Effect of Sulfate on Nitrate Transport in Volcanic Ash Soils
Sampled from the A and B Horizons

ABSTRACT

The contamination of groundwater by nitrate has become a worldwide problem. About 50% of the non-rice-producing crop areas are covered with volcanic ash soils in Japan. Therefore, it is important to analyze the nitrate movement in such soils for the conservation of groundwater quality. We investigated the nitrate transport in volcanic ash soils sampled from the A and B horizons under competitive conditions with sulfate. Miscible displacement experiments were carried out using a soil column 13-cm long and 5-cm in inside diameter. Nitrate was eluted before 1 pore volume of discharge from the A horizon soil column due to anion exclusion. On the other hand, its movement was retarded in the B horizon soil column because of electrostatic adsorption. When sulfate was adsorbed on the soil before the percolation of the nitrate solution, nitrate percolation became faster than that in the absence of sulfate adsorption. When the nitrate solution contained sulfate, nitrate moved much more faster. These faster nitrate elutions were due to the competition of adsorption with sulfate. Some sulfate was strongly adsorbed on the soil and it was not easily exchanged with nitrate in the B horizon soil. It was gradually desorbed and discharged from the soil column during the percolation of the nitrate solution. Sulfate was slightly adsorbed on the soil of the A horizon, although no positive charges were observed. The nitrate for 10 mol m$^{-3}$ solution flowed faster than that for the 1 mol m$^{-3}$ solution in the B horizon soil, because the solid-liquid distribution ratio for the 10 mol m$^{-3}$ solution was smaller than that for the 1 mol m$^{-3}$ solution. Because sulfate increased the nitrate flow rate in the B horizon soil, application of sulfate to the soil is not recommended from the viewpoint of nitrate contamination.

Keywords: groundwater contamination, nitrate, sulfate, transport, volcanic ash soil
INTRODUCTION

The contamination of groundwater by nitrate has become a worldwide problem. Nitrate-N concentration of groundwater higher than 10 mg/l (0.71 mol m⁻³) was observed in many areas in Japan (Tabuchi, 1999). About 50 % of the non-rice-producing crop areas are covered with volcanic ash soils in Japan (Wada, 1986). Therefore, it is important to analyze the nitrate movement in such soils for the conservation of groundwater quality.

Commonly, volcanic ash soils contain variable charges. Especially, their B horizon soils contain both negative and positive variable charges (Wada and Okamura, 1980; Inoue, 1986). Anion movement is retarded by electrostatic adsorption (Ishiguro et al., 1992; Ishiguro, 1992; Katou et al., 1996). Therefore, the positive charge of the soil enables to avoid nitrate contamination of groundwater. When sulfate is spread over a field as an ammonium sulfate fertilizer, for example, under upland field conditions, most of the ammonium changes into nitrate through the nitrification process, resulting in a competition between nitrate and sulfate which affects the nitrate movement. As sulfate is strongly adsorbed on positively charged soils (Gebhardt and Coleman, 1974; Rajan, 1978; Rajan, 1979; Agbenin, 1997; Yamaguchi et al., 1999) and nitrate adsorption on Andisols decreases with the increase in the sulfate concentration (Kamewada, 1996), the influence of sulfate on nitrate transport is considerable.

In this paper, we investigated the nitrate transport in volcanic ash soils sampled from the A and B horizons under competitive conditions with sulfate and analyzed the effect of sulfate on nitrate transport in the soil.

MATERIALS AND METHODS

Soils

The volcanic ash soils were sampled in the Daisen pasture halfway up Mt. Daisen in Tottori Prefecture, Japan, from the A and the B horizons. The A horizon soil consisted of Cumulic Non-allophanic Andosol. The ignition loss was 25.9 %, and the clay content was 24.6 %, the silt content was 31.8 % and the sand content was 43.6 %. The ignition loss of the B horizon soil was 7.0 %, and the clay content was 26.7 %, the silt content was 38.8 % and the sand
content was 34.5%.

**Miscible Displacement Experiment**

The breakthrough curves (BTCs) were obtained from saturated soil column tests. An acrylic column 13-cm long and 5-cm in i.d. was used. To maintain a constant hydraulic gradient at 2 m/m, a Mariotte bottle and a tube connected to the bottom of the soil column through a small water-filled head space and filter net were used. The Mariotte bottle was used to maintain a constant water pressure on top of the soil column. In order to observe the effect of sulfate on the nitrate movement, nitrate solutions and sulfate solutions were percolated into the soil column alternately as shown in Table 1. Influent solutions were percolated in the order shown in Table 1. In order to investigate the effect of the concentration on the nitrate transported in the B horizon soil, a series of higher concentration solutions (middle row of Table 1) and lower concentration solutions (right row of Table 1) were chosen. The cations in these solutions were potassium or sodium. The experimental procedure was as follows:

1. A column was packed with <2-mm sieved, field-moist soil to a bulk density of 600 kg/m$^3$ for the A and B horizons for the series of higher concentration solutions and 540 kg/m$^3$ for the B horizon for the series of lower concentration solutions.
2. The soil column was saturated by capillary rise with the initial influent solution for 1 d.
3. Each influent solution was percolated sufficiently in the order shown in Table 1. The effluent concentrations of sulfate and nitrate during the experiment were measured by ion chromatography.

The percolated amount for each higher concentration solution was about 12 pore volume and that for each lower concentration solution was about 15 pore volume for the B horizon soil, while that for the A horizon soil was about 8 pore volume.

Effluent pH values for the series of higher concentration solutions ranged from pH 6.3 to 6.7, and those for the series of lower concentration solutions from pH 5.5 to 6.2.

**Adsorbed Amounts of Ions**

The adsorbed amount of an ion during the solution percolation, $S$, was calculated from the observed BTC using the following equation:
\[ S = \int_{0}^{Q} (Ci - C)dQ - (Ci - Co)V \]  \hspace{1cm} [1]  

where \( Q \) is the total discharge during the influent percolation, \( Ci \) is the ion concentration of the influent, \( C \) is the ion concentration of the effluent, \( Co \) is the initial ion concentration in the soil column, and \( V \) is the volume of water in the soil column. When \( S \) takes a negative value, desorption occurs during the influent percolation. The adsorbed amount per unit dry soil mass, \( s \), is 

\[ s = S/W. \]  \hspace{1cm} [2]  

where \( W \) is the dry soil mass in the soil column.

RESULTS AND DISCUSSION

The A Horizon

The CEC of the soil was calculated from the potassium BTC at 1 mol·m\(^{-3}\). The CEC value was 12.3 mmol/kg. The nitrate BTC with the influent solution of “(2) 1 mol·m\(^{-3}\) NO\(_3\)" and the sulfate BTC with the influent solution of “(3) 1 mol·m\(^{-3}\) SO\(_4\)" listed in Table 1 are shown in Fig. 1. The nitrate BTC rose rather fast before 1 pore volume of discharge. If an anion is inert, the BTC rises from around 1 pore volume. In this case, because the soil contained only a negative charge, anion exclusion in the soil column resulted in faster nitrate transport. However, the effect of anion exclusion was not observed in the sulfate BTC. Based on the diffuse double layer theory, sulfate exclusion must be generated in the sulfate movement because a negative charge in the soil also excludes sulfate from the diffuse double layer. Some weak sulfate adsorption may occur in the soil. Nanzyo (1989) showed that phosphate was adsorbed on a non-allophanic andisol sampled from the A horizon, which had no positive charge. Phosphate was assumed to be adsorbed on an aluminum hydroxide and a complex of aluminum-humic substances by ligand exchange. Similar phenomena may occur in the soil with sulfate. However, further investigations should be conducted to verify this assumption.

The B Horizon

Since the B horizon soil has a positive charge, the movement of nitrate and sulfate was
delayed due to adsorption in the miscible displacement experiments. BTC during percolation of “(4) 10 mol\(\cdot\)m\(^{3}\) NO\(_{3}\) solution of higher concentration series” listed in Table 1 is illustrated in Fig. 2 and BTC during percolation of “(5) 10 mol\(\cdot\)m\(^{3}\) SO\(_{4}\) solution of higher concentration series” listed in Table 1 is illustrated in Fig. 3. Both nitrate BTC in Fig. 2 and sulfate BTC in Fig. 3 showed a delay due to adsorption.

The calculated adsorption amounts during the percolation of the solutions of higher concentration series are listed in Table 2 and those of lower concentration series in Table 3. The positive value corresponds to adsorption and the negative value to desorption during the percolation of each solution in the second and third rows in the Tables. A considerable amount of SO\(_{4}\) is adsorbed in an Andisol naturally (Kamewada, 1994; Katou et al., 1996). Some adsorbed SO\(_{4}\) was expected to be exchanged with Br and NO\(_{3}\) during the percolation of the Br and NO\(_{3}\) solutions. However, some may remain in the soil column even after the percolation of the Br and NO\(_{3}\) solutions, because some SO\(_{4}\) may be specifically adsorbed on the soil (Gebhardt and Coleman, 1974; Rajan, 1978; Rajan, 1979; Agbenin, 1997; Yamaguchi et al., 1999). The values of SO\(_{4}\) sorption listed in Tables 2 and 3 did not include such specifically adsorbed SO\(_{4}\) which was not exchanged with Br and NO\(_{3}\). Most of the specifically adsorbed SO\(_{4}\) was not considered to be involved in the anion exchange phenomena during the experiment because of its strong adsorption. In Tables 2 and 3 in the second row, the absolute value of nitrate adsorption in line (2) and that of desorption in line (3) were almost identical. Those in lines (4) and (5), (6) and (7), and (8) and (9) in the second rows in Tables 2 and 3, were also almost identical. Therefore, adsorbed nitrate was almost completely desorbed after the percolation of the sulfate solutions and the small differences were probably due to measurement errors. Nitrate adsorption was the largest before the application of the sulfate solution, amounting to 23.4 mmol/kg for “(2) 10 mol\(\cdot\)m\(^{3}\) NO\(_{3}\) solution” listed in Table 2, and 4.9 mmol/kg for “(2) 1 mol\(\cdot\)m\(^{3}\) NO\(_{3}\) solution” listed in Table 3. When sulfate was present in the nitrate solution, nitrate adsorption decreased due to adsorption competition. The smallest nitrate adsorption amounted to 2.6 mmol/kg for “(6) 10 mol\(\cdot\)m\(^{3}\) NO\(_{3}\) and SO\(_{4}\) solution” listed in Table 2, and 1.0 mmol/kg for “(6) 1 mol\(\cdot\)m\(^{3}\) NO\(_{3}\) and SO\(_{4}\) solution” listed in Table 3. The nitrate adsorption decreased to 11.1 % of the largest value for the 10 mol\(\cdot\)m\(^{3}\) nitrate solution, and 20.4 % of the largest value for the 1 mol\(\cdot\)m\(^{3}\) nitrate solution. Even when the sulfate
concentration was 1/10 of the nitrate concentration in the influent solution, nitrate adsorption decreased to about 35% of the largest value for “(8) 1 mol_c m^3 NO_3 and 0.1 mol_c m^3 SO_4 solution” listed in Table 3 and 37% of the largest value for “(8) 10 mol_c m^3 NO_3 and 1 mol_c m^3 SO_4 solution” listed in Table 2. Sulfate was highly selective over nitrate in this soil. Kamewada (1996) revealed a negative NO_3 adsorption on an Andisol when the SO_4 concentration was higher than 6 mol_c m^3. However, such NO_3 exclusion was not observed in this soil under the current solution conditions.

The influence of sulfate on the nitrate BTC can be observed in Figs. 4 and 5. The BTC that shifted to the right in Fig. 4 corresponded to the lack of sulfate application. In this case, nitrate movement was most delayed. The BTC in the middle of Fig. 4 corresponded to the presence of sulfate initially and to the adsorption in the soil column. Under these conditions, nitrate adsorption decreased to 50% of the largest value (see the second row and line (4) in Table 2). The latter nitrate moved faster than the former. The BTC that shifted to the left in Fig. 4 corresponded to the presence of sulfate in the influent solution. Due to the competition between nitrate and sulfate, nitrate adsorption became smallest and nitrate moved fastest.

The effect of the sulfate concentration of the influent nitrate solution on the nitrate BTC is depicted in Fig. 5. The nitrate concentrations of the influent solutions were all 10 mol_c m^3. The nitrate BTC for the highest sulfate concentration, 10 mol_c m^3, shifted to the left due to the smallest nitrate adsorption. The nitrate BTC for 1 mol_c m^3 sulfate concentration slightly shifted to the right of that BTC because of the increase in nitrate adsorption. The nitrate BTC for 0.1 mol_c m^3 sulfate concentration shifted more to the right of those BTCs due to the increase of nitrate adsorption.

The amount of sulfate that was adsorbed and desorbed during the percolation of influent solutions was not balanced as indicated in Tables 2 and 3, in lines (3) and (4) in the third rows. The total amount of sulfate adsorption in the soil column at the end of the percolation of each influent solution is listed in the right rows in Tables 2 and 3. Even after the percolation of the nitrate solution, sulfate remained in the soil. The sulfate BTC during percolation of “(4) 10 mol_c m^3 NO_3 solution” listed in Table 1 in the second row is illustrated in Fig. 2, as mentioned before. The sulfate concentration decreased with the percolation of the nitrate solution, but the decrease became very slow after about 4 pore volume of discharge. If the sulfate is initially
adsorbed with simple electrostatic force, it can be exchanged with percolating nitrate easily and the BTC does not show such a gradual decrease after 4 pore volume of discharge (Fig. 2). The gradual decrease occurred due to the specific adsorption of sulfate (Gebhardt and Coleman, 1974; Rajan, 1978; Rajan, 1979; Agbenin, 1997). Even after the percolation of a solution with the same sulfate concentration, total sulfate sorption values were different as indicated in Tables 2 and 3, in lines (3) and (5) in the fourth rows. The values became larger when the duration of sulfate percolation became longer. Strongly adsorbed sulfate was not easily exchanged with nitrate and the amount of adsorbed sulfate gradually increased with continuous percolation of the sulfate solution. Specifically adsorbed sulfate influenced the nitrate adsorption and transport as mentioned before.

The nitrate BTC for “(2) 10 mol·m⁻³ NO₃ solution” listed in Table 2 was compared with the nitrate BTC for “(2) 1 mol·m⁻³ NO₃ solution” listed in Table 3. The nitrate BTC for the higher concentration flowed out faster than that for the lower concentration as shown in Fig. 6, although nitrate adsorption for the former was larger than that for the latter, because the concentration of the former was ten times larger than that of the latter. When the influent concentration is higher, larger amounts of nitrate per volume are supplied to the adsorption site. Then, nitrate can flow faster than that for the lower concentration. The average penetration length of an adsorbing ion can be evaluated by the solid-liquid distribution ratio (Bolt, 1978), D, defined as,

\[
D = \frac{\rho \cdot q}{w \cdot Ci}
\]

where \(\rho\) is the bulk density (kg/m³), \(q\) is the adsorption amount (mol/kg), \(w\) is the volumetric water content (m³/m³) and \(Ci\) is the influent concentration (mol·m⁻³). The value of \(D\) for “(2) 10 mol·m⁻³ NO₃ solution” was 2.0 and the value of \(D\) for “(2) 1 mol·m⁻³ NO₃ solution” was 3.8. As the former \(D\) value is smaller, the nitrate for the higher concentration flowed out faster as observed in Fig. 6.

**CONCLUSION**

As nitrate is a contaminant of groundwater, nitrate transport in the volcanic ash soils sampled
from the A and the B horizons was investigated. Nitrate flowed out quickly in the A horizon soil due to anion exclusion. On the other hand, it moved slowly in the B horizon soil because of adsorption. Therefore, the B horizon soil exerted a good influence on groundwater conservation. However, when sulfate was initially adsorbed or was present in the influent solution, the nitrate movement became faster due to adsorption competition. As sulfate was highly selective over nitrate in the B horizon soil, its influence on the nitrate movement was considerable. Hence, the application of sulfate on that soil is not recommended. When the nitrate concentration increased, nitrate flowed faster because the solid-liquid distribution ratio decreased. Nitrogen application at higher concentrations accelerates groundwater contamination.

The amount of positive charges of the B horizon soil of this Non-allophanic Andosol was smaller than that of an Allophanic Andosol as commonly observed (Inoue, 1986). However, the positive charge considerably influenced the nitrate movement in this B horizon soil. The effect should become more appreciable for an Allophanic Andosol due to its larger positive charge content.

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Fig. 1. Nitrate BTC during percolation of “(2) 10 mol/m$^3$ NO$_3$” solution, and sulfate BTC during percolation of “(3) 10 mol/m$^3$ SO$_4$” solution for the A horizon soil. The numbers in parentheses correspond to those in Table 1.
Fig. 2. Nitrate and sulfate BTCs for the B horizon soil during percolation of “(4) 10 mol/m$^3$ NO$_3$” solution. The number in parentheses corresponds to that in Table 1.
Fig. 3. Nitrate and sulfate BTCs for the B horizon soil during percolation of “(5) 10 mol/m$^3$ SO$_4$” solution. The number in parentheses corresponds to that in Table 1.
Fig. 4.  Nitrate BTCs for the B horizon soil during percolation of “(2) 10 mol/m$^3$ NO$_3$” solution (no sulfate), “(4) 10 mol/m$^3$ NO$_3$” solution (initially sulfate was present), and “(6) 10 mol/m$^3$ NO$_3$, 10 mol/m$^3$ SO$_4$” solution. The numbers in parentheses correspond to those in Table 1.
Fig. 5. Nitrate BTCs for the B horizon soil during percolation of “(6) 10 mol./m$^3$ NO$_3$, 10 mol./m$^3$ SO$_4$” solution, “(8) 10 mol./m$^3$ NO$_3$, 1 mol./m$^3$ SO$_4$” solution, and “(10) 10 mol./m$^3$ NO$_3$, 0.1 mol./m$^3$ SO$_4$” solution. The numbers in parentheses correspond to those in Table 1.
Fig. 6. Nitrate BTCs for the B horizon soil during percolation of “(2) 10 mol/m\(^3\) NO\(_3^-\)” solution of the higher concentration series, and “(2) 1 mol/m\(^3\) NO\(_3^-\)” solution of the lower concentration series. The numbers in parentheses correspond to those in Table 1.
<table>
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<tr>
<th>Series of influent solutions for the A horizon</th>
<th>Series of higher concentration solutions for the B horizon</th>
<th>Series of lower concentration solutions for the B horizon</th>
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<tr>
<td>(1) 1 mol·m⁻³ SO₄</td>
<td>(1) 10 mol·m⁻³ Br</td>
<td>(1) 1 mol·m⁻³ Br</td>
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<tr>
<td>(2) 1 mol·m⁻³ NO₃</td>
<td>(2) 10 mol·m⁻³ NO₃</td>
<td>(2) 1 mol·m⁻³ NO₃</td>
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<tr>
<td>(3) 1 mol·m⁻³ SO₄</td>
<td>(3) 10 mol·m⁻³ SO₄</td>
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<td>(5) 10 mol·m⁻³ SO₄</td>
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Table 1. Series of influent solutions for the miscible displacement experiments.

The solutions were percolated in numerical order for each series.
Table 2. Adsorption amounts in the miscible displacement experiments for the higher concentration series of the B horizon soil.

<table>
<thead>
<tr>
<th>Influent Solution</th>
<th>NO₃ sorption (mmol/kg)</th>
<th>SO₄ sorption (mmol/kg)</th>
<th>SO₄ sorption (mmol/kg)</th>
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<td>(2) 10 mol·m⁻³ NO₃</td>
<td>23.4</td>
<td>0.0</td>
<td>0.0</td>
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<td>(3) 10 mol·m⁻³ SO₄</td>
<td>-22.2</td>
<td>31.2</td>
<td>31.2</td>
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<td>(4) 10 mol·m⁻³ NO₃</td>
<td>11.6</td>
<td>-13.0</td>
<td>18.2</td>
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<tr>
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<td>-12.4</td>
<td>19.1</td>
<td>37.3</td>
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<td>13.8</td>
<td>51.1</td>
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<tr>
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<td>-17.4</td>
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<tr>
<td>(8) 10 mol·m⁻³ NO₃, 1 mol·m⁻³ SO₄</td>
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<td>28.7</td>
</tr>
<tr>
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<td>-9.3</td>
<td>-11.2</td>
<td>17.5</td>
</tr>
<tr>
<td>(10) 10 mol·m⁻³ NO₃, 0.1 mol·m⁻³ SO₄</td>
<td>18.7</td>
<td>-0.3</td>
<td>17.2</td>
</tr>
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