Anion adsorption and transport in an unsaturated high-humic Andosol

Hidetaka Katou[A] and Nobiru Kozai[B]

[A]National Institute for Agro-Environmental Sciences, Tsukuba, 305-8604 Japan, Email katouh@affrc.go.jp
[B]Institute of Agro-environmental Research, Kumamoto Prefectural Agricultural Research Center, Koshi, Kumamoto 861-1113, Japan.

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 $CaCl_2$ or $CaCl_2$–$Ca(NO_3)_2$ 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 *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 *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 $CaCl_2$ or $CaCl_2$–$Ca(NO_3)_2$ solution at different concentrations to determine Cl^- and NO_3^- adsorption isotherms by the unsaturated transient flow method (Katou *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 *et al*. 2001; Katou 2004) as well as pesticide sorption in unsaturated soils (Ahmad *et al*. 2005; Ochsner *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

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^{2+}, Mg^{2+}, and K^+, respectively, of 138 $mmol_c$/kg, 18.1 $mmol_c$/kg, and 7.0 $mmol_c$/kg, an initial NO_3^- content of 2.3 $mmol_c$/kg, and 0.01 M NaOH-extractable SO_4^{2-} of 50.9 $mmol_c$/kg. The soil was passed through a 1-mm sieve and used without any pretreatment.

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 $CaCl_2$ or $CaCl_2$–$Ca(NO_3)_2$ 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 $\rho \approx 0.75$ Mg/m^3 so that initial volumetric water content $\theta_n \approx 0.24$ m^3/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).

$$\int_{\theta_n}^{\theta_s} x \, d\theta = \int_0^{x^*} \theta \, dx \tag{1}$$

where x is the distance (m), θ is the volumetric water content (m^3 m^{-3}), and θ_s 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 Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ by ion chromatography.

Table 1. Summary of the initial liquid-phase anion concentration, C_n, and initial anion adsorption, Q_n, determined by the unsaturated transient water absorption experiments.

| Salt solution incorporated | Column No. | Estimates from M vs. (θ/ρ) plot | | | |
| | | for Cl$^-$ | | for NO$_3^-$ | |
		C_n (mmol$_c$/L)	Q_n (mmol$_c$/kg)	C_n (mmol$_c$/L)	Q_n (mmol$_c$/kg)
0.025 M CaCl$_2$	LKZ6	5.5 ($\pm$0.6)	5.4 ($\pm$0.4)	3.1 ($\pm$0.1)	1.1 ($\pm$0.1)
0.1 M CaCl$_2$	LKZ7	29.3 ($\pm$1.2)	17.5 ($\pm$0.8)	3.5 ($\pm$0.2)	1.1 ($\pm$0.1)
0.15 M CaCl$_2$	LKZ8	52.1 ($\pm$1.2)	24.4 ($\pm$0.7)	4.6 ($\pm$0.1)	1.1 ($\pm$0.1)
0.3 M CaCl$_2$	LKZ9	144.8 ($\pm$2.0)	33.7 ($\pm$1.3)	5.5 ($\pm$0.4)	0.9 ($\pm$0.2)
0.05 M CaCl$_2$–0.05 M Ca(NO$_3$)$_2$	LKZ10	15.1 ($\pm$0.9)	7.0 ($\pm$0.5)	22.8 ($\pm$0.8)	7.2 ($\pm$0.4)

M, anion content per unit mass of soil; (θ/ρ), solution volume per unit mass of soil.

Determination of anion adsorption isotherms
The amount of anions adsorbed per unit mass of soil, Q_n (mol$_c$/kg), and the liquid-phase anion concentration, C_n (mol$_c$ m^{-3}), prior to the water imbibition were estimated from the water and anion contents in the region beyond the plane of separation ($x > x^*$) for each column. A plot of the anion content per unit mass of soil, M (mol$_c$/kg), vs. solution volume per unit mass of soil (θ/ρ) in this region gives the straight line (Katou *et al.* 2001)

$$M_i = Q_{in} + (\theta/\rho) \, C_{in} \tag{2}$$

where ρ is the bulk density (kg m^{-3}), and subscript i refers to the anion species. The anion contents in samples taken from the region $x > x^*$ were plotted against (θ/ρ) for each column. From linear regression analysis with (θ/ρ) as an independent variable (Eq. (2)), C_n and Q_n were determined for Cl$^-$, and NO$_3^-$.

Competitive Cl$^-$ and NO$_3^-$ adsorption isotherms (Katou *et al.* 1996) were inferred from the sets of C_n and Q_n for the anions obtained from a series of the column experiments listed in Table 1:

$$Q_{Cl} = \left(\frac{C_{Cl}}{C_{Cl} + K_{ex} C_{NO3}} \right) \left[\frac{K(C_{Cl} Q_{max,Cl} + C_{NO3} Q_{max,NO3})}{1 + K(C_{Cl} + C_{NO3})} \right] \tag{3}$$

$$Q_{NO3} = \left(\frac{K_{ex} C_{NO3}}{C_{Cl} + K_{ex} C_{NO3}} \right) \left[\frac{K(C_{Cl} Q_{max,Cl} + C_{NO3} Q_{max,NO3})}{1 + K(C_{Cl} + C_{NO3})} \right] \tag{4}$$

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

$$K_{ex} = Q_{NO3} C_{Cl}/(Q_{Cl} C_{NO3}) \tag{5}$$

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 $C_{Cl} = C_{Cln}$, $C_{NO3} = C_{NO3n}$, $Q_{Cl} = Q_{Cln}$, and $Q_{NO3} = Q_{NO3n}$ 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, $Q_{max,Cl} = 0.0455$ mol_c/kg and $Q_{max,NO3} = 0.0290$ mol_c/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 $mmol_c/kg$ and 2.5 $mmol_c/kg$, 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 (θ/ρ) for this column. In accord with the theory (Eq. (2)), the plot produced straight lines for the both anions. From linear regression analyses, estimates ($\pm$SE) of $C_n = 52.1$ ($\pm$1.2) $mmol_c/L$ and $Q_n = 24.4$ ($\pm$0.7) $mmol_c/kg$, and $C_n = 4.6$ ($\pm$0.1) $mmol_c/L$ and $Q_n = 1.1$ ($\pm$0.1) $mmol_c/kg$ 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).
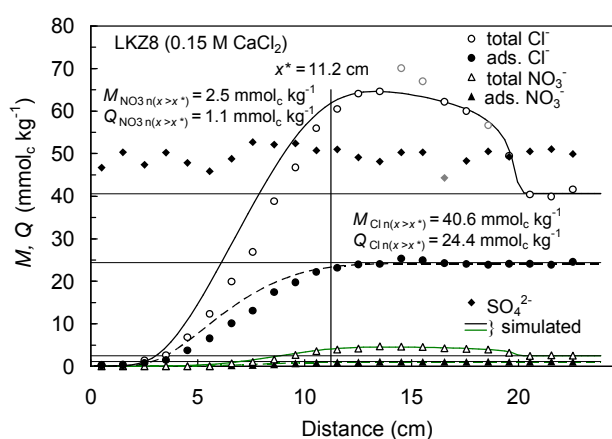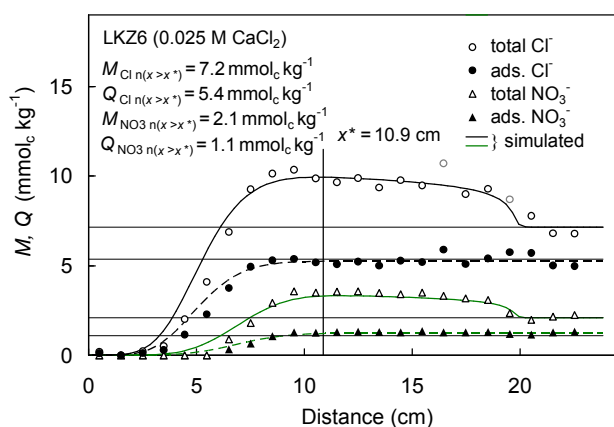

Figure 1. Profiles of anion content, *M*, and anion adsorption by soil, *Q*, upon absorption of water into Koshi soil premixed with 0.15 M CaCl₂ solution. Anion adsorption profiles were estimated from the measured *M* and volumetric water content, θ, profiles and the inferred competitive Cl⁻ and NO₃⁻ adsorption isotherm. $Q_{n(x>x^*)}$ = initial anion adsorption deduced from the *M* vs. (θ/ρ) plot in the region $x > x^*$; $M_{n(x>x^*)}$ = initial anion content; x^* = plane of separation.
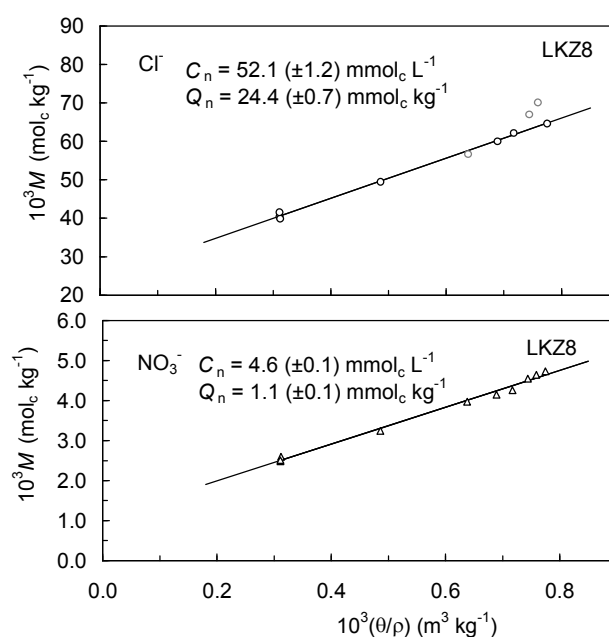
**Figure 2. Plots of anion content, *M*, against solution volume per unit mass of soil, (θ/ρ), in the region $x > x^*$ for the column LKZ8 premixed with 0.15 M CaCl₂. C_n = estimated initial liquid-phase anion concentration; Q_n = estimated initial anion adsorption.**

In Table 1, estimates of C_n and Q_n for Cl^- and NO_3^- are listed for the five column experiments. The regression analysis using the linear form of the competitive adsorption equation yielded estimates of $K = 0.0257$ ($\pm$0.0017) m^3/mol_c, $Q_{max,Cl} = 0.0444$ ($\pm$0.0074) mol_c/kg and $Q_{max,NO3} = 0.0188$ ($\pm$0.0029) mol_c/kg. All of these values are comparable to those found for the Kannondai subsoil. The adsorption parameters inferred were then used to estimate the anion adsorption profiles from the mass balance equations. They were also employed in a convective-dispersive anion transport model (Katou *el al*. 1996) to test their ability to reproduce the measured anion content profiles. In Figure 1 and 3, the estimated adsorption profiles as well as

Figure 3. Profiles of anion content, *M*, and anion adsorption by soil, *Q*, upon absorption of water into Koshi soil premixed with 0.025 M CaCl$_2$ solution. $Q_{n(x>x*)}$ = initial anion adsorption deduced from the *M* vs. (θ/ρ) plot in the region *x* > *x; $M_{n(x>x*)}$ = initial anion content.**
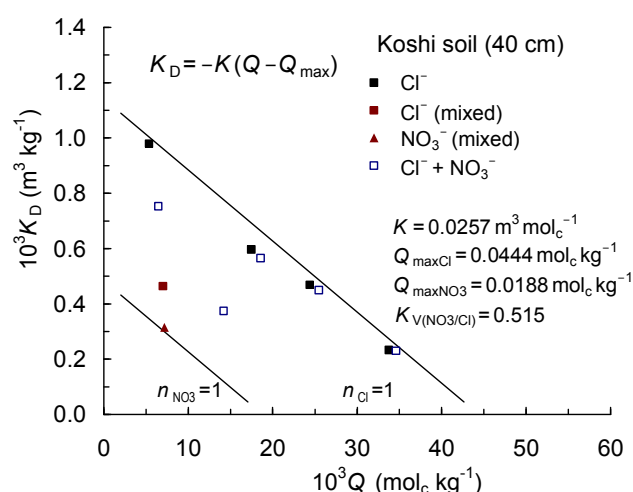
Figure 4. A plot of distribution coefficient, K_D, againt anion adsorption, *Q*, in Koshi soil. Red symbols represent anion adsorption in the column premixed with CaCl$_2$–Ca(NO$_3$)$_2$ composite solution. Other data are from the columns premixed with CaCl$_2$ solution at different concentrations. K_v = NO$_3^-$/Cl$^-$ exchange selectivity coefficient.

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

Ahmad R, Katou H, Kookana RS (2005) Measuring sorption of hydrophilic organic compounds in soils by an unsaturated transient flow method. *Journal of Environmental Quality* **34,** 1045–1054.

Dahlgren RA, Saigusa M, Ugolini FC (2004) The nature, properties and management of volcanic soils. *Advances in Agronomy* **82,** 113–182.

Katou H (2004) Determining competitive nitrate and chloride adsorption in an Andisol by the unsaturated transient flow method. *Soil Science and Plant Nutrition* **50,** 119–127.

Katou H, Clothier BE, Green SR (1996) Anion transport involving competitive adsorption during transient water flow in an Andisol. *Soil Science Society of America Journal* **60,** 1368–1375.

Katou H, Uchimura K, Clothier BE (2001) An unsaturated transient flow method for determining solute adsorption by variable-charge soils. *Soil Science Society of America Journal* **65,** 283–290.

Magesan GN, Vogeler I, Clothier BE, Green SR, Lee R (2003) Solute movement through an allopnanic soil. *Journal of Environmental Quality* **32,** 2325–2333.

Miki N, Matsumoto T, Katou H (2009) Relative velocity of nitrate transport as affected by adsorption in different Andosols in Hokkaido. *Japanese Journal of Soil Science and Plant Nutrition* **80,** 365–378. (in Japanese with English summary)

Ochsner TE, Stephens BM, Koskinen WC, Kookana RS (2006) Sorption of a hydrophilic pesticide: Effects of soil water content. *Soil Science Society of America Journal* **70,** 1991–1997.

Smiles DE, Philip JR (1978) Solute transport during absorption of water by soil: Laboratory studies and their practical implications. *Soil Science Society of America Journal* **42,** 537–544.

Wada K, Okamura Y (1980) Electric charge characteristics of Ando A$_1$ and buried A$_1$ horizon soils. *Journal of Soil Science* **31,** 307–314.