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Relating Sulfate Adsorption to Soil Properties in Japanese Forest Soils

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The relationship of sulfate adsorption capacity to the presence of aluminum, iron oxides, and organic carbon in four Japanese forest soils was investigated. Sulfate adsorption capacities were higher in subsoils than in surface soils, and their profiles were the inverse of those of organic carbon content. The black soil derived from volcanic ash had high sulfate adsorption capacity and showed no release of sulfate, while some of the surface horizons of the other soils desorbed sulfate. Oxalate extractable aluminum (Al_o) and iron (Fe_o) and ditionite-citrate-bicarbonate (DCB) extractable iron (Fe_d) were positively correlated with the sulfate adsorption capacity, and their correlation coefficients were almost identical (0.58–0.61). The lack of significant correlation between Al_d and the adsorption capacity suggests that DCB is unsuitable for extracting aluminum compounds which have the ability to adsorb sulfate. In contrast with oxides, organic carbon correlated with sulfate adsorption capacity negatively, and had a negative coefficient in a multiple regression equation, insignificantly. Furthermore, H_2O_2-treated samples containing decomposed organic matter adsorbed more sulfate than untreated samples. These results clearly indicate that organic matter hinders sulfate adsorption. A comparison of the β value (standard regression coefficient) of organic carbon with that of Al_o showed that the negative contribution of organic matter to sulfate adsorption capacity was slightly less than the positive contribution of oxides.

Key words: aluminum and iron oxides, forest soil, organic matter, sulfate adsorption

Acid deposition is a major environmental concern throughout much of the industrial world (Prenzel, 1994). This is particularly true in Asia, where sulfur emissions are expected to continue to increase dramatically, by as much as 2–7-fold between 1980 and 2020 (Galloway, 1989). Fortunately, no serious effects of acidic deposition on forest ecosystems have yet been observed in Japan, although acidity loading in Japan is not significantly different from that observed in northern Europe and eastern North America (Sato and Takahashi, 1996). Nevertheless, acidic materials are likely accumulating in forest soils, and it is thus a matter of concern to forest managers to determine when obvious effects of soil acidification will appear in Japanese forests. To determine a tolerable level of acid deposition in soils, the concept of critical load has been proposed and widely applied (Shindo *et al.*, 1995). And although this concept has also been applied to Japanese forest soils, a number of uncertainties remain, in part because of insufficient data on the extent of soil acidification in Japan.

Sulfate adsorption is recognized as the third step of the neutralization mechanism for acidity loading in soil, namely, the soil acidification process (Yoshida and Kawahata, 1988), and this step has been shown to modify the effects of elevated pollutant deposition (H^+, $SO_4{}^{2-}$) on cation leaching processes in forest ecosystems (MacDonald *et al.*, 1994). Researchers in Europe and North America have clarified the characteristics of sulfate adsorption, demonstrating that aluminum and iron oxide act as adsorbents of sulfate (Singh, 1984), while organic matter acts as a sulfate adsorption obstructer (Gobran and Nilsson, 1988). However, report on the roles of the components have sometimes been diverse and even contradictory (Johnson and Mitchell, 1998). For instance, Johnson and Todd (1983) reported that there was no significant correlation between any aluminum and sulfate fractions, and Fuller *et al.* (1985) stated that organic matter enhances sulfate adsorption. Based on these complex and equivocal results, it can at least be assumed that soil constituents have a pronounced effect on each other. Because these interactions depend on soil parent materials and soil forming conditions, original studies are also needed in Japan. Nevertheless, few studies have yet been made on sulfur behavior in soils, partly because little emphasis has been given to sulfur as a plant nutrient in Japan.

The purpose of this paper is to clarify the contribution of soil constituents, such as aluminum, iron oxide and organic matter, to the process of sulfate adsorption in typical Japanese soils. To achieve this purpose, two popular solutions were used for oxide extraction, and organic matter was decomposed by H_2O_2 in subsamples of all soils.

Materials and Methods

1 Soils

Soil samples were obtained from various horizons of four pedons. INA, DAN-1, and DAN-2 were sampled from the Chubu region, and FUC was sampled from the Kanto region. Partial characteristics of the soils are presented in Table 1, along with their minerals crystallinities as measured by X-ray diffraction analysis (Shimadzu XD-D1w, target: Cu, 35 kV, 20 mA). Soils were classified based on the "Classification of Forest Soil in Japan (1975)" (Forest Soil Division, 1976). The soil types based on the "Classification of Cultivated Soils in Japan" (Cultivated Soil Classification Committee, 1995) and the U.S. system of soil taxonomy (Soil Survey Staff, 1994) are also shown in the same table. INA was classified as a brown forest soil of a type widespread in Japan. DAN-1, DAN-2, and FUC were classified as black soils, which are also common in Japan. The black soils were further subdivided into two types: one (FUC) is originated from volcanic ash and characterized by the existence of amorphous clays such as allo-

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phane, and the other (DAN-1, DAN-2) being non-allophanic and containing crystallized minerals.

2 H_2O_2-treatment

To decrease the content of organic matter, subsamples were treated as follows. Ten grams of air-dried soil was digested with 50 ml of 6% H_2O_2 in a heated water bath at 60 to 70°C until the foam disappeared. The subsamples were then repeatedly digested with 5 ml of 30% H_2O_2 until no further visible reaction occurred. After the excess H_2O_2 was removed by heating the solution at 60 to 70°C for 2 h, the subsamples were washed with deionized water several times, centrifuged, and oven-dried at 30 to 40°C. This treatment resulted in

Table 1 Partial descriptions of soils.

Sample ID	Sampling location	Layer and depth	Classification			Parent materials	Crystallinity of minerals	Vegetation
			CFSJ[a]	CCSJ[b]	US[c]			
INA	Inabu-cho in Aichi Pref.	A (0–1) A (1–10) B (10–20) B (20–30) B (30–40)	Moderately moist brown forest soil	Brown Forest Soil	Dystrochrept	Granite	Crystalline	*Chamaecyparis obtusa* Sieb. et Zucc
DAN-1	Dando-san in Aichi Pref.	A (0–18) AB (18–33) B (33–)	Dry black soil	Non-allophanic Andosol	Dystrochrept	Granite	Crystalline	*Chamaecyparis obtusa* Sieb. et Zucc
DAN-2	Dando-san in Aichi Pref.	A (9–22) AB (92–108) B (108–)	Slightly wetted black soil	Non-allophanic Andosol	Dystrochrept	Granite	Crystalline	*Chamaecyparis obtusa* Sieb. et Zucc
FUC	Fuchu-city in Tokyo	A (0–21) A (21–36) A (36–50) AB (50–65) B (65–)	Moderately moist black soil	Andosol	Pachic Melanudand	Volcanic Ash	Amorphous	Broad-leaved trees

[a]Classification of Forest Soil in Japan. [b]Classification of Cultivated Soils in Japan. [c]U.S. System of Soil Taxonomy.

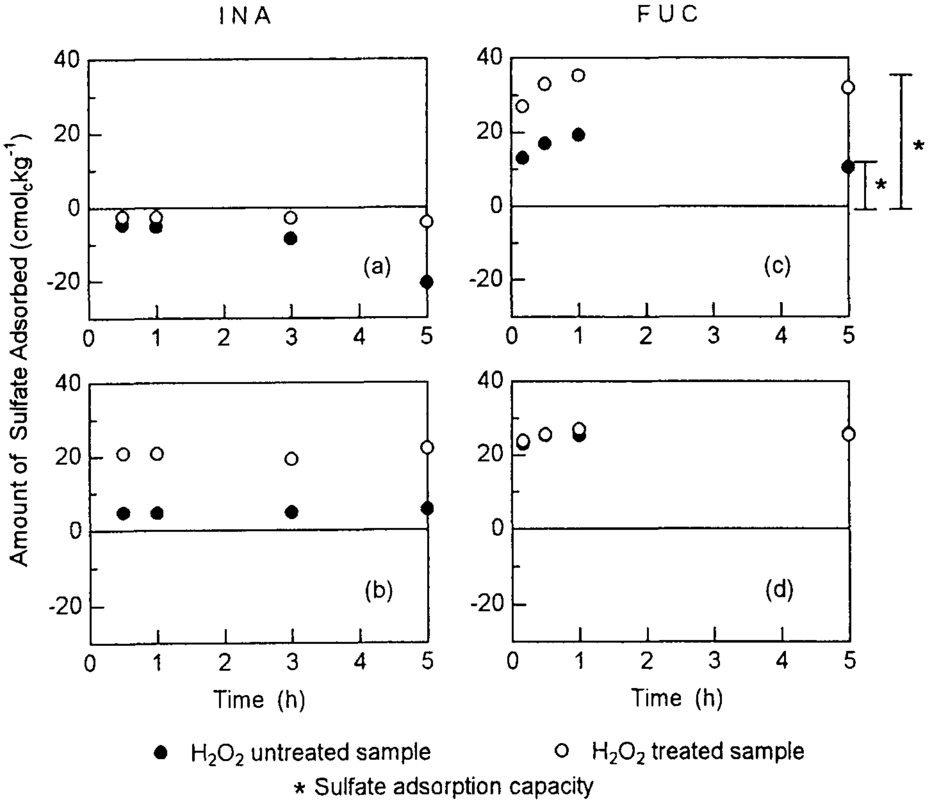

Fig. 1 Change in the amount of sulfate adsorbed with time (INA and FUC). Sampling horizons and depths were (a) A horizon (1–10 cm); (b) B horizon (30–40 cm); (c) A horizon (21–36 cm); and (d) B horizon (65–*x* cm). The amount of sulfate adsorbed appeared to increase for 1 h. The amount of sulfate adsorbed by H_2O_2-untreated samples was greater than that adsorbed by the treated ones. A release of sulfate was clearly observed in the A horizon of INA.

decomposition of about 80% of organic matter.

3 Sulfate adsorption experiment

Both H_2O_2-treated and -untreated samples were sieved through a 74 μm mesh to provide consistency in soil particle size. They were then shaken with 0.1 M NH_4Cl for 5 h to displace all exchangeable ions with NH_4^+ and Cl^-. This was followed by several additional repetition of washing with deionized water and centrifugation. And then, they were dried and sieved a second time.

A 2.5 g sample was shaken with a 40 ml of 0.001 M $(NH_4)_2SO_4$ solution at pH 5.6 ($\pm$ 0.2) to determine sulfate adsorption. After shaking for 10 min, 30 min, 1 h or 5 h, the suspensions were centrifuged and filtered through a 0.45 μm Millipore filter. Sulfate concentrations in the clear supernatants were determined by turbimetric analysis using $BaSO_4$. The amounts of sulfate adsorbed by the soil samples were calculated from the difference between sulfate concentrations before and after shaking.

4 Soil chemical analysis

The organic carbon was measured using a CN analyzer (YANACO MT500 CN CORDER). Al_o and Fe_o were determined after extracting for 2 h with an acid ammonium oxalate solution at pH 3 (Tamm, 1922). Al_d and Fe_d were determined after two extractions for 15 min at 75°C (Jackson *et al.*, 1986). The concentrations of aluminum and iron in the extracts were measured by inductively coupled plasma emission spectrometry (P_s-3000_uV; Leeman Labs. Inc.).

Results and Discussion

1 Sulfate adsorption

Typical adsorption curves for INA and FUC are shown in Fig. 1. The adsorbed amounts of sulfate increased with the shaking time and became constant after 1 h or more. Therefore, sulfate adsorption capacity was defined as the amount of sulfate adsorbed by 1 kg of dried soil after 5 h of shaking. Table 2 shows the sulfate adsorption capacities calculated for all samples using this definition, along with the results of the chemical analysis. The value of the adsorption capacities became negative when sulfate was released from soils.

Figure 2 shows depth profiles of sulfate adsorption capacity and the content of organic carbon for INA and FUC. The data for DAN-1 and 2 showed intermediate features between these two soils. In both soils, two tendencies were observed: (1) sulfate adsorption capacity was higher in subsoils than in surface soils and the distribution was the inverse of that of organic carbon content; and (2) the capacities were enhanced

Table 2 Chemical characteristics of soils.

Sample ID	Layer and depth (cm)	H_2O_2 treatment	Organic carbon (g $100g^{-1}$)	Oxides				Sulfate adsorption capacity ($mol_c\,kg^{-1}$)
				Al_o (g $100g^{-1}$)	Al_d (g $100g^{-1}$)	Fe_o (g $100g^{-1}$)	Fe_d (g $100g^{-1}$)	
INA	A (0–1)	Untreated	14.5	1.23	1.08	2.24	2.49	−4.8
		Treated	1.98	0.43	0.36	2.02	2.38	−5.2
	A (1–10)	Untreated	10.1	1.40	1.12	2.41	2.55	−20.4
		Treated	1.89	0.63	0.50	2.45	2.80	−4.0
	B (10–20)	Untreated	6.80	1.59	1.25	2.63	2.82	−1.6
		Treated	1.17	1.24	1.01	3.20	3.95	5.6
	B (20–30)	Untreated	4.31	2.17	1.36	3.26	2.90	2.0
		Treated	1.20	1.87	1.07	3.56	3.31	8.0
	B (30–40)	Untreated	3.71	2.30	1.30	3.37	2.82	5.6
		Treated	1.06	1.65	1.20	2.82	3.32	22.0
DNA-1	A (0–18)	Untreated	14.7	0.95	1.17	1.37	1.90	−8.0
		Treated	2.03	0.20	0.22	0.44	1.13	−2.0
	AB (18–33)	Untreated	7.58	1.26	1.24	1.75	3.05	16.8
		Treated	0.19	0.45	0.98	0.36	1.89	12.8
	B (33–)	Untreated	0.92	0.37	0.90	0.92	2.39	−2.0
		Treated	0.52	0.75	0.70	1.55	2.54	9.2
DNA-2	A (9–22)	Untreated	7.73	1.51	1.05	1.54	1.36	6.0
		Treated	1.18	0.64	0.39	1.28	1.06	8.4
	AB (92–108)	Untreated	0.97	0.50	0.48	0.51	0.84	−0.8
		Treated	0.18	0.65	0.44	0.78	0.92	6.4
	B (108–)	Untreated	0.43	0.40	0.33	0.46	0.86	8.8
		Treated	0.10	0.59	0.27	0.61	0.68	28.8
FUC	A (0–21)	Untreated	8.33	5.85	1.97	4.86	4.34	2.0
		Treated	1.29	6.61	2.28	6.96	5.31	20.4
	A (21–36)	Untreated	6.75	6.64	1.84	5.47	4.88	10.6
		Treated	1.18	7.23	2.09	7.28	5.29	32.0
	A (36–50)	Untreated	6.71	8.06	1.96	6.24	5.84	17.4
		Treated	1.44	9.08	2.16	8.64	6.15	30.2
	AB (50–65)	Untreated	3.09	8.72	1.54	7.59	5.60	9.8
		Treated	0.78	10.3	1.96	9.61	6.84	34.4
	B (65–)	Untreated	1.35	8.83	1.76	8.95	6.94	25.8
		Treated	0.50	8.15	1.79	8.80	6.82	25.4

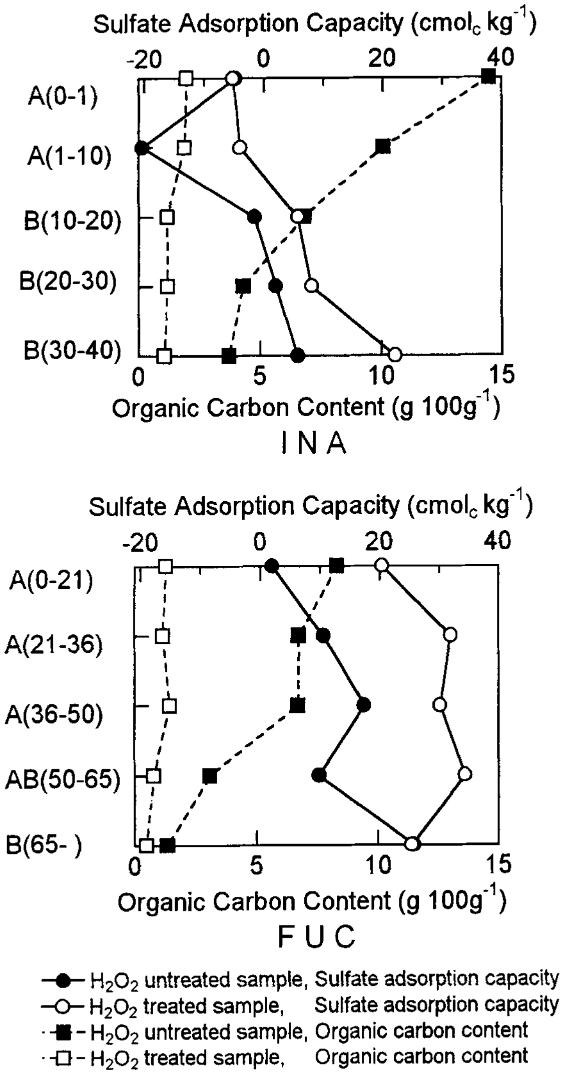

Fig. 2 The profiles of sulfate adsorption capacity and organic carbon content (INA and FUC). Sulfate adsorption capacities were higher in subsoils than in surface soils. The capacities and organic carbon contents show inverse profiles. The H_2O_2-treatment enhanced the capacities.

by H_2O_2-treatment.

It should also be noted that the desorption of sulfate ion from the surface soils of INA is pronounced in Fig. 1. Some researchers (MacDonald and Hart, 1990; Johnson and Todd, 1983) have also reported the release of sulfate ions from the surface horizons of some soils. Further, Shibata and Sakuma (1993 a, b) observed the leaching of sulfate ion from A_0 and A horizons using a field lysimeter. These results would suggest that surface horizons easily release sulfate. In the present study, however, FUC adsorbed a large quantity of sulfate and no release was observed, even from the A horizons. In a study using 11 Andisols derived from volcanic ash collected from the Kanto region and northward to Hokkaido in Japan, Fumoto *et al.* (1996) reported that not only the soils from the B and C horizons but also those from the A horizons demonstrated high capacities to adsorb sulfate ions. Their observations were similar to our present findings using FUC. Thus, even in the A horizons, sulfate seems to be adsorbed too strongly to be released when the main parent material of black soils (Andisols) is volcanic ash.

Table 3 Correlation Matrix.

	[Ad.]	[Al_o]	[Fe_o]		[Ad.]	[Al_d]	[Fe_d]
[Al_o]	0.61*			[Al_d]	0.39		
[Fe_o]	0.58*	0.97***		[Fe_d]	0.60*	0.87***	
[C]	−0.46	−0.16	−0.15	[C]	−0.46	0.21	−0.10

[Ad.], sulfate adsorption capacity; [C], organic carbon; [Al_o], oxalate extractable aluminum; [Al_d], DCB extractable aluminum; [Fe_o], oxalate extractable iron; [Fe_d], DCB extractable iron. $*p < 0.05$, $***p < 0.001$.

2 Oxides

Aluminum and iron oxides are recognized as adsorbents of sulfate (Adams and Rawajfih, 1977; Singh, 1984; Rajan, 1978; Parfitt and Smart, 1978). Accordingly, these oxides were extracted and measured to clarify their contribution to sulfate adsorption.

The extractable oxides in the soils were probably predominated by amorphous fractions. One of the reasons for this was that the soils contained large amounts of oxalate extractable oxides (Table 2). FUC, derived from volcanic ash, had much oxides (Al_o and Fe_o were about 8 % and 7 %, respectively) to be cleared the criteria for detecting andic soil property using the oxalate extractions (Soil Survey Staff, 1994). The other soils also contained more than a small amount of these oxides (Al_o and Fe_o were about 1% and 2%). The other reason for this predominance of amorphous fractions is that the DCB extractable oxides were not different from the oxalate extractable ones, with the exception of aluminum in FUC (Table 2), although DCB solution generally extracts amorphous plus crystalline fractions (Kawada, 1989).

Al_o, Fe_o, and Fe_d were significantly correlated with sulfate adsorption capacity ($p < 0.05$), and their correlation coefficients were almost the same, *i.e.*, 0.61, 0.58, and 0.60, respectively (Table 3). Since these oxides possibly consist of amorphous fraction, sulfate adsorption is associated with amorphous oxides in these soils. This phenomenon has often been observed (Rajan, 1978; MacDonald and Hart, 1990). However, some researchers have reported that the soil constituent most closely correlated with sulfate adsorption is the crystalline fraction of iron (Johnson and Todd, 1983; Fuller *et al.*, 1985), and that this correlation is related to soil weathering (Tsuji, 1986). Because we could not detect the crystalline fraction of the iron oxide and because we did not have data on the weathering, this point can not be discussed. On the other hand, Al_d did not correlate significantly with sulfate adsorption capacities ($r = 0.39$). This lack of correlation suggests that the DCB solution is unsuitable for extracting aluminum oxide that has the ability to adsorb sulfate. Fumoto *et al.* (1996) also reported a lack of correlation between Al_d and sulfate adsorption. Therefore, oxalate extractable oxides were used as the free oxides in the following discussion.

3 Organic matter

In contrast to oxides, organic carbon was negatively but insignificantly correlated with sulfate adsorption capacity (Table 3). This lack of significance could be due to such predominant factors as the presence of aluminum and iron oxides. To estimate the contribution of organic matter to sulfate retention, multiple regression analysis was applied to the data of H_2O_2-untreated soils and the following equation was obtained:

$$[\mathrm{Ad.}] = (1.93 \pm 0.68)^{*}[\mathrm{Al_o}] - (0.93 \pm 0.49)[\mathrm{C}] + (3.64 \pm 4.50) \quad r^2 = 0.51$$

$$\beta \quad [\mathrm{Al_o}]\,;\, 0.55 \quad [\mathrm{OM}]\,;\, 0.37 \quad {}^{*}p < 0.05$$

where [Ad.] stands for sulfate adsorption capacity, and $[\mathrm{Al_o}]$ and [C] are the contents of $\mathrm{Al_o}$ and organic carbon, respectively. β values for $[\mathrm{Al_o}]$ and [C] are standard regression coefficients giving the degree of contribution for each variable in the equation. In this analysis, the variable for iron oxide was excluded because of the close relationship between aluminum and iron oxides ($r = 0.97, p < 0.001$) (Table 3). Thus, the contribution of $\mathrm{Fe_o}$ to sulfate adsorption capacity is similar and comparable to that of $\mathrm{Al_o}$.

In the above equation, a positive coefficient value classifies the matter as an adsorbent, and a negative value classifies the matter as an inhibitor. Thus, the equation indicates that $\mathrm{Al_o}$ adsorbs sulfate and that organic matter acts as an inhibitor to sulfate adsorption. In addition, the result that H_2O_2-treatment increased the capacity for sulfate adsorption suggests an interference effect of organic matter. This is one of the main reasons why the profile of sulfate adsorption capacity was in contrast to that of organic carbon content, as shown in Fig. 2. Concerning the effects of organic matter on sulfate adsorption, two conflicting processes have been proposed: (1) indirect enhancement of adsorption by maintaining aluminum and iron oxides in more amorphous forms with higher adsorption capacities and (2) interference with the adsorption by competition or blockage of adsorption sites (Johnson and Mitchell, 1998). In our present results on Japanese forest soils, the interference effect was clearly observed, but the enhancement effect could not be confirmed.

In the above equation, the units of the coefficients are $\mathrm{mmol_c\,g^{-1}}$, since the unit of [Ad.] is $\mathrm{cmol_c\,kg^{-1}}$ and that of $[\mathrm{Al_o}]$ and [C] is $\mathrm{g\ 100g^{-1}}$. Thus, the coefficient of $[\mathrm{Al_o}]$ represents sulfate adsorption ability per gram of $\mathrm{Al_o}$. In the same way, the coefficient of [C] represents interference ability per gram of organic carbon. Since the coefficient and the β value of [C] were not substantially different from those of $[\mathrm{Al_o}]$ in the equation, the contribution of organic matter per gram to sulfate adsorption capacity was slightly less than that of oxides per gram, although the former was negative and the latter was positive.

On the basis of our results, a rough prediction of sulfate adsorption capacity can be made using the content of aluminum oxides and organic carbon. This estimation, along with that of the present amount of sulfate adsorbed in soils, is critical for a better understanding of the process of soil acidification. It is known that sulfate adsorption is the third stage of soil acidification, occurring just before the last stage in which aluminum is leached from soils (Yoshida and Kawahata, 1988). That is, there exists an optimum pH at which sulfate adsorption reaches a maximum in each soil, and lower pH levels typically result in solubilization of the coatings of aluminum and iron oxides (Nodvin *et al.*, 1986). Once the oxide coatings are destroyed by acidification, the sulfate adsorbed on soils is leached along with aluminum (Yoshida and Kawahata, 1988). Thus, evaluation of the balance between sulfate adsorption capacity and the present amount of sulfate adsorbed will help us to establish the critical load of acidic deposition in Japanese forest soils. For this reason, further investigation into sulfate retention mechanisms will be needed.

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