Anion adsorption and transport in an unsaturated high-humic Andosol

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Abstract
Contrary to the common notion that Andosols having a high organic carbon content possess a negligible to very weak anion exchange capacity, these soils often contain large amounts of adsorbed sulfate, implying their potential to adsorb nitrate and other weakly-adsorbing anions. The objective of this study is to determine chloride and nitrate adsorption isotherms in a high-humic Andosol under conditions that mimic those found in the field. Koshi soil (Hydric Pachic Melanudand), premixed with CaCl\textsubscript{2} or CaCl\textsubscript{2}–Ca(NO\textsubscript{3})\textsubscript{2} solution at different concentrations, was packed into columns, and one-dimensional water absorption experiments were conducted. The anion content profiles in the columns showed varying degrees of anion retardation relative to water, depending on the initial anion content. Anion adsorption by soil, \(Q_n\), and the liquid-phase concentration, \(C_n\), prior to the water imbibition were estimated from the plots of the anion content vs. water content in the region beyond the “plane of separation”, where the antecedent solution was accumulated. The anion adsorption isotherm constructed from these estimates was successfully employed in the anion transport model to reproduce the measured anion content profiles. These results show that the current notion that adsorption of monovalent electrolyte anions is negligible in high-humic Andosols should be reconsidered.

Key Words
Anion adsorption, anion exchange, humic Andosol, retardation, nitrate leaching, unsaturated flow.

Introduction
It is widely recognized that Andosols having a high organic carbon content possess a negligible to very weak anion exchange capacity (Wada and Okamura 1980; Dahlgren \textit{et al}. 2004), precluding the possibility of retarded transport and reduced leaching of nitrate in the soils. However, large amounts of adsorbed sulfate often found in high-humic Andosols, particularly those from subsurface layers (Miki \textit{et al}. 2009), suggest the existence of electrical positive charge and possibility of further anion adsorption in these soils. In the present study, we investigated adsorption/transport of weakly-adsorbing monovalent anions in a high-humic Andosol. One-dimensional water absorption experiments were conducted in soil columns premixed with CaCl\textsubscript{2} or CaCl\textsubscript{2}–Ca(NO\textsubscript{3})\textsubscript{2} solution at different concentrations to determine Cl\textsuperscript{−} and NO\textsubscript{3}– adsorption isotherms by the unsaturated transient flow method (Katou \textit{et al}. 2001). The method has an advantage that the adsorption isotherm can be determined under conditions similar to those expected during transport processes in soil, and has been successfully applied to the determination of anion adsorption in an Andosol subsoil (Katou \textit{et al}. 2001; Katou 2004) as well as pesticide sorption in unsaturated soils (Ahmad \textit{et al}. 2005; Ochsner \textit{et al}. 2006). The inferred adsorption isotherm was then employed in an anion transport model to test its ability to reproduce the measured anion content profiles.

Materials and Methods

\textit{Soil}

The soil used in the present study was the air-dried subsoil of Koshi Andosol (Hydric Pachic Melanudand) taken from the experimental field of the Institute of Agro-environmental Research, Kumamoto Prefectural Agricultural Research Center at Koshi, Kumamoto, Japan. The soil, taken from the 40 cm depth, had a total carbon content of 62.4 g/kg, exchangeable Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and K\textsuperscript{+}, respectively, of 138 mmol/kg, 18.1 mmol/kg, and 7.0 mmol/kg, an initial NO\textsubscript{3}– content of 2.3 mmol/kg, and 0.01 M NaOH-extractable SO\textsubscript{4}\textsuperscript{2−} of 50.9 mmol/kg. The soil was passed through a 1-mm sieve and used without any pretreatment.

\textit{One-dimensional water absorption experiments}

One hundred grams of the air-dried soil, at a gravimetric water content of about 0.19 kg/kg, was moistened with one of the CaCl\textsubscript{2} or CaCl\textsubscript{2}–Ca(NO\textsubscript{3})\textsubscript{2} mixed solutions listed in Table 1, to give an initial water content \(w_n \approx 0.32\) kg/kg. The moistened soil was thoroughly mixed and repacked into sectionable columns of 2.1 cm
in internal diameter to a bulk density \( \rho = 0.75 \text{ Mg/m}^3 \) so that initial volumetric water content \( \theta_0 \approx 0.24 \text{ m}^3/\text{m}^3 \). One-dimensional, horizontal water absorption experiments were conducted by supplying distilled water from a Marriotte bottle to the proximal end of the column. After terminating each experiment, the column was rapidly sectioned and the soil samples immediately weighed and air-dried. From the water content profiles, the plane of separation, \( x^* \) (m), which identifies the front of the invading water, was found for each column using the relation (Smiles and Philip 1978).

\[
\int_0^x \theta \, dx = \int_0^{x^*} \theta \, dx
\]

where \( x \) is the distance (m), \( \theta \) is the volumetric water content (m\(^3\) m\(^{-3}\)), and \( \theta_0 \) is the water content at the proximal end of the soil column. The anion contents in soil were determined by the method described by Katou et al. (1996). One gram of soil was shaken for 15 min with 100 mL of 0.01 M NaOH, and after centrifugation the supernatant solution was analyzed for \( \text{Cl}^- \), \( \text{NO}_3^- \), and \( \text{SO}_4^{2-} \) by ion chromatography.

\[
C_n = \frac{M}{\rho \cdot \omega}
\]

\[
Q_n = \frac{Q}{\rho}
\]

\[
C_{Cl} = \frac{C_{\max,Cl} + C_{NO3}Q_{\max,NO3}}{1 + K(C_{Cl} + C_{NO3})}
\]

\[
Q_{NO3} = \frac{K_{ex}C_{NO3}}{C_{Cl} + K_{ex}C_{NO3}} \left[ \frac{K(C_{Cl}Q_{\max,Cl} + C_{NO3}Q_{\max,NO3})}{1 + K(C_{Cl} + C_{NO3})} \right]
\]

where \( Q \) is the amount of the anion adsorbed per unit mass of soil (mol/kg), \( C \) is the concentration in the liquid phase (mol/m\(^3\)), \( Q_{\max,Cl} \) and \( Q_{\max,NO3} \) (mol/kg) are, respectively, the maximum adsorption of \( \text{Cl}^- \) and \( \text{NO}_3^- \) from a solution containing \( \text{Cl}^- \) or \( \text{NO}_3^- \) only, and \( K \) is an empirical constant (m\(^3\)/mol). Here, \( K_{ex} \) is the selectivity coefficient for the \( \text{NO}_3^- \)–\( \text{Cl}^- \) exchange given by

\[
K_{ex} = \frac{Q_{\max,NO3}C_{Cl}}{Q_{\max,Cl}C_{NO3}}
\]

The adsorption parameters \( K, Q_{\max,Cl} \) and \( Q_{\max,NO3} \) were determined using the linear form of the equations as described by Katou et al. (1996). The selectivity coefficient \( K_{ex} \) was evaluated by putting \( C_{Cl} = C_{\text{Cl}_{\text{air}}, C_{NO3} = C_{\text{NO3}_{\text{air}}}} Q_{\text{Cl}} = Q_{\text{Cl}_{\text{air}}} \) and \( Q_{\text{NO3}} = Q_{NO3_{\text{air}}} \) in Eq. (5).
Results and Discussion

One-dimensional absorption of water into Koshi soil premixed with CaCl$_2$ and CaCl$_2$–Ca(NO$_3$)$_2$ solutions produced anion displacement similar to that found in the Kannondai subsoil which had substantial anion adsorption properties of $K = 0.0246$ m$^3$/mol c$_i$, $Q_{\text{max,Cl}} = 0.0455$ mol/kg and $Q_{\text{max,NO$_3$}} = 0.0290$ mol/kg (Katou 2004). Figure 1 presents anion content profiles in the column LKZ8, where 0.15 M CaCl$_2$ had been incorporated. The soil had an initial Cl$^-$ and NO$_3^-$ contents of 40.6 mmol/kg and 2.5 mmol/kg, respectively. The plane of separation was located at $x^* = 11.2$ cm. Upon absorption of water, Cl$^-$ was almost completely removed from soil near the column inlet, but the center of the Cl$^-$ displacement front lagged behind $x^*$, indicating Cl$^-$ adsorption by the soil. We also see that the displacement of NO$_3^-$ was also retarded relative to water, even in the presence of much larger amounts of native SO$_4^{2-}$ and added Cl$^-$.

In Figure 2, the Cl$^-$ and NO$_3^-$ contents in the region $x > x^*$ were plotted against ($\theta/\rho$) for this column. In accord with the theory (Eq. (2)), the plot produced straight lines for the both anions. From linear regression analyses, estimates (±SE) of $C_n = 52.1 (±1.2)$ mmol/L and $Q_n = 24.4 (±0.7)$ mmol/kg, and $C_n = 4.6 (±0.1)$ mmol/L and $Q_n = 1.1 (±0.1)$ mmol/kg were deduced for Cl$^-$ and NO$_3^-$, respectively. These results clearly demonstrate that both Cl$^-$ and NO$_3^-$ had been adsorbed by the soil although the once-adsorbed anions were easily desorbed upon invasion of water.

The degree of retardation in the anion displacement was dependent on the initial anion content. In the column LKZ6 in which 0.025 M CaCl$_2$ had been incorporated, more distinct retardation was observed for Cl$^-$ and NO$_3^-$ as compared with that in the column LKZ8. This concentration-dependent anion retardation is consistent with nonlinear adsorption isotherms for these anions. A larger retardation for Cl$^-$ than NO$_3^-$ was evident in this column, confirming a larger affinity of Cl$^-$ to the adsorption sites in Andosols (Katou et al. 1996; Katou 2004).

![Figure 1. Profiles of anion content, $M$, and anion adsorption by soil, $Q$, upon absorption of water into Koshi soil premixed with 0.15 M CaCl$_2$ solution. Anion adsorption profiles were estimated from the measured $M$ and volumetric water content, $\theta$, profiles and the inferred competitive Cl$^-$ and NO$_3^-$ adsorption isotherm. $Q_{\text{initial,Cl}}$ = initial anion adsorption deduced from the $M$ vs. ($\theta/\rho$) plot in the region $x > x^*$; $M_{\text{initial,Cl}}$ = initial anion content; $x^*$ = plane of separation.](image1)

![Figure 2. Plots of anion content, $M$, against solution volume per unit mass of soil, ($\theta/\rho$), in the region $x > x^*$ for the column LKZ8 premixed with 0.15 M CaCl$_2$. $C_n$ = estimated initial liquid-phase anion concentration; $Q_n$ = estimated initial anion adsorption.](image2)
simulated anion content profiles are also shown for Cl\(^-\) and NO\(_3\)^-. The simulated anion content profiles were in reasonable agreements with measured ones, and evidence that the Koshi high-humic Andosol had anion adsorption properties described by Eqs. (3) and (4). In an allophanic topsoil having a total carbon content as high as 82 g/kg, Magesan et al. (2003) observed retardation factor of 1.5–1.8 for Br\(^-\) and Cl\(^-\). These results show that adsorption of monovalent electrolyte anions in high-humic Andosols are not exceptional, and that the common notion that anion adsorption in these soils is negligible should be reconsidered.

**References**


