S6, Supporting Information). Results show that iodide is distributed in solution more than 10-fold greater than organic iodine species. The variation in iodide fraction in water (Figure 1d) can be attributed to the difference in K_d values between iodide and organic iodine and the iodide fraction in soil, as determined by XANES (Figure S7, Supporting Information). Under oxic conditions, $K_d(\text{organic I})/K_d(\text{I}^-)$ is about 10, while the value is more than 100 under suboxic condition ($=9\text{--}12$ cm depth).

Since organification of iodine is limited under anoxic conditions, organic iodine in the pore water at 9–12 cm can be also supplied by desorption of organic iodine from the soil or degradation reactions of soil organic matter to produce dissolved organic iodine. The lower fraction of organic iodine in the water suggests that the dissociation reaction proceeds to a larger degree in water compared with reaction rates of organic iodine formation in the water. In addition, larger $K_d(\text{organic I})$ at 9–12 cm in the soil profile implied that the organic iodine ratio to organic carbon is lower in the dissolved organic matter compared with organic matter in the soil as a consequence of the dissociation of iodide from organic matter especially in water. These results reveal that the dissociation of iodine from organic iodine to iodide is a very important reaction to understand the iodine behavior under reducing conditions such as in soil–water and sediment–water systems and in groundwater–sedimentary rock systems containing organic matter.

■ ASSOCIATED CONTENT

S Supporting Information. Additional information on methods, figures, and a table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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