

## EFFECT OF PHOSPHATE ADDITION ON THE DESORPTION OF SE FROM SOILS

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### ABSTRACT

Desorption levels of soil-sorbed Se by adding phosphate (P) ion were studied for 10 typical Japanese agricultural soils. Soil-solution distribution coefficients of Se ( $K_d$ -Se) were measured using the batch technique as an index of Se sorption level in the batch process, Se-75 was added to the soils as a tracer. After the  $K_d$  measurement, added Se-75 was extracted by a 0.1 M or 1 M  $\text{Na}_2\text{HPO}_4$  solution to determine the amount of Se-75 desorbed by the P. When the 0.1 M  $\text{Na}_2\text{HPO}_4$  solution was used, 18-57% of sorbed-Se was extracted into the solution (average: 41%). The percentage of Se extracted with the 1 M  $\text{Na}_2\text{HPO}_4$  solution was 1.1-1.5 times higher than the percentage extracted with 0.1 M  $\text{Na}_2\text{HPO}_4$  for which 27-71% of sorbed-Se was extracted (average: 50%). The observed desorption rates of Se indicated the existence of an upper limit to the Se desorption by P addition. The desorption percentage of Se increased with increasing  $K_d$  values, suggesting that the soil with higher  $K_d$ -Se contains more reactive components for phosphate-sorption than the soil with lower  $K_d$ -Se. To evaluate the effect of phosphate concentration on the Se sorption, the  $K_d$ -Se was measured for two typical soils under different levels of P (0.1-20 mM  $\text{PO}_4$ ). The  $K_d$  value decreased by P addition for both soils. The  $K_d$  decrease was observed even for just 0.1 mM P. The P addition with 0.1 mM P corresponded to 0.3 g P per kg dry soil, which is the same level as in phosphate fertilizer applied to paddy fields in Japan. Therefore, it was suggested that Se desorption should occur in Japanese soils due to the phosphate input.

### INTRODUCTION

Selenium (Se) is a naturally occurring trace element found in most soils. It is an essential element for animals because it is required for normal enzyme function, however, it can cause "blind staggers" in animals that drink water or eat plants in areas with high Se contamination [1]. Among Se radioisotopes, Se-79 (half life: 65000 y) is of interest because it is a fission product of uranium and present in spent nuclear fuel and the wastes resulting from reprocessing this fuel. For these reasons, Se should be controlled in the natural environment and also in waste management sites.

Previously, we reported the soil-solution distribution coefficient ( $K_d$ ) of selenite which we measured using Japanese agricultural soils [2]. Selenite was chosen because it is the major form found in acidic soils which are common throughout Japan. Although the Se was in an anionic form, the  $K_d$  values were as high as those for Sr [2]. The primary adsorption mechanism of Se has been regarded to be ligand-exchange [3], which is the same adsorption mechanism for phosphate. The amount of phosphate in the soil probably affects the sorption-desorption reaction of Se in soil. Phosphate is added to agricultural fields as a fertilizer so that the effect of phosphate addition to the Se mobility in the soil should be clarified. Thus, in this study, we used a radiotracer to measure the desorption rate of the soil-sorbed-Se by phosphate addition. Also,

we determined the effect of phosphate concentration on the Se sorption onto soil by the  $K_d$  measurement under elevated levels of phosphate.

## **MATERIALS AND METHODS**

### **Soil samples**

Ten typical Japanese agricultural soils (5 upland soils and 5 paddy soils) were used. Andosols are the major agricultural soil for upland fields, Gray lowland soils and Gley lowland soils are the major rice paddy soils. The chemical characteristics of the soil samples are listed in Table I.

### **Measurement of the distribution coefficient ( $K_d$ ) by the batch technique**

The  $K_d$  was measured by the batch process 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 50-mL plastic bottle and 30 mL of deionized water were added. Prior to Se-75 addition, 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 the soils used in this experiment [2].

All sample suspensions were separated by centrifugation at 3000 rpm, and the supernatants were filtered through 0.45- $\mu$ m 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.

$K_d$  ( $L\ kg^{-1}$ ) was calculated as Eq. 1,

$$K_d = (C_i - C_1) \times W_1 / (C_1 \times W_g) \quad (\text{Eq. 1})$$

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).

### **Sequential extraction of Se using phosphate solution**

After the  $K_d$  measurement by a batch technique, Se-75 sorbed onto soil was extracted with a sequential extraction procedure modified from the method of Zawislanski et al. [4]. Fifteen mL of 0.25 M KCl were added to the soil, and shaken for 1h to extract the water-soluble and loosely bound Se fractions. The suspension was centrifuged at 3000 rpm, and the supernatant was filtered through a 0.45- $\mu$ m membrane filter to measure extracted Se-75. Next, 30 mL of 0.1 M  $Na_2HPO_4$  were added to the soil and the suspension was shaken for 24 h to extract the sorbed Se. This step was repeated once more with more reagents. For comparison, another sequential extraction with 0.25 M KCl and 1 M  $Na_2HPO_4$  solution was also carried out under the same extraction conditions to evaluate the effect of the amount of added phosphate.

### **Determination of the effect of phosphate concentration on the Se sorption onto soil**

Inhibition of Se sorption onto soil by phosphate ion was measured using the batch process of  $K_d$ -Se measurement. Andosol (pH 6.4) and Gray lowland soil (pH 6.0) were used. The  $K_d$ -Se was

measured under elevated levels of phosphate; the phosphate concentrations were adjusted with 0.1 M KH<sub>2</sub>PO<sub>4</sub>/0.1 M Na<sub>2</sub>HPO<sub>4</sub> buffer solution (pH 6.7). Three grams of soil sample were placed in plastic bottles with 30 mL of PO<sub>4</sub> solutions (0, 0.01, 0.1, 1, 10 or 20 mM PO<sub>4</sub>). As described above, K<sub>d</sub>s were measured by adding Se-75 to this suspension. All sample suspensions were separated by centrifugation and filtration through 0.45-μm membrane filters, then the activity concentrations of Se-75 in the filtrates were measured.

**Table I. Characteristics of Soil Samples Used in the Study**

Sample No.	Soil types	Land-use	pH	Active-Al* <sup>1</sup> (g kg <sup>-1</sup> )	Active-Fe* <sup>1</sup> (g kg <sup>-1</sup> )	Organic-C (%)
F27	Andosol	Upland	5.74	54.0	22.8	9.89
F31	Andosol	Upland	6.49	43.2	28.3	2.81
F47	Red soil	Upland	8.29	5.4	11.7	1.11
F62	Yellow soil	Upland	5.17	8.9	8.2	1.28
F78	Andosol	Upland	6.30	7.4	2.7	3.13
P10	Gray lowland soil	Paddy	5.54	11.8	15.3	2.05
P16	Gray lowland soil	Paddy	5.95	0.9	4.2	1.46
P18	Yellow soil	Paddy	6.06	2.4	7.4	2.24
P20	Gley lowland soil	Paddy	5.95	3.3	5.7	2.00
P68	Gley lowland soil	Paddy	5.41	1.9	12.8	2.56
Sample No.	Soil types	Land-use	pH	Active-Al* <sup>1</sup> (g kg <sup>-1</sup> )	Active-Fe* <sup>1</sup> (g kg <sup>-1</sup> )	Organic-C (%)
F27	Andosol	Upland	5.74	54.0	22.8	9.89
F31	Andosol	Upland	6.49	43.2	28.3	2.81
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P10	Gray lowland soil	Paddy	5.54	11.8	15.3	2.05
P16	Gray lowland soil	Paddy	5.95	0.9	4.2	1.46
P18	Yellow soil	Paddy	6.06	2.4	7.4	2.24
P20	Gley lowland soil	Paddy	5.95	3.3	5.7	2.00
P68	Gley lowland soil	Paddy	5.41	1.9	12.8	2.56

\*<sup>1</sup> Active –Al and –Fe means the acid-oxalate extractable Al and Fe.

## RESULTS AND DISCUSSION

### **K<sub>d</sub> measurement and the sequential extraction of Se using phosphate solution**

The measured K<sub>d</sub>-Se values for 10 soil samples and the extracted Se percentages by Na<sub>2</sub>HPO<sub>4</sub> solution are listed in Table II. The K<sub>d</sub> values ranged from 68 to 737 L kg<sup>-1</sup> (average: 313). These values were within the same level as reported previously [2]. The amounts of Se-75 sorbed onto soils were 87-99% of added Se.

The percentages of Se extracted by 0.25 M KCl were less than 1% of sorbed-Se, while 18-57% of added-Se was desorbed by the 0.1 M Na<sub>2</sub>HPO<sub>4</sub> solution (average = 41%).

**Table II. The K<sub>d</sub>-Se values and the Se amounts extracted by each reagent for each sample soil.**

Sample No.* <sup>1</sup>	Soil types	K <sub>d</sub> -Se (L kg <sup>-1</sup> )	The amount of Se extracted by each reagent (% of sorbed-Se)						
			0.25 M KCl	0.1M Na <sub>2</sub> HPO <sub>4</sub>			1M Na <sub>2</sub> HPO <sub>4</sub>		
				1st	2nd	total	1st	2nd	total
P20	Gley lowland soil	68	ND* <sup>2</sup>	12.7	5.3	18.0	19.9	7.3	27.2
P16	Gray lowland soil	77	ND	35.2	7.4	42.6	38.2	7.3	45.6
P18	Yellow soil	86	ND	28.2	6.2	34.3	31.4	6.4	37.8
F78	Andosol	93	ND	33.2	8.5	41.7	35.6	7.8	43.4
F47	Red soil	195	0.88	35.7	14.4	50.1	45.5	10.2	55.7
P10	Gray lowland soil	274	0.47	31.0	9.5	40.5	37.7	7.7	45.4
P68	Gley lowland soil	408	ND	27.0	12.4	39.4	41.2	13.7	54.9
F62	Yellow soil	490	0.56	26.1	9.7	35.8	41.4	12.6	54.0
F27	Andosol	708	0.06	42.6	13.9	56.5	57.6	14.1	71.7
F31	Andosol	737	0.24	35.3	16.5	51.8	52.0	15.1	67.0
Average		314				41.1			50.2
Max		737				56.5			71.7
Min		68				18.0			27.2

\*<sup>1</sup>Soil samples are sorted by the K<sub>d</sub>-Se values (smaller values-bigger values).

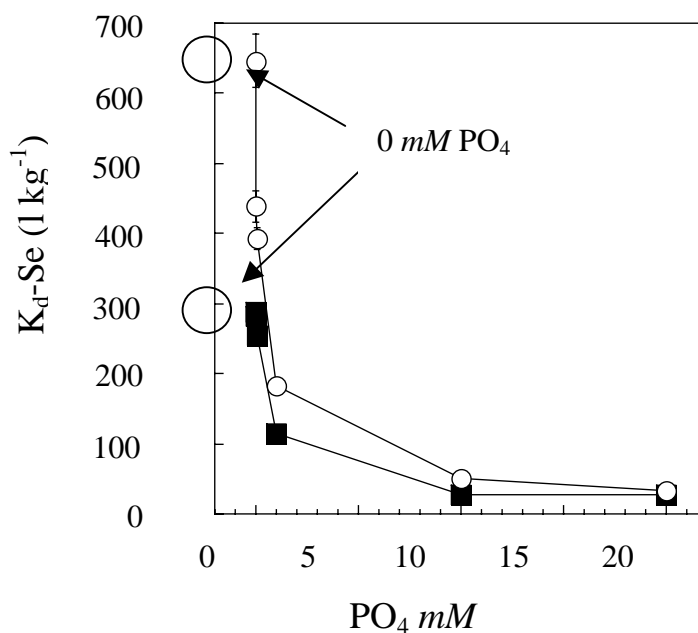
\*<sup>2</sup>ND denotes the value was lower than the detection limit.

The percentages for desorbed Se extracted with the 1 M Na<sub>2</sub>HPO<sub>4</sub> solution were 1.1-1.5 times higher than the percentages when extracted with 0.1 M Na<sub>2</sub>HPO<sub>4</sub> which were 27-72% of the sorbed-Se (average: 50%). The observed desorption rates of Se should be the upper limit of the Se desorption by phosphate addition since no big difference was found. Thus the addition of more phosphate would not be effective for enhancing removal of sorbed-Se in the soil samples. However, at least 50% of Se sorbed onto soil could be removed from the soil by the phosphate treatment.

The percentage of desorbed Se by phosphate differed with the  $K_d$  values; the desorption percentage of Se increased with increasing  $K_d$  values. This suggested that the soil with higher  $K_d$ -Se contained greater number of active components for phosphate-sorption than the soil with lower  $K_d$ -Se.

### The effect of phosphate concentration on the Se sorption onto soil

The effect of phosphate concentration on the Se sorption to soil was studied by the  $K_d$  measurement under elevated levels of phosphate. As shown in Figure 1, The  $K_d$ -Se values for both the Andosol and the Gray lowland soil were clearly decreased with increasing phosphate concentration in the soil solution;  $K_d$ -Se values of 287 and 646 for Andosol and Gray lowland soil decreased to 28 and 51 in the presence of 10  $mM$   $PO_4$  solution. This showed that the added phosphate inhibited the Se sorption and it suggested that the Se sorption in Japanese soils was affected by the phosphate concentration in the soil solution.



**Fig. 1. The changes of the  $K_d$ -Se values of Andosol (■) and Gray lowland soil (○) plotted against the phosphate concentration in the soil solution. Error bars indicate the standard deviation of three replications.**

Even in the presence of 1  $mM$   $PO_4$  in the soil solution, the  $K_d$  decrease was observed. The  $K_d$ -Se values did not change with increasing phosphate concentration above 10  $mM$   $PO_4$ , thus 10  $mM$   $PO_4$  should be the upper limit concentration for exchange of Se by phosphate. In the batch process, the added phosphate level from 30 mL of 1  $mM$   $PO_4$  solution corresponded to 0.3 g P per kg dry soil. This value is the same level as in phosphate fertilizer commonly applied to paddy fields in Japan (0.2-0.5 g P per kg dry soil). The results of the present study suggested that Se mobilization by phosphate addition could occur in Japanese agricultural fields. However, it

should be noted that phosphate is usually added before planting, and phosphate tends to be fixed to soil strongly [3]. Thus, it is probable that Se mobilization by phosphate would occur before plant growth, and would not increase Se uptake by growing crops in Japanese fields.

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