

Soil-Soil Solution Distribution Coefficients for Se, Sr, Sn, Sb, And Cs in Japanese Agricultural Soils

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ABSTRACT

In this study, soil-soil solution distribution coefficients (K_d s) for five radionuclides (Se-75, Sr-85, Sn-113, Sb-124, and Cs-137) were determined by batch sorption tests in 142 Japanese agricultural soil samples (63 paddy soil and 79 upland soil samples). The results showed that Se- and Sb- K_d data did not have a normal or a log-normal distribution, but Sr-, Sn-, and Cs- K_d data did have a log-normal distribution. Further, Se-, Sr-, and Cs- K_d values differed between paddy and upland soil samples in t -test ($p < 0.05$). Spearman's rank correlation test was carried out to investigate correlations between K_d values for each radionuclide and soil properties. The combination of the K_d value and the soil property having the highest correlation coefficient (R_s) for each radionuclide was as follows: Se- K_d – concentration of water soluble P ($R_s = -0.51$); Sr- K_d – concentration of water soluble Ca ($R_s = -0.57$); Sn- K_d – concentration of water soluble Sr ($R_s = 0.57$); and Sb- K_d – concentration of water soluble P ($R_s = -0.67$). Although there were no soil properties which had a good correlation with Cs- K_d values for all soil samples, the best correlated soil property with Cs- K_d values was concentration of water soluble ammonium ion ($R_s = -0.48$) for upland soil samples.

INTRODUCTION

One of the most important pathways of radionuclides to humans from the environment is food consumption. It is necessary to clarify behaviors of radionuclides in agricultural fields using long-term dose assessment models. One of the key parameters required in these models for the behavior dynamics of radionuclides in soils is the soil-soil solution distribution coefficient (K_d) [1]. In order to provide a more practical K_d parameter, many K_d data should be obtained for each important radionuclide in various soils, and soil properties which influence variation in K_d values should be determined. Many studies using K_d have been done, however, there are only a few studies using sufficient collected K_d data for statistical analysis.

In this study, we collected 142 agricultural soil samples throughout Japan. Since Se-79, Sr-90, Sn-126, Cs-134, and Cs-137 are important fission products [2], and Sb-126 is an important radionuclide because it is a Sn-126 progeny [3], K_d values were determined using Se-75, Sr-85, Sn-113, Sb-124, and Cs-137 as tracers. After determination of K_d values, the relationships between K_d values for each radionuclide and soil properties were analyzed statistically. The knowledge should be useful for precise long-term dose assessments.

MATERIALS AND METHODS

Soil samples

One hundred and forty-two agricultural soil samples (63 paddy soil and 79 upland soil samples) were collected throughout Japan. Soil groups of these samples were Andosol (n = 35), Cambisol (n = 25), Fluvisol (n = 77), and others (n = 5). The soil samples were dried at room temperature, and then passed through a 2-mm sieve. Soil properties are summarized in Table I. pH and electrical conductivity (EC) were measured with a pH meter (HORIBA, B-212) and EC meter (HORIBA, B-173), respectively. Total carbon (T-C) content was measured with an elemental analyzer (EuroVector, EA-3000). Cation exchange capacity (CEC) was measured by the Schollenberger method [4]. Clay content analysis was done using a recommended standard method [5]. Active Al (Al_o) and active Fe (Fe_o) contents were measured as acid-oxalate extractable Al and Fe by the method of Blakemore et al. [6]. Water soluble ionic and elemental amounts in a solid/liquid ratio of 1:5 were measured with an ion chromatograph (DIONEX, ICS-1500) and ICP optimal emission spectrometer (Seiko, Vista Pro), respectively.

Measurement of the distribution coefficient (K_d) by the batch technique

K_d of the five radionuclides was obtained by separate batch sorption tests. Each soil sample and deionized water (solid/liquid ratio, 1g: 10mL) were mixed in a plastic bottle, and initially shaken for 24 h at 23°C, and then one radionuclide (Se-75, Sr-85, Sn-113, Sb-124, or Cs-137) was added as a tracer. After shaking for 7 days, the suspension was centrifuged at 3000 rpm for 10 minutes, and the supernatant was filtered through a 0.45- μ m membrane filter. Radioactivity of the radionuclide in the filtrate was measured with a NaI scintillation counter (Aloka, ARC-380). The K_d value (L kg⁻¹) was calculated using the following equation,

$$K_d = \frac{(C_i - C_e) \cdot W_i}{C_e \cdot W_s} \quad (\text{Eq. 1})$$

where C_i (Bq L^{-1}) is the initial radionuclide activity, C_e (Bq L^{-1}) is the radionuclide activity in the liquid phase after shaking for 7 days with the tracer, W_1 is the solution volume (L), and W_s is the soil dry weight (kg).

Table I. Chemical properties of soil samples for land-use

Land use		pH (H_2O)	EC ($\mu\text{S cm}^{-1}$)	T-C (%)	CEC ($\text{meq } 100\text{g}^{-1}$)	Clay (%)	Alo ^a (g kg^{-1})	Feo ^a (g kg^{-1})
Paddy (n = 63)	GM ^b	5.7	85.4	24.9	14	22.5	3.5	6.6
	Min	4.8	48.7	13.8	< 10	10.0	0.7	1.5
	Max	6.9	252.5	125.3	27	50.6	55.4	19.3
Upland (n = 79)	GM ^b	6.2	154.4	28.1	15	18.7	6.2	7.6
	Min	4.3	23.9	2.7	< 10	1.6	0.5	1.1
	Max	8.1	2635.0	99.7	30	51.1	96.2	33.4

^a Alo and Feo mean the acid-oxalate extractable Al and Fe, respectively.

^b GM: Geometric mean

RESULTS AND DISCUSSION

Statistical characteristics of K_d values

The probability distributions of the K_d values are shown in Fig. 1. From the Shapiro-Wilk test [7], the K_d distributions for Sr-85, Sn-113, and Cs-137 are judged as not a normal type ($p < 0.05$), but a log-normal type. For Se-75 and Sb-124, their K_d distributions are not a normal or a log-normal type ($p < 0.05$).

Some statistical characteristics of K_d values are shown in Table II. The variation of K_d values is up to two or three orders of magnitude. Their geometric means are: $8.5 \times 10^1 \text{ L kg}^{-1}$ for Se-75; $2.8 \times 10^2 \text{ L kg}^{-1}$ for Sr-85; $7.2 \times 10^3 \text{ L kg}^{-1}$ for Sn-113; $6.6 \times 10^1 \text{ L kg}^{-1}$ for Sb-124; and $3.2 \times 10^3 \text{ L kg}^{-1}$ for Cs-137. In comparison with the expected K_d values for loam soil type reported by IAEA [1], the present results are one order of magnitude higher than the literature values for Sr (expected value: $2.0 \times 10^1 \text{ L kg}^{-1}$) and Sn (expected value: $4.5 \times 10^2 \text{ L kg}^{-1}$), one order of magnitude smaller for Se (expected value: $4.9 \times 10^2 \text{ L kg}^{-1}$) and Sb (expected value: $1.5 \times 10^2 \text{ L kg}^{-1}$), and the same order of magnitude for Cs (expected value: $4.4 \times 10^3 \text{ L kg}^{-1}$). The K_d values for Se-75, Sr-85, and Cs-137 differ significantly between paddy and upland soil samples in t -test ($p < 0.05$), but Sn-113 and Sb-124 do not.

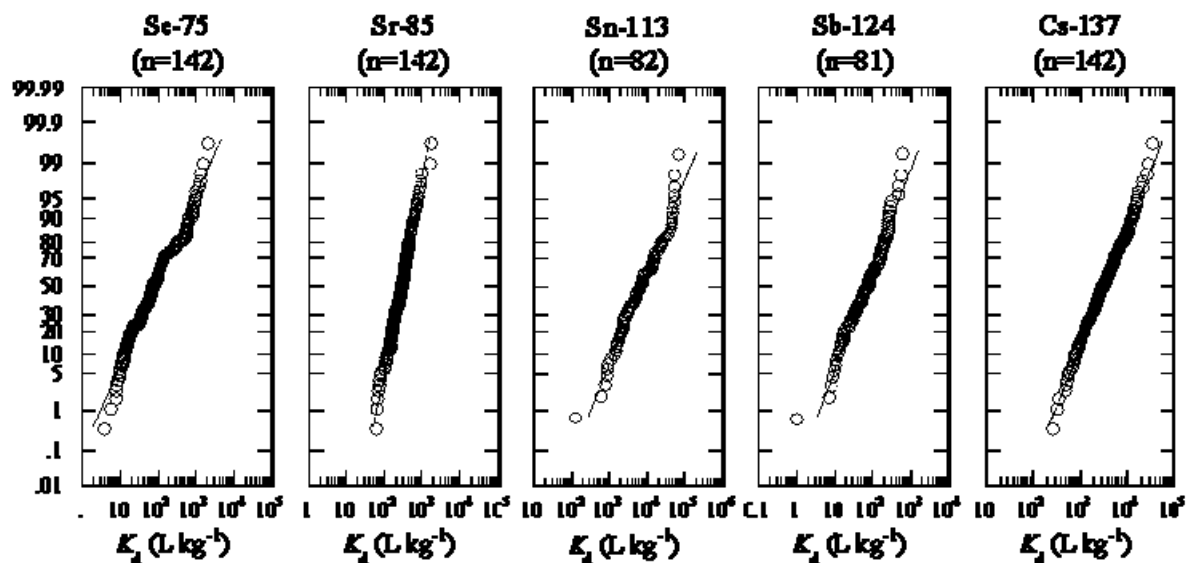


Fig. 1. Probability distributions of K_d values of the five radionuclides.

Table II Statistical characteristics of K_d values

		Se- K_d (L kg ⁻¹)	Sr- K_d (L kg ⁻¹)	Sn- K_d (L kg ⁻¹)	Sb- K_d (L kg ⁻¹)	Cs- K_d (L kg ⁻¹)
All	GM ^a	85	284	7150	66	3169
Paddy (n = 63)	n	63	63	37	36	62
	GM ^a	116	374	5518	78	2438
	Min	10	99	664	11	269
	Max	2130	1817	56350	614	28951
Upland (n = 79)	n	79	79	40	45	79
	GM ^a	67	215	9088	58	4119
	Min	4	62	128	1	360
	Max	1364	644	74347	550	35730

^a GM: Geometric mean

Correlations between K_d values and soil properties

Spearman's rank correlation test was used for evaluating correlations between K_d values and soil properties. Good correlations (Spearman's rank correlation coefficient (R_s) > 0.5) are found in the following combinations:

Se- K_d – water soluble phosphorus (P) ($R_s = -0.51$)

Sr- K_d – EC ($R_s = -0.52$)

– water soluble calcium (Ca) ($R_s = -0.57$)

Sn- K_d – EC ($R_s = -0.50$)

– water soluble Ca ($R_s = 0.50$)

– water soluble magnesium (Mg) ($R_s = 0.54$)

– water soluble Sr ($R_s = 0.57$)

Sb- K_d – pH ($R_s = -0.54$)

– Feo ($R_s = 0.58$)

– water soluble P ($R_s = -0.67$)

In Japanese agricultural soils, Se and Sb are probably present as oxyanion forms, i.e. HSeO_3^- and SbO_3^- , respectively [8,9]. Phosphate could be present as H_2PO_4^- under pH and Eh conditions in Japanese agricultural soils [10]. Thus, negative correlations between Se-, and Sb- K_d values and water soluble P can be attributed to competition by HSeO_3^- and SbO_3^- for H_2PO_4^- because these three ions can sorb on the same sorption sites in soils. In upland soil samples good correlations are found between the Se- K_d values and Alo or Feo with R_{sS} of 0.57 and 0.62, respectively ($p < 0.01$). Selenite is known to be able to associate with aluminum and iron in soil [5]. Since upland soil samples included 29 Andosol samples which have one order of magnitude higher Alo and Feo concentrations than other soil groups do, good correlation coefficients are obtained for upland soil samples but not paddy soil samples. It is reasonable that Sr- K_d values have good correlations with EC and water soluble Ca for the following two reasons: one is that the sorption mechanism of Sr in soil is cation exchange and the other is that Sr has similar chemical characteristics to Ca.

As described above, Se and Sb have similar sorption behaviors in Japanese agricultural soils. Therefore, the same reason for Se, that is, Sb would be able to associate with aluminum and iron in soil may be applicable to the good correlation between Sb- K_d values and Feo. On the other hand, only a few research studies about Sn sorption in soil have been carried out [11]. In addition, there are no reports on the relationship between Ca, Mg, or Sr and Sn in soils. Further studies are needed to clarify the reasons for the good correlations between these water soluble elements and Sn- K_d values.

No soil properties have a good correlation with Cs- K_d values in all types of soil samples. However, in upland soil samples, Cs- K_d values have quite a good correlation with water soluble ammonium (NH_4^+) with $R_s = -0.48$ and water soluble rubidium (Rb) with $R_s = -0.45$. Some types of clay minerals such as illite have specific sorption sites for Cs^+ , NH_4^+ , Rb^+ , and K^+ based on the ionic radius. This fact supports the good correlations between Cs- K_d values and water soluble NH_4^+ or water soluble Rb.

CONCLUSIONS

In this study, K_d values of five radionuclides (Se-75, Sr-85, Sn-113, Sb-124, and Cs-137) were determined by the batch sorption test for 142 Japanese agricultural soil samples. The following results were observed.

- (1) Se- and Sb- K_d data did not show a normal or a log-normal distribution, Sr-, Sn, but Cs- K_d data showed a log-normal distribution.
- (2) Se-, Sr-, and Cs- K_d values significantly differed between paddy and upland soil samples.
- (3) The combinations of the K_d values and the soil property having the highest correlation for each radionuclide were as follows: Se- K_d – water soluble P ($R_s = -0.51$); Sr- K_d – water soluble Ca ($R_s = -0.57$); Sn- K_d – water soluble Sr ($R_s = 0.57$); Sb- K_d – water soluble P ($R_s = -0.67$); Cs- K_d values – water soluble Sr ($R_s = 0.57$); and Sb- K_d – water soluble P ($R_s = -0.67$). There were no soil properties which had a good correlation with Cs- K_d values for all soil samples.

These findings should be useful for obtaining more applicable K_d values for dose assessment models.

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