Factors influencing nitrate retention in 3 Andisol profiles in Kyushu, Japan

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Abstract
We measured nitrate retention in 43 soil samples from 3 uncultivated Andisol profiles in Kyushu, Japan. In this study, nitrate retention—also termed nitrate holding capacity (NHC)—was calculated from the recovery ratio for nitrate that had been added to soils as part of a 5 mmol/L potassium nitrate solution. We then conducted a multiple regression analysis on the relationship between NHC and 3 factors that affect the soil's positive charge: total carbon, pH (H_2O), and Al_o. The multiple correlation coefficient between these 3 factors and NHC was 0.918** ($n = 43$). The partial regression coefficient yielded the following equation for NHC estimation: NHC ($cmol_c$/kg) = -0.001400 × total carbon (g/kg) - 0.124400 × pH (H_2O) + 0.004735 × Al_o (g/kg) + 0.802387. The appreciable consistency between the measured and estimated NHC suggests the possibility of broad-based estimation of nitrate retention in these soils and the development of nitrate retention characteristic maps from the existing soil analytical data and soil maps.

Key Words
NHC (nitrate holding capacity), multiple regression analysis, total carbon, pH (H_2O), Al_o

Introduction
Kyushu is one of the 4 major islands of Japan and is located in the southwest of the Japanese archipelago. Kyushu has several active volcanoes such as Aso, Unzen, Kuju, Kirishima, and Sakurajima, and Andisols are widely spread over central and southern Kyushu; their distribution area accounts for 66.9% of upland field soils in Kyushu (Soil Conservation Project 1991). Major agricultural activities in Kyushu include the cultivation of vegetables, tea, and intensive livestock farming, in which a large amount of nitrate is added to soils as chemical fertilizers and manure. As a result, there is a high risk of groundwater pollution by nitrate in these areas.

Nitrate retention due to positive charge in soil materials affects the movement of nitrate in soils. The positive charge in soil materials is pH-dependent variable. It occurs especially in Oxisols, Ultisols, Alfisols, Spodosols, and Andisols (Qafoku *et al.* 2004). In these soils, the positive charge retains the anion and retards its downward leaching (Wong *et al.* 1987; Ishiguro *et al.* 1992; Katou *et al.* 1996; Feder and Findeling 2007; Maeda *et al.* 2008). Therefore, it is important for reducing the environmental load due to nitrate leaching to determine and utilize the positive charge characteristics of Andisols in Kyushu. Since there is little data on nitrate retention of Andisols in Kyushu, we investigated its nitrate retention ability.

Nitrate retention in Andisols is affected by several factors. The positive charge in Andisols is mainly due to the protonization of Al-OH in allophane and imogolite; therefore, Si_o or Al_o that reflects the allophane and imogolite content is positively correlated with nitrate retention (Tani *et al.* 2004; Maeda *et al.* 2008). The abundance of carbon has been reported as a negative influencing factor on nitrate retention (Nanzyo *et al.* 1993; Perrott 1978; Tani *et al.* 2004). In addition, nitrate retention is influenced by soil pH because the positive charge of soils is pH-dependent.

If we can obtain clear relationships between these factors and nitrate retention in Kyushu Andisols, it is possible to derive an equation for the estimation of nitrate retention based on these factors. This equation can be applied to the existing analytical data for the broad-based estimation of nitrate retention in various Andisols and can help in the development of nitrate retention characteristic maps based on existing soil maps. This paper reports the measured nitrate retention for 43 samples from 3 Andisol profiles in Kyushu and the relationships between nitrate retention and above-mentioned factors, i.e., total carbon, pH (H_2O), and Al_o.

Materials and methods
In this study, we analyzed samples of uncultivated soils to eliminate the effect of external factors such as fertilizer application. Samples were collected from 3 Andisol profiles in Kyushu (Figure 1). The Takaono profile is located on a gentle mountain foot slope of Aso-somma in Ozu Town, Kumamoto Prefecture. Its geographic coordinates are 32º53′29″N and 130º54′29″E, and its elevation is 250 m above sea level. This soil is classified into a Hydric Pachic Melanudand, with a depth of 420 cm, and it has 15 horizons. The craters of

the Aso volcano, located 16 km eastward from this profile, were the main source of the parent material, tephra, for this soil. The Kunimi profile is located on a gentle mountain side slope in Unzen City, Nagasaki Prefecture, and its geographic coordinates are 32º48′23″N and 130º17′14″E with an elevation of 380 m above sea level. This soil is a Hydric Melanudand with a depth of 260 cm, and it has 8 horizons. The Unzen volcano, located 5 km southward from this profile, was the main source of tephra for this profile. The Hanamure profiles is located on a gentle mountain foot slope in Kokonoe Town, Oita Prefecture, and its geographic coordinates are 33º8′37″N and 131º16′5″E and it is situated 900 m above sea level. The soil here is a Hydric Melanudand, with a depth of 483 cm, and it has 22 horizons. The craters of Kuju volcano, located 5 to 7 km southward of this profile, were the main source of tephra for this profile. The Aso volcano, located 33 km southward, also provided tephra for the Hanamure profile.

No tephra layer was observed in Takaono and Kunimi profiles, whereas the Hanamure profile contained 4 layers of slightly weathered to weathered tephra. Forty-three samples, i.e., all the horizons in these profiles except for 2 very thin layers in the Hanamure profile, were collected and analyzed.

Total carbon was determined through a dry combustion method using ELEMENTAR Analysensysteme Vario EL. The pH (H_2O) value was determined by 1:2.5 extraction using a glass electrode. Al_o was measured by Blakemore *et al.*'s method (1981) using ICP-AES (Seiko Instruments SPS4000).

The nitrate retention of the soils was determined by Kubotera and Wada's method (2008). In this method, 7.5 mL of 5 mmol/L potassium nitrate solution was added to 5 g of air-dried fine earth samples in centrifuge tubes; the mixture was shaken for 30 min and centrifuged. The nitrate ion concentration of the supernatant was then measured by colorimetric analysis using Bran-Luebbe Autoanalyzer (*a* [mmol/L]). The concentration of water-soluble nitrate ions in the samples was also determined by the same procedure (*b* [mmol/L]). The sum of the concentrations of the used nitrate solution and water-soluble nitrate ions in the sample (*5+b* [mmol/L]) was considered as the concentration of the initial solution. The difference in nitrate ion concentrations between the initial solution and the supernatant after treatment (*5+b-a* [mmol/L]) was considered as the nitrate ion concentration retained by the soils. Since the samples were obtained from uncultivated soils, they contained little nitrate. Thus, the value of *b* for our samples was zero, except for the A horizons of each profile. Nitrate retention measured by this method is hereafter termed nitrate holding capacity (NHC).
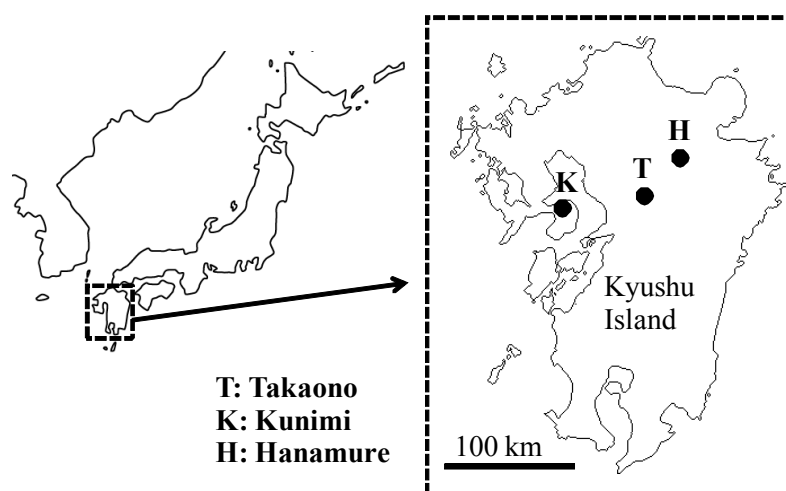

T: Takaono
K: Kunimi
H: Hanamure

Figure 1. Location of the profiles studied.

Results
NHC of the horizons and the effects of total carbon, pH (H_2O), and Al_o on NHC
The NHC, total carbon, pH (H_2O), and Al_o contents in the studied profiles are shown in Figure 2. The total carbon and pH (H_2O), which were expected to show negative relationships with NHC, are plotted inversely in the figure. In the Takaono profile, the NHC ranged from 0.100 to 0.481 $cmol_c$/kg. The NHC was smallest in the A horizon (0-24 cm), and it showed a tendency to gradually increase down the profile, but with fluctuations. The charts for total carbon and Al_o show a remarkable resemblance to that of the NHC, indicating that the NHC has a strong negative relationship with total carbon and a positive relationship with Al_o contents of the Takaono profiles. The pH (H_2O) had a small variance in this profile and did not show a relationship with the NHC.

In the Kunimi profile, the NHC ranged from 0.110 to 0.356 $cmol_c$/kg. It was smallest in the A horizon (0-35 cm) and increased down the profile in a manner similar to that found in the Takaono profile. The total carbon content showed a fluctuation similar to that of the NHC. Contrary to our expectations, a weak positive

relationship was demonstrated between pH (H_2O) and NHC. Al_o was generally small in this profile and did not show a relationship with the NHC.

In the Hanamure profile, NHC ranged from 0.0971 to 0.368 $cmol_c$/kg. It was less in the A to 3A1 horizons (0-80 cm), but increased up to 0.199 $cmol_c$/kg or more in the 3A2 to 6Bw horizons (80-265 cm); it decreased again in the deeper horizons. The fluctuation of the total carbon content was partially correlated to NHC; however, there was not much similarity between the 2 parameters. No relationship was found between pH (H_2O) and NHC. The charts of NHC and Al_o content showed a remarkable resemblance, indicating a strong positive relationship.
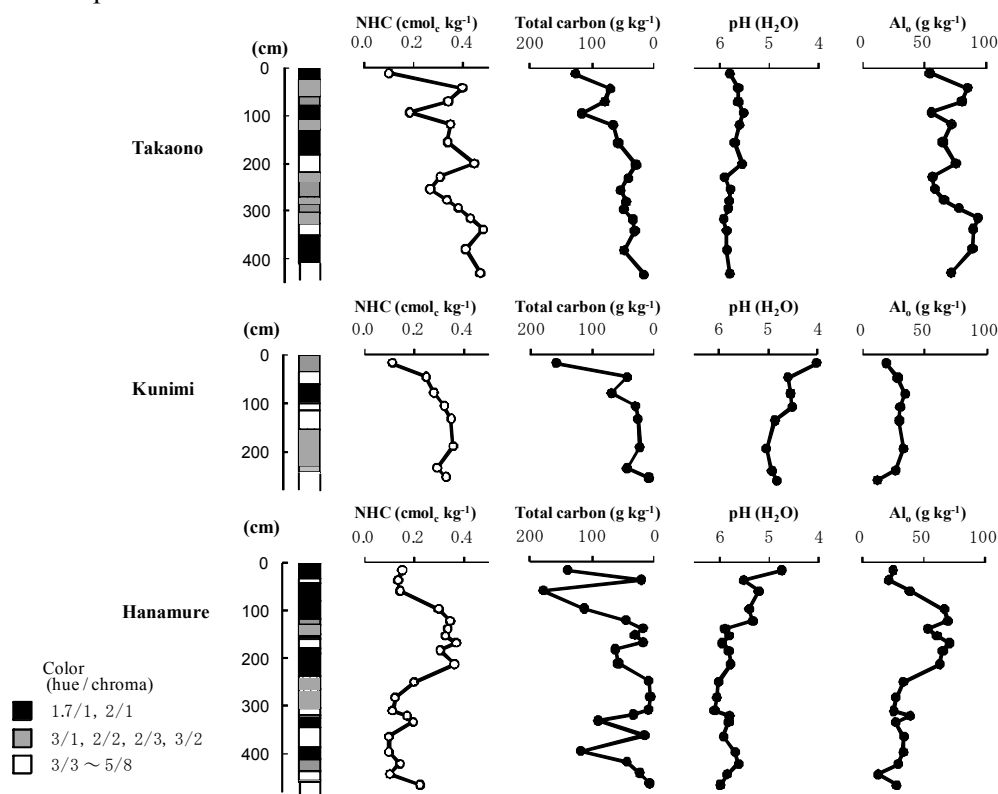

Figure 2. NHC and related properties of each horizon in the studied profiles.

Multiple regression analysis of the relationships between NHC and total carbon, pH (H_2O), and Al_o
Coefficients obtained by multiple regression analysis on all 43 samples in the 3 profiles are shown in Table 1. The partial correlation coefficients for total carbon, pH (H_2O), and Al_o were -0.772**, -0.751**, and 0.911**, respectively; all explanatory variables showed significant correlations with NHC at the 1% level of significance. The partial regression coefficients of total carbon, pH (H_2O), and Al_o were -0.001400, -0.124400, and 0.004735, respectively, and the intercept was 0.802387. The estimated NHC obtained using these partial regression coefficients showed a significant correlation with the measured NHC and had a multiple correlation coefficient of 0.918** (contribution ratio = 0.843; n = 43), as shown in Figure 3. The residual error, i.e., the difference between the measured and the estimated NHC, was relatively small in samples with large NHC. For samples with a measured NHC of 0.2 $cmol_c$/kg or more (n = 28), the residual error ranged between 0.001 and 0.081 $cmol_c$/kg, and the average was 0.027 $cmol_c$/kg. In terms of percentage of the measured NHC, the residual error ranged between 0.3% and 24.8%, with an average of 8.9% in these samples. For the samples where the NHC was smaller than 0.2 $cmol_c$/kg (n = 15), the minimum, maximum, and average residual errors were 0.001, 0.116, and 0.046 $cmol_c$/kg, respectively. The percentage error of the measured NHC ranged between 0.5% and 112.2%, with an average error of 35.9%. As shown above, the residual error was relatively large in samples with small NHC, most of which were from the Hanamure profile.

Table 1. Coefficients of multiple linear regressions. The response variable is NHC and the explanatory variables are total carbon, pH (H_2O), and Al_o. (n = 43. ** indicates the significance at 1% level.)

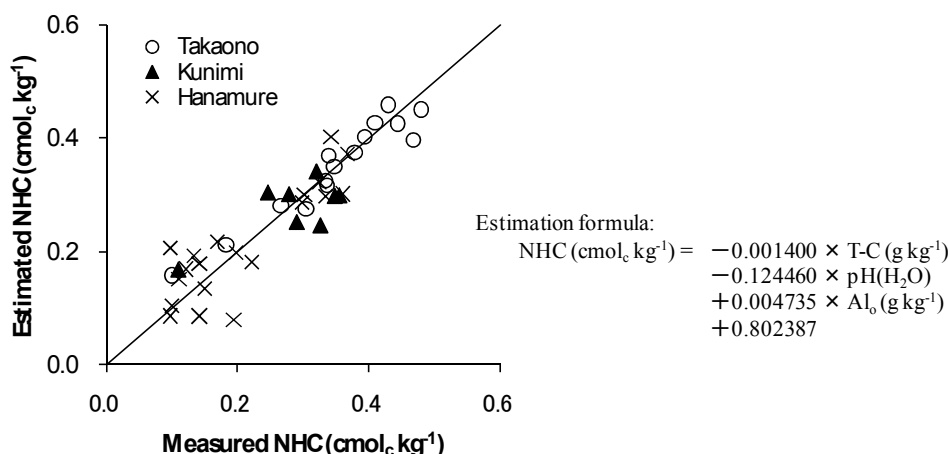| Partial correlation coefficient			Multiple correlation coefficient	Partial regression coefficient			
Total carbon	pH (H_2O)	Al_o		Total carbon	pH (H_2O)	Al_o	Intercept
-0.772**	-0.751**	0.908**	0.918**	-0.001400	-0.124460	0.004735	0.802387

Figure 3. Estimated NHC versus measured NHC values of all samples. Total carbon, pH (H₂O), and Al₀ were used as explanatory variables. Line indicates a 1:1 relationship.

Conclusion

We have shown that total carbon, pH (H_2O), and Al_o are closely correlated with the NHC of uncultivated soils from the Andisol profiles in Kyushu. The NHC can be estimated from these 3 explanatory variables. Our results suggest the possibility of deriving an equation for the broad-based estimation of the nitrate retention of soils and the development of nitrate retention characteristic maps based on existing soil analytical data and soil maps. Further studies are required for dealing with relevant issues such as improving the accuracy of NHC estimation in soils containing slightly weathered to weathered tephra layers like those found in the Hanamure profile, estimating the retardation of nitrate leaching using the NHC, and determining the influence of soil management activities in cultivated fields on the NHC.

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