C-3.2.3   Studies on Estimation of Acid-Buffering Capacity of Soils

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Abstract. (1) Soil columns of a volcanic ash soil and a granitic soil were leached with simulated precipitations for 85 weeks to compare acid-buffering capacities. Significantly higher concentration of Al was dissolved from acidified volcanic ash soil. Volcanic ash soil had significantly higher SO_4^{2-} adsorption capacity, but adsorption of input SO_4^{2-} was limited due to large amount of native SO_4^{2-}. Magnesium and Ca release rates from mineral dissolution in volcanic ash soil, estimated according to mass balances, were one order of magnitude higher than those rates reported for soil environments in Europe and North America. (2) Element release rates were measured for a volcanic ash soil and a granitic soil, employing flow-through column technique. Steady-state Mg and Ca release rates of volcanic ash soil at pH 4 were almost ten times higher than granitic soil, indicating high cation release rates from mineral dissolution. (3) Extractable SO_4^{2-} contents and SO_4^{2-} adsorption isotherms were determined on forest volcanic ash soils to investigate the effect of accumulated SO_4^{2-} on acid buffering capacity. Sulfate adsorption capacity was found to depend largely on Al content in allophane and clay content. Large amount of SO_4^{2-} had already been adsorbed to soils with high adsorption capacities, thus increase in adsorbed SO_4^{2-} was estimated to be relatively small even if soil solution SO_4^{2-} increased. Therefore, acid buffering capacity by SO_4^{2-} adsorption was considered not to correspond to SO_4^{2-} adsorption capacity of soil. (4) Throughfall and soil solution were observed in a forest to asess the effect of precipitated proton on soil. Nitrate and base cation concentrations were significantly higher in O horizon soil solution than in throughfall, suggesting that large amount of protons were being produced by nitrification and neutralized by base cation release in the O horizon. Proton production by nitrification in O horizon was estimated as much as 5 $kmol_c$ ha^{-1} yr^{-1}. Therefore, the adverse effect of precipitated protons was considered to be small on the studied soil.

Key Words Acid-buffering capacity, Sulfate adsorption, Volcanic ash soil, Soil column, Mineral dissolution

1. Introduction

In order to predict the effect of acid deposition on soil environments, it is essential

to evaluate the buffering capacities in soil which work against long-time load of relatively low concentration of acidic substances. On that view point, attention was paid to sulfate adsorption and primary mineral dissolution in this research. These acid-buffering capacities were investigated on soils from different parent materials (volcanic ash and granite) through long-term soil column leaching experiment, as well as mineral dissolution and sulfate adsorption experiment.

In soil environments, proton is loaded not only by acid deposition, also by nitrification, respiration and cation uptake by plant roots. On the other hand, proton is also consumed by anion uptake by roots and cation supply from the litter. Therefore, proton budget was studied in a forested environment to asess the effect of deposited proton on the soil.

2. Materials and Methods
Long-Term Soil Column Leaching Experiment

A volcanic ash soil and a granitic soil were packed in acrylate columns to the height of 10 cm (Fig. 1). Water condition in the soil columns was kept close to field state by applying tension of 50 cm H_2O. Three simulated precipitations (Table 1) were applied at the rate of 10 mm h^{-1} for 6 hours each week, for 85 weeks. The composition of non-acidic precipitation was set close to the average composition of throughfall of red pine in Tsukuba[11], and acidic precipitations were made by adding H^+, NH_4^+, NO_3^- and SO_4^{2-} to the non-acidic one.

Table 1 Chemical composition of simulated precipitations ($\mu mol_c L^{-1}$) .

	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Non-acidic	1	60	30	40	20	50	20	30	150
Acidic 1	100	120	30	40	20	50	20	80	260
Acidic 2	300	240	30	40	20	50	20	180	480

Leachates were collected each week and analyzed for pH, BCG alkalinity, NH_4, Na, K, Mg, Ca, Al, Cl, NO_3 and SO_4 to calculate the proton budget[8] for each soil column.

After 85 weeks of leaching, soils were removed from the columns and air-dried. Exchangeable cations (Na, K, Mg and Ca) were extracted from the air-dried soils with 1 mol L^{-1} CH_3COONH_4, and determined by flame emission or atomic absorption spectrometry.

Mineral Dissolution Experiment

The volcanic ash soil and granitic soil were treated with H_2O_2 to decompose organic compounds, and 2-2000 μm fractions were collected by sedimentation method. For the volcanic ash soil, 20-2000 μm fraction was also prepared to remove clay minerals as much as possible.

For 20-2000 μm fraction of volcanic ash soil and 2-2000 μm fraction of granitic soil, specific surface area was determined by BET method, and elemental composition was determined by XRF analysis. Primary minerals of those samples were identified as shown in Table 2 by XRD analysis. Rock type of the tephra of the volcanic ash soil is supposed to be dacitic.[10]

Table 2 Characterristics of the samples for dissolution experiment.

	Specific surface area $(m^2\ g^{-1})$	Primary minerals
Volcanic ash soil $(20-2000\mu m)$	6.4	hypersthene, plagioclase, quartz
Granitic soil $(2-2000\mu m)$	5.4	quartz, orthoclase, plagioclase

Dissolution experiment was conducted in a flow-through column system using HCl solution (Fig. 2), in order to eliminate the effects of stirring, pH-buffer and formation of secondary solid phase. Disposable syringe with $0.45\mu m$ filter (Whatman Autovial) was used as the reacting cell. One to 2.4g of mineral sample was placed in the cell, and HCl solution (0.1 or 1.0 mmol L^{-1}) was passed through the cell at the rate of 2-3 mL h^{-1} at 20 °C. Sample solution was collected in pre-weighed polyethylen bottles at intervals of several days. pH of the sample solutions was determined by glass electrode method, and Mg, Ca, Al, Si and Fe were determined by ICP-AES to calculate release rate of each element.

Extractable Sulfate Content in Forest Volcanic Ash Soil

Sulfate in volcanic ash soils of 74 horizons from 12 pedons was extracted by 0.01 mol L^{-1} Na_2HPO_4 (soil:solution = 1:50) and determined by ion-chromatography. Oxalate-extractable Al (Al_o) and pyrophosphate-extractable Al (Al_p) were extracted after Blakemore *et al.*[1] and determined by ICP-AES.

Sulfate adsorption isotherms were determined on 20 soils. Air-dried soil was shaked with 0.01 mol L^{-1} CaCl solution containing 0-0.6 mmol L^{-1} of K_2SO_4 for 12 hours. Total adsorbed SO_4 was determined from extractable SO_4 content and change in solution concentration after reaction. The adsorption data were fitted to either Langmuir or Freundlich adsorption isotherm by non-linear least square method.

Proton Budget in a Forest Soil

Duplicate zero-tension lysimeters, 10cm in length and 20cm in width, were inserted into a soil profile in a forest at National Institute of Agro-Environmental Sciences just beneath the O horizon and at the depth of 30cm. Percolated soil solution was collected after each rain event from May, 1994 to November, 1995, along with the throughfall which was collected by duplicate polyethylen funnels of 30cm in diameter. The soil solutions and throughfalls were analyzed for pH, BCG alkalinity, Na, K, NH_4, Mg, Ca, Al, Cl, NO3 and SO_4.

3. Results and Discussion
Long-Term Column Leaching Experiment

Total proton load for 85 weeks was quite different between the two soils (Fig.3). Large amounts of protons were produced by nitrification in volcanic ash soil columns. Thus, with simulated precipitation "acidic 2", the total proton load was as high as 8 0mmol$_c$ kg^{-1} in volcanic ash soil column, while it was limited to 20mmol$_c$ kg^{-1} in granitic soil column.

"Acidic 2" caused acidification in both soils (Fig. 4). For volcanic ash soil, leachate pH was decreased to 4.4 and 0.13 mmol L^{-1} Al was dissolved in 70 weeks in each of the

duplicate soil columns. For granitic soil, on the other hand, leachate pH gradually decreased to 4.2 at 85 week in only one of the duplicate soil columns. The reason for the difference among duplicate granitic soil columns is not yet clear. However, it is obvious that there is a significant difference between the two soils regarding dissolved Al concentration after acidification, i.e., Al dissolved from granitic soil was only 0.02 mmol L^{-1} even when pH had decreased to 4.2. As mentioned later in the section of minaral dissolution experiment, it is infered that fast-dissolving secandary minerals, like allphane, are one of the sources that caused high concentration of dissolved Al in the volcanic ash soil leachate.

As shown by adsorption isotherms (Fig. 5), the volcanic ash soil had a significantly higher SO_4^{2-} adsorption capacity than the granitic soil. However, the volcanic ash soil adsorbed less SO_4^{2-} from simulated precipitations "non-acidic" and "Acidic 1" than granitic soil (Fig. 3), due to the large amount of SO_4^{2-} already adsorbed to the volcanic ash soil.

Table 3   Base cation supply in 85 weeks by mineral dissolution in volcanic ash soil columns

Simulated precipitations	Proton loads	Ca	Mg	Supply rates Ca	Mg
	---------------- ($mmol_c$ kg^{-1}) ------------			--- ($mmol_c$ $kg^{-1}yr^{-1}$) ---	
Non-acidic	38	4.4	1.9	2.7	1.2
Acidic 1	50	6.4	2.3	3.9	1.4
Acidic 2	80	7.7	2.9	4.7	1.8

Mass balance calculation implies that 4.4-7.7 $mmol_c$ Ca kg^{-1} and 1.9-2.9 $mmol_c$ Mg kg^{-1} were supplied by mineral dissolution in 85 weeks in volcanic ash soil columns (Table 3). For granitic soil colmns, supply of these cations by mineral dissolution could not be detected. Calcium and Mg supply rate was 3.9 $mmol_c$ $kg^{-1}yr^{-1}$ in the volcanic ash soil column leached with non-acidic precipitation. If soil depth is assumed to be 1 m, this rate is equivalent to cation supply rate of 39 $kmol_c$ ha^{-1} yr^{-1}, whereas most of the cation supply rates observed in soil environments in Europe and North America are not more than 3 $kmol_c$ ha^{-1} yr^{-1}.[7]

Mineral Dissolution Experiment

When $2-2000\mu$m fraction of the volcanic ash soil was leached with 0.1 mmol L^{-1} HCl, pH was increased to 4.6 due to rapid release of Al and Si, making it impossible to determine cation release rates at pH4 (Fig. 6). The rapid release of Al and Si is supposed to have resulted from rapid dissolution of allophane remaining in this fraction, because the ratio of release rates (Al/Si) was almost the same as Al/Si ratio in allophane. Thus, $20-2000\mu$m fraction was prepared for volcanic ash soil in order to remove clay minerals further.

Steady-state cation release rates at pH4 were compared between $20-2000\mu$m fraction of volcanic ash soil and $2-2000\mu$m fraction of granitic soil (Fig. 7 a, b and Table 4). For volcanic ash soil, release of each element got steady before 600 h, and pH was lower than 4.2. For granitic ash soil, release of Si, Al and Mg got steady in 500 h, but steady-state release was not found either for Ca or for Fe. Nevertheless, steady-state release rates of these elements can be estimated to be less than 0.1 μmol kg^{-1} h^{-1}. Mg and Ca release rates of volcanic ash soil, 3.4 and 2.3 μmol kg^{-1}

h^{-1} respectively, were 10 times or more higher than those of granitic soil, indicating that cations are supplied at high rates in volcanic ash soil.

Ratios of release rates of Mg and Ca to Si, for volcanic ash soil, were about three times as high as ratios of contents in the 20-2000μm fraction. This means, if congruent dissolution is assumed, that major portions of Mg and Ca were supplied by dissolution of minerals that were rich in Mg and/or Ca. Taking into account the results of XRD analysis, major sources of Mg and Ca are thus to be hypersthene and plagioclase, respectively. Volcanic glass is regarded as the most susceptible to chemical weathering among primary minerals in volcanic ash soils.[6] However, Mg and Ca contents in volcanic glasses, from rhyolitic to andecitic, are not more than 1% and 3% as oxides, respectively,[12] whereas MgO content in hypersthene is as much as 17% if composition of hypersthene is $Mg_{0.5}Fe_{0.5}SiO_3$. Thus, hypersthene could be the major source of Mg in volcanic ash soil, even if volcanic glass dissolves most rapidly.

Table 4 Steady-state element release rates at pH4 or pH3

| | volcanic ash soil (20-2000μm) | granitic soil (2-2000μm) | |
	pH4	pH4	pH3
	(μmol kg^{-1} h^{-1})		
Si	11.9	3.6	16.5
Al	15.6	4.4	26.3
Mg	3.4	0.3	3.6
Ca	2.3	$\leqq$0.1	$\leqq$0.5
Fe	1.1	<0.1	
	(mol m^{-2} h^{-1})		
Si	1.9×10^{-9}	6.7×10^{-10}	3.1×10^{-9}
Al	2.4×10^{-9}	8.1×10^{-10}	4.9×10^{-9}
Mg	5.3×10^{-10}	0.6×10^{-10}	6.7×10^{-10}
Ca	3.6×10^{-10}	$\leqq$0.2×10^{-10}	$\leqq$0.9×10^{-10}
Fe	1.7×10^{-10}	<0.2×10^{-10}	
	ratios of release rates*		
Al/Si	1.31 (0.303)	1.22	1.59 (0.472)
Mg/Si	0.29 (0.083)	0.10	0.22 (0.027)
Ca/Si	0.19 (0.069)	$\leqq$0.03	$\leqq$0.03 (0.007)
Fe/Si	0.09 (0.118)	<0.03	(0.049)

*( ):Elemental ratios in mineral samples

Mg release rate from granitic soil at pH3 was 10 times higher than at pH4 (Fig. 7c, Table 4). This means that major Mg source in granitic soil has a high pH dependency for dissolution rate.

Extractable Sulfate and Sulfate Adsorption Capacity of Forest Volcanic Ash Soils

As shown in Fig. 8, SO_4^{2-} adsorption capacities of forest volcanic ash soils, which were

represented by the adsorption isotherms, varied depending on pedons and horizons. However, SO_4^{2-} adsorption at a specific concentration was able to be represented by a multiple regression equation with Al_o - Al_p and clay content as the independent variables, like equation (1).

$$Q = 2.69(Al_o - Al_p) + 0.152f_{clay} + 1.91 \quad (r^2 = 0.716^{***}, n = 16) \quad (1)$$

Q: adsorbed SO_4^{2-} at 0.1mmol L^{-1} SO_4^{2-} (mmol kg^{-1})

Al_o : oxalate-extractable Al (%)

Al_p : pyrophosphate-extractable Al (%)

f_{clay} : clay content (%)

Since Al_o - Al_p represents Al content in allophane,[9] above result implies that SO_4^{2-}adsorption capacity of volcanic ash soil depends largely on Al content in allophane and clay content.

In order to investigate the relationship between extractable SO_4^{2-} content and SO_4^{2-} adsorption capacity in forest volcanic ash soils, extractable SO_4^{2-} contents were plotted against amounts of SO_4^{2-} adsorbed in 0.1 mmol L^{-1} SO_4^{2-} solution (Fig. 9). Sulfate adsorption in 0.1 mmol L^{-1} SO_4^{2-} solution was chosen to represent the SO_4^{2-} adsorption capacity of indivisual soils, because SO_4^{2-} in forest soil solutions were generally less than 0.1 mmol L^{-1},[4, 5] and SO_4^{2-} adsorption did not show large increase over 0.1 mmol L^{-1} SO_4^{2-}(Fig. 8). It was found that extractable SO_4^{2-} content was close to adsorbed SO_4^{2-} in 0.1 mmol L^{-1} SO_4^{2-} solution. Thus, SO_4^{2-} adsorption capacity of indivisual soils is represented in the extractable SO_4^{2-} content. Moreover,taking into account the fact that most of extractable SO_4^{2-} is adsorbed SO_4^{2-}, major parts of the SO_4^{2-} adsorption capacity in these soils are already occupied.

In order to estimate the acid-buufering capacity by SO_4^{2-} adsorption, increases in adsorbed SO_4^{2-}, correponding to 0.1 mmol L^{-1} of increase in soil soluiton SO_4^{2-}, were calculated based on extractable SO_4^{2-} contents, SO_4^{2-} adsorption isotherms and field-state water contents (Fig. 10). The calculated increases were not more than 8 mmol kg^{-1}, and had no correlation with SO_4^{2-} adsorption capacities. This means that acid-buffering capacity by SO_4^{2-} adsorption in forest volcanic ash soils do not correspond to SO_4^{2-} adsorption capacity, because large amount of SO_4^{2-} is already adsoebed by soils of high SO_4^{2-} adsorption capacity.

In this research, SO_4^{2-} adsorption capacity (adsorption isotherm) was determined in 0.01 mol L^{-1} $CaCl_2$ solution without pH adjustment. Sulfate adsorption is believed to be influenced by pH, ion strength and organic substances in ecosystems.[2,3] Solution pH in SO_4^{2-} adsorption experiments was, in most cases, lower than soil pH, thus underestimation of SO_4^{2-} adsorption capacity is unlikely with regard to pH. However, ion strength was probably significantly higher than natural soil solution. Therefore, further investigation on effect of ion strength may be needed for more precise estimation of acid-buffering capacity.

Proton Budget in a Forest Soil

Discussion is done based on the volume-weighted mean concentrations of throughfall and soil solution, because ion fluxes could not be calculated due to low efficiency of the zero-tension lysimeters used. Nitrate and base cation concentrations were significantly higher in O horizon soil solution than in throughfall, suggesting that large amount of protons were being produced by nitrification and neutralized by base cation release in the O horizon. Proton

production rate by nitrification in O horizon was estimated to be as much as 5 $kmol_c$ ha^{-1} yr^{-1}, based on NH_4^+ and NO_3^- concentrations in throughfall and O horizon soil solution, and on the water flux by throughfall. Therefore, the adverse effect of precipitated protons on soil was considered to be relatively small on the studied site.

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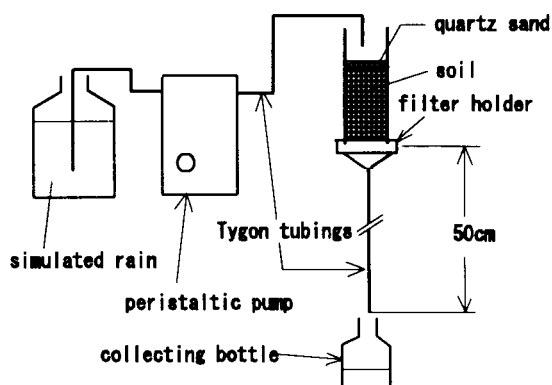
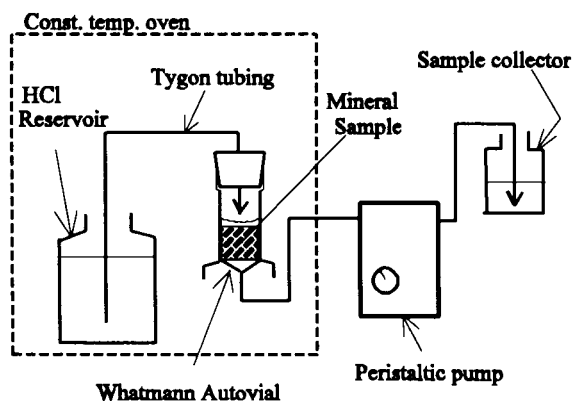Fig. 1 Apparatus for long-term soil column leaching experiment.

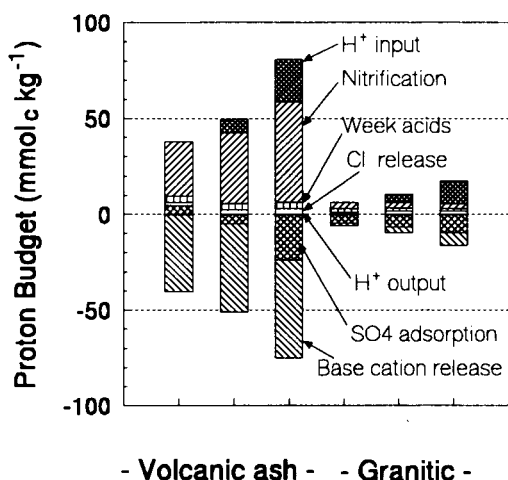
Fig. 2 Apparatus for dissolution experiment.

- Volcanic ash - - Granitic -

Fig. 3 Proton budgets of soil columns of a volcanic ash soil and a granitic soil leached with 3 kinds of simulated precipitations for 85 weeks.
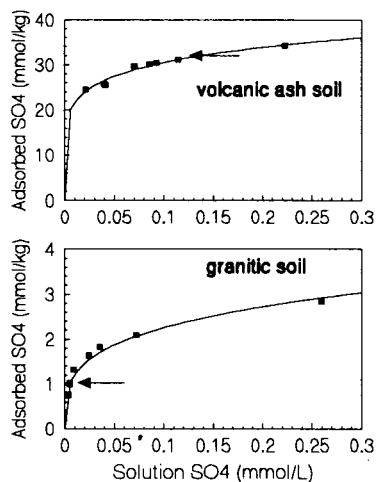

Fig.5 Sulfate adsorption isotherms of the soils used in long-term column leaching experiment. Arrows indicate extractable sulfate contents of the soils.
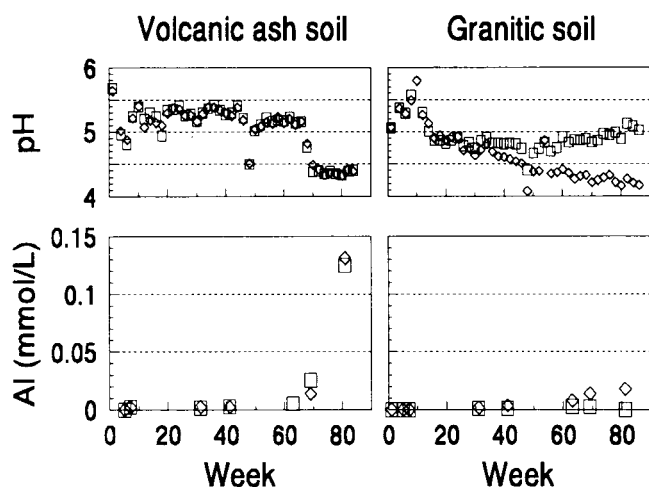

Fig. 4 pH and Al concentration in the leachates from duplicate soil columns leached with simulated precipitation 2.
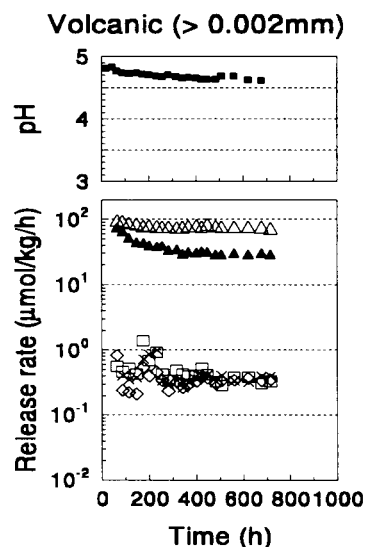
Fig. 6 Element release rates from 2-2000 μm fraction of volcanic ash aoil leached with 0.1 mmol L^{-1} HCl. $\triangle$, Al; $\blacktriangle$, Si; $\diamondsuit$, Mg; $\square$, Ca; $\times$, Fe.

Volcanic (> 0.02mm) Granitic (> 0.002mm) Granitic (> 0.002mm)
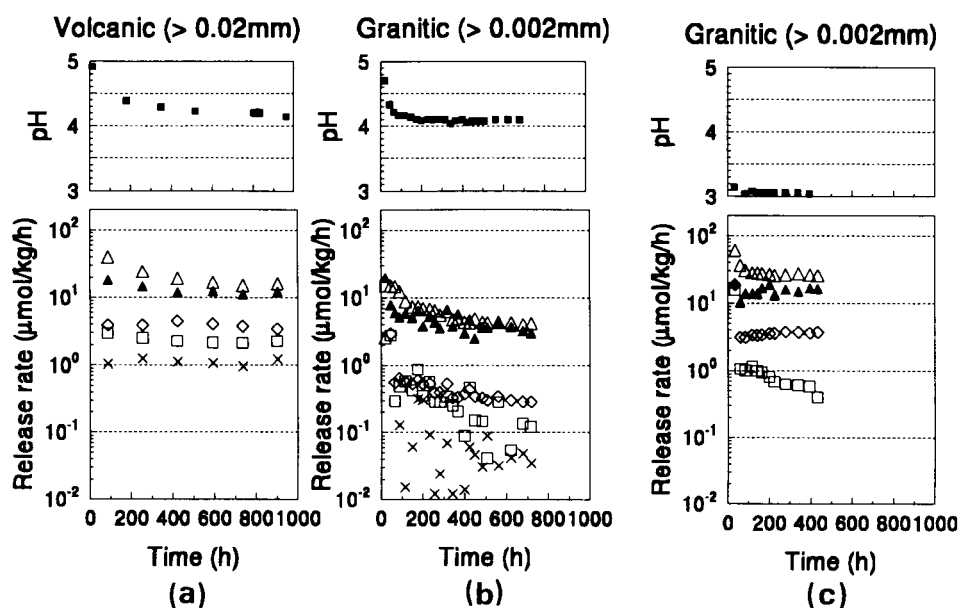

(a)   (b)   (c)

Fig.7 Element release rates from samples leached with HCl solution. (a)20-2000μm fraction of volcanic ash soil with 0.1mmol L^{-1} HCl; (b)2-2000μm fraction of granitic soil with 0.1mmol L^{-1} HCl; 2-2000μm fraction of granitic soil with 1.0mmol L^{-1} HCl. △, Al; ▲, Si; ◇, Mg; □, Ca; ×, Fe.
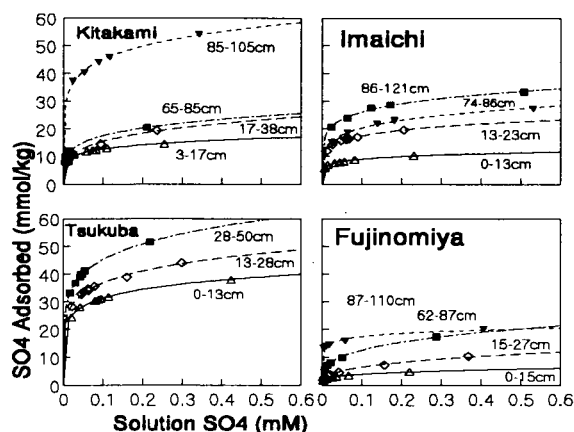
Fig. 8 Sulfate adsorption isotherms of forest volcanic ash soils from 4 pedons.
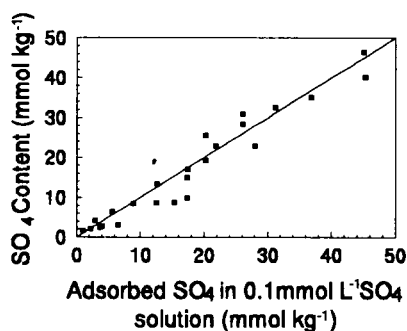
Fig. 9 Relationship between extractable sulfate content and sulfate adsorption capacity in forest volcanic ash soils.
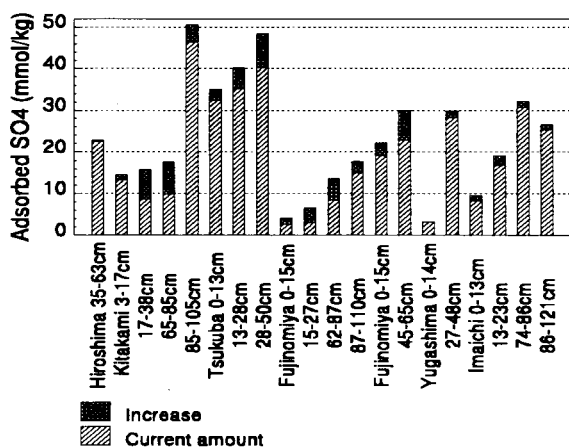

Fig. 10 Current amount of adsorbed sulfate in forest volcanic ash soils and its predicted increase when soil solution sulfate concentration has been inceased by 0.1mmol L^{-1}.
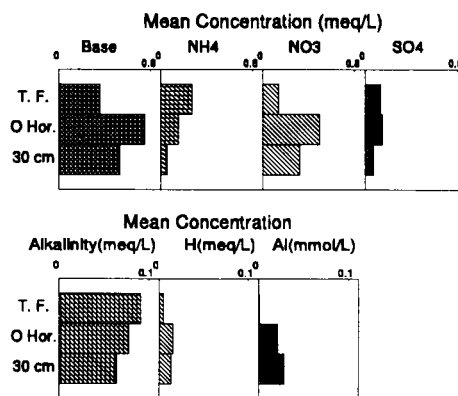

Fig. 11 Volume-weighted mean concentrations in throughfall and soil solution in a forest.