

Sulphate retention: a simplified method for categorizing soils into allophanic and non-allophanic Andosols

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Summary

Unlike phosphate, an index of sulphate retention of soils has not commonly been defined. However, sulphate sorption by soils is more sensitive than phosphate sorption to the amount of their colloidal components. Sulphate has less sorption affinity than some organic acids or phosphate, and is sorbed by hydrous Al/Fe such as allophane but not by Al-humus complexes. Therefore, we attempted to categorize soils as allophanic or non-allophanic Andosols by sorption experiments of sulphate. The method employed for sulphate retention (S-retention) was based on the common method for P-retention, using potassium sulphate solution ($3.12 \text{ mmol SO}_4^{2-} \text{ l}^{-1}$, equivalent to 100 mgS l^{-1}) buffered by potassium acetate (pH 4.0) and shaking for one hour with a soil:solution ratio of 1:5. In the results from 172 soil samples of 30 forest soils in eastern Japan, a linear regression was obtained between S-retention and $\text{Al}_o + 1/2\text{Fe}_o$ ($r = 0.780$, $P < 0.001$). All aluandic (non-allophanic) soil samples ($\text{Si}_o < 0.6\%$ and $\text{Al}_p:\text{Al}_o > 0.5$, in accordance with the WRB classification system) had poor S-retention (<60%) and were clearly divided from silandic (allophanic) soil samples. Highly weathered Cambisols with small activity ratios of free iron oxides ($\text{Fe}_o:\text{Fe}_d < 0.4$) tended to have greater S-retention (>30%) than less weathered Umbrisols and Cambisols with $\text{Fe}_o:\text{Fe}_d > 0.4$. In addition, these four soil types were separated as distinct domains on a scatter diagram of P-retention plotted against S-retention.

Introduction

Non-allophanic Andosols were first found in Japan (Shoji & Ono, 1978). Before this discovery, it was considered that the unique properties of Andosols such as large organic matter content, much phosphate fixation, good water retention and small bulk density were due to the presence of short-range-ordered allophane minerals. Although non-allophanic Andosols also have these properties, they are dominated by 2:1 layer silicates and aluminium/iron (Al/Fe)-humus complexes. Shoji (1985) subsequently showed that the genesis of non-allophanic Andosols can be attributed mainly to the leaching of silica and the formation of Al-Fe humus complexes caused by supply of a large amount of organic matter under acid conditions (pH <5) with large rainfalls. Therefore, non-allophanic Andosols in Japan are distributed in high rainfall regions such as the area adjacent to the Sea of Japan, and the Chubu district, and account for about 30% of the total (Saigusa & Matsuyama, 1998). However, there are many reports about soil profiles which have non-allophanic properties in the upper A horizon and allophanic properties in the lower part of the A horizon (Kubotera *et al.*, 2009; Van Ranst *et al.*, 2008). Vacca *et al.* (2003) showed that allophanic and non-allophanic soils in the Roccamonfina volcano, Italy, co-existed in similar landscapes under similar climatic conditions, and concluded

that allophanic soils developed in younger tephra than non-allophanic soils. It is presumed that the distribution of these two types of Andosols forms a mosaic in volcanic areas. The occurrence of non-allophanic Andosols in non-volcanic areas has also been recently found in many regions. According to Delvaux *et al.* (2004), non-allophanic Andosols in Europe are linked with Hercynian rocks in highlands with a cool and humid climate and often co-exist with Cambisols and Podzols, suggesting that non-allophanic Andosols can be regarded as further developed Cambisols with increasing Al-Fe humus complexes, and as poorly developed Podzols after carbon stabilization. The non-allophanic Andosols had a larger percentage of water-stable aggregates and a smaller carbon mineralization rate compared than Podzols, and the Al-Fe humus complexes was immobile in the non-allophanic Andosols (Aran *et al.*, 2001). In addition, Caner *et al.* (2000; 2011) found several non-allophanic Andosols derived from highly weathered soils and showed that the accumulation of organic matter in the top-soil resulted in dissolution of their secondary minerals such as gibbsite and crystalline iron oxides, and gradually replaced these with sufficient organo-metallic complexes to produce andic properties. Vacca *et al.* (2009) pointed out that andic soil properties should not just be defined according to the parent material, and the distribution of soil with andic properties might be more widespread than assumed.

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The world distribution and total area of non-allophanic Andosols have yet to be clarified fully, including in Japan.

On the other hand, it is well known that non-allophanic Andosols have lower soil pH and more extractable Al and organic carbon than allophanic Andosols (Shoji *et al.*, 1993). Therefore, it is important for not only fertilizer management but also for understanding of carbon storage to identify both types of Andosol accurately. However, it is impossible to distinguish them by morphological characteristics in the field, and so it is necessary to do this from chemical and mineralogical properties.

According to the latest Japanese soil classification system (Obara *et al.*, 2011), the phosphate absorption coefficient or phosphate retention provide diagnostic criteria for Andosols and their andic properties. However, in order to classify Andosols into allophanic or non-allophanic Andosols it is necessary to determine the acid-oxalate extractable Al, Fe and Silicon (Al_o , Fe_o and Si_o , respectively) and the pyrophosphate extractable Al (Al_p) or exchangeable acidity (y_1). In the WRB system (IUSS Working Group WRB, 2006), the values of Al_o and Fe_o are essential criteria of andic properties. In other words, the phosphate absorption coefficient or phosphate retention are not included as important components of second-level units of Andosols because the phosphate ion is sorbed not only by allophane but also by Al-humus complexes.

Sulphate ions are specifically adsorbed on the surface of hydrated Al minerals through ligand exchange reactions as well as phosphate ions (Rajan, 1978). However, the amounts of adsorbed sulphate are decreased by the presence of organic acids (Martinez *et al.*, 1998) or phosphate (Kamprath *et al.*, 1956), suggesting that these anions compete for the adsorption sites with sulphate ions and displace them. Moreover, it was found that allophanic Andosols in Japan retain significantly larger amounts of sorbed sulphate (phosphate-extractable sulphate) than brown forest soils (with no andic properties) or other soils reported in North America and Europe (Tanikawa *et al.*, 2003). However, Takahashi & Higashi (2013) reported that the amounts of sorbed sulphate in non-allophanic Andosols were similar to those in brown forest soils. These results suggest that sulphate ions have less sorption affinity than some organic acids or phosphate, and are sorbed by hydrated Al materials such as allophane but not by Al-humus complexes.

In the present study, in order to separate allophanic Andosols from non-allophanic Andosols we conducted sulphate sorption experiments using the normal method for phosphate retention (Blakemore *et al.*, 1987) using samples of various soil types under forest vegetation. We also propose a simplified method for categorizing soils on the criteria of extractable Al and Fe in combination with sorption of sulphate (S-retention) and phosphate (P-retention).

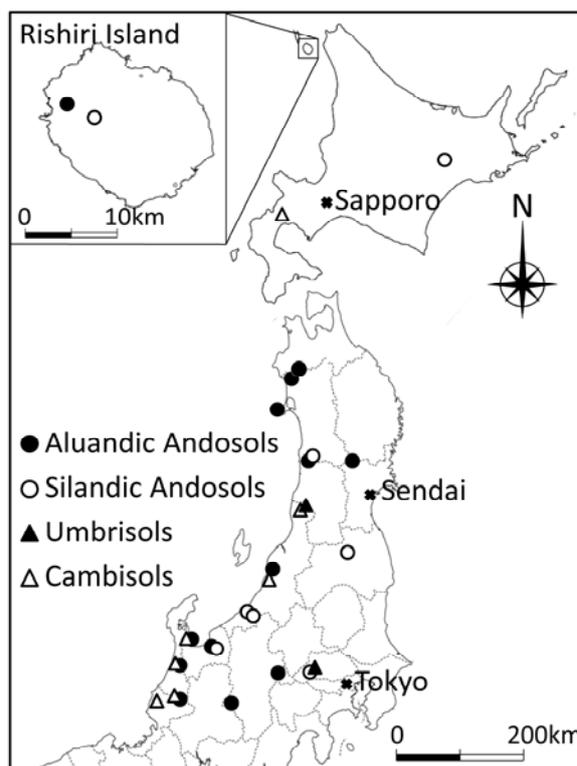


Figure 1 Locations of the study sites.

Materials and methods

Soil samples

Soil samples (a total of 172) were taken from each horizon of 30 soil profiles under forest vegetation in eastern Japan (Figure 1). The soil profiles were classified as 13 aluandic Andosols, eight silandic Andosols, two Umbrisols and seven Cambisols as classified by the WRB system. These samples came from areas with mean annual temperatures of 6.3-15.2°C, annual precipitation of 895-2640 mm and altitudes of 44-1350 m above sea level. The parent materials of Andosols are mainly cumulative volcanic ashes and those of Umbrisols and Cambisols are igneous and sedimentary rocks. Vegetation is broad-leaved deciduous forest dominated by *Fagus crenata* Blume or *Quercus crispula* Blume and evergreen needle-leaf forest dominated by *Pinus densiflora* Siebold & Zucc. Only natural or secondary forests were included. The details including the chemical properties of some of these soil profiles were previously described by Takahashi & Higashi (2013).

Analytical methods

All soil samples were air-dried and passed through a 2 mm or 0.5 mm sieve prior to chemical analyses. Acid oxalate-extractable Al, Fe and Si (Al_o , Fe_o and Si_o), pyrophosphate-extractable Al and Fe (Al_p and Fe_p) and dithionite-citrate-extractable Al and Fe (Al_d and Fe_d) were extracted according

to Blakemore *et al.* (1987). The pyrophosphate extracts were centrifuged with Accofloc and then passed through a 0.025- μm membrane filter to remove colloidal iron compounds. The Al, Fe, and Si concentrations were determined by inductively coupled plasma atomic emission spectrophotometry (ICP-AES) using ICPS-8100 (Shimadzu, Tokyo, Japan). Soil pH was measured in H_2O and 1 M KCl (soil:solution 1:2.5). Exchangeable Al in the 1 M KCl extracts was determined by ICP-AES. Total carbon (TC) and total nitrogen (TN) were determined by dry combustion using an NC analyser (Sumigraph NC-900, Sumika Chemical Analysis Service, Tokyo, Japan). Phosphate retention (P-retention) was measured according to Blakemore *et al.* (1987) by shaking samples for 16 hours with potassium dihydrogen phosphate solution (1000 mgP l^{-1} , pH 4.6) at a soil:solution ratio of 1:5. Phosphate concentrations were determined by the vanadomolybdate spectrophotometric method with a V-660 instrument (JASCO Corporation, Tokyo, Japan).

Sorption of sulphate (S-retention)

Unlike phosphate, the index of sulphate retention or sorption capability of soils has not been commonly defined although numerous sulphate-sorption experiments have been conducted under various conditions. On the other hand, many characteristics related to sulphate sorption, especially sulphate concentration and solution pH, have been investigated. Thus apparent sulphate sorption increases exponentially at equilibrium concentrations $>100 \text{ mmol SO}_4^{2-} \text{ l}^{-1}$ because of precipitation (Ishiguro *et al.*, 2004). Delfosse *et al.* (2006) reported that $\text{Al}_x(\text{OH})_y(\text{SO}_4)_z$ minerals might be formed under large sulphate concentrations ($>6 \text{ mmol SO}_4^{2-} \text{ l}^{-1}$). In addition, Barreal *et al.* (2001) showed that sorption of sulphate tended to be about one tenth of that of phosphate sorption. On the basis of these results and the standard experiment conditions for phosphate retention (Blakemore *et al.*, 1987), in the present study we adopted 100 mgS l^{-1} (3.12 mmol $\text{SO}_4^{2-} \text{ l}^{-1}$) potassium sulphate as our standard condition.

Pigna & Violante (2003) reported that the sorption of sulphate by Andosols was almost absent at pH >5.5 and increased with soil acidification. However, Nodvin *et al.* (1986) showed that samples from spodic horizons sorb maximum amounts of sulphate at pH 4 because the dissolution of the solid phase of sorbent begins at pH <3.5 . Therefore, a preliminary assessment of sulphate sorption by one allophanic Andosol sample was conducted at pH 3.0 to 6.0 in potassium acetate buffer. In addition, the effect of shaking time (ranging from one minute to 16 hours) on sulphate sorption was tested using the same sample. The results, discussed later, showed that pH 4.0 and one hour were optimal for measurement of S-retention.

Sulphate-retention solution was prepared according to the following procedure. Anhydrous potassium sulphate (1.089 g) and anhydrous potassium acetate (3.926 g) were dissolved in 1.8 L water, and glacial acetic acid (about 9 ml) added to bring the mixture to pH 4.0. This was made up to volume with water in a 2-L volumetric flask. A sorption experiment was conducted by shaking this solution for one hour at 25° C with soil sample at a soil:solution ratio of 1:5. After centrifugation, the liquid phase was filtered through a 0.45- μm membrane filter and sulphate concentration determined by ion chromatography (HIC-SP; Shimadzu, Tokyo, Japan).

Results and discussion

Effects of pH and shaking time on sulphate sorption

Two preliminary experiments were conducted to determine suitable pH and shaking time for sulphate sorption. The soil sample studied was from a Bw horizon with allophanic soil properties. The values of $(\text{Al}_0 + 1/2\text{Fe}_0)$, Si_0 , exchangeable Al and native sorbed sulphate (phosphate-extractable sulphate) were 53.1 g kg^{-1} , 27.3 g kg^{-1} , 51.8 mg kg^{-1} and 17.3 mmol kg^{-1} , respectively. The equilibrium pH values of the supernatant after shaking were within the pH of the original added solutions ± 0.2 in all cases. As shown in Figure 2, the amount of sulphate sorbed from the added solution was greatest at pH 3.5–4.0 and decreased with both increasing and decreasing pH. On the other hand, the amount of Al dissolved from soil drastically increased at pH <3.5 , as reported by Nodvin *et al.* (1986). The amount of sulphate sorption slightly increased with shaking time (Figure 3). However, the difference between one hour and 16 hours was less than 2%, indicating that the equilibrium was approximately reached within one hour. Therefore, pH 4.0 and one hour were employed throughout in this study.

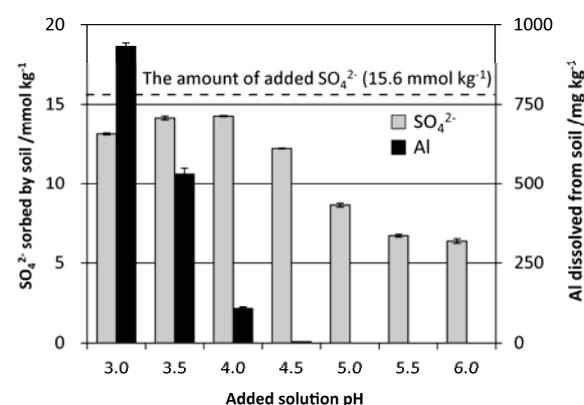


Figure 2 Amounts of sulphate sorbed by, and Al dissolved from one silandic soil sample at pH 3.0 to 6.0 using potassium sulphate solution (100 mgS l^{-1}) buffered by potassium acetate. Error bars = standard deviation.

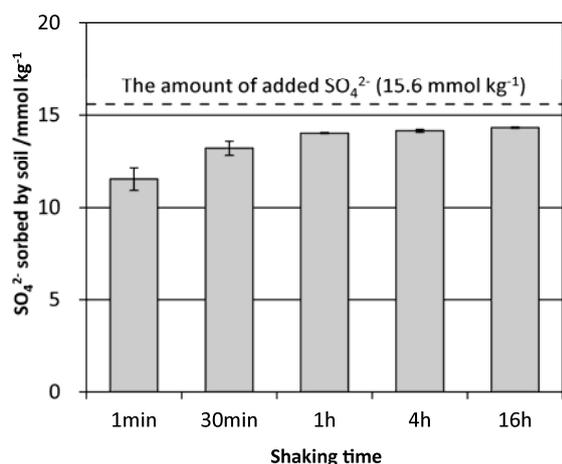


Figure 3 Amounts of sulphate sorbed by one silandic soil sample at different shaking time (ranged from one minute to 16 hours). Error bars = standard deviation.

It is to be noted that the amount of added sulphate (15.6 mmol kg⁻¹) was less than the native sorbed sulphate (17.3 mmol kg⁻¹) of this sample in our experiment conditions. According to previous research, the amounts of native sorbed sulphate in most non-volcanic soils (not Andosols) are <2 mmol kg⁻¹ (e.g. Singh, 1980; Johnson & Todd, 1983), while those in some volcanic Andosols are >20 mmol kg⁻¹ (Hasan *et al.*, 1970; Tanikawa *et al.*, 2003). Therefore, the S-retention values under our experiment conditions should not be regarded as total sorption capacity.

Comparison of the chemical properties of soil samples by soil type

Table 1 summarises the means and ranges of some chemical properties of soil samples for A and B horizons from each soil type. Although there was no a great difference in the pH_{H2O} between A horizons of either type of Andosol, the mean value of pH_{H2O} of B horizons in aluandic Andosols was 4.92, lower than for silandic Andosols (5.21). In agreement with Shoji (1985), the formation of allophane has been inhibited under acid conditions (< pH5). The pH values in KCl (pH_{KCl}) of silandic Andosols were higher than those of aluandic Andosols for both A and B horizons. In accordance with this result, the amounts of exchangeable Al of silandic Andosols were less than those of aluandic Andosols. Umbrisols and Cambisols had low pH_{KCl} values and large amounts of exchangeable Al similar to aluandic Andosols. Total carbon values in Cambisols were clearly smaller, but there was little difference among other three soil types, unlike Shoji *et al.* (1993)'s study who reported that aluandic Andosols can accumulate more organic carbon than silandic Andosols. Only the Al_o and Si_o contents of silandic Andosols were greater than those of

aluandic Andosols. On the other hand, extractable Al, Fe (except Fe_a) and Si of Umbrisols and Cambisols were smaller than those of Andosols, indicating that Fe oxides predominate in Umbrisols and Cambisols unlike Andosols which are dominated by short-range-ordered iron oxyhydroxides. According to the US Soil Survey Staff (2004), Al_d represents the Al-humus complexes plus the Al substituted in Fe oxides (Al_{sub}). In our study, good correlation between (Al_d-Al_p) and (Fe_d-Fe_p) was obtained in Umbrisols and Cambisols ($r = 0.832$, $P < 0.001$), suggesting that (Al_d-Al_p) represents Al_{sub}. However, in Andosols (Al_d-Al_p) correlated well with Al_o ($r = 0.736$, $P < 0.001$) rather than with (Fe_d-Fe_p) ($r = 0.310$, $P < 0.05$). Therefore, we consider that Al_d of Andosols represents the Al partly dissolved from allophane or Al-humus complexes (Parfitt & Childs, 1988).

Characteristics of phosphate and sulphate retention

The amount of sulphate sorbed from 100 mgS l⁻¹ solution (S-retention) was calculated as percent S retained, as with P-retention (Blakemore *et al.*, 1987). The results of analyses of 172 soil samples indicated that the distribution of S-retention was even and symmetrical around a central score (40–50%). However, the values of P-retention were more than 70% in 144 samples, and less than 50% in only eight samples.

With the relationships between P-retention or S-retention and Al_o + 1/2Fe_o (Figures 4 and 5), a logarithmic regression was obtained for P-retention ($r = 0.863$, $P < 0.001$), agreeing with the relationships reported by Shoji *et al.* (1993). However, a linear regression was obtained for S-retention ($r = 0.780$, $P < 0.001$). According to the WRB system, an Al_o + 1/2Fe_o value of 20 g kg⁻¹ or more and a P-retention of 85% or more are required for andic properties. The approximate curve obtained from P-retention passed close to the intersection of these criteria lines (Figure 4), confirming that P-retention is useful for identifying andic properties. In fact, the latest Japanese soil classification system (Obara *et al.*, 2011) requires only the P-retention or phosphate absorption coefficient as the diagnostic criteria of andic properties. On the other hand, the values of S-retention even in Andosols varied from 0% to 99%, although the sulphate concentration of the S-retention standard solution was only one tenth of the phosphate concentration of P-retention solution (Figure 5). The Cambisols and Umbrisols samples tended to deviate upward from this regression line, indicating these soils have greater sulphate retention in relation to Al_o and Fe_o contents. Therefore, it is assumed that sorbents other than Al_o and Fe_o are important for S-retention of these soils. The correlation coefficients between extractable Al/Fe and S- or P-retention are shown in Table 2 in order to help to identify the dominant sorbent by soil type. Results from Cambisols and Umbrisols were combined for statistical analysis because the number of Umbrisol samples was small.

Table 1 Chemical properties of soil samples by soil type.

	A horizons				B horizons			
	Aluandic Andosols (n=37)	Silandic Andosols (n=24)	Umbrisols (n=4)	Cambisols (n=12)	Aluandic Andosols (n=34)	Silandic Andosols (n=28)	Umbrisols (n=5)	Cambisols (n=28)
pH _{H2O}	4.70 (3.47-5.51)	4.77 (3.8-5.58)	5.21 (4.30-5.55)	4.61 (4.02-4.92)	4.92 (4.02-5.63)	5.21 (4.68-5.98)	5.19 (4.78-5.61)	4.95 (4.68-5.26)
pH _{KCl}	3.88 (2.85-4.63)	4.07 (3.26-4.69)	3.60 (3.30-3.96)	3.68 (2.94-4.12)	4.23 (3.36-4.84)	4.73 (4.07-5.28)	4.06 (3.95-4.18)	3.90 (3.68-4.25)
Total Carbon / g kg ⁻¹	108.5 (33.1-222.8)	145.0 (64.1-295.6)	124.7 (54.3-218.9)	63.0 (19.8-201.3)	37.8 (4.4-125.2)	48.7 (15.9-115.0)	25.7 (2.4-83.3)	8.8 (0.2-22.0)
Al _o / g kg ⁻¹	16.0 (3.6-33.5)	26.5 (2.4-74.8)	9.0 (7.2-10.2)	7.1 (3.0-11.9)	22.5 (6.4-47.6)	43.6 (12.2-86.1)	7.4 (2.5-13.8)	6.8 (2.7-13.5)
Fe _o / g kg ⁻¹	15.0 (6.8-24.6)	13.4 (2.4-25.3)	11.3 (10.1-12.3)	6.5 (3.3-9.8)	18.1 (4.4-33.9)	19.4 (7.5-36.2)	7.0 (2.2-11.7)	5.9 (1.7-13.0)
Si _o / g kg ⁻¹	1.14 (0-7.4)	6.5 (0-23.7)	0.2 (0-0.3)	0.4 (0-1.4)	4.6 (0.2-20.7)	15.8 (0.9-33.1)	0.5 (0-1.0)	0.7 (0.2-3.0)
Al _p / g kg ⁻¹	11.1 (2.7-20.3)	13.7 (2.2-33.6)	7.2 (6.2-7.9)	4.5 (2.3-6.4)	10.3 (1.9-20.1)	9.7 (4.7-27.3)	5.0 (0.8-10.2)	3.3 (1.2-6.3)
Fe _p / g kg ⁻¹	8.1 (4.1-13.8)	7.7 (1.6-13.6)	8.0 (7.3-8.7)	3.8 (2.0-6.0)	7.4 (1.0-18.9)	4.1 (0.4-12.2)	4.0 (0.2-7.4)	2.4 (0.2-5.2)
Al _d / g kg ⁻¹	12.7 (3.3-21.2)	18.3 (3.9-28.5)	8.9 (6.9-10.7)	6.1 (2.8-9.5)	14.6 (3.9-28.5)	17.6 (4.1-32.0)	6.0 (1.4-11.1)	6.0 (1.6-9.2)
Fe _d / g kg ⁻¹	17.1 (9.1-28.0)	13.0 (2.0-21.3)	16.9 (12.7-19.7)	12.6 (5.9-17.3)	19.5 (5.6-33.8)	15.6 (5.2-28.3)	10.8 (2.9-14.6)	15.2 (3.7-35.0)
Exchangeable Al / mg kg ⁻¹	459.6 (15.1-1421.8)	269.2 (7.1-790.5)	682.8 (560.5-854.7)	625.5 (293.6-1357.5)	441.9 (25.6-1892.7)	108.7 (10.9-410.4)	371.9 (255.8-455.4)	617.0 (158.2-2131.9)

For each parameter, the upper line shows the mean value and the lower line shows the range (minimum - maximum) values.

Table 2 Correlation coefficients (r) between extractable Al/Fe and phosphate or sulphate retention.

		Al					Fe				
		Al _d	Al _o	Al _p	Al _d :Al _p	Al _o :Al _p	Fe _d	Fe _o	Fe _p	Fe _d :Fe _p	Fe _o :Fe _p
S-retention											
Aluandic Andosols	(n=71)	0.677	0.827	<u>0.369</u>	0.526	0.776	<i>0.392</i>	0.546	-0.062	0.499	0.668
Silandic Andosols	(n=52)	0.485	0.848	0.018	0.566	0.880	<u>0.308</u>	<i>0.453</i>	-0.549	0.695	0.689
Other soil types	(n=49)	<i>0.478</i>	<i>0.392</i>	-0.026	0.799	0.663	0.677	0.170	-0.214	0.753	<i>0.466</i>
P-retention											
Aluandic Andosols	(n=71)	0.714	0.647	0.650	0.284	0.421	<i>0.368</i>	0.480	0.129	<i>0.344</i>	0.464
Silandic Andosols	(n=52)	0.565	0.623	<i>0.381</i>	0.472	0.565	<i>0.426</i>	<i>0.438</i>	-0.064	0.513	0.462
Other soil types	(n=49)	0.880	0.879	0.711	<i>0.416</i>	0.613	<i>0.463</i>	0.622	<i>0.440</i>	<u>0.300</u>	0.487

Values in underline, italic and bold type are significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

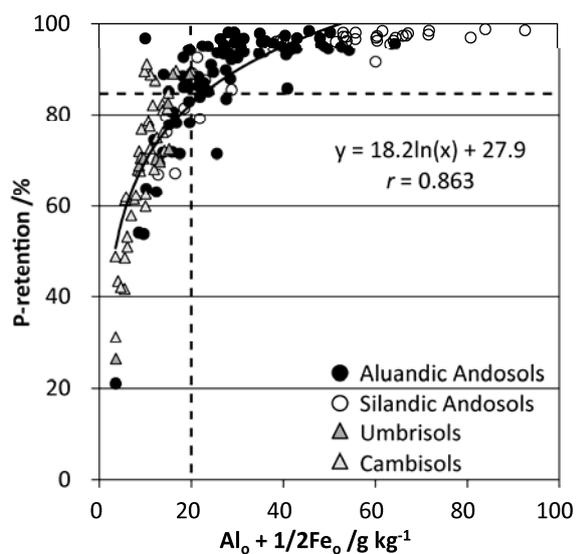


Figure 4 Relationship between Al_o + 1/2Fe_o and P-retention of 172 soil samples. The two broken lines shows the diagnostic criteria of andic properties according to the WRB system.

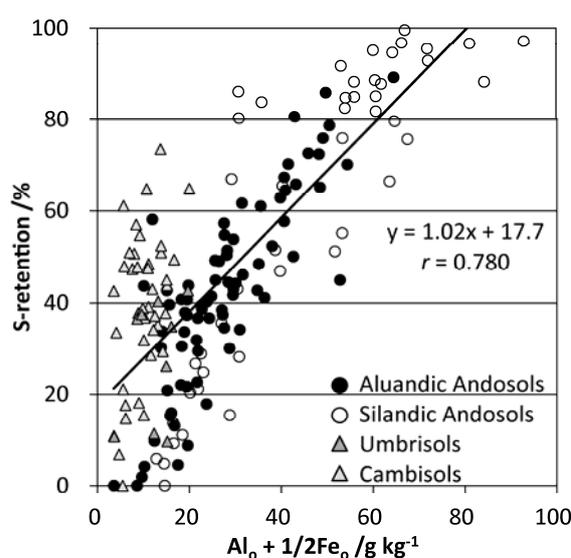


Figure 5 Relationship between Al_o + 1/2Fe_o and S-retention of 172 soil samples.

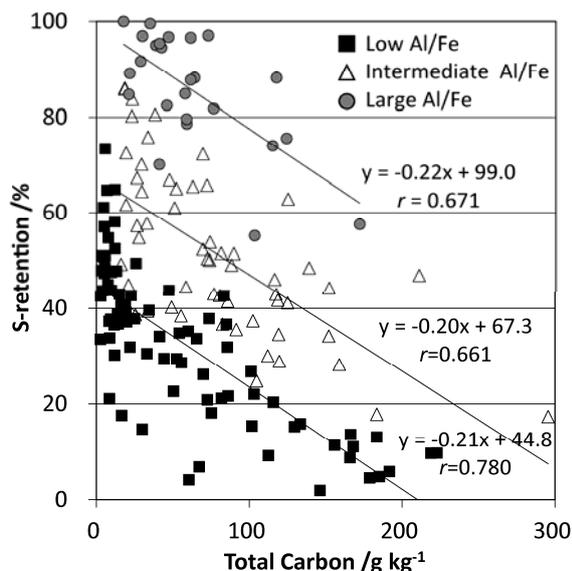


Figure 6 Relationship between Total carbon and S-retention. Low Al/Fe samples are $(Al_o + 1/2Fe_o) < 20 \text{ g kg}^{-1}$, intermediate Al/Fe samples are $20 \text{ g kg}^{-1} < (Al_o + 1/2Fe_o) < 50 \text{ g kg}^{-1}$, and large Al/Fe samples are $(Al_o + 1/2Fe_o) > 50 \text{ g kg}^{-1}$.

For S-retention, both Andosols had similar trends of correlation coefficients, but Cambisols and Umbrisols had poorer correlation with Al_o and Fe_o and better correlation with $(Al_d - Al_p)$ and Fe_d than for Andosols. As discussed previously, $(Al_d - Al_p)$ in Cambisols and Umbrisols represents the Al_{sub} in Fe oxides. Barreal *et al.* (2003) reported that goethite with more Al_{sub} had greater sulphate sorption capacity because specific surface area increased by substitution of Al. Therefore, it is considered that not only Fe_d but also $(Al_d - Al_p)$ contribute to increase S-retention in these soil types. Whereas in P-retention, all soil types had similar trends and positive correlations were found between every extractable Al/Fe category except Fe_p . Unlike P-retention, there was no correlation between Al_p and S-retention, suggesting that sulphate was not sorbed by Al-humus complexes. Moreover, for soil samples with similar $Al_o + 1/2Fe_o$ contents, S-retention tended to decrease with increasing soil organic carbon (Figure 6).

Categorizing method using S-retention and P-retention

Since it is clear that the dominant sorbents of sulphate were different between Andosols and Umbrisols/Cambisols, further correlation analysis was performed for each soil type. Figure 7 shows the relationship between S-retention and the dominant sorbents $[(Al_o - Al_p) + (Fe_o - Fe_p)]$ for Andosols: closed circles are soil samples with the criteria for aluandic Andosols ($Si_o < 0.6\%$ and $Al_p:Al_o > 0.5$) based on the WRB system. The values of S-retention in all aluandic samples were less than

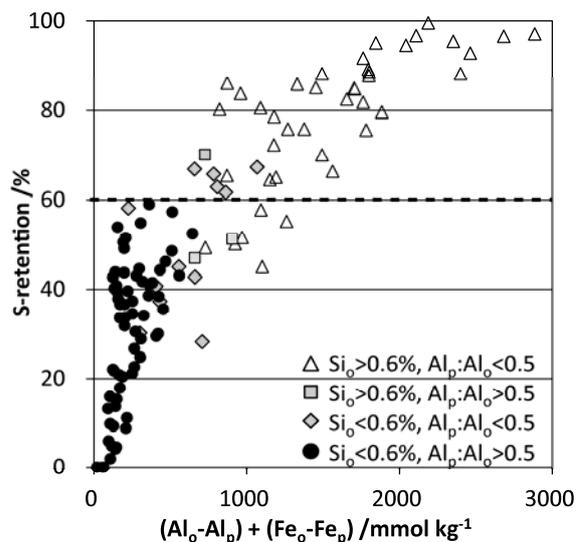


Figure 7 Relationship between $[(Al_o - Al_p) + (Fe_o - Fe_p)]$ and S-retention of Andosols. All aluandic samples (●) have S-retention $< 60\%$ as indicated by the broken line.

60% and were clearly separated from silandic samples ($Si_o > 0.6\%$ or $Al_p:Al_o < 0.5$). Unlike the WRB system, the criteria for aluandic Andosols in the Japanese soil classification system (Obara *et al.*, 2011) is $Si_o < 0.6\%$ or $Al_p:Al_o > 0.5$. In this case, aluandic soil samples were separated from silandic samples by the criterion of S-retention $< 70\%$. In Soil Taxonomy (Soil Survey Staff, 2010), there is no criteria to categorize either allophanic or non-allophanic Andosols although the classification scheme for the new soil order of Andisols was first published by Soil Survey Staff (1990).

Some silandic soil samples with S-retention of $< 60\%$ contained large amounts of total carbon ($> 100 \text{ g kg}^{-1}$) or Si-rich allophane (molar ratio of $(Al_o - Al_p):Si_o < 1.6$). Delmelle *et al.* (2003) reported that Al-rich allophane might permit more sulphate sorption at the mineral surface because allophane with a $(Al_o - Al_p):Si_o$ ratio close to 2 develops variable negative and positive charges than does Si-rich allophane. This explains why our samples had less S-retention than typical silandic samples.

With Umbrisols and Cambisols, a stronger correlation was obtained between S-retention and $[(Al_d - Al_p) + (Fe_d - Fe_p)]$ rather than $[(Al_o - Al_p) + (Fe_o - Fe_p)]$ (Figure 8). Soil samples with a small activity ratio of free iron oxides ($Fe_o:Fe_d < 0.4$) tended to have greater S-retention ($> 30\%$): this ratio is used as a relative measure of the degree of aging or crystallinity of free iron oxides (Blume & Schwertmann, 1969). According to Nagatsuka (1972), the criterion of $Fe_o:Fe_d < 0.4$ is useful to differentiate 'yellow-brown forest soil' which develops in the warm-temperate region of Japan. This soil type usually does

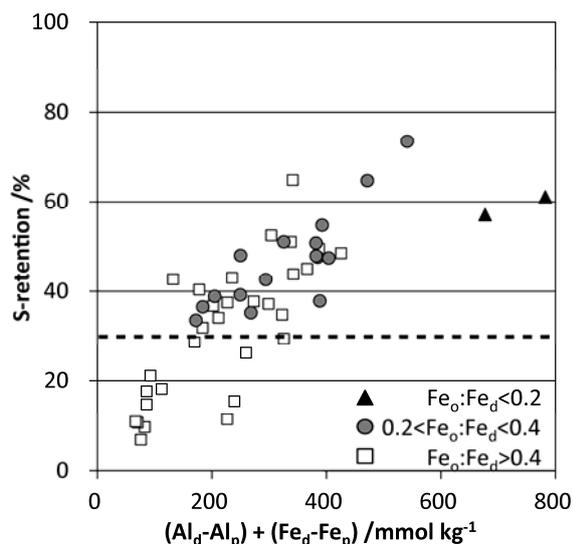


Figure 8 Relationship between $[(Al_d - Al_p) + (Fe_d - Fe_p)]$ and S-retention of Umbrisols and Cambisols. Highly weathered Cambisols with a small activity ratio of free iron oxides ($Fe_o:Fe_d < 0.4$) tend to have a relatively large S-retention ($>30\%$) as indicated by the broken line.

not have a definite Argic horizon, however it is more highly weathered than ‘brown forest soil’ in the cold-temperate region but less weathered than ‘red-yellow soils’ in the humid subtropical climate region of Japan. In regions such as Japan, which are covered by relatively young soils, it is important in the management of agriculture and forestry to divide Cambisols into brown forest soil and yellow-brown forest soil. The trend of soils with a small activity ratio having a large S-retention was not found for P-retention, for which the values were little different regardless of the amount of extractable Al/Fe or ratio of $Fe_o:Fe_d$.

The trends of P-retention and S-retention are different for each soil type as the scatter diagram of P-retention and S-retention in Figure 9 shows. Using the criteria of extractable Al and Fe from the WRB system and the activity ratio, each soil sample was easily categorized as follows: (i) P-retention $>85\%$ and S-retention $>60\%$ are silandic soils; (ii) P-retention $>85\%$ and S-retention $<60\%$ are aluandic soils; (iii) P-retention $<85\%$ and S-retention $>30\%$ are samples of highly weathered Cambisols with $Fe_o:Fe_d < 0.4$ (yellow-brown forest soils); and (iv) P-retention $<85\%$ and S-retention $<30\%$ are samples of Umbrisols or Cambisols with $Fe_o:Fe_d > 0.4$ (brown forest soil).

The amounts of native sorbed sulphate of the forest soil samples used in this study ranged from 0.15 to 47.7 $mmol\ kg^{-1}$, so we considered this method to be useful regardless of the content of native sulphate in the case of forest soils. However, it is necessary to assess its applicability to agricultural soil samples heavily fertilized with phosphate. In addition, only the amounts of extractable Al and Fe were discussed as the sorbent

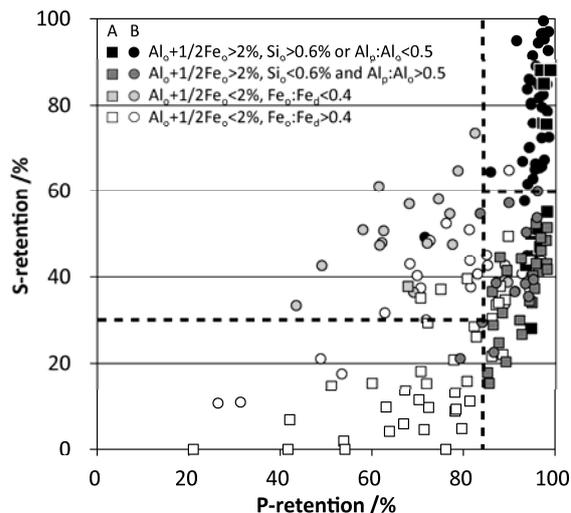


Figure 9 Scatter diagram of P-retention and S-retention. A vertical broken line marks P-retention of 85%; the two horizontal broken lines are at S-retention of 60% and 30%.

of sulphate in the present study. However, the amount of sulphate sorption cannot be necessarily predicted on the dominant type of the minerals or their contents (Barreal *et al.*, 2003), and depends more on the degree of crystallinity and the specific surface than on the total content (Borggaard, 1983). Further mineralogical study is required to understand the characteristics of sulphate sorption by soils with more complicated colloidal components such as aluandic Andosols derived from highly weathered soils reported by Caner *et al.* (2000).

Conclusions

The sulphate-sorption experiment (sulphate retention) was conducted by modifying the common method for phosphate retention. The results from correlation analyses with extractable Al and Fe showed that the characteristics of sulphate retention are different from phosphate retention. Namely, little sulphate is sorbed by Al-humus complexes (Al_p), and the values of sulphate retention even in Andosols varied from 0% to 99% and closely reflect the amount of extractable Al and Fe. Therefore, sulphate retention in the present study can be proposed as a simplified method for categorizing Andosols into silandic and aluandic Andosols. Moreover, Fe oxides (Fe_d and Al_{sub}) largely contribute to sulphate retention in non-Andosols with small amounts of Al_o and Fe_o , indicating that highly weathered Cambisols has relatively large sulphate retention despite of low phosphate retention. Since the amounts of these anion sorption might be determined by the quantity and quality of the colloids in soils, it would be possible to develop a more effective method for categorizing

soils using the combination of different characteristics of anion sorption. Further study is required to obtain the chemical and mineralogical information on the sorption of sulphate.

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