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Sulfate Sorption in Soils under Acid Deposition: Comparison of Two Modeling Approaches

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Abbrevations: BEM, Batch Equilibrium Model; IAP, ion activity product; p$K = -\log_{10} K$ for any positive number K

ABSTRACT

Soil acidification under the impact of acid deposition is often modeled by adsorption isotherms. The assumption of solubility equilibria for basic Al sulfates is an alternative modeling approach. Similarities and differences between both concepts are discussed. A simple solubility equilibrium model is defined and used to demonstrate that the second model can explain results that are well described by typical adsorption isotherms. The same model can also explain a pH dependency of adsorption isotherms that has been widely reported. In the application to assumed soil acidification scenarios, predictions are presented that could not be described by an adsorption isotherm approach.

INTRODUCTION

Acid deposition is a major environmental concern in much of the industrial world and it may become more widespread if more and more countries start using more and more fossil fuels.

Soils have a buffering effect that mediates the impact of acid deposition. But this buffering capacity can become exhausted leading to the acidification of the soil solution and subsequently streams and lakes. Macroscopic soil acidification models have been set up to predict the velocity of this process.

A main component of man–made acid deposition is H_2SO_4. Soils often have the ability to sorb SO_4 and this process seems to be an important part of their buffering power against the impact of acid deposition. But the process is reversible: SO_4 can be desorbed again and reappears as H_2SO_4 in the soil solution (25,28).

There are at least three ways in which macroscopic soil acidification models include the process of SO_4 sorption: (i) the adsorption isotherm approach, (ii) the solubility product approach, and (iii) the anion exchange approach (13). Concept (i) has found application in several published models during the 1980s (9,29), while concepts (ii) and (iii) have been used less often.

In most applications of concept (i) the adsorption isotherms are not pH–dependent. In these cases SO_4 sorption is described as function of a single state variable, the SO_4 concentration in solution. Concept (ii) uses an equation where at least three solution concentrations are combined (Al, OH, and SO_4). Concept (iii) involves specific exchange between two of the ions (SO_4 and OH) and is in this sense intermediate between (i) and (ii).

This paper compares concepts (i) and (ii). A model is set up which uses the solubility product approach. This model shows adsorption isotherm behavior if certain sorption experiments are modeled, demonstrating that concept (ii) can include concept (i) under certain circumstances. In other situations solubility product models differ significantly from adsorption isotherm models. This is the case when acidification has used up available Al that may react with SO_4 and also when soil acidification is neutralized by liming.

The modeling approaches are related to microscopic chemical concepts (33): The adsorption isotherm and the anion exchange concepts are connected to the concept of *adsorption*, which defines sorption as an interfacial, two–dimensional process. The solubility product, on the other hand, is derived from thermodynamic considerations regarding the chemical potential of a *bulk precipitate*. It is difficult to design experiments that can distinguish between these two microscopic concepts. Often sorption experiments can be explained by either concept (33). No attempt is made to decide what really happens at the soil solution interface when SO_4 is sorbed. Rather, a strictly macroscopic view is taken.

The concepts discussed here are narrower than those of adsorption and precipitation in general. They are the concept of a *single* adsorption isotherm on the one hand and of *constant* solubility products on the other. The limitations of both are easily demonstrated: empirical SO_4 adsorption isotherms are pH–dependent and relevant empirical ion activity products are not constant in soils. However for macroscopic models one has to use simplifications and approximations if one cannot incorporate the empirical variance into a theory and this into the model.

MODELING APPROACHES

Common Features

All models to be discussed suppose that SO_4 sorption can be described by

$$X(OH)_2 + SO_4^{2-} \rightleftharpoons XSO_4 + 2OH^- \qquad [1]$$

with X denoting the soil matrix.

In adsorption isotherm models this assumption is usually not made explicitly. But many models behave in this way because they indirectly calculate the solution pH from a charge balance equation and, if SO_4^{2-} disappears from solution, H^+ must also disappear. This is equivalent to the appearance of OH^- in order to maintain the dissociation equilibrium for water.

The solubility product model presented in this paper uses $AlOHSO_4$ as the sink for SO_4 ions with $Al(OH)_3$ as the principal source for the necessary Al ions:

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

In this way both modeling approaches predict an influence of SO_4 sorption on soil pH. The sorption process is seen as a buffer mechanism against acidification by H_2SO_4. The reversal of reaction, Eq. [1] leads to a consumption of OH^- or to the appearance of H_2SO_4 as result of SO_4 desorption.

Adsorption Isotherms

A SO_4 adsorption isotherm is a monotonically increasing function f

$$q = f(c) \qquad [3]$$

where q is the amount of SO_4 sorbed per unit mass of soil matrix and c is the concentration of SO_4 in the soil solution (33: p. 117).

For many years the retention of SO_4 by soils under the impact of H_2SO_4 deposition has been studied in the field and in sorption experiments. In many experiments results could be described by adsorption isotherms (6,21,30,37).

In most cases it has been found that SO_4 sorption depends on pH (6,21,23,31,37). In some studies the sorption of SO_4 is restricted to pH values near 4.0, with a sorption maximum at pH $\approx$ 4.0 and about 40% less sorption at pH values 3.5 and 4.5 respectively (37,23,6). An adsorption isotherm for a range of pH conditions therefore should read

$$q = f(c, \mathrm{pH}) \qquad [4]$$

The function f in Eq. [3] or [4] is specific for any one soil material. One factor that has been found to correlate strongly with the ability of a soil horizon to sorb SO_4 is the concentration of dithionite– or citrate–extractable Al oxides (6,12,36).

Reuss et al. (29) and Eary et al. (9) reviewed models that deal with acidification on a watershed or larger scale. In many cases a SO_4 adsorption isotherm is incorporated in the models. The models BIRKENES (38), ETD (22), ILWAS (14), and MAGIC (5) are discussed in more detail. They all include some form of a ionic charge balance for the solution phase enabling them to be described by Eq. [1].

In BIRKENES the concentrations of Ca^{2+} and Mg^{2+} are either functions of pH because cation exchange equilibria at constant saturation percentages are assumed, or they are defined by a weathering flux, and $[Al^{3+}]$ is a function of pH because equilibrium with gibbsite is assumed. Among the ions considered by the model only H^+ is free to vary and is thus implicitly assumed to be cosorbed with sulfate.

The chemical part of ETD is built around the concept of conservation of alkalinity. SO_4 sorption is considered as a source for alkalinity. Alkalinity can be defined as (28):

$$alk = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

The first two of these concentrations are functions of pH and the partial pressure of CO_2. If this partial pressure is thought to be fixed independently, SO_4 sorption can be understood as generating OH^- or removing H^+ in accordance with Eq. [1].

ILWAS includes SO_4^{2-} in its operational definition of alkalinity (Eq. 22 of (14)) which is used to calculate the pH. Because all other concentrations are either fixed by mass balances or equilibria (Tab. 1 of (14)), only H^+ remains to maintain electroneutrality if SO_4 is sorbed.

MAGIC explicitly incorporates a charge balance equation (3). All total concentrations except H^+, OH^-, Al–species and inorganic carbon are fixed by mass balances. Al species and carbonic acid species are fixed at given pH and partial pressure of CO_2. Therefore, also in this model the sorption of SO_4 is accompanied by a rise in pH (cf. Eq. [1]).

Each of the four models has been calibrated and tested to explain the present variation in streamwater chemistry for certain watershed systems. Streamwater chemistry depends on seasonal hydrological fluctuations and the models explain well such changes in pH, alkalinity and other solution concentrations. But longer term trends in acidification of catchments are difficult to isolate from short observation records of streamwater chemistry. It seems that these models have not been compared with soil solution data from the field or to laboratory experiments with soils, though soil chemistry is incorporated in some of them. With larger changes in soil pH it might be necessary to include the pH dependency of sulfate sorption.

Solubility Products

The concept of a solubility product is founded on chemical thermodynamics and describes the relationship between activities in a chemical equilibrium. The attainment of equilibrium for any chemical reaction depends on its reaction velocity. In complicated models that include several reactions together with transport processes, an equilibrium assumption is appropriate if the reaction is fast compared with other processes, like diffusion, bulk transport, or uptake. Singh (32) has found 90% completeness of SO_4 sorption within 10 d. For our present purpose of comparison it is not necessary to dwell further on this issue because the adsorption isotherm models rely on equilibrium concepts too; time is not a variable in adsorption isotherms. Therefore they assume implicitly an equilibrium between solution and matrix with respect to SO_4 sorption.

The theoretical derivation of the solubility product equation (8: p. 308) further assumes the existence of a solid phase that has a fixed chemical potential at a given temperature and pressure. This is plausible if we deal with a salt of constant internal composition and negligible surface energy. In this case the specific Gibbs energy of any ion in the salt does not depend on the ratio of salt to solution nor can it depend on varying compositions of the salt. The equilibrium considered is for the dissolution or precipitation of such a salt to or from its ionic components in aqueous solution. Let X_i $(i = 1, \ldots, n)$ be the components of the salt X. Then the solubility product is

$$K_{sp}^{(\mathrm{X})} = (\mathrm{X}_1) \cdot \ldots \cdot (\mathrm{X}_n) \qquad [5]$$

where (X_i) stands for the *activity* of X_i in solution and $K_{sp}^{(\mathrm{X})}$ depends only on temperature and pressure and the state (chemical potential) of X. For well defined pure substances $K_{sp}^{(\mathrm{X})}$ is a universal constant. But in soils it may describe a solubility equilibrium with an impure or metastable (e.g., amorphous) solid phase. If $K_{sp}^{(\mathrm{X})}$ is not really a constant but varies with changing composition of X and with time (as a metastable X is transformed into a more stable form) then justification for using Eq. [5] as an approximate model has to be tested against empirical evidence.

The assumption of one or more equations like Eq. [5] is the core of the solubility product approach to soil chemical modeling. The assumed constants $K_{sp}^{(\mathrm{X})}$ may be specific for local conditions. This is comparable to adsorption isotherm functions being not universal but dependent on local conditions.

The right hand side of Eq. [5] can be determined for any given solution. This expression is called an (empirical) ion activity product IAP. The condition of solubility equilibrium for X then can be expressed as

$$IAP^{(\mathrm{X})} = K_{sp}^{(\mathrm{X})} \qquad [6]$$

One approach in studying solubility equilibria in soils is to test the hypothesis $IAP^{(\mathrm{X})}$ = constant for a given X and varying solution compositions. This method has found wide application on acid soils, in both, field and laboratory studies.

Salts that may be involved in the sorption of SO_4 have been compiled by Nordstrom (24). He used results from experiments with defined substances and concluded that when acid soils received H_2SO_4 depositions the formation of jurbanite, $AlOHSO_4$, or alunite, $KAl_3(OH)_6(SO_4)_2$, was probable.

In Spodosols from Quebec, Canada, the IAPs seemed to indicate joint equilibria with $Al(OH)_3$ and $KAl_3(OH)_6(SO_4)_2$ at $\mathrm{p}K_{sp}$ values of 33.2 and 85.4 respectively (7).

Danish Podzols and podzolized brown earths were subjected to enhanced acid input in the laboratory and ist was found that a possible equilibrium with $AlOHSO_4$ ($\mathrm{p}K_{sp}$ = 17.2) existed in one case and a probable joint equilibrium with $Al(OH)_3$ ($\mathrm{p}K_{sp}$ = 33.9) and $AlOHSO_4$ ($\mathrm{p}K_{sp}$ = 17.8) in another case (15).

Weaver et al. (37) studied a soil from Göttingen, Germany, that developed from limestone residuum over limestone and has a pH near 6 measured in water. After addition of SO_4 the IAP indicated a possible equilibrium with $AlOHSO_4$ ($\mathrm{p}K_{sp}$ = 17 to 18) if the pH was lowered to

< 5.5 by addition of HCl.

In the Solling forest research area of Germany, IAPs from suction lysimeter solutions taken at 20–, 40– and 80–cm depth indicate joint equilibria among $Al(OH)_3$ (pK_{sp} = 33.1 to 33.9), $KAl_3(OH)_6(SO_4)_2$ (pK_{sp} = 82.2 to 83.8), and $AlOHSO_4$ (pK_{sp} = 17.2 to 17.8) (19). The solutions from 10–cm depth appear undersaturated with respect to all three salts. There is a systematic difference in IAPs for jurbanite and alunite between the beech and the spruce site in the Solling. The soil solutions under the beech forest seem to be undersaturated or in contact with less soluble basic Al sulfates.

A review of $>$ 2000 soil saturation extracts from German forest soils (27) showed relationships between ion activities in accordance with Eq. [5] for gibbsite between pH 4 and 7, for alunite betweeen pH 3.8 and 7, and for jurbanite between pH 3.8 and 4.2. Outside these pH ranges the activities did not follow the form of Eq. [5]. Inside these ranges the IAP values were between 32 and 34 for $Al(OH)_3$, between 81 and 85 for alunite, and between 17 and 18 for jurbanite.

In none of these IAP studies is Eq. [6] strictly obeyed. There is a considerable variance. This can be explained by (i) lack of chemical equilibrium or (ii) impurities or varying composition of the salt phase (solid solution) (16). It is not possible to deduce the existence of alunite, jurbanite or gibbsite in the soil from IAP studies (33: p. 122–128). From a chemical point of view there remains the need for direct identification of the chemical state of sorbed sulfate.

The IAP studies on basic Al sulfates show a more or less consistent picture with a range of different soils. The salts involved have been prepared in the laboratory and the possibility of their existence in acid soils has been shown. It seems justified, therefore, to incorporate the concept of solubility equilibrium for basic Al sulfates into models and to test such models against empirical evidence.

Few models of this kind have been published. Förster (10,11) used an equilibrium with $AlOHSO_4$ in a model that included cation exchange, complexation and diffusion. He was able to describe a soil column that exhibited SO_4 retention when a concentration pulse of neutral salt was added. He was also able to explain qualitatively the SO_4 dynamics of the spruce plot in the Solling area, which shows SO_4 retention for several years followed by SO_4 release in the following years without much change in the SO_4 input (16).

Lükewille and Prenzel (18) used a model with solubility equilibria for jurbanite– and alunite–like minerals to reconstruct the acidification history of a small catchment in Germany. They were able to reproduce present day concentrations in soil and stream water.

General Comparisons

The adsorption isotherm models discussed above follow Eq. [1] and thereby allow SO_4 sorption to control soil pH. But as they make the amount sorbed a function of dissolved SO_4 alone, (Eq. [3],) they do not take into account the control pH may have over SO_4 sorption. Models of the anion exchange type (13) would include this control.

Models of the solubility product type that use Al ions from soil Al hydroxides as the source of precipitating cations for sulfate include not only control of SO_4 sorption over pH, and vice versa, but also the influence of Al availability in the soil.

Such differences between modeling approaches may be especially important if pH changes across a wide range. On the one hand, in extreme acidification the availability of Al may affect SO_4 sorption. If, on the other hand, a soil is limed, SO_4 desorption is to be expected, but cannot be described by a simple adsorption isotherm, (Eq. [3]).

The concept of an adsorption isotherm is usually linked to the idea of a limited adsorption capacity that is reflected in the isotherm function as decreasing slope with higher values of c in Eq. [3]. The solubility product approach has a comparable limit in the amount of available $Al(OH)_3$ for Eq. [2]. Available Al here will not include all Al in the soil. But there is another mechanism which limits the SO_4

sorption in models based on Eq. [2]: any increase in pH will shift the equilibrium of Eq. [2] to the left. This will be demonstrated by the example model calculations below.

METHODS

Defining the Model

The simplified soil chemical equilibrium model includes only the cations Ca, Al and H and the anions SO_4, Cl and OH. Ca represents all basic cations (Na, K, Ca, Mg) and Cl represents all anions of strong acids, other than SO_4. Only one of the possible basic Al sulfates is included: $AlOHSO_4$. The model assumes chemical equilibrium for the 13 reactions shown in table 1. enter Tab. 1

The solubility product for $Al(OH)_3$ ($\mathrm{p}K_1^\circ$ in table 1) is set to 33.5. This is almost the solubility of synthetic gibbsite given by May and Nordstrom (recalculated as $\mathrm{p}K_{sp} = 33.88$) (20) with a slight shift towards natural or microcristalline Al hydroxide. It is also a value which is commonly found as the ion activity product in soil solutions from German forest soils (27).

The solubility product for $AlOHSO_4$ ($\mathrm{p}K_2^\circ$) is set to 17.8, which is found as a typical ion activity product in German forest soils (27) and has been reported by Nordstrom (24) for jurbanite.

Cation exchange is modeled using selectivity coefficients as defined by Bruggenwert and Kamphorst (2). The parameter values 0.0 and -1.5 for $\mathrm{p}K_3^\circ$ and $\mathrm{p}K_4^\circ$ respectively are typical values for German forest soils, if the calculation is based on water saturation extracts for solution cations and $1\,\mathrm{mol\,L^{-1}}$ NH_4Cl extracts for exchangeable cations (27).

K_5° is the ionic product of water. All other K_i° values define the stability of complexes, and have the form of the mass action law .

One additional ion is Cl^-. It is not involved in equilibria but is necessary for the simulation of additions of neutral salt ($CaCl_2$), or acid that is not H_2SO_4 (HCl).

The equilibrium expressions are complemented by element balances for Al, Ca, and Cl, and by the charge balance for ions in solution and by the Davies equation for activity corrections. No attempt is made to use equilibrium constants for any temperature other than the standard temperature of 25 °C.

The cation–exchange capacity is assumed to be 50 $mmol_c\,kg^{-1}$. The initial saturation of cation exchanger is 2.5% Ca and 97.5% Al in most cases, but these parameters are reset for the first simulated experiment.

The bulk density of the soil is assumed to be 1 $kg\,L^{-1}$.

The initial amounts of $Al(OH)_3$ and $AlOHSO_4$ are assumed to be 20 and 5 $mmol\,kg^{-1}$ respectively. These parameters influence the model behavior because the salts can dissolve completely during model runs. The values have been chosen to include this disappearance of salts in the simulations. The value for $AlOHSO_4$ is in the range of results for extractable SO_4 as found by Meiwes et al. (21) in the Solling area of Germany. The value for $Al(OH)_3$ is rather low if compared with amounts of extractable amorphous Al oxides in acid forest soils (12,36).

The model has been implemented using BEM (26). BEM (Batch Equilibrium Model) is a general chemical equilibrium model that allows the user to specify complexation for ions in solution, cation exchange at a fixed cation–exchange capacity and precipitation and dissolution. The pH in solution is calculated assuming a charge balance equation.

Using the Model

Three laboratory experiments are simulated in order to demonstrate that the model can produce results that are similar to published experimental findings. In all three experiments the sorption or desorption of SO_4 is observed. A batch reactor is simulated where the addition of certain chemicals is assumed, similar to a titration experiment.

The fourth application of the model simulates the acidification of a soil. In this case the exchange of the total solution phase is assumed for each step: the equilibrium solution is replaced by an input solution of known composition.

Simulation 1. This simulation resembles an experiment where SO_4 is added stepwise as neutral salt to the system. In this model a neutral sulfate can only be $CaSO_4$. Three different initial Ca–saturations of the cation exchanger, 2.5, 10, and 40%, are used to show differences for soils in different soil chemical states.

Simulation 2. This simulation is quite similar. It uses 2.5 % initial Ca saturation throughout, but it varies the form of the sulfate: SO_4 is added as $CaSO_4$, as H_2SO_4, or as an equimolar mixture of both.

Simulation 3. This simulation resembles an experiment where SO_4 is desorbed by the addition of either H^+ or OH^-. The additions are simulated as additions of HCl and $Ca(OH)_2$, respectively.

Simulation 4. This simulation assumes a batch reactor with solution throughput which is identified with a soil as follows:

Let the soil compartment have a thickness of 30 cm, let the percolation flow be $300\,\mathrm{L\,m^{-2}\,yr^{-1}}$, let the time step be 1 yr. In this case the model calculates in each step the equilibrium between 300 L of input solution and 300 kg of soil matrix. At completion of the step the equilibrium solution leaves the system and is replaced by a new batch of input solution.

If we had chosen 3 cm as the depth of the soil layer and 0.1 yr as the time step, the same model would have been defined (now equilibrating 30 L with 30 kg in each step). The results can be interpreted as a 300–yr development in a 30–cm layer or as quicker change in a shallower one.

A background input flux of neutral salt equivalent to concentrations of 25 $\mu mol\,L^{-1}$ of $CaSO_4$ and 5 $\mu mol\,L^{-1}$ of $CaCl_2$ is assumed.

The H_2SO_4 deposition in the standard run is assumed to be constant at 1.5 $kmol_c\,ha^{-1}\,yr^{-1}$, which is not very high for German forests today (35). The corresponding input concentration is 250 $\mu mol(H_2SO_4)\,L^{-1}$

In addition to this standard scenario, three scenarios have been defined where the input fluxes are changed after step 50 assuming

1. All acid deposition ends;
2. Continuing H_2SO_4 deposition and input of alkalinity amounting to 1.92 $kmol_c\,ha^{-1}\,yr^{-1}$ or an input concentration of 320 $\mu mol\,L^{-1}$ Ca , which could stem from surface liming of the soil, and
3. Continuing H_2SO_4 deposition with an additional input of nonsulfuric acid of 0.75 $kmol_c\,ha^{-1}\,yr^{-1}$ (250 $\mu mol\,L^{-1}$ HCl which may be thought to stem from excess nitrification (35) (HCl and HNO_3 being equivalent in this model)

RESULTS AND DISCUSSION

A key reaction for the sorption of SO_4 in the model is Eq. [2]. If SO_4 ions are added to the system, this reaction can proceed to the right but the equilibrium concentration of SO_4 will depend on the pH.

In simulation 1, SO_4 is added as a neutral salt. This leads to some precipitation of $AlOHSO_4$ but at the same time the pH is raised according to Eq. [2] and after some SO_4 has been added the precipitation ceases. The pH in turn is influenced by cation exchange. The increase in pH has to be accompanied by an increase in the Ca–saturation of the cation exchanger in the model. These two processes may explain the curves in Fig. 1 which show the appearance of adsorption isotherms as described by many authors (6,21,30). enter Fig. 1

The influence of the cation exchanger is obvious in simulation 1 (Fig. 1): the lower the initial Ca–saturation, the more the exchanger can counteract the increase in pH and the more SO_4 can precipitate. Certainly the exchange capacity and the cation exchange selectivity constants would also modify the apparent adsorption isotherms. In this way the model could explain the variability of SO_4 sorption characteristics in different soils.

If SO_4 is added as H_2SO_4, the situation is different

$$\mathrm{Al(OH)_3 + H_2SO_4 \rightleftharpoons AlOHSO_4 + 2\,H_2O} \qquad [7]$$

In this case no alkalinity is accumulated nor is any other solution concentration affected by this reaction.

Therefore, in Simulation 2 (Fig. 2) the sorption of H_2SO_4 occurs at constant sulfate concentration and constant pH in solution. This is a clear difference to any adsorption isotherm model, be it pH–independent or not. Courchesne and Hendershot (6) presented adsorption isotherms rather similar qualitatively to Fig. 2 with a very steep curve at pH 3.97. enter Fig. 2

If the pH is changed by addition of OH^-, the sorption reaction (Eq. [2]) would be forced to the lefthand side and desorption would occur. If the pH is lowered by the addition of nonsulfuric acid, $AlOHSO_4$ can dissolve in the following way

$$\mathrm{AlOHSO_4 + H^+ \rightleftharpoons Al^{3+} + SO_4^{2-} + H_2O}\ . \qquad [8]$$

Eq. [8] is clearly another instance of SO_4 desorption.

Fig. 3 shows the effect of such pH changes in the model. The sorption of SO_4 shows a maximum at pH values around 4 as has been observed in experimental studies (6,23,34). enter Fig. 3

The standard run of simulation 4 assumes constant inputs for 300 pore volumes. Despite this, the pH (Fig. 4) drops drastically at ≈ 120 enter Fig. 4

pore volumes and more slowly from about pore volume 180 on. This behavior of the model can be best understood if we look at the salt concentrations: $Al(OH)_3$ dissolves at a constant rate (Fig. 5) until it is exhausted at about pore volume 120. During this period, which is characterized by Eq. [7], $AlOHSO_4$ is formed. But as soon as $Al(OH)_3$ is exhausted, $AlOHSO_4$ starts to dissolve (Fig. 6) and Eq. [8] consumes H ions. As soon as $AlOHSO_4$ is also exhausted, the pH starts to drop to the level of the input solution.

enter Fig. 5

enter Fig. 6

This pattern is also reflected by the SO_4 concentrations. The right hand side of the curve for the standard run in Fig. 7 indicates the level of SO_4 in the input solution. Up until step 120 SO_4 is sorbed and then rather suddenly desorbed again, despite a constant input level. This is clearly different to the behavior of models that use pH–independent adsorption isotherms (Eq. [3]). If the adsorption isotherm is not of the linear type, those models would predict a saturation of the sorbent and subsequently cease sorbing more SO_4 (4,28).

enter Fig. 7

If the model is realistic this particular behavior might be of ecotoxicological significance. The drop in pH to the level of input pH after the exhaustion of all buffer mechanisms is not surprising. But the Al concentrations rise to rather high values in this model (Fig. 8). According to Eq. [8] one equivalent of H^+ is sufficient to release three equivalents of Al^{3+} in the dissolution of $AlOHSO_4$.

enter Fig. 8

The model exhibits SO_4 sorption only if gibbsite is present as a source of Al according to Eq. [2] or [7]. This parallels the empirical finding that SO_4 sorption is correlated to extractable Al in soils (6,12,36).

Ending acid deposition in Simulation 4 has no immediate influence on the soil solution concentrations (Figs. 4, 7, and 8). Dissolution of $AlOHSO_4$ and precipitation of $Al(OH)_3$ only begin at step 50 (Figs. 5 and 6). But as long as some $AlOHSO_4$ is left over, the solution composition is fixed. Around step 100 the system suddenly shifts to pH values > 4.6 and low sulfate and Al concentrations. The delayed effect of ending acid deposition in soils that have sorbed SO_4 is also predicted by adsorption isotherm models (4,28). But they predict a greater effect immediately after the end of acid deposition which then tails off with time.

The liming of forests is now a widespread practice in German forests affected by acid deposition. The lime is deposited on the forest floor. In addition to neutralizing the acid deposition, some alkalinity is generated by H_2CO_3 dissolution of the lime and is transferred as $Ca(HCO_3)_2$ to the soil. Simulation 4 assumes that this additional alkalinity amounts only to 640 $\mu mol_c\,L^{-1}$ which is not very high compared with the equilibrium solubility of calcite. The model shows immediate effects of liming on the soil solution (Figs. 4, 7, and 8), but these effects are somewhat subdued as long as $AlOHSO_4$ has not completely disappeared (Fig. 6).

To raise the pH above 4.4, the accumulated sorbed sulfate, which is $AlOHSO_4$ in this model, has to be desorbed first. This process uses up alkalinity according to the reverse of Eq. [2]. The model therefore predicts that sorbed SO_4 has to be included into the lime requirement for an acidified soil.

An additional input of acid, as would be generated by nitrification of deposited ammonium in excess of NO_3 uptake, does not alter the principal pattern shown by Simulation 4 in the standard run. But the changes in solution concentrations are steeper in this case (Figs. 4, 7, and 8). First, as long as $AlOHSO_4$ accumulates (Fig. 6) SO_4 sorption is slightly furthered by additional acid. Later, as it dissolves, the Al and SO_4 concentrations rise to higher values than in the standard run.

The spruce plot in the Solling research area of Germany receives extremely high acid depositions of $\approx 5\,kmol_c\,ha^{-1}\,yr^{-1}$ (35). This system shows a desorption of SO_4 at high SO_4 inputs similar to the predictions of the model presented here. Other soils may still be in an earlier phase of acidification with the rise in solution acidity caused by dissolution of basic Al sulfate still to occuur.

CONCLUSION

Sulfate sorption by soils described by classic adsorption isotherms can also be explained by a model that assumes joint equilibrium with $Al(OH)_3$ and $AlOHSO_4$. Such a model also reproduces the dependency of SO_4 sorption on pH providing qualitative agreement with published experimental results. As a model of SO_4 sorption it is therefore more comprehensive than a simple adsorption isotherm.

Simulation of a hypothetical field situation, using the same model, shows that even a constant load of H_2SO_4 deposition can lead to SO_4 desorption if the availability of reactive Al in the soil is limited. This desorption amounts to an additional acid load for the soil. The simulation of liming shows that the accumulated sorbed SO_4 has to be included in the lime requirement.

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Table 1: Chemical reactions for which equilibrium is assumed in the model

i	reaction			pK_i°
1	$Al(OH)_3{}^{(s)}$	$\rightleftharpoons$	$Al^{3+} + 3\,OH^-$	33.5†
2	$Al(OH)(SO_4)^{(s)}$	$\rightleftharpoons$	$Al^{3+} + OH^- + SO_4^{2-}$	17.8†
3	$\frac{1}{3}\,Al^{3+} + \frac{1}{2}\,CaX_2$	$\rightleftharpoons$	$\frac{1}{2}\,Ca^{2+} + \frac{1}{3}\,AlX_3$	0.0†
4	$\frac{1}{3}\,AlX_3 + H^+$	$\rightleftharpoons$	$\frac{1}{3}\,Al^{3+} + HX$	$-1.5^\dagger$
5	H_2O	$\rightleftharpoons$	$H^+ + OH^-$	14.0‡
6	$AlSO_4^+$	$\rightleftharpoons$	$Al^{3+} + SO_4^{2-}$	3.2‡
7	$AlOH^{2+}$	$\rightleftharpoons$	$Al^{3+} + OH^-$	9.0§
8	$Al(OH)_2^+$	$\rightleftharpoons$	$Al^{3+} + 2\,OH^-$	18.7§
9	$Al(OH)_3^0$	$\rightleftharpoons$	$Al^{3+} + 3\,OH^-$	27.0§
10	$Al(OH)_4^-$	$\rightleftharpoons$	$Al^{3+} + 4\,OH^-$	33.0§
11	$Al_2(OH)_2^{4+}$	$\rightleftharpoons$	$2\,Al^{3+} + 2\,OH^-$	20.3§
12	$Al_3(OH)_4^{5+}$	$\rightleftharpoons$	$3\,Al^{3+} + 4\,OH^-$	42.1§
13	$Al_{13}(OH)_{32}^{7+}$	$\rightleftharpoons$	$13\,Al^{3+} + 32\,OH^-$	349.3§

†estimated from a survey of field data (27)

‡from Lindsay (17)

§from Baes and Mesmer (1)

Captions

Fig. 1: Sorbed SO_4 as $AlOHSO_4$ in Simulation 1. $CaSO_4$ is added to the soil suspension. Three different Ca–saturations at the start of the simulated experiment result in different apparaent adsorption isotherms. Initial and final pH is indicated.

Fig. 2: Sorbed SO_4 as $AlOHSO_4$ in Simulation 2. The uninterrupted line is identical to the same in Fig. 1. The more the form of added SO_4 shifts towards H_2SO_4, the more sorption occurs at constant concentrations. Initial and final pH are indicated.

Fig. 3: Sorbed SO_4 as $AlOHSO_4$ in Simulation 3. pH is changed by addition of HCl or $Ca(OH)_2$.

Fig. 4: Solution pH in Simulation 4. The model batch reactor with throughput simulates development in a 30–cm soil layer in 300 years (1 pore volume = 1 year) of H_2SO_4 deposition ($\square$). The input concentrations are modified at step 50 to no more acid deposition ($\circ$), alkalinity input from liming ($+$), and additional nonsulfuric acid input ($\times$).

Fig. 5: Amount of $Al(OH)_3$ in the soil matrix in Simulation 4. Same symbols as in Fig. 4.

Fig. 6: Amount of $AlOHSO_4$ in the soil matrix in Simulation 4. Same symbols as in Fig. 4.

Fig. 7: Total SO_4 concentration in the soil solution in Simulation 4. Same symbols as in Fig. 4.

Fig. 8: Total Al concentration in the soil solution in Simulation 4. Same symbols as in Fig. 4.