Chapter 17

Model of Ion Dynamics and Acidification of Soil: Application to Historical Soil Chemistry Data from Sweden

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Summary

A dynamic model of soil processes was applied to soil chemistry data from four forest sites in southern Sweden. The sites were sampled in 1949 and resampled in 1984. The model simulates transport of ions with percolating water, cation exchange, weathering of base cations and dissolution of Al³⁺. The model is driven by deposition of H⁺ and base cations which cause changes in the simulated base saturation and the concentration of ions in solution. After calibration, the model results are in reasonable agreement with observed changes in base saturation whereas the changes in pH are underestimated. The simulated trends are correct, and the results correspond qualitatively to those obtained by another model, the RAINS soil model.

Introduction

The objective of the dynamic model of soil processes presented here is to simulate quantitatively the changes in forest soil chemistry that are due to the combined impact of deposition of H⁺ and base cations, nutrient cycling in soil and biomass, weathering of minerals and the dissolution of aluminum. The model simulates the dynamics of base saturation and the concentrations of base cations, H⁺ and Al³⁺ in soil solution. It is formulated in terms of kinetic equations for cation exchange and an equilibrium equation for the dissolution of Al³⁺. It falls in a category between the kinetic model of Gobran and Bosatta (1988) and the equilibrium models of Reuss and Johnson (1986), Cosby et al. (1985), Kauppi et al. (1986) and Posch et al. (this volume). The model is based on a dynamic model (Oksanen et al. 1984), which was modified to account for the continuous vertical distribution of soil moisture and ionic concentrations (Holmberg et al. 1985a,

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1985b). In the version presented here, the vertical distributions are lumped to average values over the entire soil profile.

Here we apply the model to historical Swedish soil chemistry data. Few data sets are available that provide long-term actual measurements of soil acidification. Falkengren-Grerup et al. (1987) have re-analyzed old soil samples from 1949 using the same procedures as for the analysis of the samples taken in 1984. The sites are located in Skane, southernmost Sweden, and currently receive high levels of acid deposition.

Model Structure

MIDAS (Model of Ion Dynamics and Acidification of Soil) simulates the time development of H⁺, Al³⁺, Ca²⁺ and Mg²⁺ in one layer of mineral soil, subject to the deposition of H⁺ and base cations. The concentrations of H⁺, Al³⁺ and the sum of Ca²⁺ and Mg²⁺ in soil solution and the fractions of the sum of H⁺ and Al³⁺ and of the sum of Ca²⁺ and Mg²⁺ on the exchanger are calculated at each time step. These are the model's state variables (the description of the sympols used is provided in Appendix 17.1): $y = (y_1, y_2)^T$ and $x = (x_1, x_2)^T$, $(eq m^{-2})$. Changes in state variables are driven by deposition $u = (u_1, u_2)^T$, $(eq m^{-2} yr^{-1})$, weathering $w = (w_1, w_2)^T$, $(eq m^{-3} yr^{-1})$, and biological turnover $s = (s_1, s_2)^T$, $(eq m^{-2} yr^{-1})$. Soil depth z(m) and volume wetness $\theta(m^3m^{-3})$ are fixed parameters. The model accounts for the vertical transport of ions with percolating water, cation exchange, weathering of minerals, nutrient uptake by the vegetation, decomposition of litter and the dissolution of Al(OH)₃.

Transport

The soil is considered to be horizontally homogenous and unrestricted, and thus only vertical flux of water is taken into account. Ions are transported with the water that moves through the soil. In a humid climate the predominant direction of water flow is downwards. The part of precipitation $P \text{ (m yr}^{-1)}$, that is not intercepted by the canopy or lost by surface runoff, infiltrates into soil and increases its volume wetness $\theta \text{ (m}^3\text{m}^{-3)}$. Vegetation withdraws water from the soil by transpiration and evaporates the intercepted water directly from the leaves $ET \text{ (m yr}^{-1)}$. Any surplus water that exceeds the field capacity of the soil percolates to groundwater $Q \text{ (m yr}^{-1)}$.

$$\frac{d\theta}{dt} = P - ET - Q \tag{17.1}$$

Although the volume wetness varies over the yr as the soil dries out by transpiration in early summer and rewets by infiltration in the fall, the seasonal dynamics in the hydrology are here neglected in order to keep the calculations simple. On an annual time scale the assumption of a hydrological steady state $(\frac{d\theta}{dt} = 0)$ is well founded, and so the annual percolation may be represented as the difference between precipitation and evapotranspiration

$$Q = P - ET \tag{17.2}$$

This is used to calculate the residence time τ (yr) of the soil solution in a layer of thickness z(m)

$$\tau = \frac{\theta \cdot z}{Q} = \frac{\theta \cdot z}{P - ET} \tag{17.3}$$

In a hydrological steady-state, with constant θ , the residence time τ decreases and the leaching rate $(1/\tau)$ increases with the annual percolation Q. The flux of ions through the soil q_i (eq m⁻²yr⁻¹) is calculated from the input with deposition u_i (eq m⁻²yr⁻¹) and the output with leaching

 $q_i = u_i - \frac{y_i}{\tau} \tag{17.4}$

This is to say that the net leaching of ions from the soil increases with the annual percolation, as long as the amount of ions in solution y_i or the rate of deposition u_i do not change. However, y_i changes as soon as the chemical and biological processes in soil are not in steady state.

Cation Exchange, Weathering and Nutrient Cycling

Cation exchange modifies the chemical composition of the percolating solution. Here the simplification is made that cations in soil solution are comprised of the base cations Ca²⁺ + Mg²⁺ and acid cations H⁺ + Al³⁺. Further it is assumed that the acid cations behave as a trivalent species in the exchange and the equation is written

$$2A_s + 3B_a \rightleftharpoons 2A_a + 3B_s \tag{17.5}$$

where A stands for the sum of H^+ and Al^{3+} and B for the sum of the divalent base cations Ca^{2+} and Mg^{2+} . The subscript a denotes the aqueous phase and s the solid phase. The assumption of a trivalent exchange is acceptable when the bulk of the exchangeable acid ions are Al^{3+} , which is the case for the mineral soils of the Swedish forest sites of this application (Falkengren-Grerup et al. 1987). The cation exchange reaction is quantified using the Gaines-Thomas exchange equation (Gaines and Thomas 1953), slightly modified in that equivalent concentrations are used instead of activities in solution. (Thus the equilibrium coefficient incorporates the activity coefficients.) According to this equation the exchange equilibrium is determined by the fraction of base cations on the exchanger BS and the concentrations in solution C_i (eq l^{-1})

$$K_{exch} = \frac{(1 - BS)^2 \cdot C_2^3}{BS^3 \cdot C_1^2} \tag{17.6}$$

where the subscript 1 denotes the sum of H⁺ and Al³⁺ and 2 the sum of Ca²⁺ and Mg²⁺. For the purpose of the kinetic model equations the selectivity coefficient is split into rate coefficients

$$K_{exch} = \frac{k_2}{k_1} \tag{17.7}$$

The values of the rate coefficients are chosen so that the cation exchange is always faster than the transport of ions through the soil. The auxiliary variables BS and C_i are calculated from the state variables in the following way

$$BS = \frac{x_2}{cec} \tag{17.8}$$

$$C_i = \frac{y_i}{\theta \cdot z \cdot 1000} \tag{17.9}$$

where cec (eq m⁻²) is the cation exchange capacity expressed in charge equivalents

$$cec = x_1 + x_2. (17.10)$$

The partitioning of the exchangeable sites to base cations and H⁺ and Al³⁺ in equilibrium is determined by the fractions of these cations in solution. The larger the cation exchange capacity, and the further away the initial state is from equilibrium with respect to cation exchange, the longer it takes to reach a new equilibrium with constant deposition. The time it takes for the solution to reach equilibrium after a change in deposition also depends on the residence time of the water in the soil.

Weathering replenishes the pool of base cations on the soil exchange complex at the rate w_2 (eq m⁻³yr⁻¹) and consumes an equivalent amount of hydrogen ions w_1 (eq m⁻³yr⁻¹). The assumption of a constant weathering rate was made for simplicity, although the rate may depend on the soil solution composition as well as on the mineralogy of the site (Sverdrup and Warfvinge 1988).

Decomposition of organic material releases base cations into solution and consumes H^+ . Nutrient uptake by plants, on the other hand, consumes base cations and releases H^+ . Net production of H^+ by the organic cycle is here denoted by s_1 (eq m⁻²yr⁻¹) (uptake - release) and that of base cations by s_2 (eq m⁻²yr⁻¹) (release - uptake). The net contribution of the organic cycle to H^+ and base cations in soil depends primarily on the type of vegetation cover and its stage of development. A young rapidly-growing forest consumes more base cations than are released from decomposing litter and thus contributes to the acidification of the soil.

The kinetic equations that combine transport, cation exchange, weathering and nutrient cycling are

$$\frac{dx_i}{dt} = (-1)^i \cdot k_1 \cdot (1 - BS)^2 \cdot C_2^3 - (-1)^i \cdot k_2 \cdot BS^3 \cdot C_1^2 + (-1)^i \cdot w_i \cdot z$$
 (17.11)

$$\frac{dy_i}{dt} = -(-1)^i \cdot k_1 \cdot (1 - BS)^2 \cdot C_2^3 + (-1)^i \cdot k_2 \cdot BS^3 \cdot C_1^2 + q_i + s_i$$
 (17.12)

They are solved numerically by a fourth-order Runge-Kutta algorithm. The model is programmed in Pascal, and the simulation of 100 yrs takes about 10 minutes on an IBM AT microcomputer.

The concentration of acids in solution C_1 (eq l^{-1}) is expressed in charge equivalents,

$$C_1 = 3 \cdot [Al^{3+}] + [H^+],$$
 (17.13)

where square brackets denote molar concentrations. The apportioning of acid cations into H⁺ and Al³⁺ in soil solution is calculated from an equilibrium with a solid aluminum hydroxide phase

$$[Al^{3+}] = K_{Al}[H^+]^3 (17.14)$$

The equilibrium coefficient again includes the activity coefficients. The equations 17.13 and 17.14 are solved numerically by a Newton-Raphson iteration algorithm.

Application to Swedish Sites

Soils data from the sites in Skåne include measurements of cation exchange capacity and exchangeable ions (Al³⁺, H⁺, Ca²⁺, Mg²⁺, Na⁺ and K⁺) at several depths within soil profiles that range from 0.3 to 1.0 m. Four sites were selected for the model application: sites 2, 3 and 6 in deciduous forest and site 7 in spruce forest (Falkengren-Grerup et al.

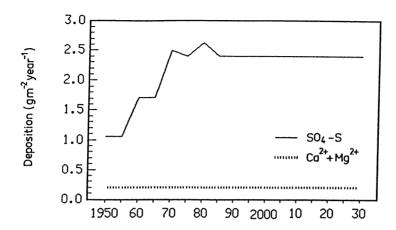


Figure 17.1. Assumed deposition history and future scenario of SO₄-S and base cations used to simulate soil chemistry by the MIDAS model for the coniferous stand (site 7). For sulfur, this deposition was 1.6 times higher than that to the deciduous stands (sites 2, 3, 6).

Table 17.1. Parameter values

θ	$0.25 \text{ m}^3\text{m}^{-3}$
P	600 mm
ET	200 mm
$oldsymbol{w}$	$0.05 \mathrm{eq} \mathrm{m}^{-3} \mathrm{yr}^{-1}$
K_{Al}	$5.89 l^2 mol^{-2}$
$log K_{Al}$	8.77

1987). Site 2 is a beech forest which was clear-felled a few months before resampling. The soil is a podzol with a thin mor layer and an eluvial horizon of ca 10 cm, developed from a sandy moraine. Site 3 is a beech forest growing on a well developed podzol with a mor layer thicker than 5 cm and an eluvial horizon of ca 15 cm, on a moraine formed by Cambrian sandstone. Site 6 is a mixed deciduous forest on a soil developed from a sandy moraine with a mull humus layer. Site 7 is former arable land, planted in 1889 with *Picea abies*, replanted with a second generation in about 1965. The soil is developed from a sandy moraine and the humus layer is a mull (Falkengren-Grerup et al. 1987).

For the purpose of comparison with MIDAS, which treats soil as one homogenous layer, the measured mineral soil characteristics were averaged over the entire profile. The values of the parameters θ , P, ET, w, K_{Al} and K_{exch} were chosen to facilitate a comparison with the RAINS and SMART model results (Posch et al. this volume). These values are listed in Table 17.1.

The SO₄-S deposition history (1949-1984) at these sites shown in Figure 17.1 was estimated by the Energy-Emission and Long-Range Transport Module of the RAINS model (Alcamo et al. 1987). The filtering efficiency of the coniferous stand was assumed to be 1.6 times that of an open field, while no significant filtering was assumed for deciduous

	site 2	site 3	site 6	site 7
measured:				
z(m)	1.0	0.9	0.85	1.0
calibrated:				
$k_1 \left(l^3 qe^{-2} m^{-2} yr^{-1} \right)$	$1.0\cdot 10^7$	$1.0 \cdot 10^7$	$1.0 \cdot 10^7$	$1.0 \cdot 10^{6}$
$k_2 \left(l^2 qe^{-1} m^{-2} yr^{-1} \right)$	$1.0\cdot10^{12}$	$1.5\cdot 10^{11}$	$2.0\cdot10^{11}$	$3.0 \cdot 10^{10}$
$Kexch$ (eq l^{-1})	$1.0\cdot 10^{5}$	$1.5\cdot 10^4$	$2.0 \cdot 10^4$	$3.0 \cdot 10^{4}$
$s_1 \left(\text{eq m}^{-2} \text{yr}^{-1} \right)$	0.04	0.04	0.07	0.07
$s_2 \left(\text{eq m}^{-2} \text{yr}^{-1} \right)$	-0.04	-0.04	-0.07	-0.07

Table 17.2. Site-specific parameter values

forest (Ivens et al. this volume). The deposition of calcium and magnesium was assumed to show no trend, since there is little evidence of long-range transport of base cations originating in energy production (Wiman and Ågren 1985). The level of base cation deposition used in the simulations $(0.2 \text{ g m}^{-2}\text{yr}^{-1})$ is lower than that used in the RAINS-application, which peaks at $1.0 \text{ g m}^{-2}\text{yr}^{-1}$ in the 1970's (Posch et al. this volume). This peak is of the order of magnitude of base cations in throughfall in the Gårdsjön area as reported by Grennfelt et al. (1985), where bulk deposition of $\text{Ca}^{2+} + \text{Mg}^{2+}$ is 0.3 $\text{g m}^{-2}\text{yr}^{-1}$. The base cations leached from the canopy are part of the nutrient cycle and in the MIDAS-application they are incorporated in s_2 , the net production of base cations by biological activity (release - uptake).

The simulated time development of base saturation and the annual rate of change in BS are presented in Figures 17.2 and 17.3. The simulated soil solution chemical composition and the molar ratio of Al3+ to Ca2+ + Mg2+ are shown in Figures 17.4 and 17.5. A fit with observed BS in 1984 was achieved by altering the ion-exchange equilibrium and the rate of nutrient uptake by vegetation. The values of the parameters k_2 and s_2 were changed until a good fit was obtained. The site specific parameter values are summarized in Table 17.2. The best fit for sites 2 and 3 is reached with $s_2 = -0.04 \text{ eq m}^{-2} \text{yr}^{-1}$ and for sites 6 and 7 with $s_2 = -0.07 \text{ eq m}^{-2} \text{yr}^{-1}$. This means that, at all sites, more base cations are bound into growing vegetation than are released from decomposing organic matter and leached from the canopy. Considering only Ca2+, 8 kg ha-1 is annually accumulated into wood at sites 2 and 3, and 14 kg ha⁻¹ at sites 6 and 7. Assuming an average Ca²⁺ content of 2.5 g kg⁻¹ dry weight of the trees the corresponding annual wood production would be 3200 kg ha⁻¹ and 5600 kg ha⁻¹. Compared with the assumed rate of weathering, the values for the net nutrient uptake that gave a good fit with the observed BS in 1984 represent in two cases (sites 2 and 3) a situation where 80 % of the base cations produced in weathering are sufficient for the plants' nutrient demand. For the sites 6 and 7 only 70 % of the vegetation's nutrient demand is supplied by weathering. In other words, the observed changes in BS were produced by introducing natural acidification by growing forest which partly consumes the base cations produced in weathering.

The simulations were continued into next century with a 10 % reduction of acid deposition from the 1980 level. The base saturation is still decreasing at site 7 in 2030, while it has stabilized for site 2 to 1.0 %, for site 3 to 1.7 % and for site 6 to 1.4 % (Figure 17.2). The maximum rate of change in BS occurs in 1980 for site 7 and in 1970 for the other

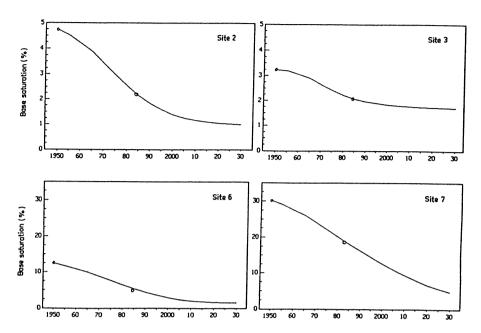


Figure 17.2. Simulated base saturation obtained by the MIDAS model for sites 2, 3, 6 and 7 that were sampled in 1949 and 1984 by Falkengren-Grerup and co-workers (1987). Measurements are indicated by circles.

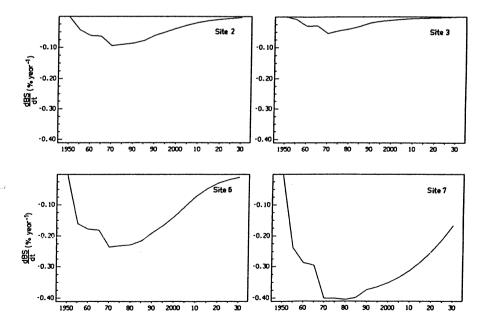


Figure 17.3. Simulated rate of change in base saturation obtained by the MIDAS model for sites 2, 3, 6 and 7 that were sampled in 1949 and 1984 by Falkengren-Grerup and co-workers (1987).

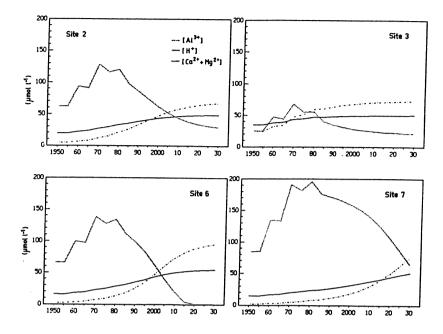


Figure 17.4. Simulated soil solution concentrations obtained by the MIDAS model for sites 2, 3, 6 and 7 that were sampled in 1949 and 1984 by Falkengren-Grerup and co-workers (1987).

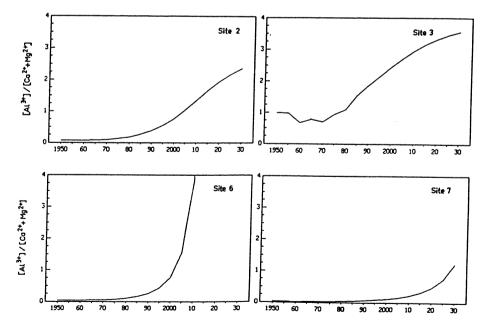


Figure 17.5. Simulated molar ratio of Al³⁺ to Ca²⁺ + Mg²⁺ in soil solution obtained by the MIDAS model for sites 2, 3, 6 and 7 that were sampled in 1949 and 1984 by Falkengren-Grerup and co-workers (1987).

	site 2	site 3	site 6	site 7
simulated:				
$BS_{1985} - BS_{1950}$	-2.6	-1.2	-7.2	-12.1
$pH_{1985} - pH_{1950}$	-0.2	-0.1	-0.3	-0.2
observed:				
$BS_{1984} - BS_{1949}$	-2.6	-1.2	-8.4	-12.4
$pH_{1984} - pH_{1949}$	-0.5	-0.3	-1.2	-0.9

Table 17.3. Observed and simulated changes in base saturation and pH

Table 17.4. Initial values of exchangeable base cations, total decrease in exchangeable base cations 1950 to 2030 and the maximum rate of change in BS.

	· · · · · · · · · · · · · · · · · · ·	site 2	site 3	site 6	site 7
$x_{2(1950)}$	(eq m ⁻²)	4.0	2.3	6.6	11.9
$x_{2(2030)} - x_{2(1950)}$	$(eq m^{-2})$	3.2	1.1	5.8	10.0
$x_{2(2030)} - x_{2(1950)}$	(%)	-80	-48	-89	-84
dBS_	$(\%yr^{-1})$	-0.09	-0.05	-0.23	-0.41

sites (Figure 17.3). This maximum rate is largest for site 7, which has the largest initial amount of exchangeable base cations and receives a larger acid load than the other sites. Correspondingly, site 7 shows the largest total leaching of base cations (Table 17.4). Site 3, with the smallest initial amount of exchangeable bases, shows the smallest maximum rate of change in BS and the smallest total leaching of base cations.

Keeping the vegetation's nutrient demand constant over the yrs leads to very low nutrient concentrations in solution in the case of site 6 (Figure 17.4). In reality, the demand would decrease as the forest matures. It is also likely that very a very low concentration of base cations in solution would increase the weathering rate. The molar ratio of Al^{3+} to $Ca^{2+} + Mg^{2+}$ in solution remains below 1 during this century for all sites except site 3 (Figure 17.5). The measured value of exchangeable cations was in 1949 the lowest for site 3 (Table 17.4), its simulated base saturation changes the least over the years (Figure 17.3) and so its $Ca^{2+} + Mg^{2+}$ concentration in soil solution is the lowest of all the simulated sites (Figure 17.4).

As regards the impact of soil acidification on the vegetation, different hypothetically harmful situations can be illustrated with this kind of a simulation experiment. If a high Al³⁺ relative to Ca²⁺ concentration in soil solution is assumed to have a detrimental impact on tree roots (Rost-Siebert 1983), soils with low amounts of exchangeable base cations, such as site 3, can be singled out as sensitive to acid deposition with respect to tree growth. If on the other hand, unstable nutrient supply is considered potentially harmful for the trees, forests on soils with high, but highly varying Ca²⁺ + Mg²⁺ concentrations, such as site 7, may be assumed to experience future nutrient imbalance.

A fit with observed changes in pH was not attempted because an average pH value is not informative of the chemical changes in a 1 m deep soil horizon, and also because the

interpretation of the pH-measurements of old air-dried samples is problematic. Soil data acquired from field and laboratory studies may not accurately reflect the properties of the natural soil (Driessen 1986). Considering the uncertainty inherent in measurements of pH and exchangeable cations, attempts to exactly predict soil acidity or base saturation are questionable. More interesting is the observed or predicted change.

Compared with SMART (Posch et al. this volume), MIDAS predicts similar changes in pH. MIDAS was calibrated to fit the observed changes in BS by changing the value of the Gaines-Thomas selectivity coefficient and by increasing the rate of nutrient uptake (sites 6 and 7) as compared to the values used in the SMART runs. Like SMART, MIDAS' response to the deposition pattern is more realistic than the RAINS soil model, primarily because of the non-linearity introduced by representing cation exchange by a Gaines-Thomas equation.

MIDAS is, as is evident from equations 17.11 and 17.12, a kinetic parallel to the cation exchange part of SMART, and so it should to perform similarly with respect to those features that involve only cation exchange. MIDAS' advantage is that observed trends in base saturation can be produced with a minimum of calibration with a simple model that includes only the lumped cation exchange of $H^+ + Al^{3+}$ versus $Ca^{2+} + Mg^{2+}$.

Conclusions

A simple dynamic model structure is sufficient to illustrate the combined impact of acid deposition, constant-rate weathering, cation exchange with constant selectivity coefficients, and constant-rate binding of nutrients into growing vegetation. Although these processes hardly occur at constant rates in reality, the simulated results could not be shown to be unrealistic using a set of observations of only two points in time.

In order to account for the variable chemical characteristics at different depths of forest soils models should be developed to deal with consecutive soil layers. A simple model structure, such as MIDAS', is advantageous. For studying the impact of the seasonal variation in hydrology on soil chemical response, the assumption of steady-state hydrology will have to be abandoned. To improve the ability of models to describe reality, experimental work is needed on the solubility of different Al-compounds in variable circumstances in the soil, as well as on the change in selectivity coefficients with large changes in base saturation.

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Appendix 17.1. List of Symbols.

Symbol	Unit	Description
$\boldsymbol{x}=(x_1,x_2)^T$	$eq m^{-2}$	ions on the exchanger
$oldsymbol{x}_1$	$eq m^{-2}$	sum of H ⁺ and Al ³⁺
x_2	$eq m^{-2}$	sum of Ca ²⁺ and Mg ²⁺
$\boldsymbol{y}=(y_1,y_2)^T$	$eq m^{-2}$	ions in solution
$oldsymbol{y}_1$	eq m ⁻²	sum of H ⁺ and Al ³⁺
y ₂	$eq m^{-2}$	sum of Ca ²⁺ and Mg ²⁺
$\boldsymbol{u}=(u_1,u_2)^T$	$eq m^{-2} yr^{-1}$	annual deposition
u_1	$\rm eqm^{-2}yr^{-1}$	deposition of H ⁺
u_2	$eq m^{-2} yr^{-1}$	deposition of Ca ²⁺ and Mg ²⁺
$q=(q_1,q_2)^T$	$ m eqm^{-2}yr^{-1}$	ion flux
q_1	$eq m^{-2} yr^{-1}$	flux of $H^+ + Al^{3+}$
q_2	$eq m^{-2} yr^{-1}$	flux of $Ca^{2+} + Mg^{2+}$
$\boldsymbol{w} = (\boldsymbol{w_1}, \boldsymbol{w_2})^T$	$ m eqm^{-3}yr^{-1}$	annual weathering
$oldsymbol{w_1}$	$ m eqm^{-3}yr^{-1}$	H ⁺ consumed by weathering
$oldsymbol{w_2}$	$ m eqm^{-3}yr^{-1}$	Ca ²⁺ and Mg ²⁺ produced by weathering
$\boldsymbol{s}=(s_1,s_2)^T$	$eq m^{-2} yr^{-1}$	biological cycling
s_1	$\rm eqm^{-2}yr^{-1}$	net production of H ⁺
s ₂	$ m eqm^{-2}yr^{-1}$	net production of Ca ²⁺ and Mg ²⁺
cec	$eq m^{-2}$	cation exchange capacity
C_1	$eq l^{-1}$	concentration of H ⁺ + Al ³⁺ in solution
C_{2}	$eq l^{-1}$	concentration of $Ca^{2+} + Mg^{2+}$ in solution
BS		fraction of $Ca^{2+} + Mg^{2+}$ on the exchanger
K_{exch}	$eq l^{-1}$	Gaines-Thomas selectivity coefficient
k_1	$l^3 eq^{-2} m^{-2} yr^{-1}$	rate coefficient for ion exchange
k_2	$l^2 eq^{-1} m^{-2} yr^{-1}$	rate coefficient for ion exchange
K_{Al}	$l^2 mol^{-2}$	aluminum hydroxide solubility coefficient
$oldsymbol{ heta}$	$m3m^{-3}$	volume wetness of the soil
z	m	soil depth
au	yr	residence time of soil solution
\boldsymbol{P}	$m yr^{-1}$	precipitation
ET	$ m myr^{-1}$	evapotranspiration
Q	m yr ⁻¹	percolation