JP&KJM – manuscript – March 17, 1994

PREPRINT: This manuscript has been accepted for publication by *J. Environ. Qual.*, March 1, 1994.

Sulfate Sorption in Soils under Acid Deposition: Modeling Field Data from Forest Liming

Jürgen Prenzel * and Karl–Josef Meiwes

J. Prenzel, Institute for Soil Science and Forest Nutrition, Göttingen University, Büsgenweg 2, Göttingen, Germany; K.–J. Meiwes, Forest Experiment Station of Lower Saxony, Grätzelstraße 2, Göttingen, Germany.
* Corresponding author.

Abbrevations: BEM, Batch Equilibrium Model; CEC, cation–exchange capacity; K_{sp}, solubility product; M_b cation, one of the following: Na, K, Ca, Mg; $\mathrm{pK_{sp}} = -\log_{10} \mathrm{K_{sp}}$;

ABSTRACT

Sulfate sorption can modify the reaction of a soil to acid depositions. Different models of this process exist. In a preceeding paper (21) the adsorption isotherm and the solubility product modeling approach have been compared and a solubility product model has been introduced. The latter model is tested using a forest liming experiment. Concentration data from canopy drip and seepage covering a 20–yr observation period are used as 3–yr moving averages. The model assumes a steady seepage flow and uses only one 1–m compartment. The model considers joint chemical equilibria for gibbsite, jurbanite, cation–exchange and complexation. The seepage pH and concentrations of Al and sulfate under the unlimed reference plot can be modeled if a reduced CEC and a free parameter function for alkalinity production are used. The sulfate desorption caused by liming can be explained by the model. It is concluded that sorbed sulfate contributes to the lime requirement of an acidified soil.

INTRODUCTION

If the soil response to acid deposition is modeled, the process of SO_4 sorption is usually included. SO_4 sorption is understood as reversibly storing not only sulfur but also acidity in the soil matrix and thereby delaying and modifying the acidification of the soil solution (4,18,22).

From laboratory studies it has been known for a long time that SO_4 sorption on soils is pH–dependent (5,23). But many models that aim at understanding and predicting soil acidification under acid deposition impact ignore this pH–dependency (p. 47 in 6). Recently a model has been proposed that includes a pH–dependent SO_4 sorption mechanism by assuming joint solubility equilibria with $AlOHSO_4$ and $Al(OH)_3$ (21).

Applied to liming, this model predicts that the amount of sorbed SO_4 has to be included in the lime requirement for a soil. One question is, whether this conclusion holds if the model is tested against field data. Soil acidification and deacidification are supposed to be influenced by SO_4 sorption or desorption. A second question is, whether a model of this type can predict the development of such changes under field conditions.

The model is tested against field data from the Solling forest research area of Germany. In one plot lime was applied on the forest floor in 1982. Soil solution data from monthly sampling from 1970 to 1991 in 1 m depth are used. An unlimed reference plot is used for comparison. This reference plot shows changes in pH, SO_4, and Al concentrations in the soil solution that can be explained by the model if several ad–hoc assumptions are introduced. If the validity of these assumptions is put into question it still remains possible to interpret the success or failure of the model in predicting the *differences* between limed and unlimed plots.

The interpretation of the field data is restricted to 36–month moving averages of concentrations. No attempt is made to model processes with seasonal or shorter time domain. Rather it is attempted to detect long term trends within the data and to explain them by a model that assumes steady flow conditions.

MATERIALS AND METHODS

Site Description

The Solling mountains are found in the middle of Germany between Hannover and Frankfurt. The forest research area is situated on a flat upland, 500 m above sea level. Mean annual precipitation is 1088 mm, the mean temperature is 6.4 °C. The soil derived from weathered triassic sandstone with loess intermixed by periglacial solifluction. It is a Typic Dystrochrept ("acid podzolic brown earth" in the german soil taxonomy system). Soil texture is dominated by silt, the clay content is 17% by weight. The soils are rich in quartz ($\approx$ 60%), major clay minerals are mica (30%) and kaolinite (5%). Further soil chemical characteristics are given by Matzner and others (14,15,16).

The Solling forest research area is under intensive investigation since 1966 (7). Part of this research has been the estimation of biogeochemical cycling in beech and spruce forests based on monthly sampling of precipitation, canopy drip and soil solution since $\approx$ 1970 (15).

Data from two subplots are used. The reference plot has been described elsewhere as $B1$ and the liming experiment has the internal label BK. They are adjacent parts of a beech (*Fagus sylvatica*, L.) forest, now 146 years old, which is classified as *Luzulo fagetum*. Their size is 10 000 (reference plot) and 1 500 m^2 (limed plot).

Liming Experiment

On plot BK in 1982 the rather high amount of 3 $kg\,m^{-2}$ of finely ground dolomitic limestone has been applied which had been found sufficient to raise soil pH up to 5.5 for the main rooting zone in laboratory soil titration experiments. The lime has been put on top of the forest floor without mixing it into the soil. Details may be found in (2,3,17).

Sampling and Analytics

For canopy drip collection 15 rain gauges were used at each site. They were sampled every week. Solutions were mixed to obtain three composite samples from subsets of the gauges every month for analysis.

For soil solution analysis ceramic suction lysimeters had been installed in 0.9 (reference plot) or 1 m depth (limed plot) in at least threefold replicate. The concentrations observed in these depths are referred to as output concentrations. The suction was applied continuously and the soil solution was collected as monthly sample.

Samples were analyzed for pH using a glass electrode. Aluminum was determined colorimetrically by aluminon (11) before 1980 and by AAS (9) from 1980 on, NO_3 colorimetrically by biacetylmonoxime after reduction by $SnCl_2$ (10) before 1980 and by the Cd reduction method (1) from 1980 on, and SO_4 by potentiometric titration of excess Ba (8) before 1981 and colorimetrically by a modified methylthymol blue method (1) from 1981 on. Any time a new method was introduced its performance and accuracy were tested comparing 100 – 200 analyses by old and new methods.

Data Presentation

For setting boundary conditions and as test of the model measured concentrations in either canopy drip or output soil solution are used. The data are presented as moving averages: Each data point shown is the arithmetic mean of all analysed samples from a symmetric 36–month time interval around this point. At the beginning and at the end of measured time series the interval is no longer symmetrically occupied because it extends into the time not covered by measurements. This averaging procedure is used to filter seasonal and to some degree also yearly fluctuations.

MODEL

General Structure

The core of the model is a system of chemical reactions for which joint equilibrium is assumed. This reaction system is the same as presented recently (Tab. 1 in 21). It consists of 13 reactions: dissolution of $Al(OH)_3$, dissolution of $AlOHSO_4$, exchange between Al^{3+}, Ca^{2+} and H^+, dissociation of H_2O and dissociation of 8 different inorganic Al–complexes. One further anion is included, that does not enter any reaction within the model. This is interpreted as NO_3 in this paper, instead of Cl in (21).

The solubility product of $AlOHSO_4$ has been set to $pK_{sp} = 17.8$ which is a representative value for this site as calculated from soil solution data (Fig. 5 in 16). The same value has been used in the preceding paper (21). The solubility product for $Al(OH)_3$ is set to $pK_{sp} = 33.0$ which is again a representative value for the beech site in the Solling research area (Fig. 3 in 16) and well within the range reported for soils (13). The remaining 10 equilibrium constants have been chosen as in (21).

The model considers the upper meter of the soil as one compartment. The dry soil density is set to 1.3 $\mathrm{Mg\,m^{-3}}$, which is a median value for this site (p. 96 in 15). The time step is one year. The mean annual seepage at the beech sites in the Solling research area is 578 $\mathrm{L\,m^{-2}}$ (15). This flow is assumed as constant in the model. In each time step the equilibrium between one years's seepage and the soil matrix is calculated.

Boundary conditions for the model are the concentrations in the input solution that enters the model reaction system at each time step. In this input solution H^+ is defined implicitely by the charge balance rule: The absolute value of the sum (in equivalents) of all cations minus the sum of all anions specified is the concentration of H^+ if the sum is negative, or of alkalinity, if it is positive. Calcium in this model is meant to represent the M_b cations (K+Na+Mg+Ca).

The input concentrations of SO_4 and NO_3 have been taken from measurements.

The input concentration of Ca has a complex interpretation. Part of the SO_4 and NO_3 deposition is neutralized by M_b cations prior to deposition. Ecosystem internal processes like ion uptake, mineralization, and silicate weathering produce or consume alkalinity. The input flux of Ca is used to lump all such processes together. In other words, it is meant to be the input of alkalinity to the mineral soil that results from deposition and from ecosystem internal processes. The Ca input has been used here as free parameter–function in the fitting of model behavior to the data.

Further parameters are the CEC and the initial amounts of Al, Ca, and SO_4 in the model. These amounts are sums over all phases: solution, salts, and exchangeable cations (20).

The model calculations have been carried out using the program BEM (batch equilibrium model), which is a general program for the calculation of coupled chemical equilibria including complexation, precipitation, and cation-exchange (20). Specific models are defined for BEM in model files. The model files that were used here are available via internet (anonymous ftp retrieval from ftp.gwdg.de in pub/forest-soils/bem/models/prenzel.94a). The program description (20) is found also there (in pub/forest-soils/bem/doc).

Modeling the Reference Plot

Fig. 1 *sulfate input*

The input of SO_4 is based on measured concentrations in the canopy drip of the reference plot times a factor of 2.25 (Fig. 1). The ratio between water input to the soil and seepage is on average 1.5 at this stand (15), due to evapotranspiration. The total input of SO_4 to the soil is greater than the input by canopy drip alone, due to stem flow. The ratio of total to canopy drip input is again 1.5 (15). The product of both factors is 2.25. It is assumed that mineralization and uptake of sulfur balance each other, therefore not influencing the SO_4 input to the mineral soil.

Fig. 2 *nitrate input*

The input of NO_3 to the model has been taken as the measured concentration in the output soil solution (Fig. 2). It can be said that nitrogen deposition to this stand consists of NH_4 and NO_3 in approximately equal concentrations (15). In this case complete uptake of deposited nitrogen has no side effect in producing or consuming H^+. The seepage output of nitrogen, on the other hand, is rather NO_3 alone and not NH_4 (15). Therefore, the seepage output of NO_3 is equivalent to the input of nitric acid to the soil (p. 47 in 24).

Fig. 3 *Ca input*

The assumed Ca input, which is to be interpreted as alkalinity input to the mineral soil, is shown in Fig. 3. It can not be compared to a single measurable quantity but the net input of acid or negative alkalinity can be compared with estimates that are based on measured ion fluxes. This will be done in the discussion section.

The soil solution pH at this site drops from ≈ 4.3 to ≈ 3.8 in 1975 to 1977 and recovers in 1978 to 1983 (Fig. 5). pH values as low as 3.8 would result in unrealistically high Al concentrations if a solubility equilibrium with $Al(OH)_3$ were assumed. Therefore the initial element stores had to be low enough that $Al(OH)_3$ was not present in 1977 (Fig. 7).

Meiwes (12) found $1\,\mathrm{mmol\,kg^{-1}}$ of extractable SO_4 at this site. This value is used as initial amount of $AlOHSO_4$. But $AlOHSO_4$ remains present during all simulations. Therefore the initial amount does not influence the calculated solution concentrations.

The limited amount of $Al(OH)_3$ assumed is in a sense balanced by the assumption of an input flux of Al to the model. This is interpreted as a result of the weathering of layer silicates. This input flux is equivalent to an input of $Al(OH)_3$. But instead of an unlimited amount of salt that is assumed to be in equilibrium we use a defined flux of $230\,\mu$mol(Al) L^{-1}, which is equivalent to $4\,\mathrm{kmol_c\,ha^{-1}\,yr^{-1}}$.

The measured soil solution concentrations change more than twofold within less than 5 yr (Fig. 5, 4, and 6). This behavior can not be reproduced by the model if we use CEC values as determined by routine laboratory methods. Matzner (p. 96 in 15) gives a median value of $413\,\mathrm{kmol_c\,ha^{-1}}$ and a median bulk density of $1.3\,\mathrm{t\,m^{-3}}$ for 0 – 0.5 m at this site. Assuming the same properties for the soil in 0.5 – 1 m a CEC of $64\,\mathrm{mmol_c\,kg^{-1}}$ results. We use a value of 18, which is 28% of 64. This difference may be caused by different kinetic availability of sites: while the CEC determination in the laboratory is based on a soil suspension, under field conditions intra–aggregate surfaces may not be available for exchange reactions within a few years.

Modeling the Limed Plot

The model for the liming experiment has different input functions for Ca and for NO_3 but is otherwise the same as for the reference plot.

The lime deposited on the forest floor is dissolved mainly by carbonic acid (19)

$$CaCO_3^{(s)} + CO_2^{(g)} + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad [1]$$

The bicarbonate then is transported by seepage to the mineral soil. For the model this reaction generates only an additional input of Ca because HCO_3^- is not a specified input concentration but is implicitely calculated from the charge balance and the partial pressure of CO_2.

As for the reference plot, the additional Ca input flux (Fig. 3) is not based on measurements but is used as (almost) free parameter function.

The response of the soil solution pH in 1 m depth to liming is very quick. Immediately after liming pH rises to ≈ 4.9 and falls to ≈ 4.5 within 10 years. The immediate response may be interpreted as macropore transport of lime suspension. We take this into account in the model by a pulse of $3000\,\mu$mol(Ca) L^{-1}. A more measured response of $800\,\mu\mathrm{mol\,L^{-1}}$ is assumed only from 1988 on. The delay between 1982 and 1988 in the assumed additional alkalinity input counterbalances the spatial crudity of the model. In the model each change in the input concentrations immediately affects the whole 1-m compartment while in reality a gradient will develop with early response at the top and later response at the bottom of a soil layer.

The output concentration of NO_3 at the limed plot is increased for 10 years after liming. This is considered in the model as additional input of NO_3, that is of acid (Fig. 2).

RESULTS AND DISCUSSION

Model Assumptions

The resolution of the model in space and time is obviously very coarse, one 1–m compartment and a time step of one year at an assumed steady seepage flow. The purpose of such a model can be the prediction of long term trends in soil acidification, certainly not the fluctuations between or within years.

It was not possible to explain the variability of observed pH and SO_4 and Al concentrations if the full CEC as determined in the laboratory was used in the model. If that was done the concentration curves became far too dampened. This experience leads to the idea of internal or intra–aggregate surfaces that are not quickly reacting in the field but are so in the laboratory, where aggregates are destroyed. Another observation pointing in the same direction is the sudden strong response in 1–m depth to liming (Fig. 5). A possible explanation is the transport of fine lime particles as suspension. Here again, not the whole bulk soil is reacting.

The model has been tuned to follow observed fluctuations that occur within ≈ 5 yr. If trends within, say, 50 or 100 yr were studied, it might be appropriate to include the total CEC because internal surfaces are not really cut off from the transport flow but are connected to it by slow diffusion.

pH values as low as 3.8, which have been observed in 1977, cannot be assumed to be in equilibrium with $Al(OH)_3$. Using the equilibrium constants of this model this would lead to an Al^{3+} concentration of more than $100\,\mathrm{mg\,L^{-1}}$, which is almost never observed. On the other hand, aluminous minerals are still present in the soil. This leads to the assumption that Al silicates do not dissolve quickly enough to maintain equilibrium. A dissolution rate of $4\,\mathrm{kmol_c\,ha^{-1}\,yr^{-1}}$ is assumed here. If the maximum weathering rate of $0.38\,\mathrm{kmol_c\,ha^{-1}\,yr^{-1}\,m^{-1}}$ estimated by Matzner (p. 105 in 15) is attributed to muskovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, this would mean $3.42\,\mathrm{kmol_c\,ha^{-1}\,yr^{-1}}$. Kaolinite dissolution, which is not included in the term silicate weathering as used by Matzner, may also contribute. So the assumed Al input into the model system is not exeedingly high.

The assumed input concentrations for this model implicitely define the assumed input of alkalinity

$$\mathrm{alk} = [\mathrm{Ca}] - [\mathrm{SO_4}] - [\mathrm{NO_3}]$$

where [ ] denote concentrations in units of equivalent charge. For the reference plot *alk* is negative indicating an input of acidity. While the

SO_4 and NO_3 inputs are based directly on measurements (Fig. 1,2), the Ca input (Fig. 3) is used as a free parameter function that has to represent all processes that produce or consume alkalinity, like ion uptake, mineralization, and silicate weathering.

Matzner (p. 93 in 15) gives an estimate for the H^+ load to the mineral soil that may be compared to the net alkalinity input used for this model. The SO_4, NO_3, and Ca input functions are equivalent to an acidity input of $3.5\,\mathrm{kmol_c\,ha^{-1}\,yr^{-1}}$ on average for 1970 to 1985. This is the same order of magnitude as the value of 2.9 $\mathrm{kmol\,(H^+)\,ha^{-1}\,yr^{-1}}$ given by Matzner for this period. No explanation can be offered for the form of the Ca input curve used for the reference plot model (Fig. 3). This form has been found by trial and error in attempts to fit the model to the measured output concentrations.

The additional Ca input assumed for the limed plot (Fig. 3) is interpreted as lime dissolution. But there is no direct way to measure this process. Therefore, this Ca input function is a free parameter function too. The observations show an immediate response, especially in pH (Fig. 5) in 1982 and a second response, especially in SO_4 (Fig. 4) from 1988 on. As discussed above, this may be due to a quick reaction of fine particles transported as suspension and a slower proceed of soil deacidifcation from the top soil downwards.

The model assumes a Ca pulse in 1982 of 3000 and a constant input of $800\,\mu\mathrm{mol\,L^{-1}}$ from 1988 on. The maximum solubity of calcite can be calculated from thermodynamics. It depends on temperature and CO_2 partial pressure. The values of 800 and 3000 $\mu\mathrm{mol\,L^{-1}}$ are in the range to be expected (19).

Model Output

Fig. 4 *sulfate output*

Fig. 5 *output pH*

Fig. 6 *Al output*

The concentrations of SO_4 and Al and the pH in the soil solution in 1 m depth are more or less reproduced by the model (Fig. 4, 5, and 6). The main deviations occur for Al that is underestimated by $\approx 50\%$ from 1982 on.

Fig. 7 *salts*

The sorption of SO_4 can be seen directly as change in the store of $AlOHSO_4$ (Fig. 7). This curve for the reference plot is different in shape from the measured and simulated SO_4 concentration curves (Fig.

4). While the $AlOHSO_4$ curve is monotonically increasing, the SO_4 curve has a main maximum in 1979. Such a result cannot be produced by adsorption isotherm models (21). The reduced SO_4 input from $\approx$ 1988 on leads to a leveling off of $AlOHSO_4$ precipitation in the reference plot model while $Al(OH)_3$ is again formed.

The desorption of SO_4^{2-}on liming exhibited the model (Fig. 4) can be explained by

$$2HCO_3^- + AlOHSO_4^{(s)} \rightleftharpoons SO_4^{2-} + Al(OH)_3^{(s)} + 2CO_2^{(g)} \qquad [2]$$

where HCO_3^- stems from lime dissolution (Eq. 1). Fig. 7 shows the steep increase in $Al(OH)_3$ and the decrease in $AlOHSO_4$ calculated by the model for the limed plot. This desorption effect can not be explained by models that are based on pH–independent adsorption isotherms (21).

The relative success of the model in reproducing measured soil solution data does not prove that these salts are present in the soil in a sense that might be detectable by optical of difractrometric methods. It is only shown that the assumption of joint solubility equilibria of these types can be used as an approximate model for the interaction of soil solution and soil matrix. Probably a closer look would reveal solids that are not pure and not homogeneous. A hint in this direction is the observed variability of ion activity products (16,21).

The model for the reference plot cannot be called predictive in the form presented here. Especially the Ca input function is a parameter function that had to be adapted to the test data set. Also, the reduction in CEC could not be determined indepentently. But, on the other hand, the proposed model mechanisms have not been falsified by this data set. It may be possible to use the model for more long term predictions if unknown parameters can be replaced by reasonable guesses. Such guesses may stem from steady state assumptions for the biotic parts of the ecosystem. Such more long term scenarios have been presented in (21).

The additional assumptions that were introduced in modeling the liming experiment are not many. The prediction of the response to liming is a major test for this model.

CONCLUSION

If soils that contain sorbed SO_4 are limed, the SO_4 is desorbed. A model is presented that can explain this observation at least qualitatively. The model could be fitted to an existing data set by several ad–hoc hypotheses. The general applicability of this model for short term predictions is open for further investigations. The use of the model in scenarios for > 50 yr may be reasonable.

REFERENCES

1. American Public Health Association. 1985. Standard methods for the examination of water and waste water. 16th ed. APHA, New York.
2. Beese, F. 1989. Wirkungen von Kalkungs– und Düngungsmaßnahmen auf die chemische Zusammensetzung der Bodenlösung. Rep. Forest Ecosystem Research Center at the Göttingen University (Göttingen, Germany), Ser. A 49:27–48.
3. Beese, F. and J. Prenzel. 1985. Das Verhalten von Ionen in Buchenwald–Ökosystemen auf podsoliger Braunerde mit und ohne Kalkung. Allg. Forst Zeitschr. 41:1162–1164.
4. Cosby, B. J., G. M. Hornberger, R. F. Wright, and J. N. Galloway. 1986. Modeling the effects of acid deposition: control of long–term sulfate dynamics by soil sulfate adsorption. Water Resour. Res. 22:1283–1291.
5. Courchesne, F. and W. H. Hendershot. 1989. Sulfate retention in some podzolic soils of the southern Laurentians, Quebec. Can. J. Soil Sci. 69:337–350.
6. Eary, L. E., E. A. Jenne, L. W. Vail, and D. C. Girvin. 1989. Numerical models for predicting watershed acidification. Arch. Evironm. Contam. Toxicol. 18:29–54.
7. Ellenberg, H., R. Mayer, and J. Schauermann (ed.). 1986. Ökosystemforschung: Ergebnisse des Sollingprojekts 1966–1986. Ulmer, Stuttgart, Germany.
8. Grether, C. 1965. Die Bestimmung von Sulfat mit potentiometrischer Titration. Application Bulletin (Metrohm Comp., Herisau, Switzerland) A38d.
9. Heinrichs, H., N. König, and R. Schultz. 1985. Atomabsorptions– und emissionsspektroskopische Bestimmungsmethoden für Haupt– und Spurenelemente in Probelösungen aus Waldökosystem–Untersuchungen. Rep. Forest Ecosystem Research Center at the Göttingen University (Göttingen, Germany) 8:1–92.
10. Holz, F. and H. Kremers. 1973. Automatische photometrische Simultanbestimmung von Sulfat und Nitrat in Trink–, Fluß– und Dränwasser. Landw. Forsch 28 (Sonderheft I):189–201.

11. Hsu, P. H. 1963. Effect of initial pH, phosphate and silicate on determination of aluminum with aluminon. Soil Sci. 96:230–238.

12. Khanna, P. K., J. Prenzel, K. J. Meiwes, B. Ulrich, and E. Matzner. 1987. Dynamics of sulfate retention by acid forest soils in an acidic deposition environment. Soil Sci. Soc. Am. J. 51:446–452.

13. Lindsay, W. L. 1979. Chemical equilibria in soils. Wiley, New York.

14. Matzner, E., P. Khanna, K. Meiwes, and B. Ulrich. 1983. Effects of fertilization on the fluxes of chemical elements through different forest ecosystems. Plant Soil 74:343–358.

15. Matzner, E. 1988. Der Stoffumsatz zweier Waldökosysteme im Solling. Rep. Forest Ecosystem Research Center at the Göttingen University (Göttingen, Germany), Ser. A 40.

16. Matzner, E. and J. Prenzel. 1992. Acid deposition in the German Solling area: Effects on soil solution chemistry and Al mobilization. Water Air and Soil Pollution 61:221–234.

17. Meiwes, K. J. and F. Beese. 1992. Chemical changes in an ammonium sulphate fertilized and a limed soil under beech. p. 825–826. *In* A. Teller, P. Mathy, and J. Jeffers (ed.) Responses of forest ecosystems to environmental changes. Elsevier.

18. Prenzel, J. 1983. A mechanism for storage and retrieval of acid in acid soils. p. 157–170. *In* B. Ulrich and J. Pankrath (ed.) Effects of accumulation of air pollutants in forest ecosystems. Reidel, Dordrecht, Netherlands.

19. Prenzel, J. 1985. Die maximale Löslichkeit von oberflächlich ausgebrachtem Kalk. Allg. Forst Zeitschr. 41:1142.

20. Prenzel, J. 1991. Introduction to BEM (Batch Equilibrium Model). Rep. Forest Ecosystem Research Center at the Göttingen University (Göttingen, Germany), Ser. B 28.

21. Prenzel, J. 1994. Sulfate sorption in soils under acid deposition: Comparison of two modeling approaches. J. Environ. Qual. 23:188–194.

22. Reuss, J. O. and D. W. Johnson. 1986. Acid deposition and the acidification of soils and waters. No. 59 in Ecological Studies. Springer-Verlag, New York etc.

23. Singh, B. R. 1984. Sulfate sorption by acid forest soils: 3. Desorption of sulfate from adsorbed surfaces as a function of time,

desorbing ion, pH, and amount of adsorption. Soil Sci. 138:346–353.

24. Ulrich, B. 1991. An ecosystem approach to soil acidification. p. 28–79. *In* B. Ulrich and M. E. Sumner (ed.) Soil acidity. Springer, Berlin.

CAPTIONS

Fig. 1: SO_4 concentrations in the canopy drip under beech at the reference plot (REF. exp.) multiplied by 2.25 and assumed input concentrations of SO_4 in models for reference (REF.) and limed (LIME) plot.

Fig. 2: NO_3 concentrations in the output soil solution under reference plot (REF. exp.) and limed plot (LIME exp.) and assumed input concentrations of NO_3 in models for reference plot (REF. mod.) and limed plot (LIME mod.).

Fig. 3: Assumed input concentrations of Ca in the models for reference (REF.) and limed (LIME) plot.

Fig. 4: SO_4 concentrations in the output soil solution under reference plot (REF. exp.) and limed plot (LIME exp.) and simulated output concentrations from models for reference plot (REF. mod.) and limed plot (LIME mod.).

Fig. 5: pH in the output soil solution under reference plot (REF. exp.) and limed plot (LIME exp.) and simulated output pH from models for reference plot (REF. mod.) and limed plot (LIME mod.).

Fig. 6: Aluminum concentrations in the output soil solution under reference plot (REF. exp.) and limed plot (LIME exp.) and simulated output concentrations from models for reference plot (REF. mod.) and limed plot (LIME mod.).

Fig. 7: Simulated soil matrix concentrations of salts in models for reference plot (REF. mod.) and limed plot (LIME mod.).