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Adsorption of nitrate as a groundwater pollutant by soil particles

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ABSTRACT

This study discusses nitrogen adsorption in several soil samples of the Kanto loam collected from two locations in the Kanto plain. Their chemical properties were assessed on each of the soil samples as well as on pure allophane clay by instrumental analysis using batch and soil column tests.

Nitrogen–nitrate adsorption by soil samples was determined by a 10-hour batch test using a nitric acid solution of 0.14 mmol. A saturation column test was conducted to obtain a breakthrough curve and calculate the coefficients of dispersion and retardation. The extent of nitrate adsorption in soil samples was confirmed by percolation with 0.14 mmol nitric acid through columns packed with the soil sample and silicate sand.

In the batch test, it was found that the amount of nitrate adsorption was greater in allophane-rich volcanic ash soils with the amount of nitrate adsorption increasing under conditions of low pH. The breakthrough curve determined by the column test showed that the coefficient of retardation increased in allophane-rich soils.

Adsorption of nitrates by Kanto loam soils was thus found to be dependent upon the content of allophane and amorphous material in the soil. Since the positive charge of allophane has the potential to reduce the nitrate content in groundwater, it can be effectively applied to reduce nitrate contamination in groundwater.

INTRODUCTION

Nitrogen-based fertilisers used in agriculture are the main sources of nitrate to the groundwater and the soil in many areas of the world. The potential for accumulated nitrates to leach out of the soil and contaminate groundwater has resulted in an increased awareness among the public regarding the health risks posed by nitrate in groundwater supplies used for drinking purposes. The World Health Organisation (WHO) recommends a standard for nitrate concentration levels of less than 50 mg/l (nitrogen–nitrate of less than 10 mg/l) in the groundwater for drinking purposes. As reviewed by Follett et al. (1989), methemoglobinemia (blue baby syndrome) is suspected of being associated with drinking water contaminated by nitrate when it is used to prepare infant feed, and chronic nitrate exposure from drinking water is suspected of being responsible for stomach cancer. In European countries, nitrogen concentration in drinking water is a particularly severe problem.

The Japanese Ministry of Environment investigated the groundwater quality across the country in 2004. A groundwater quality survey revealed several areas with nitrogen–nitrate concentrations exceeding 10 mg/l. The survey showed that 421 of the 5,129 (6.5%) wells sampled exceeded nitrogen–nitrate environmental quality standards. High nitrogen–nitrate concentrations were obtained in the diluvial terrace areas of the Kanto plain in Japan.

The surface layer of the terrace is a volcanic ash soil consisting of the Kanto loam with allophane-rich clay. Generally, these soil types have a high cation exchange capacity. The negative charge of soil particles promotes leaching of nitrate through the soil profile. However, the allophane in clay shows the positive charge under the conditions of low pH. The sorption of anions is a characteristic feature of allophane-rich volcanic ash soils. This study investigated the adsorption of nitrogen–nitrate in several soil samples of the Kanto loam in Japan.

MATERIALS AND ANALYTICAL METHODS

Allophane

Mineral allophane is a naturally occurring, amorphous, hydrous alumino-silicate. This mineral is the most common constituent of clay soils derived from volcanic ash over a wide range of climatic conditions. As reviewed by Wada (1978), it has been estimated that volcanic ejecta once covered approximately 20% of the total land surface area of Japan. Consequently, approximately 60% of the total upland soil volume is derived from such volcanic materials. A characteristic feature of allophane is the cationic condition that the mineral assumes due to an increased affinity for H^+ by Al-OH groups on its surface under conditions of low pH (Henmi et al. 2001). The positive charge is also dependent upon the chemical composition of the allophane, specifically on the SiO_2/Al_2O_3 ratio, and is more pronounced when the ratio is closer to 1.0 than 2.0 (Henmi 1988).

Soil samples

The three soil samples (U-1.2, U-2.0, K-2.2) were obtained from the Ibaraki (Site 1) and Saitama prefectures (Site 2) of Japan in the Kanto plain (Fig. 1). A control sample consisting of pure allophane clay was also used. Generally, these soils are found in the diluvial terraces consisting of loam. However, at Site 1, clay deposits were found below the loam at a depth of 190–210 cm. Chemical constituents and properties of the samples were as follows:

(a) X-ray diffraction pattern

X-ray diffraction (XRD) patterns of the soil samples are shown in Fig. 2. The XRD patterns of both U-1.2 and U-2.0 were characterised as having bands at 14.7, 9.7, 7.0, 4.2, 3.5, 3.34 Å, indicating that these samples contained chlorite, goethite, and quartz (Oinuma 1980). A broad band appeared at 4.7–3.0 Å in the XRD patterns of U-1.2, K-2.2, and allophane soil, as well as a broad peak that was similar to the XRD pattern of mineral allophane (Wada 1978).

(b) Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric (TG) curves are shown in Fig. 3. Samples U-1.2 and K-2.2 exhibited a large endothermic peak between 100 and 300 °C, and a short exothermic peak between 800 and 1000 °C. As reviewed by Mackenzie (1970), these peaks on the DTA curve are considered to be features common to mineral allophane. However, U-2.0 had an endothermic peak at 500 °C. The DTA curve obtained for U-2.0 indicated the hydration of iron oxides (Oinuma 1997). The TG curves of all samples exhibited continuous water loss with increasing temperature, implying that these samples contained mineral allophane.

(c) Chemical composition of soil samples

The chemical composition of soil samples assayed using fluorescent X-ray spectrometry is shown in Table 1. Findings indicated that U-1.2, U-2.0, and K-2.2 all contained more than 20% of Fe_2O_3. The peak on the XRD pattern of U-2.0 shows the existence of goethite. On the DTA curve, U-2.0 was observed to contain hydrated iron oxide. Taken together these findings indicated that the chemical properties of U-2.0 were different from those of the other soil samples. The SiO_2/Al_2O_3 ratios in U-1.2, K-2.2, and allophane soil were all less than 2.00.

(d) Quantitative determination of mineral allophane

The content (wt %) of allophane in soil samples is shown in Table 2. Mineral allophane was quantified by alternate dissolution of soil samples in HCl and NaCl solutions (Kitagawa 1977). Mineral allophane content was 58.9% for U-1.2, 13.7% for U-2.0, 77.3% for K-2.2, and 94.1% for allophane soil.

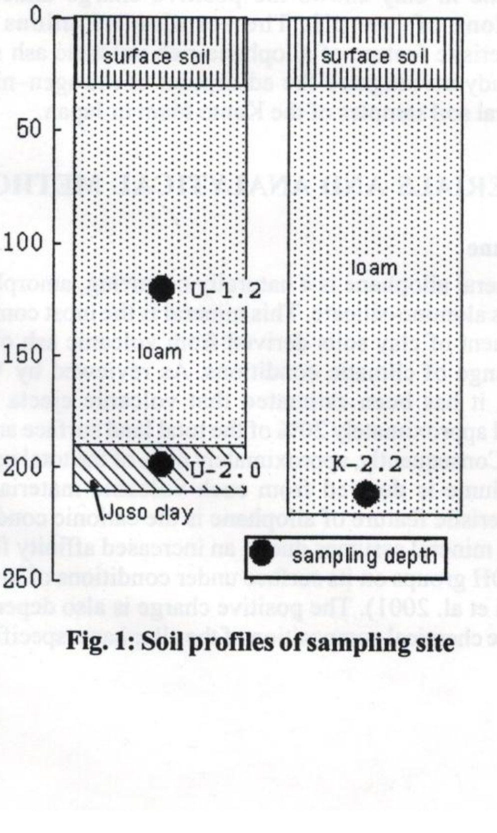

Fig. 1: Soil profiles of sampling site

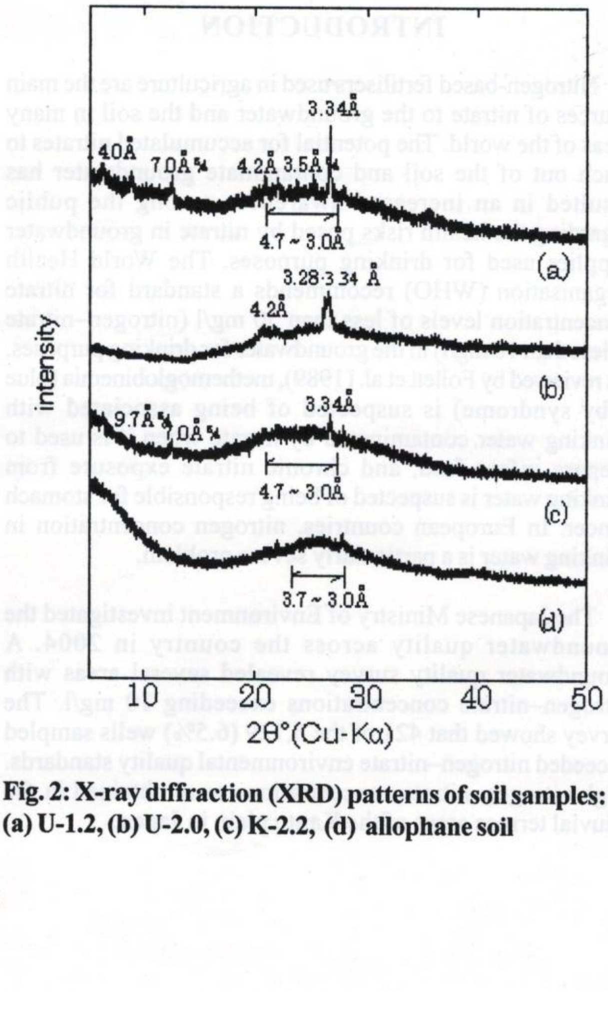

Fig. 2: X-ray diffraction (XRD) patterns of soil samples: (a) U-1.2, (b) U-2.0, (c) K-2.2, (d) allophane soil

Table 1: Chemical composition of soil samples

Attribute	U-1.2	U-2.0	K-2.2	Allophane soil
SiO_2	37.63	38.45	40.00	50.37
Al_2O_3	36.08	23.37	33.56	43.52
Fe_2O_3	25.3	33.15	20.95	3.32
TiO_2	2.29	2.25	2.41	0.51
MgO	0.66	0.00	0.36	0.21
MnO	0.43	0.44	0.42	0.00
CaO	0.41	0.19	0.31	0.82
K_2O	0.99	0.36	0.72	0.41
P_2O_3	0.12	1.30	0.46	0.00
Total (wt %)	103.91	99.51	99.19	99.16
SiO_2/Al_2O_3 ratio	1.04	1.65	1.19	1.16

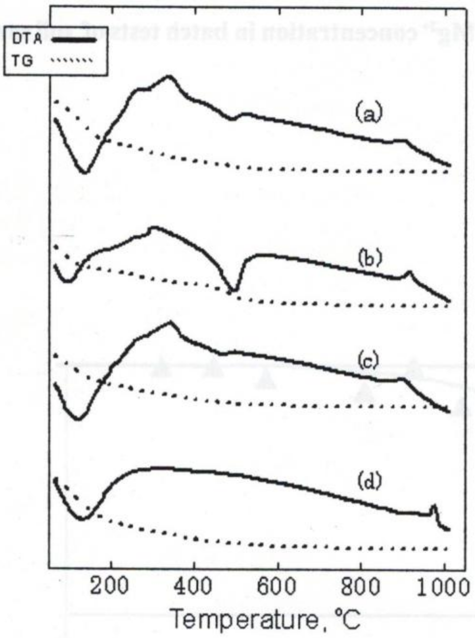

Fig. 3: Thermal analysis: (a) U-1.2, (b) U-2.0, (c) K-2.2, (d) allophane soil

Table 2: Mineral allophane content (wt%) in soil samples

U-1.2	U-2.0	K-2.2	Allophane soil
59.80%	13.70%	77.30%	94.10%

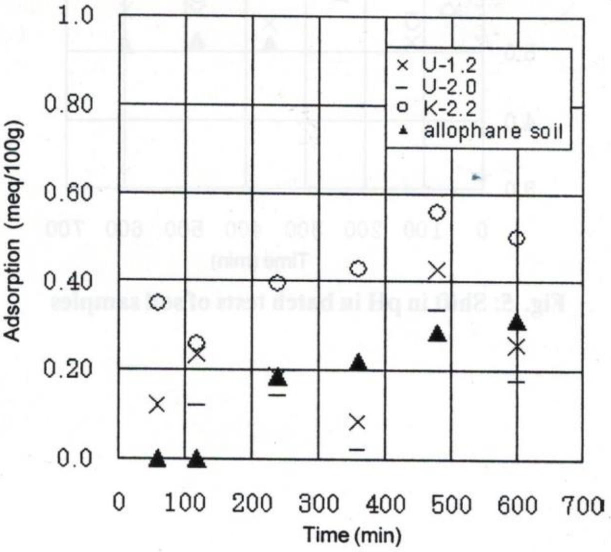

Fig. 4: N–NO_3^- adsorption in batch tests of soil samples

EXPERIMENT

Batch tests

Nitrogen–nitrate adsorption by soil samples was determined using a 10-hour batch test with an HNO_3 solution of 0.14 mmol/l. In the batch test, 5 g of oven-dried soil was added to 100 ml of 0.14 mmol/l of HNO_3 solution. The test was performed as follows: 1) After washing with distilled water, the soil samples were passed though a 2-µm screen sieve before being oven dried at 60 °C; 2) The soil samples were then saturated with HNO_3 solution and shaken for 1 hour; 3) After being allowed to settle for 1 hour, nitrogen–nitrate, cations and pH concentrations in the solution were measured every 2 hours over a 10-hour period; and 4) Nitrogen–nitrate, Mg^{2+} and Ca^{2+} ion concentrations of the supernatant were determined by ion-chromatography and pH using a pH analyser.

The column test

The column saturation test was conducted to obtain a breakthrough curve and to calculate the coefficients of dispersion and retardation. For this purpose an acrylic column (length = 40 cm, diameter = 5 cm) was used. Flow control was affected by the constant hydraulic gradient and flow percolation through the column was maintained at 3.0 ml/min. To the bottom of the soil column was set a filter of 2 cm thickness connected to an intake tube. The extent of nitrate adsorption in soil samples was confirmed by percolation with 0.14 mmol nitric acid through columns packed with 25 g of the soil sample and 2500 g of silicate sand. The breakthrough curve was used to determine the coefficients of retardation and dispersion.

RESULTS AND DISCUSSION

Batch tests

The adsorption of nitrogen–nitrate by samples is shown in Fig. 4. The amount of nitrogen–nitrate adsorbed by K-2.2 and allophane was greater than the amount adsorbed by

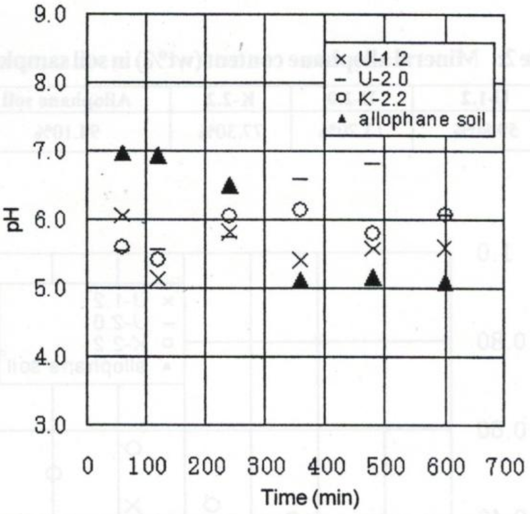

Fig. 5: Shift in pH in batch tests of soil samples

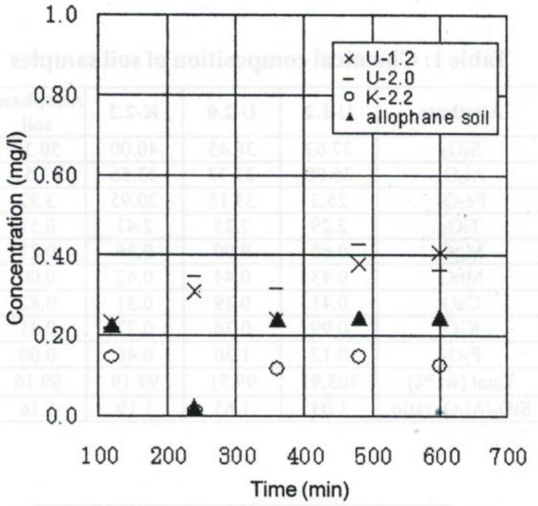

Fig. 6: Mg^{2+} concentration in batch tests of soil samples

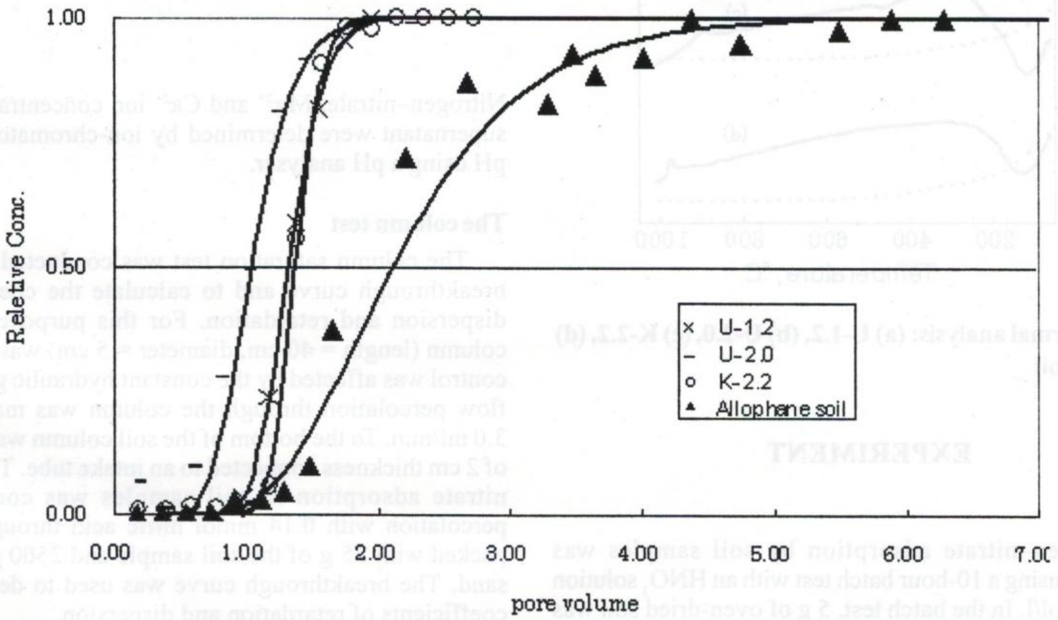

Fig. 7: Breakthrough curves describing percolation of 0.14 mmol nitric acid solution

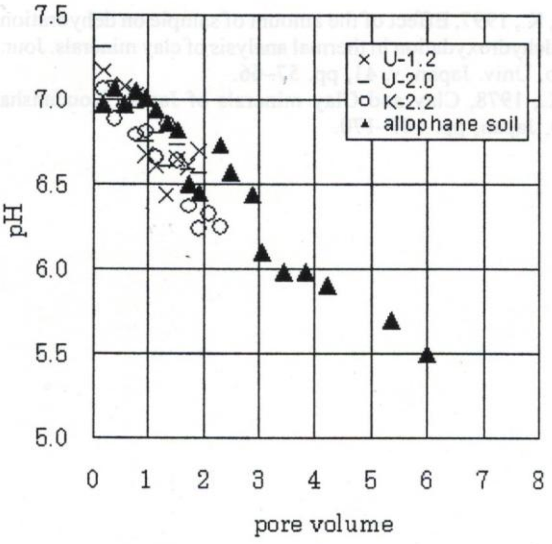

Fig. 8: Shift in pH within the column

other samples over 600 minutes. Conversely, nitrogen–nitrate adsorption by U-1.2 and U-2.0 was markedly less.

A shift in the pH with reaction time is shown in Fig. 5. A 0.14 mmol/l HNO_3 solution had a pH value of 4.2, but the pH in the K-2.2 and allophane soil samples of the batch ranged between 5 and 7. Allophane had a positive charge under low pH. Consequently, it appears that the adsorption of nitrogen–nitrate was accelerated by the positive charge in K-2.2 containing mineral allophane.

The concentration of Mg^{2+} is shown in Fig. 6. The concentration of Mg^{2+} was observed to increase in the batch solutions of U-1.2 and U-2.0 due to the dissolution of minerals other than allophane in these samples. Fig. 5 shows the maintenance of pH in U-1.2 and U-2.0 at a value of approximately 6 for the duration the reaction time. This was due to the buffering effect associated with the dissolution of Mg^{2+}, which prevented the soil solution from attaining a low pH.

The column test

The breakthrough curve obtained from the column test with HNO_3 solution is shown in Fig. 7. The breakthrough curves of U-1.2, U-2.0, and K-2.2 showed that nitrogen–nitrate percolated rapidly through the soil column. The breakthrough curve obtained for the allophane soil indicated that nitrogen–nitrate exhibited the slowest movement in this sample. It is therefore proposed that the adsorption of nitrogen–nitrate in the Kanto loam can be ascribed to the presence of mineral allophane.

The shifts in pH observed in the column tests are shown in Fig. 8. A 0.14 mmol/l HNO_3 solution had a pH value of 4.2.

Table 3: Coefficients obtained from the breakthrough curve

Soil sample	Dispersion coefficient (cm^2/min)	Retardation coefficient	Seepage velocity (cm/min)
U-1.2	0.12	1.31	0.20
U-2.0	0.33	1.01	0.20
K-2.2	0.10	1.36	0.20
Allophane soil	0.65	2.00	0.20

However, the pH of the column containing U-1.2 and K-2.2 ranged from 6 to 7, with minerals other than allophane influencing the pH variation in the column. The pH in the column containing the allophane soil declined to 5.5. This decline in the pH of the control sample was associated with the increased adsorption of nitrogen–nitrate.

Several factors exhibited by the breakthrough curve are shown in Table 3. The retardation factor was calculated as 1.31 for U-1.2, 1.01 for U-2.0, 1.36 for K-2.2, and 2.00 for the allophane soil. The mineral allophane content in samples increased in the order: U-2.0 (13.7%) < U-1.2 (58.9%) < K-2.2 (77.3%) < the allophane soil (94.1%). The coefficient of retardation correspondingly increased in proportion to the content of mineral allophane in each of the soil samples.

CONCLUSIONS

The adsorption of nitrogen–nitrate in the Kanto loam revealed the following: 1) a low pH resulted in the development of a positively charged soil profile; 2) adsorption of nitrogen–nitrate was observed to increase in proportion to the mineral allophane content in the Kanto loam; and 3) minerals other than allophane had a buffering effect on the soil solution and prevented the occurrence of a low pH in the soil samples.

Adsorption of nitrates by the Kanto loam soils was thus attributed to the mineral allophane content of the soil. Given that allophane assumes a positive charge under conditions of low pH, the application of this mineral to areas polluted by nitrates has the potential for alleviating nitrate contamination in groundwater.

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