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# Soil-soil solution distribution coefficient of soil organic matter is a key factor for that of radioiodide in surface and subsurface soils

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## ABSTRACT

We investigated the vertical distribution of the soil–soil-solution distribution coefficients ($K_d$) of $^{125}$I, $^{137}$Cs, and $^{85}$Sr in organic-rich surface soil and organic-poor subsurface soil of a pasture and an urban forest near a spent-nuclear-fuel reprocessing plant in Rokkasho, Japan. $K_d$ of $^{137}$Cs was highly correlated with water-extractable $K^+$. $K_d$ of $^{85}$Sr was highly correlated with water-extractable $Ca^{2+}$ and SOC. $K_d$ of $^{125}I^-$ was low in organic-rich surface soil, high slightly below the surface, and lowest in the deepest soil. This kinked distribution pattern differed from the gradual decrease of the other radionuclides. The thickness of the high-$^{125}I^-$ $K_d$ middle layer (*i.e.*, with high radioiodide retention ability) differed between sites. $K_d$ of $^{125}I^-$ was significantly correlated with $K_d$ of soil organic carbon. Our results also showed that the layer thickness is controlled by the ratio of $K_d$-OC between surface and subsurface soils. This finding suggests that the addition of SOC might prevent further radioiodide migration down the soil profile. As far as we know, this is the first report to show a strong correlation of a soil characteristic with $K_d$ of $^{125}I^-$. Further study is needed to clarify how radioiodide is retained and migrates in soil.

## 1. Introduction

Some long-lived radionuclides released to the atmosphere are deposited on the ground, where they move down through the soil and eventually reach the groundwater. For assessing risks to human health, it is important to understand their behavior in soil. The emission of long-half-life iodine ($^{129}$I) from nuclear fuel reprocessing plants is of public concern (Kaplan et al., 2014), therefore, it is important for public acceptance of such plants to understand its migration in each specific soil surrounded a nuclear facility.

The behavior of iodine in soils is affected by physical, chemical, and biological processes. Its mobility in surface soils varies widely with soil type. A substantial proportion of soil iodine exists in the soil solid phase through adsorption to metal oxides or the formation of irreversible covalent bonds to organic matter (OM) (Bors et al., 1988; Hou et al., 2003; Shetaya et al., 2012; Yoshida et al., 1992; Whitehead, 1973; Yamada et al., 2002; Yu et al., 1996). Although the proportion of soil iodine in the liquid phase is generally considered to be low, Hou et al. (2003) found that around 20% of total $^{129}$I in Chernobyl soil occurred in water-soluble and exchangeable fractions. The content of radioiodide in the liquid phase is crucial because it could pollute groundwater in the long term.

The soil–soil-solution distribution coefficient ($K_d$) is used to estimate the migration of various substances in soils. In aerobic conditions, it is considered that iodine is bound to soil organic matter (SOM), and that immobilization increases with the content of SOM (Kaplan et al., 2014); the IAEA (2010) lists the $K_d$ of I as increasing with the SOM content. Our previous study showed that in a high-OM soil, exogenous inorganic iodine was rapidly transformed to organically bound forms, depleting water-extractable iodine (Takeda et al., 2015). However, some SOM remains dissolved and retains covalently bonded iodine in the liquid phase (Shetaya et al., 2012). The relationship between iodine partitioning and OM partitioning in soil is not clear. In addition, the distribution of $K_d$ to several meters depth is not known.

In this study, we measured the $K_d$ of radioiodide in soil cores collected from a pasture and from an urban forest near a nuclear fuel reprocessing plant. Both soils were OM-rich in the surface and OM-poor in the subsurface. We selected $I^-$ because $I^-$ is a major

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*Abbreviations:* Distribution coefficient ($K_d$), Organic matter (OM); Molecular-weight (MW), Soil organic carbon (SOC); Soil organic matter (SOM), Water-extractable (W.E.).

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form of iodine in soils (Kaplan et al., 2014), and our previous research found only I$^-$ in the soil solution as an inorganic iodine species (Takeda et al., in press). We also measured the $K_d$ of radiocesium and radiostrontium, which are important fission radionuclides. We relate these $K_d$ values to depth distribution patterns, land use, and soil properties, including OM content.

## 2. Materials and methods

### 2.1. Soil core samples

We collected soil samples from a pasture (40°99′91″N, 141°28′95″E, 75.2 m a.s.l.) and an urban forest (40°57′48″N, 141°22′06″E, 18.6 m a.s.l.) near a spent-nuclear-fuel reprocessing plant in Rokkasho, Aomori, Japan. The region has as oceanic climate (Cfb) with monthly average temperatures between −1.7 °C + 21.3 °C, and an average annual rainfall of 1427 mm. Soil cores from the pasture were collected from 0 to 0.5 m depth on 25 to 28 September 2012 and from 0.5 to 3.0 m depth on 4 to 8 August 2014. Cores from the forest were collected from 0 to 0.5 m depth on 25 to 28 September 2013 and from 0.5 to 3.0 m depth on 15 to 18 August 2015. Cores of up to 1 m in length with a diameter of 86 mm were collected with a triple-wall core barrel system, which covers the cores immediately with a vinyl sleeve with little disturbance. The samples were stored in a cool dark place until analysis.

The soils at both sites were Andosols derived from volcanic ejecta. Both sites had an OM-rich humic silt A horizon (0–0.40 m in the pasture and 0–0.64 m in the forest), a B horizon (0.40–1.54 m and 0.64–1.37 m), and C horizon (>1.54 m and >1.37 m; Fig. S1). The samples were cut into 10-cm slices (Table S1) and passed through a 4-mm sieve. All samples were analyzed fresh for $K_d$ measurement and the liquid phase analysis mentioned later. The clay content was analyzed according to the JSA (2009). For practical reasons, we determined the levels of soil organic carbon (SOC) instead of SOM. The total soil organic carbon (SOC) content was measured by the method of Schumacher (2002) with an elemental analyzer (FLASH 2000; Thermo Fisher Scientific).

### 2.2. Batch sorption experiment

Fresh samples of 2 g were mixed with 19 mL of deionized water in a 50-mL tube and then shaken for 24 h at 60 rpm at 20 °C. Then 1 mL of tracer solution containing about 5 kBq of carrier-free $^{125}$I$^-$ ($T_{1/2} = 59.4$ days), $^{137}$Cs ($T_{1/2} = 30.1$ years), or $^{85}$Sr ($T_{1/2} = 64.9$ days) was added. $^{125}$I and $^{85}$Sr are not a fission product. However these isotopes have characteristics suitable for the use in measurement of the $K_d$, since they have relatively long half-life, can be detected by gamma-counter crystal detectors and behave in the same way as fission products such as $^{129}$I and $^{131}$I, or $^{90}$Sr. For these reasons, we used $^{125}$I and $^{85}$Sr for our batch sorption experiment. After further shaking for 14 days, which preliminary testing showed was enough time to reach sorption equilibrium (data not shown), the soil suspension was centrifuged at 3180 × g for 10 min, and the supernatant was filtered through a 0.22-μm membrane filter (Millipore Steriflip). Radioactivities of $^{125}$I, $^{137}$Cs, or $^{85}$Sr in the filtrate were measured with a NaI scintillation counter (Aloka, ARC-7001R48-1).

### 2.3. Liquid-phase analysis

Solution samples were prepared as for the batch sorption experiment, except for the tracers, at a solid-to-liquid ratio of 1:10. Water-extractable (W.E.) OC was measured by TOC analyzer (Shimadzu, TOC-5000). W.E.-Ca and W.E.-K were measured by ion chromatography (Thermo Fisher, Dionex AS-AP).

### 2.4. $K_d$ calculation

$K_d$ values of radionuclides were calculated as:

$$K_d = \frac{q}{C_f} = \frac{VL \times \left(C_i - C_f\right)}{Ms \times C_f}$$

where $q$ (Bq/kg) and $C_f$ (Bq/L) are the $^{125}$I, $^{137}$Cs or $^{85}$Sr activities in the solid phase and the liquid phase, respectively, at 14 days after addition of the tracers; $C_i$ (Bq/L) is the initial $^{125}$I, $^{137}$Cs, or $^{85}$Sr concentration in the liquid phase; $VL$ (L) is the solution volume; and $Ms$ (kg) is the soil dry weight.

$K_d$ of organic carbon ($K_d$-OC) was calculated as:

$$K_d\mathrm{OC} = \frac{q_{\mathrm{OC}}}{C_{f\mathrm{OC}}} = \frac{Ms \times \mathrm{SOC} - VL \times \mathrm{W.E.OC}}{VL \times \mathrm{W.E.OC}}$$

where $q_{\mathrm{OC}}$ (g/kg) is the OC concentration in the original soil sample and $C_{f\mathrm{OC}}$ is that (g/L) in the liquid phase after 15 days of incubation. SOC (g/kg), W.E.-OC (mg/L), $VL$, and $Ms$ were measured as above. $K_d$-OC might be slightly overestimated because a minor proportion of the OC was dissolved or decomposed during the shaking.

### 2.5. Statistics

Correlation analysis was performed using Spearman's rank correlation coefficients (Aabel, Gigawiz). To assess the relationship between the $K_d$ of organic C and the $K_d$ of $^{125}$I$^-$ at each sites, ordinary least squares regression was performed by means of the R library SMATR (Warton et al., 2012). In addition, common slopes across sites were tested using a likelihood ratio test, and intercepts were compared between sites by calculating the Wald statistic.

## 3. Results and discussion

### 3.1. Distribution coefficients of radionuclides

The values varied depending on the depth, land use, or tracer.

$K_d$-$^{125}$I$^-$ ranged from $8.2 \times 10^0$ to $3.8 \times 10^3$ L/kg in the pasture soil and from $1.2 \times 10^0$ to $1.4 \times 10^4$ L/kg in the forest soil (Fig. 1; Table S1a; Table S1b). $K_d$-$^{125}$I$^-$ in 142 dried agricultural soils in Japan ranged from $4.4 \times 10^0$ to $1.8 \times 10^2$ L/kg (Ishikawa et al., 2013). $K_d$-I values from around the world ranged from $1.0 \times 10^{-2}$ to $5.8 \times 10^2$ L/kg, but the moisture status of the samples was not reported (IAEA, 2010). Our $K_d$ values measured in fresh soil ranged higher than those of the two previous studies. On the other hand, they were in the range of values of 68 Japanese soils ($1.1$–$1.0 \times 10^5$ L/kg) measured fresh by Yoshida et al. (1998).

The formation of covalent bonding between iodine and OC, known as iodination, can be caused by enzymes, quinolic moieties, or free radicals (Pommier et al., 1973; Huber et al., 1989; Steinberg et al., 2008; Li et al., 2011). I$^-$ rapidly binds to organic substances in the presence of hydrogen peroxidase, laccase or lactoperoxidase (Pommier et al., 1973; Huber et al., 1989; Seki et al., 2013), and also the iodination rate decreases rapidly in OM-rich surface soil, which inhibits laccase activities (Seki et al., 2013). Iodine mobility in soil is also affected by soil microorganisms, and $K_d$-$^{125}$I$^-$ was remarkably decreased under conditions that inhibit microbial activity (Yoshida et al., 1998; Seki et al., 2013). The reason for the different $K_d$ values between fresh and dry soils may be related to the suppression of microbial activity in dry soil. These results suggest that the use of dried soil underestimates $K_d$-$^{125}$I$^-$, and the use of fresh soil gives a more realistic estimate.

$K_d$-$^{137}$Cs and $K_d$-$^{85}$Sr in pasture soil ($^{137}$Cs, $4.1 \times 10^3$–$5.2 \times 10^4$ L/