MODEL OF ION DYNAMICS AND ACIDIFICATION OF SOIL: 
SIMULATING RECOVERY OF BASE SATURATION

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ABSTRACT

Recovery of base saturation in response to reduced acid deposition was simulated with MIDAS (Model of Ion Dynamics and Acidification of Soil). The model accounts for the vertical transport of ions with percolating water, cation exchange and dissolution of Al(OH)$_3$. MIDAS is driven by deposition of acid and base cations, weathering of base cations and the turnover of base cations with the organic matter. The time development of base saturation and the concentrations of Ca$^{2+}$, Mg$^{2+}$, H$^+$ and Al$^{3+}$ in soil solution were calculated from 1950 to 2070 for two forest soils in southern Sweden. As reported elsewhere, base saturation of these soils decreased in the period 1950 to 1985 from 30% to 18% at the coniferous site and from 3% to 2% at the deciduous site. These sites were assumed to receive deposition that peaked in 1984 at 2.6 and 1.65 g m$^{-2}$ SO$_4^-$-S, respectively. Here I report model runs in which the deposition of H$^+$ was reduced by 30%, 60% or 80% of the 1980 level, fully effective from 1995. At the deciduous site, reducing the deposition by 80% caused the base saturation to increase past the 1950 value by the year 2030, while a 30% or 60% reduction stabilized the base saturation at a lower level. Base saturation continued to decline for all scenarios at the coniferous site, slightly less with the larger reduction. In response to the decreasing deposition, base saturation and pH followed different pathways than when responding to increasing deposition. It was concluded that the base saturation of forest soils recovers slowly, if at all, as the deposition of acidifying compounds is reduced, and the recovery is not symmetrical to the acidification. Low acid deposition is required over long periods of time to restore acidified soils and surface waters.

1. INTRODUCTION

The acidification of soils and surface waters has been observed in many regions of Europe and Northamerica and the linkage to acid deposition has been demonstrated (Likens, Bormann, Pierce, Eaton and Johnson 1977; Overrein, Seip and Tollan 1980; Ulrich 1983; Kämäri 1985; Falkengren-Grerup, Linnermark and Tyler 1987). Several models have been developed to explain past and predict future acidification (Reuss 1980; Cosby, Wright, Hornberger and Galloway 1985; Holmberg, Mäkelä and Hari 1985; Kauppi, Kämäri, Posch, Kauppi and Matzner 1986; Reuss and Johnson 1986; Kämäri 1988). Political efforts are being made to reduce acid deposition and criteria for the reduction decisions are being sought (Critical loads for sulphur and nitrogen 1988).
Important questions to be addressed when reduction strategies are planned include: to which extent is the acidification of soil and surface waters reversible; how long does the recovery take? Few have managed to study the reversibility of acidification experimentally, Wright, Lotse and Semb (1988) being the exception. Cosby, Hornberger, Galloway and Wright (1985) used the MAGIC model to simulate soil and streamwater response to abruptly reduced deposition. They found that initial recovery rates are rapid compared with initial acidification rates, whereas the total recovery times are longer by a factor of two or more than total acidification times. Reuss, Cosby and Wright (1987) illustrate the asymmetrical pathways followed by pH and alkalinity of surface water in response to changes in soil sulphate concentration using the Reuss and Johnson (1986) model.

The response of base saturation to different reduction scenarios for two forest soils in southern Sweden was studied. Base saturation of these soils have decreased considerably since 1950 (Falkengren-Grerup et al. 1987). The simulations were made with MIDAS (Model of Ion Dynamics and Acidification of Soil), which has earlier been calibrated to the Swedish soil data (Holmberg, Nissinen and Hari). MIDAS evolved from the model by Oksanen, Mäkelä, Heikkilä and Hari (1985). It consists of a kinetic formulation of cation exchange combined with constant rate weathering, percolation, nutrient uptake and decomposition. The primary objective of this modeling work is to estimate changes in base cation status in forest soils in response to changing fluxes of H⁺ and base cations. The model is intended to be coupled to a stand-growth model to study the role of soil-mediated effects in forest die-back. The purpose of this report is to illustrate the use of a simple kinetic model for studying the effects of emission reductions, and to point to the different response patterns that may be expected.

2. MODEL STRUCTURE

MIDAS simulates the concentrations of H⁺, Al³⁺, Ca²⁺ and Mg²⁺ in one homogenous layer of mineral soil that receives deposition of H⁺, Ca²⁺ and Mg²⁺ (Holmberg et al.). The model is driven by deposition of acid and base cations, weathering of base cations and turnover of base cations with the organic matter. Ions are transported vertically with percolating water and are exchanged for those adsorbed to the solid phase.

Fig. 1. MIDAS simulates the amounts of ions on the exchanger and in soil solution by combining deposition and cation exchange with percolation, biomass turnover and weathering at a constant rate.
The rate of water turnover \( \lambda \) (year\(^{-1} \)) in a layer of thickness \( z \) (m) is calculated from the annual percolation \( P \) and evapotranspiration \( ET \) (m year\(^{-1} \))

\[
\lambda = \frac{P - ET}{\theta \cdot z},
\]

(1)

where \( \theta \) (m\(^3\) m\(^{-3} \)) is soil volume wetness. The flux of ions \( q_i \) (eq m\(^{-2}\) year\(^{-1} \)) through the soil is the difference between input with deposition \( u_i \) (eq m\(^{-2}\) year\(^{-1} \)) and outflow with percolation

\[
q_i = u_i - y_i \cdot \lambda; \quad i = 1, 2,
\]

(2)

where \( y_i \) (eq m\(^{-2}\)) is the amount of ions in soil solution. In MIDAS, the simplification is made that cations in soil solution are comprised of the acid cations \( H^+ + Al^{3+} \) (subscript 1) and base cations \( Ca^{2+} + Mg^{2+} \) (subscript 2). Further it is assumed that the acid cations behave as a trivalent species in the exchange

\[
2[H + Al]_a + 3[Ca + Mg]_a \rightleftharpoons 2[H + Al]_a + 3[Ca + Mg]_a.
\]

(3)

The Gaines-Thomas exchange equation is used, slightly modified in that the activity coefficients are incorporated in the equilibrium coefficient (Gaines and Thomas 1953). According to this equation the exchange equilibrium is determined by the fraction of base cations on the exchanger \( BS \) and the concentrations of ions in solution \( C_i \) (eq l\(^{-1} \))

\[
K_{exch} = \frac{(1 - BS)^2 \cdot C_i^2}{BS^3 \cdot C_i^2}.
\]

(4)

Base saturation is calculated from the amount \( x_2 \) (eq m\(^{-2}\)) of base cations on the exchanger

\[
BS = \frac{x_2}{ccc},
\]

(5)

where \( ccc \) (eq m\(^{-2}\)) is the cation exchange capacity expressed in charge equivalents

\[
ccc = x_1 + x_2.
\]

(6)

The molar concentrations \( C_i \) of ions in solution are calculated from the amounts \( y_i \) of ions in solution

\[
C_i = \frac{y_i}{\theta \cdot z \cdot 1000}.
\]

(7)

Weathering replenishes the pool of base cations on the soil exchange complex at the rate \( w_2 \) (eq m\(^{-3}\) year\(^{-1} \)) and consumes an equivalent amount of hydrogen ions \( w_1 \) eq m\(^{-3}\) year\(^{-1} \). 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 Warvinge 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\(^{-2}\) year\(^{-1} \)) (uptake - release) and that of base cations by \( s_2 \) (eq m\(^{-2}\) year\(^{-1} \)) (release - uptake).
The kinetic equations that combine transport, cation exchange, weathering and nutrient cycling are

\[
\frac{dx_i}{dt} = (-1)^i \cdot k_1 \cdot (1 - BS)^2 \cdot C_i^2 - (-1)^i \cdot k_2 \cdot BS^3 \cdot C_i^2 + (-1)^i \cdot w_i \cdot z
\]

\[
\frac{dy_i}{dt} = (-1)^i \cdot k_1 \cdot (1 - BS)^3 \cdot C_i^2 + (-1)^i \cdot k_2 \cdot BS^3 \cdot C_i^2 + q_i + \dot{\lambda}_i
\]

They are solved numerically by a fourth-order Runge-Kutta algorithm. The model is programmed in Pascal, and the simulation of 100 years takes about 10 minutes. The rate coefficients \( k_1, k_2 \) are chosen so that the cation exchange is always faster than the transport of ions through the soil, and their ratio is the Gaines-Thomas selectivity coefficient

\[
K_{\text{exch}} = \frac{k_2}{k_1}
\]

(9)

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

\[
C_1 = 3 \cdot [Al^{3+}] + [H^+],
\]

where square brackets denote molar concentrations. The apportioning of acid cations into \( H^+ \) and \( Al^{3+} \) in soil solution is calculated from an equilibrium with a solid aluminum hydroxide phase

\[
[Al^{3+}] = K_{\text{Al}}[H^+]^3
\]

(11)

The equilibrium coefficient again includes the activity coefficients. The equations (10) and (11) are solved numerically by a Newton-Raphson iteration algorithm.

3. ACIDIFICATION PHASE

The acidification of forest soils in southern Sweden has been simulated with MIDAS (Holmberg et al.). The model was calibrated with historical soil chemistry data from Sweden consisting of soil samples from 1949 and 1984 (Falkengren-Gerup et al. 1987). The sites are located in Skåne, and currently receive high levels of acid deposition. Two sites were selected for simulating recovery of base saturation: site 3 in beech and site 7 in spruce forest (Falkengren-Gerup et al. 1987). The beech site is 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. \( CEC \) was 71.2 eq m\(^{-2}\) and the amount of exchangeable bases was 2.3 eq m\(^{-2}\) in 1950. The spruce site 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 null, with a \( CEC \) of 39.5 eq m\(^{-2}\) and 11.9 eq m\(^{-2}\) exchangeable base cations in 1950 (Falkengren-Gerup et al. 1987).

The \( SO_4 - S \) deposition history (1949-1984) was estimated by the Energy-Emission and Long-Range Transport Module of the RAINS model (Alcamo et al. 1987). The spruce forest (Fig. 2) was assumed to receive 1.6 times the deposition of \( H^+ \) at the beech site. The annual base-cation deposition (0.2 g m\(^{-2}\)) was held constant over the years.
Deposition to spruce stand
SO4-S

Fig. 2. Assumed deposition history and future scenarios of $SO_4 - S$ used to simulate soil chemistry by the MIDAS model at the spruce stand.

Base saturation decreased from 30% to 18% at the spruce site and from 3% to 2% at the beech site in the period 1949 to 1984 (Falkengren-Grerup et al. 1987). MIDAS was calibrated to fit the observed BS in 1984 by altering the ion-exchange equilibria and the rate of nutrient uptake by vegetation (Holmberg et al.). The obtained parameter values are given in Table 1. The pool of exchangeable base cations is larger at the spruce site than at the beech site, and in 1985 the spruce site is still far from steady-state. The beech site, with its high CEC and small initial BS is almost completely depleted of exchangeable bases by the year 1985. Weathering substitutes more base cations than are removed by growing vegetation at the beech site, the net effect of weathering and biomass turnover being an addition of 0.005 eq m$^{-2}$ year$^{-1}$Ca$^{2+}$ + Mg$^{2+}$, which is half the input of base cations with deposition. At the spruce site, 0.03 eq m$^{-2}$ year$^{-1}$Ca$^{2+}$ + Mg$^{2+}$ in addition to the amount supplied by weathering are removed from the soil and bound into biomass.

Table 1. Parameter values for the MIDAS model calibrated to historical soil chemistry data from Sweden (Holmberg et al.).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>value</th>
<th>unit</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>0.25</td>
<td>m$^3$ m$^{-3}$</td>
<td>soil volume wetness</td>
</tr>
<tr>
<td>( P )</td>
<td>600</td>
<td>mm</td>
<td>annual precipitation</td>
</tr>
<tr>
<td>( ET )</td>
<td>200</td>
<td>mm</td>
<td>annual evapotranspiration</td>
</tr>
<tr>
<td>( w )</td>
<td>0.05</td>
<td>eq m$^{-3}$ year$^{-1}$</td>
<td>weathering rate</td>
</tr>
<tr>
<td>( \log K_{Al} )</td>
<td>8.77</td>
<td></td>
<td>aluminum solubility</td>
</tr>
<tr>
<td>beech :</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( z )</td>
<td>0.9</td>
<td>m</td>
<td>soil depth</td>
</tr>
<tr>
<td>( K_{exch} )</td>
<td>1.5 \cdot 10^4</td>
<td>(eq l$^{-1}$)</td>
<td>selectivity coefficient</td>
</tr>
<tr>
<td>( s_1 )</td>
<td>0.04</td>
<td>eq m$^{-2}$ year$^{-1}$</td>
<td>net $H^+$ production by biomass turnover</td>
</tr>
<tr>
<td>( s_2 )</td>
<td>-0.04</td>
<td>eq m$^{-2}$ year$^{-1}$</td>
<td>net Ca$^{2+}$ + Mg$^{2+}$ production</td>
</tr>
<tr>
<td>spruce :</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( z )</td>
<td>1.0</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>( K_{exch} )</td>
<td>3.0 \cdot 10^4</td>
<td>(eq l$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>( s_1 )</td>
<td>0.07</td>
<td>eq m$^{-2}$ year$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>( s_2 )</td>
<td>-0.07</td>
<td>eq m$^{-2}$ year$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>
4. REDUCING DEPOSITION

The responses of base saturation and soil solution pH to decreasing deposition were studied by reducing the input of $H^+$ to the soils. Three scenarios for emission reductions were used in the predictions for the period 1985 to 2070. The deposition of $H^+$ was reduced by 30%, 60% and 80% of the 1980 level, fully effective from 1995 (Fig. 1). At the deciduous site, reducing the deposition by 80% increases base saturation (Fig. 3a). By the year 2030, base saturation has reached its 1950-level, and the soil continues to accumulate base cations. The increase is faster, at first, than the decrease in the acidification phase. Towards 2070 the rate of change in BS approaches a small positive value (Fig. 3b), determined by the surplus of base cations supplied by weathering over those consumed by growing vegetation.

**Fig. 3a.** Simulated base saturation obtained by the MIDAS model for the deciduous stand. The 30% reduction stabilizes BS to the 1995 value. Although the amount of base cations lost in 1950 to 1985 was only 0.8 eq m$^{-2}$, the net effect of weathering and biomass turnover is not enough to restore base saturation with the 30% reduction scenario.

**Fig. 3b.** Simulated rate of change in base saturation. For the 60% and 80% reduction, the rate of change in BS is still positive in 2070.

The deposition scenario with a 60% reduction was almost symmetrical, although not a square-wave, whereas the response of base saturation is asymmetrical. The trajectory of the rate of change in BS is steeper in 1985-1995, in response to the decreasing acid deposition, than in the acidification phase 1950-1985. This is in accordance with the results obtained with MAGIC (Cosby et al. 1985b), an equilibrium model which incorporates more detailed chemistry than MIDAS.
Base saturation continued to decline for all scenarios at the coniferous site, slightly less with the larger reduction (Figs. 4a and b). The initial amount of exchangeable base cations and the total acid load were larger at this site than at the beech site. Correspondingly, the annual change in base saturation is larger at the spruce site, but BS stabilizes later than at the beech site.

Fig. 4a. Simulated base saturation obtained by the MIDAS model for the coniferous stand. The net acidifying effect of weathering and biomass turnover at this site makes it impossible for the soil to recover with any of the reduction scenarios and the small input of base cations with deposition.

Fig. 4b. Simulated rate of change in base saturation obtained by the MIDAS model for the deciduous stand.

The reversibility of soil acidification clearly depends on the initial pool of exchangeable base cations and the cation exchange capacity of the soil. Other factors that influence the response time of the soil are the hydrological conditions and the weathering properties of the site. In these runs the rates of nutrient uptake and decomposition were assumed to be constant over the whole time-span. In reality, forest management practices, such as clearcutting and reforestation, change the rate at which nutrients are bound into vegetation and released from decomposing organic matter, and thereby influence the reversibility of soil acidification. Soils in which sulphate adsorption occur may decacidify slower than these model runs suggest. Furthermore, if the rate of weathering increases strongly with the acidity of soil solution, as suggested by e.g. Sverdrup and Warvvinge (1988), the recovery of base saturation may be slower than expected with a constant rate of weathering.
The response of soils to a pulse in deposition was studied by plotting transient base saturation and soil solution pH simulated with the 60% reduction scenario versus average deposition of $SO_4 - S$ of the past five years (Figs. 4 and 5). Transition from point 1 to point 2 in Figs. 4 and 5 represent the period of increasing deposition, from 1950 to 1985, and corresponding acidification. Reducing the deposition in the period 1985 to 1995 (going from point 2 to 3) stops the acidification of the soil at the beech site: BS decreases no more and soil solution pH increases (Fig. 4). As weathering replenishes the pool of exchangeable base cations in absence of a large flux of mobile anions, BS of the beech site slowly increases towards the initial value. It takes 75 years to go from point 3 to 4, and in 2070 the 1950-level is still not reached. The long recovery times were already demonstrated by Coeby and co-workers (1985b). The hysteresis character of the response of the soil at the beech site resembles the pH pathways of surface waters in response to changes in soil sulphate concentrations shown by Reuss and co-workers (1987). If the soil would behave like a system without memory, BS and pH would resume the initial values following the pathways of the acidification phase (from 1 to 2 in Figs. 4 and 5).

**BS pathways**

- beech; - 60%

![BS pathways](image)

**pH pathways**

- beech; - 60%

![pH pathways](image)

Fig. 4. Pathways followed by base saturation and soil solution pH at the beech site upon increasing deposition (from 1 to 2) and decreasing deposition (from 2 to 3) as simulated by the MIDAS model with the 60% reduction scenario.

**BS pathways**

- spruce; - 60%

![BS pathways](image)

**pH pathways**

- spruce; - 60%

![pH pathways](image)

Fig. 5. Pathways followed by base saturation and soil solution pH at the spruce site upon increasing deposition (from 1 to 2) and decreasing deposition (from 2 to 3) as simulated by the MIDAS model with the 60% reduction scenario.
Base saturation and soil solution $pH$ do not recover their initial values at the spruce site, but keep decreasing at the constant deposition maintained after 1995. This is due to the removal of cations by growing vegetation, which was assumed to occur at a constant rate, faster than the rate of weathering.

5. CONCLUSIONS

The reversibility of soil acidification depends on the initial base saturation, the weathering properties of the soil and the vegetation's base cation demand. In predictions with the MIDAS model, only a large reduction of acid deposition (80% of the 1980-level) resulted in a recovery of base saturation at a site with an initially low base saturation and a positive net effect of weathering and biomass turnover. These runs also suggest that recovery of lost base saturation is a slow process, although the initial response to reducing acid deposition may be fast. Only small changes in soil chemistry are reversible in a reasonable time. The pathways followed by base saturation and soil solution $pH$ are not symmetrical in the acidification and recovery phases. This implies that low acid deposition is required over long periods of time to restore acidified soils and surface waters. Forest management also influences the soil's chances to recover lost base saturation.

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