Aluminum Dynamics in Nonallophanic Andosols from Northeastern Japan

著者	TAKAHASHI Tadashi, NANZYO Masami
journal or publication title	Journal of Integrated Field Science
volume	2
page range	77-82
year	2005-03
URL	http://hdl.handle.net/10097/30944

JIFS, 2 : 77 - 82 (2005)

Special review

Aluminum Dynamics in Nonallophanic Andosols from Northeastern Japan

Tadashi TAKAHASHI and Masami NANZYO

Graduate School of Agricultural Science, Tohoku University,
1-1, Tsutsumidori Amamiya-mach, Aoba-ku, Sendai, 981-8555 Japan

Key words : aluminum-humus complexes, aluminum release rate, aluminum solubility, aluminum toxicity, exchangeable aluminum, liming.

Abstract

We studied Al dynamics in nonallophanic Andosols from northeastern Japan by determination of Al solubility and Al release rates, selective dissolution analyses of active Al fractions, and examination of liming effect on the active Al. Aluminum solubility of the nonallophanic Andosols was lower than that of gibbsite in the lower pH range and showed oversaturation in the higher pH range, indicating that the Al solubility was controlled by Al-humus complexes. There was a close relationship between Al saturation (KCl-extractable Al / effective CEC) and the amount of pyrophosphate extractable Al, indicating that exchangeable Al is equilibrated with organically complexed Al. Liming ($CaCO_3$ treatment) largely reduced the amount of organically complexed Al (pyrophosphate- and $CuCl_2$-extractable Al), confirming that a portion of Al-humus complexes are labile.

Introduction

The processes regulating aluminum solubility and release/retention kinetics play a major role in determining the productivity of acid soils. Dissolved Al in soil solutions has been recognized to be a limiting factor for plant root growth. The exchangeable Al fraction, such as 1 M KCl-extractable Al, has also been found to be toxic to plant roots due to its presumed rapid release kinetics to the soil solution (Saigusa et al., 1980). Therefore, information on the factors controlling the concentrations of aqueous Al is critical for elucidating the potential toxicity of Al in soils.

Andosols are divided into two major groups on the basis of their colloidal compositions : "allophanic" Andosols dominated by allophanic clay materials and "nonallophanic" Andosols dominated by Al - humus complexes and 2 : 1 type aluminosilicates. Both groups of Andosols show unique properties characteristic of volcanic ash derived soils, such as high reactivity with phosphate and fluoride ions and a low bulk density. However, there are large differences in soil acidity and Al toxicity between the two groups of Andosols. Allophanic Andosols are moderate to slightly acid even when the base saturation is very low and rarely contain toxic levels of KCl-extractable Al. In contrast, nonallophanic Andosols are strongly acid when the base saturation is low and possess a high KCl-extractable Al (Nanzyo et al. 1993). The origin and status of the toxic Al are not yet clear although the exchangeable Al is assumed to be adsorbed mainly in permanent negative charges of 2 : 1 type minerals.

To clarify Al dynamics in nonallophanic Andosols, we analyzed Al solubility of A horizons of soils from northeastern Japan. Then, we investigated the relationship between 1 M KCl-extractable Al and organically complexed Al that is a major Al pool in nonallophanic Andosols. Finally, we examined the effects of liming ($CaCO_3$ treatment) on Al-humus complexes.

Materials and methods

Soil samples. Soil samples of nonallophanic Andosols were collected from northeastern Japan. Sampling points were distributed in Aomori, Akita, Iwate and Miyagi Prefectures. As comparisons, we used some allophanic Andosols and a Bhs horizon of a Spodosol.

Determinations of active Al pools. Selective dissolution techniques were used to remove operationally defined solid-phase pools of Al : 1) acid ammonium oxalate at pH 3 in the dark (Al_o) (McKeague 1976); 2) sodium pyrophosphate at pH 10 (Al_p) (McKeague 1967); 3) 0.5 M $CuCl_2$ (Al_{Cu}) (Hargrove and Thomas 1981); and 4) 1 M KCl

(Al_{KCl}) (Blakemore et al. 1981).

Aluminum release rates and Al solubility of soils. Rates of Al release from non-treated soil samples and residues obtained from the selective dissolution extraction were determined using a stirred, flow-through reaction vessel with an extracting solution which consists of a 10^{-3} M sodium acetate / acetic acid solution adjusted to pH 3.5. (Takahashi et al. 1995). The reacted solution was continuously injected into an auto-analyzer equipped with the pyrocatechol violet method for determination of monomeric Al.

An equilibrium study was conducted to determine the solubility of Al as a function of pH. A 0.01 M $CaCl_2$ solution was added to soil samples and HCl or NaOH was added to provide a pH range from 3 to 5. After 30 d incubation at 25°C, monomeric Al concentrations in the solution were determined and Al^{3+} activity was estimated.

Comparison between Al saturation and pyrophosphate-extractable Al. Extractable Al (1 M KCl and sodium pyrophosphate (Al_p)) was determined to characterize soil aluminum pools for 25 surface soil samples from Noshiro City, Akita Prefecture. The relationship between Al saturation (KCl-extractable Al / effective CEC) and Al_p was examined.

Liming and analyses of limed soils. Based on the lime requirement with respect to a pH of 6.5, the mixture of soil samples and $CaCO_3$ was incubated at field water capacity for 30 d. After air-drying, the limed and unlimed samples were used for determination of 1 M KCl-extractable Al, Al_p, and so on.

Results and discussion

Solid-phase pools of active Al for representative soil horizon samples (Takahashi et al. 1995).

Table 1 shows the properties of three representative soil horizons : a nonallophanic Andosol A horizon, an allophanic Andosol A horizon, and a Spodosol Bhs horizon. The nonallophanic A horizon (Noshiro) and the spodic Bhs horizon (Hubbard Brook) showed high Al_p/Al_o ratios (0.88 and 0.97, respectively) indicating that Al-humus complexes are dominant form of active Al. In contrast, the allophanic Andosol A horizon (Hiyamizu) showed a lower Al_p/Al_o ratio and a high content of Si_o (acid oxalate-extractable Si) indicating that allophanic materials dominate the active Al fraction.

The amount of 1 M KCl extractable Al, approximating easily exchangeable Al, is high for the nonallophanic A horizon and the spodic Bhs horizon (5.4 and 6.7 $cmol_c\ kg^{-1}$) , whereas the value for the allophanic A horizon was very low (0.4 $cmol_c\ kg^{-1}$).

Aluminum solubility of soils (Takahashi et al. 1995).

It is generally assumed that Al solubility of mineral soils is regulated by a solid $Al(OH)_3$ mineral phase (e.g. gibbsite). However, aqueous Al concentrations in humus-rich soil horizons are considered to be regulated also by humic substances. Although Andosols are included in mineral soils, they have a lot of organic matter especially in A horizons.

Results of Al release rates are shown in Fig. 1. Following the treatment with the pyrophosphate reagent, the Al release rates from the nonallophanic A horizon and the spodic Bhs horizon dropped to very low levels. In contrast, the Al release rates from the allophanic A horizon slightly decreased by the

Table 1. Some properties of the representative soil horizons.

	pH(H_2O)	Organic C $g\ kg^{-1}$	KCl-Al $cmol_c\ kg^{-1}$	Al_p $g\ kg^{-1}$	Al_o $g\ kg^{-1}$	Al_p/Al_o	Si_o $g\ kg^{-1}$
Noshiro (nonallophanic)	5.1	41.4	5.4	9.2	10.5	0.88	0.7
Hubbard rook (Spodosol Bhs)	4.7	53.7	6.7	6.5	6.7	0.97	0.4
Hiyamizu (allophanic)	5.4	67.7	0.4	8.3	30.2	0.27	10.9

pyrophosphate treatment. Following acid oxalate treatment, all soils showed virtually no Al release. Therefore, Al released from non-treated soil samples was attributed primarily to the Al-humus complexes for the nonallophanic A horizon and the spodic Bhs horizon. In contrast, Al released from the allophanic A horizon originated largely from allophanic materials.

Figure 2 and Table 2 show pH-pAl relations obtained by the equilibrium study. The dotted line in Fig. 2 indicates the solubility of synthetic gibbsite with a slope of 3.0 and log K^*_{so} of 8.1 for the reaction :

$$Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O.$$

The solubility of the allophanic A horizon (Hiyamizu) was nearly identical with that of synthetic gibbsite (Fig. 2 and Table 2). The saturation index (SI) of imogolite for the soil calculated from H^+, Al^{3+} and H_4SiO_4 activities showed +0.4 to +1.0, indicating slight oversaturation with respect to imogolite. Thus, the allophanic Andosol horizon appears to be in near equilibrium with both $Al(OH)_3$ and imogolite. On the other hand, the value of the slope of the solubility line for the nonallophanic A horizons and the spodic Bhs horizon ranged between 2.0-2.4 and was significantly lower than the value of 3.0 of the slope for $Al(OH)_3$ minerals (Table 2). The calculated log K^*_{so} value of these horizons ranged between 3.4-5.2 as compared with the value of 8.1 for the gibbsite (Table 2).

These results obtained from the Al release rates and the solubility experiments strongly suggest that in nonallophanic Andosol A horizons, the Al concentration is controlled by ion exchange reaction of H^+ and Al^{3+} ions on negatively charged sites of humus and that Al solubility is regulated by Al-humus complexes.

Relationship between exchangeable Al and organically complexed Al in A horizons (Takahashi et al. 2003). The above results indicate that organically complexed Al controls Al concentration in soil solution of nonallophanic Andosols. Exchangeable Al estimated by 1 M KCl extraction is thought to be easily released into soil solution. Therefore, exchangeable Al should be related to organically complexed Al. To confirm this

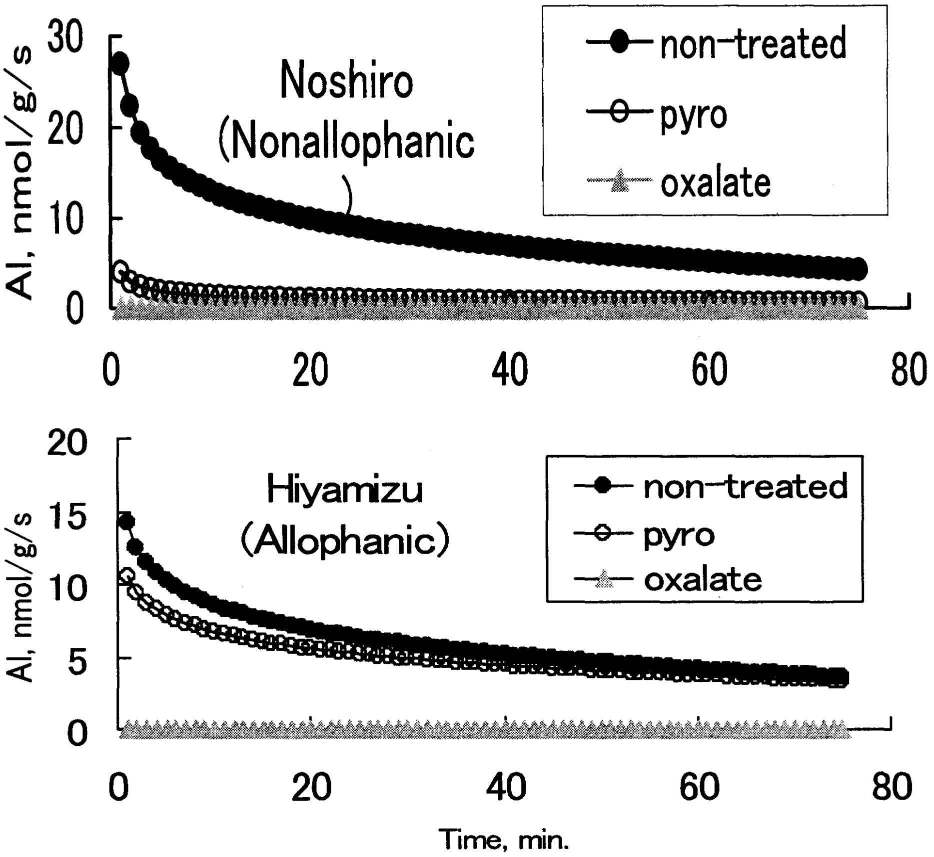

Fig. 1. Aluminum release rate for non-treated, pyrophosphate, and oxalate treated soil samples.

Table 2. Slopes and log K^*_{so} (intercept) values obtained from Al solubility data.

	Nonallophanic			Spodosol	Allophanic
	Mukaiyama	Noshiro	Wakami	Hubbard Brook	Hiyamizu
Slope	2.4	2.2	2.3	2.0	2.9
log K^*_{so}	5.2	4.5	4.8	3.4	7.5

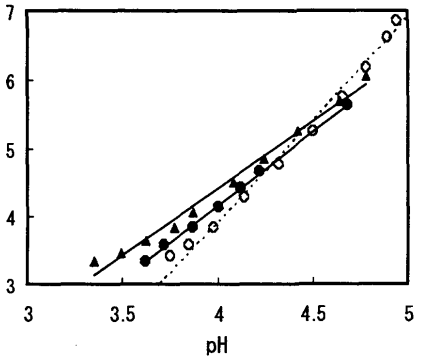

Fig. 2. Plot of equilibrium Al solubility versus pH. The solubility of synthetic gibbsite is indicated by the dotted line for comparison

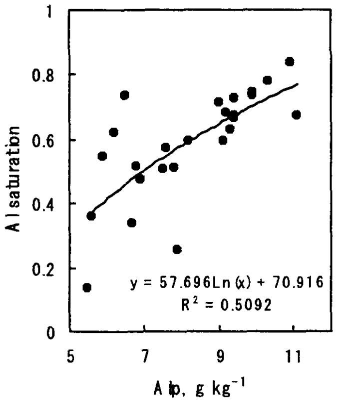

Fig. 3. Relationship between the concentration of pyrophosphate-extractable Al (Al_p) and Al saturation for A horizons of Noshiro soils.

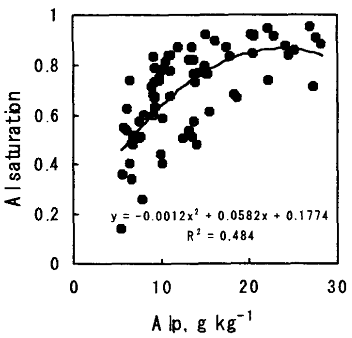

Fig. 4. Relationship between the concentration of pyrophosphate-extractable Al (Al_p) and Al saturation for A horizons of Noshiro soils and those of Shoji et al. (1985).

hypothesis, we investigated the relationship between Al saturation (exchangeable Al / effective CEC) and Al_p contents of nonallophanic Andosol A horizons from Noshiro City, Akita Prefecture.

As shown in Fig. 3, a significant, positive correlation was observed between Al saturation and Al_p content ($r = 0.714$, $p < 0.001$). Though there was a significant correlation between the two values, the soil pH must have affected the solubility and release/retention of Al. We analyzed a multiple regression of Al saturation on two variables, Al_p and $pH(H_2O)$. Because of the absence of a significant correlation between the Al_p concentration and $pH(H_2O)$ value ($r = -0.054$), these factors can be used as independent variables. The resultant regression is as follows :

$$\text{Al saturation} = 0.070 \times Al_p\ (\text{g kg}^{-1})^{***} - 0.426 \times pH(H_2O)^{***} + 2.277$$

$R = 0.895$, ***Significant at 0.1% level.

Eighty percent of Al saturation can be explained using the regression equation.

Although a significant positive correlation was observed between Al saturation and the Al_p concentration in the soils from Noshiro city, the

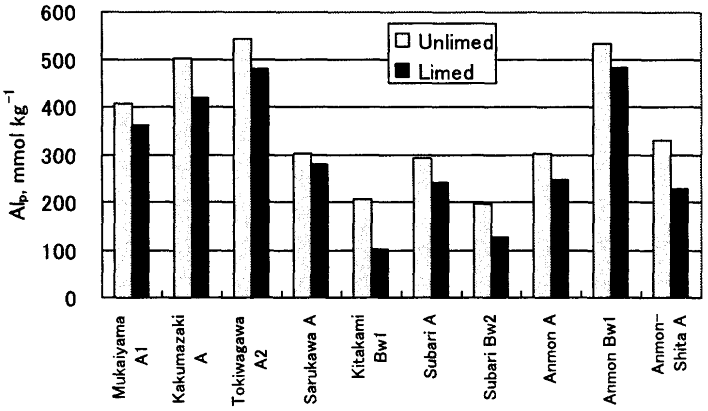

Fig. 5. Amounts of pyrophosphate-extractable Al from unlimed and limed soil samples.

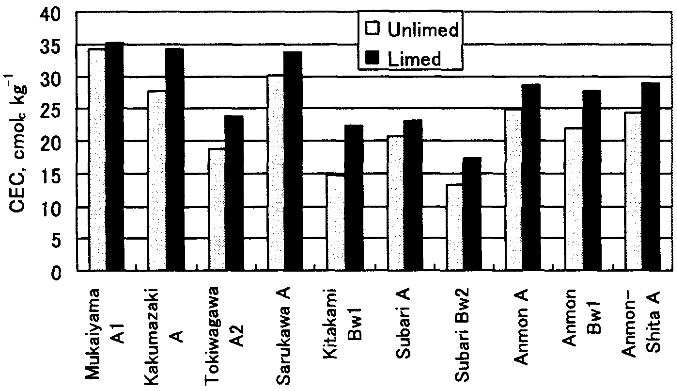

Fig. 6. Cation exchange capacity (CEC) of unlimed and limed soil samples.

concentrations of Al$_p$ were rather low (5.5–11.1 g kg^{-1}). To confirm the relationship for other soils with higher Al-humus contents, the data for the Noshiro soils were combined with the data from the A horizons of a wide range of nonallophanic Andosols in Japan (Shoji et al. 1985). As shown in Fig. 4, a significant relationship was also observed between Al saturation and the Al$_p$ concentration over a wide range of Al$_p$ concentrations from 5 to 28 g kg^{-1} though the parent materials and ages of soils were different. In these soil horizons, aqueous Al is considered to be equilibrated as follows : humus-complexed Al ⇔ aqueous Al ⇔ exchangeable Al.

Effect of liming on organically complexed Al (Takahashi et al. 2004). From the results of the Al solubility and the relationship between exchangeable Al and organically complexed Al, it was indicated that a portion of Al-humus complexes are labile and are easily altered by rather simple chemical treatment such as liming. Because nonallophanic Andosols usually show low pH values and high levels of toxic Al, liming is commonly performed.

Figure 5 shows the pyrophosphate-extractable Al (Al$_p$) of limed and unlimed soil samples. A large decrease of Al$_p$ value with liming was observed (decrease rate of 9–43%), and the decrease is significant ($p < 0.001$) according to the result of the t-test (for paired samples) for the Al$_p$ values of the two groups, unlimed and limed samples. The decrease of Al$_p$ values cannot be explained only by the disappearance of the KCl extractable Al (data not shown). These results strongly indicate that liming reduces significant amounts of organically complexed Al as well as exchangeable Al. As shown in Fig. 6, the increase in the cation exchange capacity (CEC) at pH 7 after liming further suggested that the carboxyl group was partly liberated from Al complexation and became to develop negative charges.

This phenomenon is very important because the dominance of Al-humus complexes is considered to be the essential characteristics for nonallophanic Andosols.

References

Blakemore, L.C., Searle, P.L. and Daly, B.K., 1981. Soil Bureau Laboratory Methods : A. Methods for chemical analysis of soils. New Zealand Soil Bureau Scientific Report, 10A (revised).

Hargrove, W.L. and Thomas, G..W., 1981. Extraction of aluminum from aluminum-organic matter complexes. Soil Sci. Soc. Am. J., 45 : 151-153.

McKeague, J.A., 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci., 47 : 95-99.

McKeague, J.A., 1976. Manual on Soil Sampling and Methods of Analysis. Soil Resource Institute, Agriculture Canada, Ottawa.

Nanzyo, M., Dahlgren, R. and Shoji, S., 1993. Chemical characteristics of volcanic ash soils. In : S. Shoji, M. Nanzyo and R.A. Dahlgren (Editors), Volcanic Ash Soils -Genesis, Properties and Utilization. Elsevier, Amsterdam-London-New York-Tokyo, pp.145-187.

Saigusa, M., Shoji, S. and Takahashi, T., 1980. Plant root growth in acid Andosols from northeastern Japan : 2. Exchange acidity Y_1 as a realistic measure of aluminum toxicity potential. Soil Sci., 130 : 242-250.

Shoji, S, Ito, T, Saigusa, M, and Yamada, I., 1985 : Properties of nonallophanic Andosols from Japan. Soil Sci., 140 : 264-277

Takahashi, T., Fukuoka, T. and Dahlgren, R.A., 1995. Aluminum solubility and release rates from soil horizons dominated by aluminum-humus complexes. Soil Sci. Plant Nutr., 41 : 119-131.

Takahashi, T., Sato, T., Sato, A. and Nanzyo, M., 2003. Relationship between 1 M KCl-extractable aluminum and pyrophosphate-extractable aluminum in A horizons of non-allophanic Andosols. Soil Sci. Plant Nutr., 49 : 729-733.

Takahashi, T., Ikeda, Y., Fujita, K. and Nanzyo, M. 2004. Effect of liming on organically complexed aluminum of nonallophanic Andosols from northeastern Japan. Geoderma (in press).