The Study on Behavior of Selenium in Soils from the Difference of Selenite and Selenate Adsorption by Soils

Kazutoshi SAEKI* and Satoshi MATSUMOTO*

Abstract

The adsorption of selenite and selenate by four types of soil in humid regions of Japan was investigated with respect to the effects of pH. Selenite and selenate adsorption by the soils increased as pH of the suspension decreased. Selenate was less strongly adsorbed than selenite over the entire pH range. The results suggest the following ability sequence for used soils to adsorb selenium; the andosol > the acrisol > the fluvisol > the cambisol. The selenium adsorption capacities of the four soils were related to increases in the specific surface area, phosphate adsorption coefficient, and oxalate extractable Al content of the soils. The sorption of selenite released the much amount of Si from the andosol to solutions.

Desorption of selenate and selenite was investigated using a sequential extraction. Much of the adsorbed selenite (>60%) was not released by nitrate and sulfate. In contrast, more than 70% of adsorbed selenate was desorbed with nitrate and sulfate extracts, indicating the difference of adsorption mechanism of selenite and selenate. The low pH in soils results in low mobility of Se and selenate has the higher mobility in soils than selenite.

Key Words: anion adsorption mechanism, anion desorption, selenite, selenate, humid-zone soils.

Introduction

Selenium is both an essential and a hazardous element for animals and humans. The range between sufficient and toxic levels of Se in animal nutrition is very narrow. There are problems both of Se-toxicity diseases and Se-deficiency diseases in animals and human in various countries. In Japan, because of the large amount of Se produced and consumed as an industrial material, Se may pose a new environmental problem in the future. In agriculture, Se also may be used as additives of feed or fertilizer to protect Se deficiency of livestock.

Therefore, it is important to understand the behavior of Se in soils, in order to grasp the environmental and agricultural effects of Se. The importance of adsorption phenomena in soil systems is well known, particularly with respect to limiting the movement and availability of inorganic ions in the soil profile.

The oxidation states of Se which may be found in soils under various conditions are mainly -II, 0, IV and VI. Selenium in aqueous systems is most mobile in Se (IV) and Se (VI) forms, and both of these species are found as anions under the prevailing Eh-pH conditions in soils. Selenate and selenite are the most important species, as indicated in Fig. 1.

Many researchers have investigated selenite and selenate adsorption by specimen minerals contained in soils to give insight into the mechanical aspects of Se solubility in soils.
The adsorption mechanism of selenite and selenate was recently presented in the studies of Se adsorption by goethite\(^1,12\). There have been studies on Se adsorption by soils\(^13-18\). However, Se adsorption by acidic or weakly-acidic soils from humid regions has rarely been reported\(^16,17\). An exception is the study of selenite retention by John et al.\(^19\). Moreover, there are contradictory reports on selenate adsorption by soils under experimental conditions; Singh et al.\(^13\) reported that selenate was adsorbed more by soils than selenite, whereas Neal & Sposito\(^18\) were unable to detect any significant selenate adsorption by alluvial soils from California. However, Barrow & Whelan\(^16\) revealed that selenite was adsorbed to a greater extent than selenate by the yellow-brown, loamy sand from Western Australia.

The purpose of the present study was to investigate the adsorption of selenite and selenate by different soils in order to grasp the behavior or mobility of selenium in Japanese soils, in which Se pollution or accumulation may be of potential and Se may be used as fertilizer or feed to overcome Se deficiency of livestock.

**Materials and Methods**

Four types of soil (Humic andosol, Dystric fluvisol, Orthic acrisol, Dystric cambisol) were used in this study to represent main soil types in Japan. All samples were collected from the surface to 15 cm deep and prepared after air-drying and sieving through 0.5 mm sieve. The physical and chemical properties of these soils are summarized in Table 1. Mineralogy was determined by X-ray diffraction. The clay fraction of the acrisol is dominated by kaolinite and the main clay minerals of the cambisol are vermiculite and quartz. The fluvisol contains kaolinite, quartz, halloysite and vermiculite. The clay fraction of the andosol is considered to be dominated by allophane.

**Adsorption study**

Solutions of Se (IV) and Se (VI) were prepared from Na\(_2\)SeO\(_3\) and Na\(_2\)SeO\(_4\) with distilled water. Ten milliliters of 0.5 M NaCl and 5 ml of 2.5 mM Na\(_2\)SeO\(_3\) or Na\(_2\)SeO\(_4\) solution was placed in a 50 ml measuring flask, whereupon dilute HCl or NaOH was added to adjust the

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**Table 1. Physical and chemical properties of the soils.**

<table>
<thead>
<tr>
<th>Soil sample (Location)</th>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
<th>pH</th>
<th>T-C</th>
<th>CEC</th>
<th>S. surface area(^a)</th>
<th>P-adsorption coefficient(^b)</th>
<th>Oxalate extractable(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic andosol (Tanashi)</td>
<td>23.9</td>
<td>27.1</td>
<td>49.0</td>
<td>5.3</td>
<td>8.29</td>
<td>54.3</td>
<td>215</td>
<td>2550</td>
<td>4.91</td>
</tr>
<tr>
<td>Dystric fluvisol (Saitama)</td>
<td>24.0</td>
<td>35.0</td>
<td>41.0</td>
<td>5.6</td>
<td>1.61</td>
<td>18.0</td>
<td>36.1</td>
<td>565</td>
<td>0.189</td>
</tr>
<tr>
<td>Orthic acrisol (Ishikawa)</td>
<td>29.2</td>
<td>18.7</td>
<td>52.1</td>
<td>4.9</td>
<td>1.39</td>
<td>34.6</td>
<td>156</td>
<td>1700</td>
<td>0.617</td>
</tr>
<tr>
<td>Dystric cambisol (Aichi)</td>
<td>18.4</td>
<td>12.7</td>
<td>68.9</td>
<td>4.2</td>
<td>6.50</td>
<td>29.5</td>
<td>51.5</td>
<td>712</td>
<td>0.410</td>
</tr>
</tbody>
</table>

\(^a\) Diamond, S. & Kinter, E. B. (1958) method\(^20\)

\(^b\) Nanjyo, M. (1986) method\(^21\)

\(^c\) Schwertmann, V. U. (1964) method\(^22\)
solution to the desired pH. Then distilled water was added to make up the solution to 50 ml. The Se concentration of the working solution was 0.25 mM. Air-dried samples containing 0.500 g (±1%) of oven-dry soil were placed into 50 ml polyethylene centrifuge tubes. Twenty-five milliliters of 0.1 M NaCl containing 0.25 mM Se was added. The suspensions were placed in an air-conditioned room at 298 ± 1 K and were stirred for 6 hours using N₂ gas introduced via manifold. A 6 hr agitation time was chosen on the basis of the results of the contact period study described in Results and Discussion. Thereafter, the pH of the suspension was measured and the suspension was centrifuged at 2100 G for 15 min. The supernatant solution was passed through a 0.22 μm Millipore filter. The selenite content was determined by atomic adsorption spectrophotometer (AAS) with a hydride generator. As this method only measures the selenite oxidation state, the selenate samples were reduced to selenite by heating in glass test tubes in a water-bath at 368 K for 30 min in 50% (vol/vol) HCl before measurement. The adsorption of selenium was expressed quantitatively as the percentage of the initial concentration lost from the solution during the reaction period of the experiments.

Desorption study

The residue separated in Adsorption study was washed 3 times with 10 ml of 90% ethanol. To the residue samples were added 20 ml of 0.1 M NaNO₃. The suspensions were stirred for 30 min by N₂-gas and were centrifuged at 2000 G for 15 min. The supernatant solutions were passed through a 0.22 μm Millipore filter. The residue was extracted with 0.5 M Na₂SO₄ and 0.33 M NaH₂PO₄ sequentially in the same procedure as described above. The selenium content in each filtrate was determined by the same method as described in Adsorption study.

Results and Discussion

1. Selenium adsorption study

The sorption reaction in soil solutions is affected by many factors: temperature, adsorbate concentration, solution pH, competitive ions, and contact period. In the present study, the relationship between the contact period and the amount of Se adsorbed was measured, and the effect of the solution pH on Se adsorption was investigated.

Contact period

The relationship between the reaction time and the amount of selenium and selenate adsorbed by soils (the andosol and the fluvisol) is shown in Figure 2. The amount of Se adsorbed was dependent upon the type of soil and on the Se oxidation state. The adsorption in each of three cases increased rapidly with time before 2 or 3 hrs. Afterthen, it increased very slightly.

![Fig. 2](image-url)
with time. In all cases, the difference between adsorption for 6 hrs and for 24 hrs was less than 5%, and changes in the final pH of the solutions were rarely found. Therefore, a 6 hr contact period was chosen in the following adsorption experiments, because in the present study it was purpose to grasp only the sorption reaction for brief period. If the longer reaction between Se and soils is studied, the more factors should be considered in addition to sorption. They would include reduction of selenate to selenite, assimilation and volatilization of Se by microorganism. The contact periods in published Se adsorption experiments have been fairly variable, ranging from 2 hrs to 1 week. It is expected that the reaction of selenite to the soils continues gradually for a long time, which is similar to that for phosphate, molybdate and fluoride. Barrow and Whelan (1989b) indicated with a mechanistic model that the reaction consisted of an initial selenite adsorption followed by a diffusive penetration and also reported that the effects of time for selenate adsorption reaction was much smaller than for selenite.

Effect of pH on Se adsorption

Figure 3 shows the percentage of Se adsorbed by the four soils as a function of pH. Except for selenate which was scarcely adsorbed by the fluvisol, the adsorption of selenite and selenate mostly increased with decreases in suspension pH. This is similar to the results for specimen minerals reported by Benjamin, Balistrieri & Chao, Bar-Yosef & Meek, and Okazaki et al, and is also in agreement with the results for alluvial soils reported by Neal et al.

Generally, the adsorption of anions by soils is dependent on solution pH, which varies the

![Fig. 3](image_url)  

The adsorption of selenite (closed symbols) and selenate (open symbols) by four soils as a function of pH. Initial concentration of selenium = 0.25 mM. Ionic strength = 0.1 M NaCl.
positive charge on the soil particle surface. Selenite and selenate were no exceptions, and their behavior in soils and their effects on plants and microorganisms are changed considerably with the soil pH.

Selenate was only slightly adsorbed by soils under alkaline conditions (pH \geq 8), although all soils could adsorb a small amount of selenite even in high pH conditions from pH 8 to 9. In all soils, the adsorption of selenate was much less than selenite over the entire pH range. A similar difference of adsorption of selenite and selenate can be found in specimen minerals such as goethite. In selenate adsorption by soils under experimental conditions in comparison to selenite, there are contradictory references: Singh et al. reported that selenate was adsorbed more by various soils than selenite, while Barrow & Whelan and Neal & Sposito showed that selenate was less adsorbed than selenite by the yellowish-brown, loamy sand and by the alluvial soils, respectively. One can conclude that selenate tends to be adsorbed by soils which have variable charge characteristics under low pH conditions and the amount of selenate adsorbed is clearly less than that of selenite. It can be viewed as an inherent difference in the affinity to the soil particle surface and in the adsorption mechanism of the two oxidation states. The results also suggest that selenate could be more highly mobile than selenite even in acidic soils if selenium is discharged into the soils as a form of selenate.

Barrow & Whelan emphasized that for both selenate and selenite the effects of pH on sorption depended on the background electrolyte in which the measurement were made. Therefore, the results would be a little changed at a different concentration of background electrolyte. It is expected that the selenium behavior in soils is affected by content and kind of salts contained in soils.

The four soils varied appreciably in their ability to adsorb selenite and selenate. The highest amount of selenite and selenate was adsorbed by the andosol, followed by the acrisol. The fluvisol and the cambisol adsorbed fairly less selenite and selenate than the andosol and the acrisol. The variation in their capacity to absorb Se may be explained by their physical and chemical properties (Table 1). The Se adsorption capacities of the four soils were related to increases in the specific surface area, phosphate adsorption coefficient, and oxalate extractable Al content of the soils. John et al., in a study of 66 New Zealand soils, concluded that selenite sorption increased as a function of soil weathering and significant correlations were also found with surface area, organic C and extractable Al, Si, and Fe. Neal et al. also attributed differences in selenite sorption by alluvial soils below pH 6 to the amounts of solubilized Al, Fe, and Mn. There is little evidence in literature for the factor of selenate adsorption by soils. However, it is possible that free-form oxides with a large surface area bear the positive charges which are variable with the solution pH and the active sites for both selenite and selenate adsorption on the surface of the soil particles.

Release of inos from soils with adsorption of selenium

Iron, Al, and Si released from the soils to the extracts with Se adsorption were determined by ICP. Figure 4 shows the release of Al, Fe and Si from the andosol as a function of pH. No differences in Al and Fe concentrations were observed at each pH value of the solutions between three cases, selenite, selenate and no Se addition (Blank). Although the Si concentration with selenate addition did not differ from that with no Se addition, the amount of Si released into the selenite added solutions was clearly more than in the other two cases. This indicate that added selenite replaces silicate contained in the andosol and the silicate is released into a liquid phase. The same reaction takes place in selenite and phosphate sorption by allophane clay and in phosphate sorption by andosols. No symptom of this phenomena was found in the other three soils. It can therefore be presumed that the released silicate is from allophane in the andosol. These results substantiated that selenite is sorbed on soil particles by ligand exchange like as phosphate.
2. Selenium desorption study

In order to evaluate the differences in the adsorption mechanism of selenite and selenate, the relative strength of adsorption and the affinity of Se to the soil particle surfaces were supposed by the desorption of adsorbed Se with nitrate, sulfate, and phosphate. The affinities of these anions to the soil particle surfaces is in the order, phosphate $>$ sulfate $>$ nitrate. Phosphate is fixed on soils by ligand exchange, while nitrate is adsorbed only by electrostatic bonding as a diffuse-ion swarm or outer-sphere complexes$^{26}$. Figure 5 indicates the desorption partitions of selenite and selenate adsorbed by the acrisol and the andosol. The desorption partitions of selenite in each soil were not clearly affected by the final pH of the suspensions in the adsorption experiments. Selenium released by each anion extract from the soils adsorbing selenate contained only a small amount of selenite ($<0.5\%$). Selenate added to the suspensions was scarcely reduced to selenite for the contact period. Barrow and Whelan$^{17}$ also reported that there was no indication of reduction of selenate to selenite under the condition of their selenate incubation experiment.

Much of the selenite ($>60\%$) adsorbed on soils was not released by nitrate and sulfate, indicating that selenite binds to soil particle surfaces strongly. Selenite is generally thought to be sorbed by ligand exchange, like as phosphate$^{5,23,27}$, and to form inner-sphere surface complexes on goethite$^{11-12}$. The present
results did support this concept. Zhang & Sparks\(^{12}\) indicated that the formation of the inner-sphere surface complexes involves two steps: selenite first forms an outer-sphere surface complex at the \(\beta\) layer, and then a ligand is replaced from the surface site by adsorbed selenite, forming an inner-sphere surface complex. The second step is much slower than the first step\(^{12}\). Therefore, selenite released by nitrate, which is a small percentage of the total adsorbed selenite (Fig. 5), is suspected to be in the first step, in which selenite ions retain a hydration shell around them.

In contrast to selenite, a large amount (> 70\%) of selenate adsorbed by the soils was desorbed with nitrate and sulfate extracts. It is particularly significant that much of the selenate was released by nitrate. These results indicate that much of the selenate is retained on soils only by the coulomb force between the selenate ions and the positive charge sites on the soil particles, from the consideration that nitrate is unable to penetrate to the inner-sphere surface or to exchange anions fixed by ligand exchange. The results also indicate that selenate adsorbed by soil particles is ion-exchangeable with other anions. The adsorptive strength and affinity of selenate to soil particle surfaces were very weak in comparison to selenite. The finding of Hayes et al.,\(^{11}\) indicate that selenate retains a hydration shell when adsorbed by goethite and forms a weakly bonded, outer-sphere surface complex. Zhang & Sparks\(^{12}\) concluded from the equilibrium and the kinetics studies that selenate adsorption by goethite occurs at the \(\beta\) layer via electrostatic attraction to from outer-sphere surface complexes. The results of the present study confirms this theory positively. In summary, the adsorption structures of selenite and selenate which are supposed from the discussion are schematically shown in Figure 6. The data both in the adsorption study and in the desorption study confirm that selenite is adsorbed by soil particle surfaces by ligand exchange, forming the inner-sphere complexes, and that selenate is attracted as an ion-pair, outer-sphere surface complex with water molecules.
between the selenate ion and the soil surface.

This work shows that the reaction of selenite with soils is similar to that for phosphate, molybdate and fluoride, while selenate behaves in soils like nitrate, chloride and perchlorate. If soils are polluted with selenium in the form of selenate, the hazard and the effect on microorganism and plants would be larger than selenite. On the other hand, if selenium is considered as a fertilizer, selenate would be expected to have more effectiveness than selenite.

References

Selenite and Selenate Adsorption by Soils


亜セレン酸イオンとセレン酸イオンの吸着の特異性から見た
土壤中のセレンの挙動に関する研究

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摘 要
セレンの主要形態である亜セレン酸イオン, セレン酸イオンの土壤に対する吸着性を,
pH の影響の観点から 4 種の土壤を用いて調べた。亜セレン酸イオン, セレン酸イオン共に
pH 低下に伴って吸着量は増加した。セレン酸イオンの吸着量は亜セレン酸イオンに比べ,
全 pH ではるかに少なかった。使用土壤のセレン吸着能は次のような順になった。黒ボク土 >
赤黄色土 > 灰色低地土 > 褐色森林土。この吸着能は、土壤の比表面積、リン酸吸着係数,
しゅう酸可溶性アルミニウム量の増加と関係があった。亜セレン酸イオンの黒ボク土に対
する吸着で、黒ボク土からのケイ素の放出が認められた。
連続抽出法を用いて、亜セレン酸イオン、セレン酸イオンの土壤からのの脱着を調べた。
吸着した亜セレン酸イオンの大部分（＞60 ％）は、硝酸イオン、硫酸イオンでは通りしなか
った。反対に、吸着したセレン酸イオンの 70 ％以上が硝酸イオン、硫酸イオンで脱着し、
亜セレン酸イオンとセレン酸イオンの吸着機構の違いが示唆された。土壤中では、pH が低
いほどセレンは動きにくく、セレン酸塩は亜セレン酸塩に比べ、かなり移動性に富むこと
がわかった。

キーワード：亜イオン吸着機構、亜イオン脱着、亜セレン酸塩、セレン酸塩、湿潤気候の
土壤