

USING A SEQUENTIAL EXTRACTION PROCEDURE FOR SELECTIVE DETERMINATION OF SOIL-ADSORBED Se

Y. Nakamaru, K. Tagami, S. Uchida

Office of Biospheric Assessment for Waste Disposal, National Institute of Radiological Sciences
Anagawa 4-9-1, Inage, Chiba City, 263-8555, Japan

ABSTRACT

To understand Se adsorption behavior in acid soils, soil/soil solution distribution coefficient (K_d) was obtained for 58 Japanese agricultural soil samples using Se-75 as a tracer. It was found that the K_d -Se values, ranged from 12 to 1060 (arithmetic mean =315), were highly correlated to the soil active-aluminum (Al) and active-iron (Fe) contents. Those two components were considered to be the major adsorbents of Se in Japanese soils. The mechanism of Se adsorption by the active-Al and active-Fe is regarded to be ligand-exchange, which is the same adsorption mechanism for phosphorus (P). Therefore, using a modified sequential extraction procedure proposed for soil adsorbed P, the adsorbed Se-75 was extracted from 12 selected soil samples. In this procedure, we employed $1 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$, $4 \text{ mol L}^{-1} \text{ NH}_4\text{F}$ and $0.1 \text{ mol L}^{-1} \text{ NaOH}$ for extracting loosely bound Se, active-Al bound Se and active-Fe bound Se, respectively. The results showed that 80-100% of the adsorbed Se was recovered as active-Al and active-Fe bound forms. The loosely bound Se was less than 2% of the total amount of Se sorbed on each soil. The active-Al bound Se was the dominant form in the soils that had higher K_d values, while the active-Fe bound Se was the dominant form in the soils that had lower K_d values. Therefore, we considered that the higher values of K_d -Se were mainly caused by the sorption on active-Al.

INTRODUCTION

Selenium-79 (Se-79) is one of the important radionuclides for management of high-level radioactive waste because of its long radiological half-life ($1.1 \times 10^6 \text{ y}$). Additionally, Se is an essential nutrient for animals so that it is an important trace element in the agri-ecosystem. At high concentrations, however, Se becomes toxic to animals.

The amount of Se in soil that is available to plants could be a main factor for its mobility in the food chain. In soil-solution system, Se forms selenate, selenite, elemental Se, and organic Se species. For growing plants, selenate is the most available Se species, while selenite is less available because of its high degree of adsorption onto soil particles [1]. However, under an acidic soil environment, selenate is unstable and not resistant to leaching [2]. Therefore, the adsorption level of selenite may be the limiting factor of Se bioavailability in acid soils, which a lot of Japanese soils are. In Japan, about 50% of the upland field soils are classified as acid volcanic ash soils (Andosols), which contain large amounts of active-Al and active-Fe [3].

To understand Se adsorption behavior in acid soils, we employed the soil/soil solution distribution coefficient (K_d). Since there are not many reports on the K_d of Se (K_d -Se) in Japanese soils, the K_d values were obtained in 58 agricultural soils sampled throughout Japan in order to evaluate their Se adsorption level. Then, Se bound to active-Al and active-Fe, which are

regarded as reactive components for Se adsorption [2, 4, 5, 6] was extracted sequentially to clarify the contribution levels of each reactive component in soils.

In this study, we applied a modified extraction method for adsorbed Se in different soil fractions. Originally, the method was for phosphorus (P) extraction [7]. Generally, phosphate buffer solution has been used to extract soil-adsorbed Se [8, 9, 10], because the primary adsorption mechanism of Se has been regarded to be ligand-exchange, which is the same adsorption mechanism for phosphorus (P) [2, 10], and we tried to clarify and quantify the dominant form of soil-adsorbed Se using the sequential extraction procedure. The adsorbed Se-75 was separated into the following three fractions: soluble and loosely bound Se, Al-bound Se, and Fe-bound Se. The proportion of each fraction was compared with the soil properties and the K_d-Se values of soil samples.

MATERIALS AND METHODS

Soil Samples

Fifty-eight agricultural soil samples (29 upland soils and 29 paddy soils) were collected throughout Japan. They were air-dried at room temperature and passed through a 2-mm mesh sieve. The following soil properties were measured for all soils: pH (H₂O), cation exchange capacity (CEC, mmol_c kg⁻¹), anion exchange capacity (AEC, mmol_c kg⁻¹), the contents of exchangeable potassium (ex. K, mmol kg⁻¹), exchangeable calcium (ex. Ca, mmol kg⁻¹), acid oxalate extractable aluminum (Al_o, g kg⁻¹), acid oxalate extractable iron (Fe_o, g kg⁻¹), total carbon (T-C, g kg⁻¹) and total nitrogen (T-N, g kg⁻¹). The classification of soil samples [11, 12] and the characteristics are shown in Table I.

Measurement of the Distribution Coefficient (K_d)

The K_d was measured by the batch technique using Se-75 (half life: 119.8 d) as a tracer. The Se-75 was provided as a selenite solution. Three-gram amounts of each soil were placed in a plastic bottle (50 mL) and 30 mL of deionized water were added. Prior to adding Se-75, the suspension was shaken at 120 reciprocations per min (rpm) for 24 h at 23°C using an end-over-end shaker. About 10 kBq of Se-75 with 21 ng of stable Se as a carrier were then added, and the suspension was shaken for 7 d. The 7-d shaking time was sufficient to achieve equilibrium of Se adsorption for Gray Lowland soil and Andosol samples (data not shown).

All sample suspensions were separated by centrifugation at 3000 rpm, and the supernatants were filtered through 0.45-μm membrane filters. Gamma rays of Se-75 in the filtrates were measured with a NaI scintillation counter (Aloka, ARC-300) to determine Se-75 concentration. The pH and the electrical conductivity (EC) (mS cm⁻¹) values in the solutions were also measured with a pH meter (Horiba, B-212) and an EC meter (Horiba, B-173), respectively.

K_d (L kg⁻¹) was calculated as Eq. 1.

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

where C_i is the initial concentration of Se-75 in the solution (Bq L^{-1}), C_1 is the concentration of Se-75 in the supernatant solution after shaking with soil (Bq L^{-1}), W_1 is the solution volume (L), and W_g is the soil weight (kg).

Table I Characteristics of soil samples used in the study

Soil groups ^a	Andosols	Gray Lowland soils	Gley Lowland soils	Yellow soils	Red soils	Sand-dune Regosols	Brown Lowland soils
Classification of FAO ^b	Andosols	Fluvisols	Fluvisols	Alisols, Acrisols, or Cambisols	Alisols, Acrisols, or Cambisols	Regosols, Alenosols	Cambisols
Number of samples	20	15	7	8	5	2	1
pH	5.1-7.0	4.8-7.0	5.4-7.7	5.2-6.5	4.7-8.3	6.5-6.8	7.1
CEC ($\text{mmol}_c \text{kg}^{-1}$)	70-427	8-235	98-286	60-160	80-181	14	166
AEC ($\text{mmol}_c \text{kg}^{-1}$)	0.8-8.1	0.7-3.7	0.6-4.8	0.8-8.2	0.6-3.1	0.5-1.0	1.4
Ex. Ca (mmol kg^{-1})	19-157	25-95	39-196	14-50	10-110	1.9-3.3	82
Ex. K (mmol kg^{-1})	0.6-7.2	1.1-9.4	0.9-16.3	0.9-8.8	1.0-4.5	0.3-0.4	8.6
Alo (g kg^{-1})	7.4-65.1	0.9-11.8	1.3-3.3	0.8-10.8	0.9-5.9	0.3	1.8
Feo (g kg^{-1})	2.7-76.3	2.8-29.7	5.7-18.1	1.5-13.6	1.6-11.7	0.4-1.6	5.4
T-C (g kg^{-1})	17-109	9-24.2	17-31	3-22	9-17.2	0-1	12.6
T-N (g kg^{-1})	1.5-7.6	0.8-2.2	2-13	0.5-2.9	1.3-1.7	0.10	1.40

^a See Ref. 11.

^b See Ref. 12.

Sequential Extraction of Adsorbed Se

Sequential extractions were carried out to identify and quantify the dominant Se fractions of soil-adsorbed Se for 12 selected samples. The soil samples that had been treated by the batch process for Kd analysis as described above were reused, since they had some Se-75 remaining from added tracer. The sequential extraction procedure used in this study was based on existing techniques applied to soil phosphorus fractionation [7]. Twenty-five mL of $1 \text{ mol L}^{-1} \text{NH}_4\text{Cl}$ were added to the soil. This suspension was shaken automatically for 30 min to extract the water-soluble and loosely bound Se fraction. The suspension was centrifuged at 3000 rpm, and the supernatant was filtered through a $0.45\text{-}\mu\text{m}$ membrane filter. The filtrate was used for determination of water-soluble and loosely bound Se-75. Then, 30 mL of $4 \text{ mol L}^{-1} \text{NH}_4\text{F}$ were added to the soil and the suspension was shaken for 1 h to extract the Al-bound Se. This step was repeated once more with more reagents. The soil was washed with 25 mL of saturated NaCl solution. Then, 30 mL of $0.1 \text{ mol L}^{-1} \text{NaOH}$ were added, and this was shaken for 17 h to extract the Fe-bound Se. The extraction was also repeated once more. For all of the supernatant solutions, Se-75 concentration was determined, and the proportion of each fraction was obtained.

RESULTS AND DISCUSSION

The range of Kd-Se in Japanese agricultural soils

The Kd-Se values determined for the 58 Japanese agricultural soils ranged between 12-1060, indicating that 55-99 % of added Se was adsorbed for soil samples, and the mean value was 315 (97% of Se adsorbed). No significant difference in soil Kd-Se was found between upland and paddy soils. The range was similar to Kd ranges expected for soils in the temperate environments [13]. Comparison of soil types showed the Kd-Se values for Andosols were higher than for the others [14]. About 75% of the Kd-Se values of Andosols were higher than the median value (>95% of Se adsorbed) of all samples.

Effects of Soil Components for Se Adsorption

The correlation coefficients between Kd-Se and the measured properties of the soil samples are summarized in Table II. All the Kd-Se values were significantly correlated with Alo and Feo at the 0.1% level. Alo content refers to the amount of non-crystalline or short-range-ordered aluminosilicates (allophane, imogolite), and Al-humos complex, and the Feo content refers to the amount of Fe-humos complex or non-crystalline Fe minerals (ferrihydrite). These soil components were considered to be active-Al and active-Fe, those were adsorbents of phosphate and selenite [2, 5].

These results indicated that the active-Al and the active-Fe were the major adsorbents of Selenite in Japanese agricultural soils; the same results have also been reported for New Zealand soils [4].

Table II Correlation coefficients between kd values and soil properties

Soil properties	pH	CEC	AEC	Ex. Ca	Ex. K	Alo	Feo	T-C	T-N
Correlation coefficients	0.01	0.13	0.08	0.01	0.00	0.46 [†]	0.35 [†]	0.21 ^{††}	0.10

[†] Significant at 0.1 % level.

^{††} Significant at 0.5 % level.

Fractionation of Adsorbed Se in Soils

According to previous studies [2, 15], it was assumed that the sorption mechanisms of Se were similar to those of P, thus, the sequential extraction procedure provided for P [7] was modified to determine the soil-adsorbed Se forms. In the original method, 50 mL of 0.5 mol L⁻¹ NH₄F was used for 1 g soil to extract Al-bound P, however, in this study, 30 mL of 4 mol L⁻¹ NH₄F were used for 3 g soil and the extraction step was repeated, that is, total fluoride (F) content per 1g soil was tripled. Previously, Sekiya [16] reported that the F content in the original method was insufficient for extraction of P and they recommended that F content should be increased four times over the original. The proposed amount would be reasonable because Japanese volcanic soils contain large amounts of active-Al.

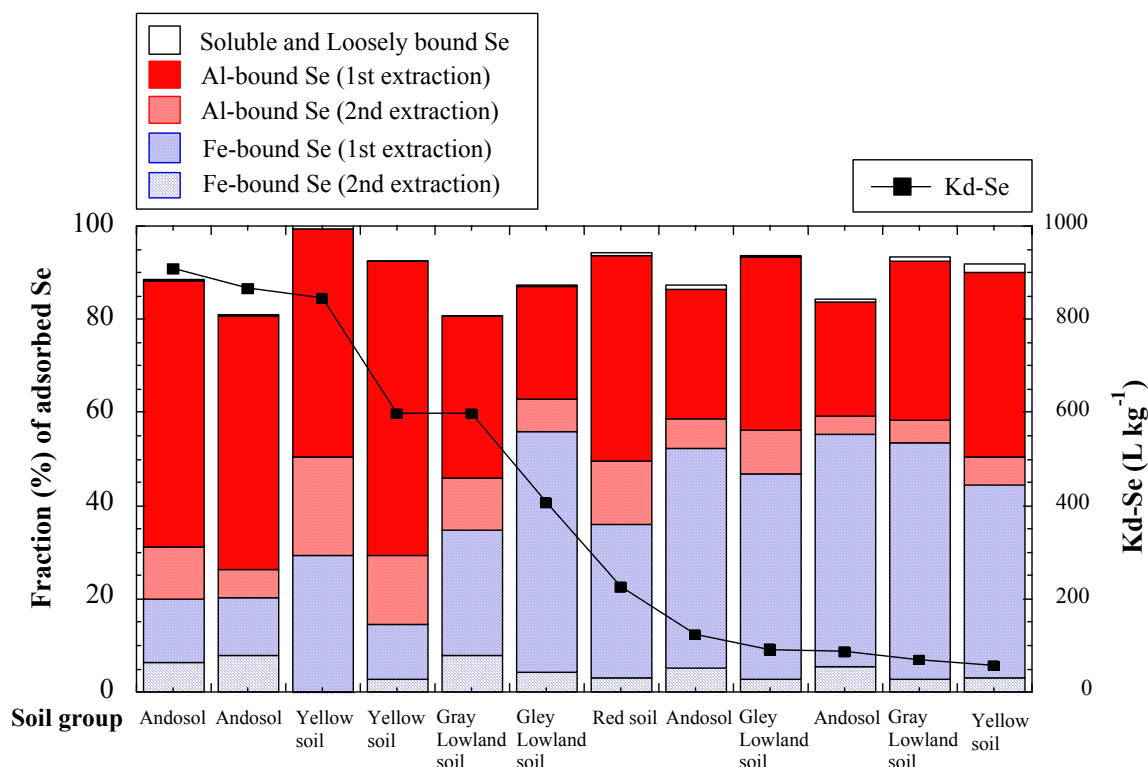


Fig. 1 Percentages of the amounts of adsorbed se in the soil samples extracted as soluble- and loosely-bound, al-bound and fe-bound forms, and the kd-se values

The results of the sequential extraction were shown in Fig. 1. The soluble and loosely bound Se fraction was the smallest among the fractions. The result of the lower amount of Se extracted by chloride ion implied that most of the adsorbed Se was not in anion exchangeable forms.

As shown in Fig. 1., the amounts of Se-75 extracted in the second extractions with NH_4F and NaOH decreased. Thus, it was assumed that the fractions extracted by NH_4Cl , NH_4F and NaOH were independent of each other. Total recovery of Se was 80-100%, which showed that the dominant fractions of the soil-adsorbed Se were extracted by this method. Thus, the proposed sequential extraction procedure would be suitable for evaluation of soil-adsorbed Se forms.

The comparison of each fraction determined by the sequential extraction showed that the Al-bound Se and the Fe-bound Se were the dominant fractions of the soil-adsorbed Se. The proportions of the Al-bound Se and the Fe-bound Se differed by soil. The amount of Al-bound Se was relatively higher in the soils with high Kd values ($\text{Kd} > 400$), and Fe-bound Se was relatively higher in the soils with low Kd values ($\text{Kd} < 400$). These results suggested that the dominant form of adsorbed Se differed with the level of Kd-Se. For Japanese agricultural soils, we assumed that the higher values of Kd were mainly caused by the sorption of active-Al.

CONCLUSION

Soil/soil solution distribution coefficient of Se (K_d -Se) for Japanese agricultural soils were obtained and the major adsorbents were studied using the sequential extraction procedure. The K_d -Se values obtained covered a wide range, from 12 to 1060, and their arithmetic mean was 315. The proposed extraction procedure could extract 80-100% of Se adsorbed by soil. The NH_4Cl extractable fractions were lower than 2%, indicating that negligible amount of Se was Cl^- exchangeable. For the Japanese soils, it was suggested that the most of added Se was strongly adsorbed by the soil. The extraction results showed that the Al-bound Se and the Fe-bound Se were the dominant forms of soil-adsorbed Se. The higher K_d values found for some Japanese soils were explained by the Se sorption to the active-Al. This method can evaluate the contributions of these components separately. Therefore, the method can be a powerful tool to investigate the behavior of Se in acid soils such as Japanese agricultural soils.

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