

C-1.1.3 Research on critical load estimation with soil response models to acidic substances

Contact Person Junko Shindo

Global Agro-Environment Research Team, National Inst. of Agro-
Environmental Sciences, Ministry of Agriculture, Forestry and Fisheries
3-1-1 Kannondai, Tsukuba, Ibaraki 305 Japan
Phone +81-298-38-8356, Fax +81-298-38-8199
E-mail shindo@ss.niaes.affrc.go.jp

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Abstract

To evaluate the acid buffering capacity of chemical processes, the following models were developed: 1) An extended constant capacitance model was valid to simulate SO_4^{2-} adsorption to soils, assuming protonation of surface hydroxyl groups and formation of outer sphere complex with SO_4^{2-} . 2) Dissolution rate constants of volcanic glasses were derived from dissolution experiment data and introduced into a existing mineral weathering model (PROFILE model). 3) A dynamic model was applied to the field condition and changes in soil solution chemistry agreed with the observations. According to the field measurements, base cation budget was investigated. Net production of base cation in soil was negative and contribution of plant uptake and release from soil were evaluated. Measurement of Sr isotope ratio made it possible to give tentative estimation of mineral weathering rate in the field. Comparison of measured weathering rate to the estimation with modified PROFILE suggested that the base cation is mainly supplied from sandy fraction of soil.

Key Words: Soil acidification model, Mineral weathering, Sulfate adsorption, Ion budget

1. Introduction

Acidic substances of anthropogenic and natural origin are neutralized in soil by the chemical reaction in soil solution and in the adsorption layer on the colloidal surface. Acidic substance are also neutralized through material cycle between atmosphere, vegetation and soil. Acid neutralizing capacity of soil is an important factor to determine the ecosystem sensitivity to the acidic deposition. Therefore, it is necessary to evaluate the buffering mechanisms and their capacity of various soils quantitatively in order to estimate the ecosystem impact due to acid deposition.

Cation exchange was well formulated in the existing soil acidification models. In recent years mineral weathering has recognized as an important mechanism in a long-term evaluation and several kinds of methods were proposed for estimation of weathering rate mainly in Europe and in North America. In Japan, however, there are few data on it. Moreover, it has been pointed out that the estimated weathering rates differ markedly according to the method.

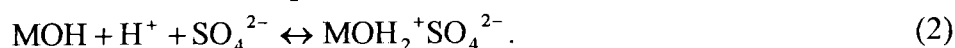
The first objective of the research is to extract the processes for which numerical estimation and modeling are not sufficient and to investigate the method of quantification of buffering capacity of these processes. We especially focus on the mineral weathering and sulfur adsorption. The second objective is estimation of material flow in forest ecosystems and contribution of buffering mechanisms by means of field observation and a model considering various chemical processes.

2. Research Method

(1) Sulfate adsorption model

Sulfate adsorption experiment was carried out for three volcanic soils and three granitic soils with the solutions of three levels of pH and several levels of SO_4^{2-} concentrations to obtain the SO_4^{2-} adsorption as a function of pH and SO_4^{2-} concentrations.

The model based on the extended constant capacitance model¹⁾ was developed. It assumes protonation of surface hydroxyl groups of oxide minerals on the inner plane, and formation of complex with SO_4^{2-} on the outer plane, as



This model determines SO_4^{2-} and H^+ adsorption as the functions of two independent variables, SO_4^{2-} and H^+ concentrations, while including six soil dependent parameters, *i.e.* $[\text{MOH}]_{\text{tot}}$ (mol kg^{-1}), the amount of surface hydroxyl groups per unit mass of soil; S ($\text{m}^2 \text{kg}^{-1}$), surface area of the SO_4^{2-} adsorbing minerals per unit mass of soil; C_1 ($\text{C m}^{-2} \text{V}^{-1}$), capacitance between the inner plane and the outer plane; C_2 ($\text{C m}^{-2} \text{V}^{-1}$), capacitance between the outer plane and the bulk solution; $K_{\text{OH}_2}^{\text{intr}}$, intrinsic equilibrium constant of reaction (1); $K_{\text{SO}_4}^{\text{intr}}$, intrinsic equilibrium constant of reaction (2).

In the model application, $[\text{MOH}]_{\text{tot}}$ was assumed to be $0.1 \times (\text{Al}_0 - \text{Al}_p)$, where Al_0 (mol kg^{-1}) is the acid oxalate extractable Al content, Al_p (mol kg^{-1}) is the pyrophosphate extractable Al content of the soil. S , C_1 and C_2 were bundled into two parameters, $S C_1$ and $S C_2$, since they appear in the governing equations only in the forms of the two products. The values of $K_{\text{SO}_4}^{\text{intr}}$, $S C_1$ and $S C_2$ were optimized to fit calculated SO_4^{2-} adsorption to the experimental data. The value of $K_{\text{OH}_2}^{\text{intr}}$ was optimized so that the highest net surface charge is approximately zero.

(2) Estimation of base cations budget based on field surveys

The field survey was initiated from August in 1997 in a red pine forest in Kannondai (Light Colored Andosols) and mixed deciduous forest in Yasato (granitic Brown Forest Soils).

The following parameters were measured for surface soil (0 to 20 cm of depth) and subsoil (sampled from 20 to 50cm of depth) in both sites; soil pH, concentration of exchangeable cations, element contents and particle size distribution. Mineral composition and surface area were also measured for each of the clay, silt, fine sand and coarse sand fraction.

Rain, throughfall, O-horizon leachate and soil solution were collected every 10 to 14 days in Kannondai and every month in Yasato and ionic concentrations were measured. Soil solution was collected at the boundary of A and B horizon (20 cm in depth) and at the depth of 50 cm with ceramic porous cups. Precipitation and water contents in soil horizons of 0 to 20 cm and 20 to 50 cm were measured every hour with TDR and were used for estimating water flux through soil layers with the following equation:

$$W_{\text{flux}}(t) = \max(W(t-1) + W_{\text{in}}(t) - \max(W(t), W_f), 0) \quad (3)$$

where $W_{\text{flux}}(t)$, $W_{\text{in}}(t)$ and $W(t)$ denote water flux from objective soil layer, water input to the layer and water contents, respectively, of the t th day. W_f means field capacity that was estimated as the average water content of the second day after heavy rain.

(3) Estimation and modeling of mineral weathering rates

(a) Mineral weathering based on strontium isotope ratio

Sr isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) has been used for estimation of biogeochemical cycling of Ca, based on the inherent isotope ratio of parent rocks, eolian minerals from desert, sea salt etc.²⁾. Isotope ratios were measured for soil and water samples collected in Kannondai and in Yasato.

Isotope ratio of soil solution was considered to be determined by mixing the BC release from soil minerals and input through the O-horizon, whose contribution were X and 1-X, respectively. Weathering rate of Ca, for instance, was estimated based on X derived by the following equation and Ca flux measurements from O-horizon..

$$X = \{R_S / (1 + R_S) - R_O / (1 + R_O)\} / \{R_M / (1 + R_M) - R_O / (1 + R_O)\} \quad (4)$$

where R_S , R_O , and R_M are isotope ratio of soil solution, O-horizon leachate and soil minerals, respectively.

(b) Mineral Weathering Model

PROFILE³⁾ was modified for application to volcanic soils, by introducing dissolution rate constants of volcanic glasses. In PROFILE, the dissolution rate of each mineral, r (keq base cations $m^{-2} s^{-1}$), is described as

$$r = k_H \frac{[H^+]^{n_H}}{f_H} + \frac{k_{H_2O}}{f_{H_2O}} + k_{CO_2} P_{CO_2}^{n_{CO_2}} + k_R \frac{[R^-]^{n_R}}{f_R}, \quad (5)$$

where k_H , k_{H_2O} , k_{CO_2} and k_R are the rate constants of dissolution reactions with H^+ , water, dissolved CO_2 and organic acid anions, respectively, n_H , n_{CO_2} and n_R are reaction orders, f_H , f_{H_2O} and f_R are coefficients of inhibiting effects of Al^{3+} , base cations and organic acid anions. In order to derive the dissolution rates constants of volcanic glasses, k_H , k_{H_2O} and n_H with respect to Si were determined from the data of dissolution experiment of obsidian⁴⁾. Then, k_H and k_{H_2O} with respect to base cations were derived for basaltic and dacitic volcanic glasses considering the chemical composition of these types of glasses⁵⁾. Values of f_H , f_{H_2O} and f_R were set to 1.0.

Modified PROFILE was applied to the Kannondai soil and other two volcanic soils (Fujinomiya III C horizon and Yugashima II C horizon) for which weathering rates were determined in dissolution experiments at pH 4.

(4) Development and application of a dynamic soil acidification model

A dynamic model was developed that predict temporal changes of soil chemical properties. Cation exchange, dissolution of Al-hydroxide, sulfate adsorption etc. were incorporated in the model as equilibrium reactions. Validity of the model was investigated by applying the model to the soil acidification experiments with respect to 12 soil samples. The model was also applied to the result of the field measurements in Kannondai and Yasato, and buffering mechanisms controlling the soil chemistry and their relative contribution were examined for each forest.

3. Results and Discussion

(1) Sulfate adsorption model

As shown in Table 1, experimental SO_4^{2-} adsorption was precisely reproduced by an empirical equation

$$E_{SO_4} = q [H^+]^m [SO_4^{2-}]^n, \quad (6)$$

where E_{SO_4} ($mol\ kg^{-1}$) is SO_4^{2-} adsorption, $[H^+]$ and $[SO_4^{2-}]$ ($mol\ L^{-1}$) are concentrations of H^+ and SO_4^{2-} , respectively, q , m and n are soil dependent parameters.

The electrostatic SO_4^{2-} adsorption model was applied on the soils from Tsukuba, Morioka and Makabe. By optimizing the values of $K_{OH_2}^{intr}$, $K_{SO_4}^{intr}$, $S C_1$ and $S C_2$, this model precisely reproduced the experimental SO_4^{2-} adsorption data (Table 2), showing its validity to simulate the SO_4^{2-} adsorption to soils. The calculated SO_4^{2-} adsorption isotherms of Tsukuba soil are shown in Figure 1. According to this model, moreover, H^+ adsorption increases almost linearly with SO_4^{2-} adsorption at constant pH (Fig. 1), being approximated by the equation

$$E_H = (a \text{ pH} + b)E_{\text{SO}_4} + c \text{ pH} + d, \quad (7)$$

where a , b , c and d are soil dependent parameters (Table 3). Thanks to their simplicity, equations (6) and (7) are useful as the SO_4^{2-} adsorption submodel for soil acidification models, which calculates SO_4^{2-} and H^+ adsorption as functions of SO_4^{2-} and H^+ concentrations.

Table 1. Parameters in the empirical SO_4^{2-} adsorption model

soils	Experimental SO_4^{2-} adsorption (mmol kg^{-1})	q	m	n	r^2
Tsukuba	24.2 - 41.6	0.372	0.140	0.137	0.983
Morioka	1.0 - 8.1	3.674	0.342	0.385	0.983
Naruko	1.4 - 7.2	1.404	0.269	0.414	0.988
Makabe	9.4 - 23.6	0.610	0.194	0.203	0.995
Hiura	0.6 - 1.4	0.022	0.184	0.172	0.967
Sainomae	0.6 - 1.6	0.014	0.107	0.197	0.934

Table 2. Assumed and optimized parameters of the electrostatic SO_4^{2-} adsorption model

soils	$[\text{MOH}]_{\text{tot}}$ (mol kg^{-1})	$S \cdot C_1$ ----- (C $\text{V}^{-1} \text{kg}^{-1}$) -----	$S \cdot C_2$	$\log K_{\text{OH}_2}^{\text{intr}}$	$\log K_{\text{SO}_4}^{\text{intr}}$	r^2
Tsukuba	0.137	4.45×10^4	3.62×10^4	4.9	9.75	0.975
Morioka	0.064	1.68×10^4	2.41×10^4	3.0	7.80	0.970
Makabe	0.043	4.21×10^4	3.07×10^4	4.4	9.34	0.980

Table 3. Equations to approximate H^+ adsorption to soils

soils	Equations
Tsukuba	$E_H = (-0.00388\text{pH} + 1.046)E_{\text{SO}_4} - 0.0091\text{pH} + 0.057$
Morioka	$E_H = (0.00136\text{pH} + 0.902)E_{\text{SO}_4} - 0.0016\text{pH} + 0.0088$
Makabe	$E_H = (0.0801\text{pH} + 0.618)E_{\text{SO}_4} - 0.0070\text{pH} + 0.038$

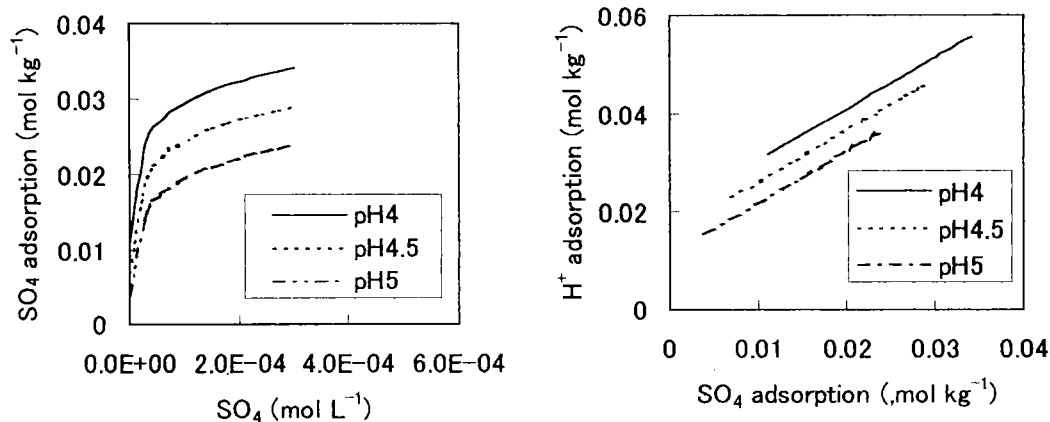


Figure 1. The SO_4^{2-} adsorption isotherms and the relationship between H^+ and SO_4^{2-} adsorption of Tsukuba soil calculated by the extended constant capacitance model

(2) Estimation of base cations budget based on field surveys

Element contents of soils were similar each other between Kannondai and Yasato. Magnesium was the dominant base cation in both soils. Dominant exchangeable cation was Ca^{2+} in Kannondai soil and Al in Yasato soil, and soil pH in Yasato was lower than in

Kannondai. Mineral composition and the surface area of 0.02 - 2 mm fraction or 0.002 - 2 mm fraction of Kannondai soil were shown in Table 4 together with the data of other volcanic soils used for soil dissolution experiments. Yasato soil had similar mineral composition with Kannondai soil, suggesting influence of volcanic ash on the granitic parent material.

One year's data were analyzed to estimate the base cation budget in the forest ecosystems. Annual fluxes of divalent base cation due to deposition, through canopy, O-horizon and soil horizons were shown in Fig. 2 together with the water fluxes. The water fluxes from soil horizons derived by TDR measurements were considered adequate because water flux from A horizon is almost same with that from B horizon. It was also supported by the result that Cl^- discharge from soil horizon calculated from water flux was almost same with the input to the soil layer, because Cl^- was considered an inert ion in the biogeochemical cycle.

Large amounts of base cation leached from canopy and O-horizon and infiltrated into soil. Net supply of base cation to the soil solution was negative: plant uptake, BC_U , was larger than base cation release from soil, BC_{SS} . BC_{SS} was described as

$$BC_{SS} = BC_{out} - BC_{in} + BC_U, \quad (6)$$

where BC_{out} and BC_{in} denotes base cation output from soil and input into soil, respectively. BC_{SS} includes mineral weathering, release of exchangeable cation and organic matter decomposition. Plant uptake was divided into growth uptake (GU) and return uptake (RU) that was regarded as the sum of canopy and O-horizon leaching. Calculated BC_{SS} was $0.94+GU$ (keq $ha^{-1}yr^{-1}$) for Kannondai and was $2.02+GU$ (keq $ha^{-1}yr^{-1}$) for Yasato. Granitic soil in Yasato had rather larger BC_{SS} though values of GU are not known.

Table 4. Mineral composition and surface area of the soils entered in the mineral weathering model

soils	mineral composition						surface area	
	Fd	VG	Opx	Cpx	Ho	Ol	0.02-2 mm	0.002-2 mm
	----- (%) -----						----- (m ² g ⁻¹ soil) -----	
Kannondai A	31.3	27.5	8.9	2.0	0.5	0.3	0.54	17.12
Kannondai B	34.6	27.5	11.0	1.5	0.4	1.3	0.30	35.16
Fujinomiya [†]	22.8	70.6	0.0	0.0	0.0	6.7	0.92	6.23
Yugashima [†]	24.3	64.8	4.9	0.4	0.7	0.0	1.16	5.99

Fd, feldspar; VG, volcanic glass; Opx, orthopyroxene; Cpx, clinopyroxene; Ho, hornblend; Ol, olivine
[†]Wada (1986)

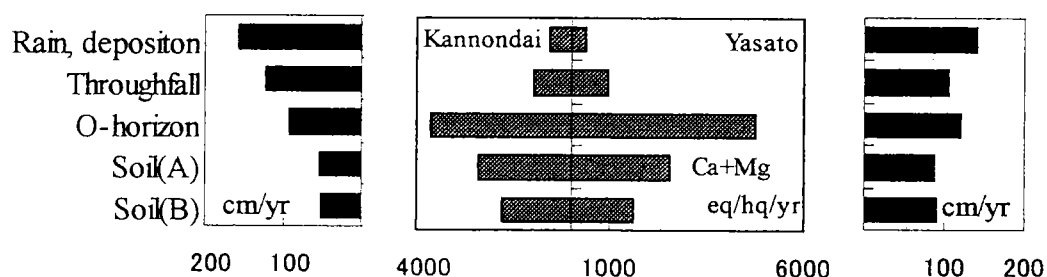


Figure 2. Estimated water and base cation (Ca+Mg) fluxes in Kannondai and in Yasato

(3) Estimation and modeling of mineral weathering rates

(a) Mineral weathering based on strontium isotope ratios

As Sr concentration was strongly correlated with Ca and Mg, it was thought that behavior of Ca and Mg could be represented by that of Sr. Isotope ratio became smaller gradually from rain to soil solution. Ratios in rain and throughfall were 0.7089 and 0.7081, respectively, and values for the other parts were shown in Figure 3 for the case of Kannondai. With respect to the soil, isotope ratio of fine fraction was large and coarse fraction had the smaller value.

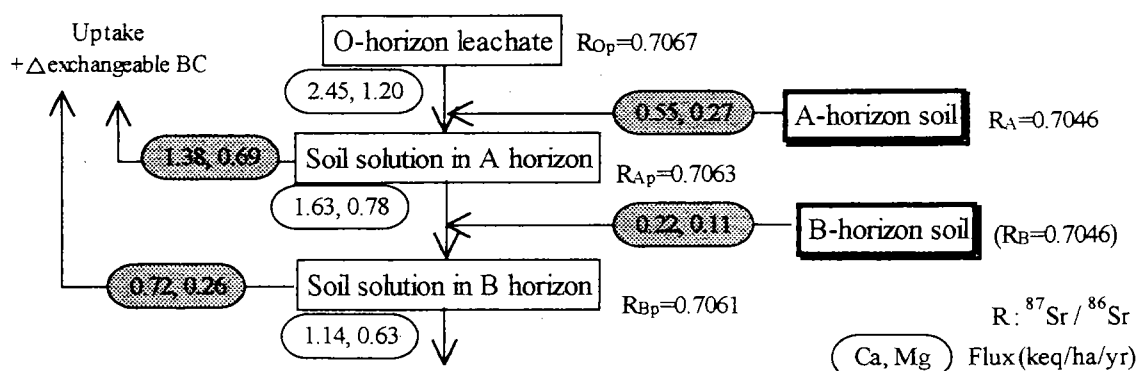


Figure 3. Ca and Mg flow in soil of Kannondai estimated from ion budget and Sr isotope ratios

Value of the leachate of 0.02-2 mm fraction treated with 0.1 M HCl was used for the tentative calculation of Ca and Mg budgets (Figure 3).

(b) Mineral weathering model

Dissolution rate constants of volcanic glasses (Table 5) were derived from the experimental data⁴⁾, and introduced into PROFILE model. Weathering rates were compared between field estimation, dissolution experiments and model calculation (Fig. 4). When the surface area of 0.02 - 2 mm fraction was assumed as the total surface area of primary minerals, the model calculation fairly agreed with the measurements, in contrast with much larger estimation for the usage of 0.002 - 2 mm fraction. This suggest the base cation is mainly supplied from sandy fraction of the volcanic soil.

Table 5. Dissolution rate constants of volcanic glasses

Rock type of glass	$-\log k_H$	n_H	$-\log k_{H_2O}$
Basaltic	14.00	0.39	15.16
Dacitic	14.49	0.39	15.65

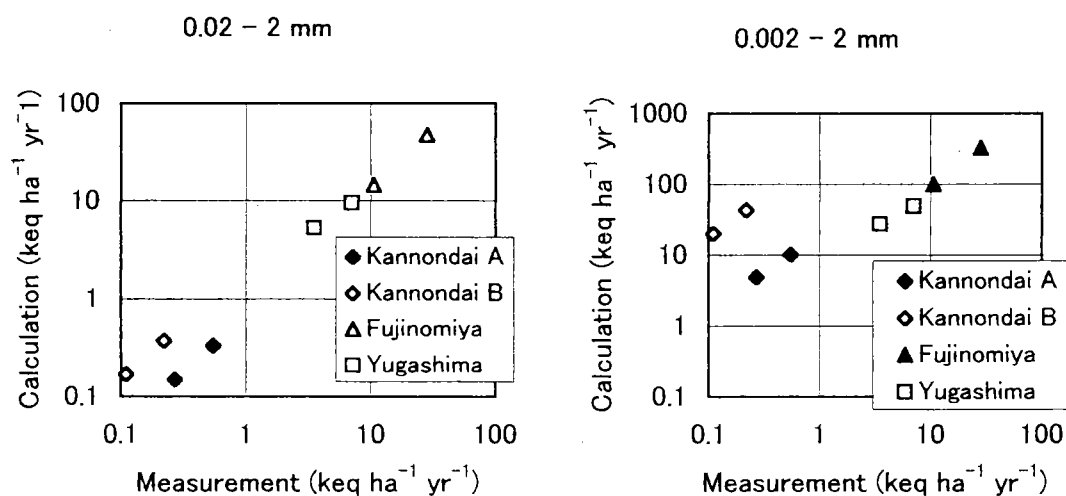


Figure 4. Comparison of model calculation and measured weathering rates of volcanic soils when the surface area of 0.02-2 mm fraction or 0.002-2 mm fraction was assumed as the total surface area of primary minerals.

(4) Development and application of a dynamic soil acidification model

Changes of pH, concentration of base cation ($Ca^{2+}+Mg^{2+}+K^{+}+Na^{+}$) and nitrate ion in

Kannondai were compared between measurements and model predictions in Figure 5. In the model application, net consumption of elements in soil horizon was determined to have the calculated discharge of each element nearly equal to the measurement. Observed changes in Kannondai soil solution were well reproduced with the model, assuming constant net consumption. In the case of Yasato, however, it was necessary to assume seasonal changes in net consumption to reproduce the observed changes, indicating that magnitude of seasonal change in nutrient uptake by plants was significant compared to the seasonal change in mineral weathering.

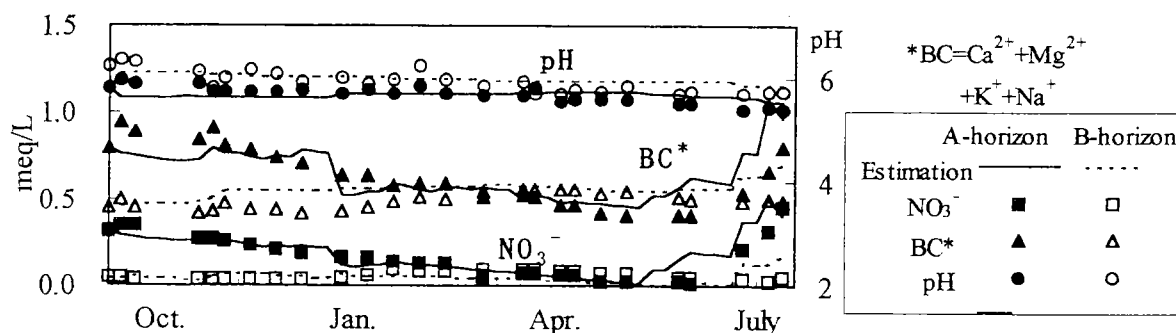


Figure 5. Comparison of model estimation to the measurements of soil solution chemistry in Kannondai

4. Conclusions

In order to evaluate the dynamics of acidity loaded from atmosphere and produced in ecosystems, the following three models were developed. 1) An extended constant capacitance model was used to simulate sulfate adsorption. According to the model, SO₄²⁻ and H⁺ adsorption can be approximated. 2) Existing mineral weathering model (PROFILE) was modified to involve the weathering of volcanic grasses that is important constituent in volcanic soils. 3) A dynamic model was made to predict temporal change of soil chemistry based on soil chemical processes and applied to the field data.

Field survey in forest ecosystems were conducted for understanding the material cycle that was considered important to evaluate impact of acidic deposition to the ecosystems. Base cation budget between atmosphere, vegetation and soil each other and acid neutralization capacity were focused. Mineral weathering rate in soil was evaluated by means of base cation budget and Sr isotope ratio. These data was useful for validation and improvement of the models.

Nitrogen plays an important role in ecosystems and is controlling acidity of ecosystems through nitrogen transformation. It would be necessary to evaluate contribution of the microbiological processes such as denitrification, nitrogen fixation etc., to nitrogen budget and impact of acidic deposition on these processes.

5. References

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