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The study of soil chemistry through quasi-steady-state models: I. Mathematical definition of model

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Abstract—A mathematical method for studying the composition and speciation of soil solutions is presented. The method is formulated in general algebraic terms, and is adaptable to soil-water systems of virtually any chemical composition. Chemical processes in three different time frames are considered: fast, reversible processes, described in terms of chemical equilibrium; slow processes, described by kinetic equations for which the steady-state solution is found; and very slow processes, which are considered to be invariant in time for the solution of the system. The rates of the slow processes are written as functions of concentrations of species at chemical equilibrium. The numerical algorithm STEADYQL, which incorporates these principles, has been developed.

This approach permits the calculation of sensitivity coefficients, that is, the partial derivative of the concentration of any species with respect to the value of any of the parameters that describe influx or efflux. The approach, which allows systematic and rapid computation of the speciation and sensitivity of any soil-water system, is illustrated with a simple example. A formal mathematical description of the method is given in an appendix.

INTRODUCTION

SEVERAL MODELS HAVE been developed to assess the acidification of soils and waters by anthropogenic or natural processes, notably ILWAS (GOLDSTEIN *et al.*, 1984), the "trickle-down" model (SCHNOOR *et al.*, 1984), and the "magic" model (COSBY *et al.*, 1986). Some of these models are reviewed by EARY *et al.* (1989). While designed mainly to guide research, such models might ultimately be used to evaluate strategies for controlling acidification of the environment.

These models vary greatly in comprehensiveness. Some are oriented towards chemical processes, others towards biological processes, and others include many different types of processes. In principle, if more processes are included in a model, the model is more complete and represents the natural system better. In practice, however, if more processes are included, it is more difficult to recognize those processes to which the model is most sensitive, and to select the processes that should be the subject of further laboratory, field, and theoretical investigations. The analysis of sensitivity of these models is often an arduous task, requiring long integrations over time for many combinations of factors.

In recognition of this situation, we have developed an alternative approach for formulating and solving the chemical flux and equilibrium equations for ecosystem acidification. This approach, similar to the one in the multicomponent chemical equilibrium program MICROQL (WESTALL, 1986), provides a general matrix-algebra framework for formulating biogeochemical processes mathematically, solving the equations, and analyzing sensitivity.

The approach focuses on the steady-state solution of the equations that define the state of the system. Three time frames are considered in the model, and processes can be assigned to any one of the three. The time frames are: fast, reversible processes, described in terms of chemical equilibrium; slow processes, described by kinetic equations; and very slow processes, which are considered to be independent of time for the period under consideration.

Two factors argue for a steady-state approach, even for systems known not to be at steady state. First, the steady-state solution is unique and independent of initial state of the system; thus the steady-state approach provides a framework for systematic comparison of the relative importance of parameters within a model. Second, since processes can be assigned to any of the three time frames, the approach is not locked into any particular time scale.

These concepts are developed in two papers. In this, the first, a simple example is used to illustrate the mathematical approach. In the second, the method is applied to problems of geochemical significance (FURRER *et al.*, 1989).

Important to our approach is the distinction between the conceptual model and the data for any particular system. The conceptual model refers to the principles discussed above: the steady-state condition, the assignment of processes to one of three time frames, and the formulation of the equations through matrix algebra. Based on these principles, the numerical algorithm STEADYQL was developed.

The data for any particular system refers to the set of equilibrium reactions, stoichiometry, equilibrium constants, kinetically controlled processes, and rate expressions that are used to describe the geochemistry of that system. These are defined independently of the algorithm. Thus, we distinguish between the model itself, as represented by the numerical algorithm, and the database used to define the processes for any particular system.

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THEORY

The system

To facilitate the exposition of the theory, an example involving a compartment of saturated soil and soil solution (Fig. 1) is considered. The slow processes considered are: (i) inflow of acid, in this case dilute sulfuric acid; (ii) weathering of minerals, represented by dissolution of gibbsite ($Al(OH)_3(s)$); and (iii) outflow of the soil solution. The chemical species in the system include all of the products of reactions of H_2SO_4, $Al(OH)_3(s)$, and water (Table 1a). These species are in solution or adsorbed to the surface of solids, and the reactions between these species are considered to be at chemical equilibrium. Although no natural system is this simple, the example serves to illustrate the theory. Since the mathematical formulation is completely general, more complex systems can be treated in exactly the same way.

The goal of this exercise is to determine the composition and speciation of a soil solution (focusing on acidity and free aluminum), the rate of weathering loss from the system at steady state, and the sensitivity of the steady-state solution to the parameters that control the state of the system, namely, input of H_2SO_4 and weathering rate. We first formulate the equations that define the system, next show how the equations are solved, and then discuss the results for this example. A formal algebraic definition of the problem, the steady-state solution, and the sensitivities are given in the appendix.

Table 1. Definition of the problem: 19 equations for the 19 unknowns (12 unknown concentrations and 7 unknown fluxes).

a. Species:
mobile: H^+, OH^-, SO_4^{2-}, Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, $AlSO_4^+$
immobile: XOH_2^+, XOH, XSO_4^-

b. Components:
mobile: H^+, SO_4^{2-}, Al^{3+}
immobile: XOH_2^+

c. Mass-action equations[a]
(1) $[OH^-] = K_w\,[H^+]^{-1}$
(2) $[AlOH^{2+}] = K_1\,[Al^{3+}]\,[H^+]^{-1}$
(3) $[Al(OH)_2^+] = K_2\,[Al^{3+}]\,[H^+]^{-2}$
(4) $[Al(OH)_3] = K_3\,[Al^{3+}]\,[H^+]^{-3}$
(5) $[Al(OH)_4^-] = K_4\,[Al^{3+}]\,[H^+]^{-4}$
(6) $[AlSO_4^+] = K_5\,[Al^{3+}]\,[SO_4^{2-}]$
(7) $[XOH] = K_6\,[XOH_2^+]\,[H^+]^{-1}$
(8) $[XSO_4^-] = K_7\,[XOH_2^+]\,[SO_4^{2-}]$

d. Fluxes of the components through inflow and dissolution
(9) $J(in,H^+) = 2\,v\,c$
(10) $J(in,SO_4^{2-}) = v\,c$
(11) $J(diss,H^+) = -\,3\,k\,[H^+]^{0.4}$
(12) $J(diss,Al^{3+}) = k\,[H^+]^{0.4}$

e. Fluxes of the components through outflow
(13) $J(out,\ H^+) = -\,v\,([H^+] - [OH^-] - [AlOH^{2+}]$
$- 2\,[Al(OH)_2^+] - 3\,[Al(OH)_3] - 4\,[Al(OH)_4^-])$
(14) $J(out,\ SO_4^{2-}) = -\,v\,([SO_4^{2-}] + [AlSO_4^+])$
(15) $J(out,\ Al^{3+}) = -\,v\,([Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+]$
$+ [Al(OH)_3] + [Al(OH)_4^-] + [AlSO_4^+])$

f. Mole-balance equation for the immobile component
(16) $[XOH_2^+] + [XOH] + [XSO_4^-] - T_{XOH_2^+} = 0$

g. Flux-balance equations for the mobile components
(17) $J(out,\ H^+) + J(in,\ H^+) + J(diss,\ H^+) = 0$
(18) $J(out,\ SO_4^{2-}) + J(in,\ SO_4^{2-}) = 0$
(19) $J(out,\ Al^{3+}) + J(diss,\ Al^{3+}) = 0$

[a] Values of stability constants in Table 2a.

Definition of the problem

The problem definition has three parts: (i) chemical equilibrium equations, which describe the fast processes; (ii) reaction stoichiometries and rate equations, which describe the slow processes; and (iii) mole-balance equations, which provide for conservation of matter (and charge).

Species. This system contains 12 chemical species which interact through fast reactions considered to be at equilibrium. These species, listed in Table 1a, comprise the soluble reaction products of sulfuric acid and gibbsite. Since the species are in solution, they are classified as mobile. We also consider products of adsorption reactions; these adsorbed species are classified as immobile, since they do not flow out of the system with the solution.

The adsorption reaction could be represented formally in many different ways, for example, as an ion-exchange process, by a Freundlich or Langmuir isotherm, or as a surface-complexation process (SCHINDLER and STUMM, 1987). Here we use the surface complexation model, without consideration of the electrostatic energy, in order to simplify exposition of the theory. The theory, however, is not limited to any particular model of adsorption.

Components. In order to define the problem mathematically, a set of "components" must be selected (MOREL, 1983; WESTALL, 1986). The components comprise a complete and independent set of reactants, such that every species can be represented as the sole product of a reaction involving only the components, and no component can be represented as the product of a reaction involving only the other components. The particular set of components for a given system is not unique, but once the set of components has been selected, each species is uniquely represented in terms of this set. The set of components selected for this example is given in Table 1b.

If the system contains both mobile and immobile species, there must be both mobile and immobile components. All species that include an immobile component are themselves immobile. The total concentrations of the mobile components at steady state are regulated by the slow processes, whereas the total concentrations of the immobile components remain constant.

The mass-action equations (Table 1c) relate the concentrations of the species to the concentrations of the components. These equations describe the fast, equilibrium processes. The stability constants are conditional constants, correct for the temperature and ionic strength of the solution under study.

Fluxes. In this simple example, three slow processes add or remove material from the system (Fig. 1): (i) the inflow of dilute H_2SO_4, (ii) the dissolution of gibbsite, $Al(OH)_3(s)$, and (iii) the outflow. Fluxes that add material to the soil system are designated as positive, those that remove material from the system are negative. Fluxes are represented by the symbol J [mol dm^{-2} s^{-1}].

The fluxes of the components H^+ and SO_4^{2-} that result from the inflow process are given by Eqns. (9) and (10) in Table 1d, where v is the flow velocity [dm s^{-1}] and c is the concentration of sulfuric acid in the inflow [mol dm^{-3}]. Note that the hydrogen ion flux is twice as large as the sulfate flux, on account of the stoichiometry of sulfuric acid.

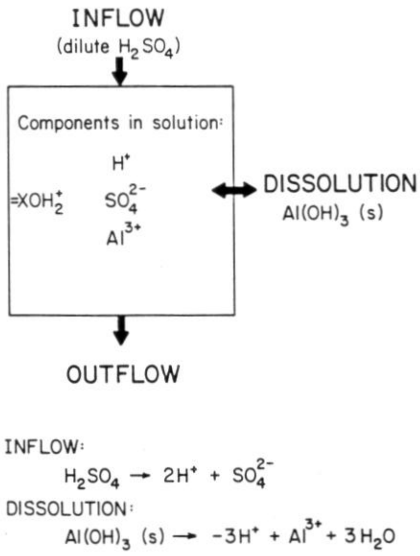

FIG. 1. A simple box model of a compartment of soil and soil water. The chemical components are H^+, SO_4^{2-}, Al^{3+}, H_2O and the surface hydroxyl group, XOH_2^+. The processes resulting in fluxes of these components into and out of the box are inflow, dissolution, and outflow. The rates of all processes are expressed relative to the surface area of the compartment; thus the depth of the compartment is implicit in the rates, but does not appear explicitly in the model.

The stoichiometry of the dissolution reaction is

$$Al(OH)_3(s) = Al^{3+} + 3H_2O - 3H^+ \tag{1}$$

and an empirical rate law is (STUMM *et al.*, 1985)

$$R = k[H^+]^{0.4} \tag{2}$$

where R is the area-specific rate [mol $dm^{-2}\ s^{-1}$] and k is the reaction rate constant when $[H^+]$ is expressed in mol dm^{-3}. For this example it is assumed that the solution remains undersaturated and that the back reaction can be neglected. A more complex rate law could be substituted readily.

The fluxes of the components H^+ and Al^{3+} corresponding to the stoichiometry and rate law given above are represented by Eqns. (11) and (12) in Table 1d. The flux of H_2O in the dissolution reaction is not taken into account because it is insignificant compared with the total amount of H_2O in the system.

Since the soil solution is assumed to be well mixed, the outflow solution must have the same composition and speciation as the solution in the system. Therefore, the flux of a component in the outflow is simply the product of the total concentration of the component in solution and the flow velocity, v (Table 1e, Eqns. 13–15).

Mole balance. For each component there is exactly one mole-balance (mass-balance) equation. For the immobile component, the mole-balance equation is of the conventional form (Table 1f); the symbol $T_{XOH_2^+}$ represents the total concentration of immobile exchange sites (mol dm^{-3}). For the mobile components, the steady-state mole-balance equations take the form of flux-balance equations (Table 1g) that express the condition that the net flux through the system at steady state is zero, that is, influx is equal to efflux.

It might be noted that the flux-balance equations in Table 1g are formulated without an explicit electroneutrality equation. This equation could be formulated through a linear combination of Eqns. (17–19) in Table 1: Eqn. (17) minus two times Eqn. (18) plus three times Eqn. (19). Thus the information on electroneutrality is included in Eqns. (17–19), but it is unnecessary (and less convenient) to express it explicitly.

The whole problem is thus defined by 19 equations with 19 unknowns (12 concentrations of species and 7 fluxes).

Solution of the problem

The chemical equilibrium/steady-state problem is solved iteratively as follows: (i) An initial estimate of the free concentrations of the components at steady state is made; (ii) From this initial estimate, the corresponding concentrations of all of the species are computed from the mass-action equations (Table 1, Eqns. 1–8); (iii) From the concentrations of the species, the fluxes are calculated using Eqns. (9–15) in Table 1; (iv) The concentrations of the species and the fluxes are then substituted into the mole-balance equations (Table 1, Eqns. 16–19). The sums of the terms on the left-hand side of the mole-balance equations are referred to as the difference functions for the components; (v) If all of the difference functions are equal to zero, the mole balance equations are satisfied, and the problem is considered to be solved; (vi) If some of the difference functions are not equal to zero, the value of the difference functions, and their derivatives with respect to the free concentrations of the components, are used to calculate improved values for the free concentration of components with the Newton-Raphson method. The process is repeated with the improved values until the mole-balance equations are satisfied. A general mathematical description of this procedure is given in Appendix 1.

Sensitivity analysis

After the problem is solved for the composition/speciation at steady state, the sensitivity analysis is performed. The sensitivity analysis is an important aspect of any model since it identifies which parameters must be most carefully measured or estimated.

The mathematical description of the sensitivity analysis is given in Appendix 2. From inspection of the equations in Table 1, it can be seen that the only independent variables in these equations are the parameters v, c, k, and the total concentration of immobile exchange sites, $T_{XOH_2^+}$. (Formally the elements of the *A*, *K*, *W*, *N*, and *S* matrices, defined in the appendix, Table A1, are independent variables as well, but they are not considered in this analysis.) Thus the steady-state value of any property of the system (*e.g.*, concentrations of species or fluxes) is ultimately determined only by the values of these independent variables.

There are several ways to express the sensitivity of the system to changes in these parameters. One of the most convenient is the normalized sensitivity coefficient, $Q(i, m)$, which we define by

$$Q_{i,m} = \frac{\partial \ln C_i}{\partial \ln P_m} \tag{3}$$

where $C(i)$ is the concentration of species i, $P(m)$ is the value of parameter m, and the partial derivative is taken subject to the mole-balance and flux-balance constraints. The sensitivity coefficients are not global; they are partial derivatives, valid for the set of parameter values at which they were calculated.

This normalized sensitivity coefficient can be interpreted for practical purposes in the following way: a one percent change in the parameter m will cause a $Q(i, m)$ percent change in the concentration of species i. This interpretation is based on a finite-difference approximation to the derivatives in Eqn. (3):

$$Q_{i,m} = \frac{\partial \ln C_i}{\partial \ln P_m} = \frac{\partial C_i}{\partial P_m}\frac{P_m}{C_i} \approx \frac{\Delta C_i}{\Delta P_m}\frac{P_m}{C_i}. \qquad (4)$$

In this example the sensitivity is calculated only for the three parameters related to the slow processes: the flow velocity, v, the concentration of the sulfuric acid in the inflow, c, and the rate constant for the dissolution of gibbsite, k. The sensitivities with respect to other parameters such as the stability constants could be obtained in a similar manner.

Table 2. Numerical example.

a. Stability constants (298 K) and parameter values

$K_w = 10^{-14.0}$	$v = 3.17 \times 10^{-7}$ dm s^{-1}
$K_1 = 10^{-5.4}$	$c = 5.00 \times 10^{-5}$ mol dm^{-3}
$K_2 = 10^{-10.0}$	$k = 1.40 \times 10^{-10}$ (^{a})
$K_3 = 10^{-15.7}$	
$K_4 = 10^{-23.5}$	$T_{XOH_2^+} = 1.00 \times 10^{-4}$ mol dm^{-3}
$K_5 = 10^{3.2}$	
$K_6 = 10^{-7.5}$	
$K_7 = 10^{4.5}$	

b. Speciation

Species	$C(i)^b$ (mol/L)	log C(i)
H^+	7.21×10^{-5}	-4.14
OH^-	1.39×10^{-10}	-9.86
SO_4^{2-}	4.94×10^{-5}	-4.31
Al^{3+}	7.90×10^{-6}	-5.10
$AlOH^{2+}$	1.10×10^{-6}	-5.96
$Al(OH)_2^+$	1.21×10^{-7}	-6.92
$Al(OH)_3$	2.10×10^{-9}	-8.68
$Al(OH)_4^-$	2.92×10^{-12}	-11.54
$AlSO_4^+$	6.18×10^{-7}	-6.21
XOH_2^+	3.90×10^{-5}	-4.41
XOH	1.71×10^{-8}	-7.77
XSO_4^-	6.10×10^{-5}	-4.22

c. Composition

Component	$X(j)^c$ (mol/L)	log X(j)	$T(j)^d$ (mol/L)
XOH_2^+	3.90×10^{-5}	-4.41	1.00×10^{-4}
H^+	7.21×10^{-5}	-4.14	7.08×10^{-5}
SO_4^{2-}	4.94×10^{-5}	-4.31	5.00×10^{-5}
Al^{3+}	7.90×10^{-6}	-5.10	9.74×10^{-6}

d. Normalized Sensitivity Coefficients^e $\partial \ln C_i / \partial \ln P_m$

	Parameter m		
Species i	v	c	k
H^+	0.329	1.180	-0.329
OH^-	-0.329	-1.180	0.329
SO_4^{2-}	0.010	0.993	-0.010
Al^{3+}	-0.824	0.572	0.824
$AlOH^{2+}$	-1.153	-0.608	1.153
$Al(OH)_2^+$	-1.482	-1.788	1.482
$Al(OH)_3$	-1.811	-2.968	1.811
$Al(OH)_4^-$	-2.140	-4.147	2.140
$AlSO_4^+$	-0.814	1.565	0.814
XOH_2^+	-0.006	-0.605	0.006
XOH	0.335	-1.785	0.335
XSO_4^-	0.004	0.388	-0.004

[a] Units defined with description of Equation 2 in text.
[b] Concentration of species i.
[c] Free concentration of component j.
[d] Total (analytical) concentration of component j.
[e] Normalized sensitivity coefficient defined in Equation 4.

RESULTS

A numerical example illustrating the steady-state soil acidification model is shown in Table 2. The values of the independent parameters, which determine the state of the system, are given in Table 2a. The composition and speciation of the system at steady state are given in Tables 2b and 2c, and the normalized sensitivity coefficients in Table 2d.

The stability constants and parameter values are given in Table 2a. The flow velocity v is equivalent to a net precipitation rate of 1000 mm per year, and the concentration of 50 μmol/L sulfuric acid in the inflow corresponds to pH = 4.0. The reaction constant k is calculated for approximately 2 m^2 of gibbsite surface per dm^2 of watershed surface area. The total concentration of the immobile component, $T_{XOH_2^+}$, is 100 micromoles per liter of soil solution.

The concentrations of all of the species and the total concentrations of all of the components are shown in Tables 2b and 2c. At steady state, the log concentration of H^+ in the soil solution is -4.14, down from the value of -4.00 in the inflow due to the weathering reaction. The predominant aluminum species in solution at this pH value is Al^{3+}. The total concentration of SO_4^{2-} in the soil solution is equal to that in the inflow, even though much sulfate is present in the adsorbed form (XSO_4^-). The adsorption sites are occupied by sulfate and H^+; virtually no sites are free.

The fluxes of the mobile components H^+, SO_4^{2-} and Al^{3+} are shown in Fig. 2. About 30% of the H^+ in the inflow is consumed in the dissolution process. The corresponding flux of aluminum into solution is one third of the H^+ flux, in keeping with the stoichiometry of the dissolution reaction (Eqn. 1). At steady state the flux of sulfate in the outflow equals that in the inflow. This condition arises because no other slow processes add or remove sulfate.

The sensitivities of the steady-state concentrations to the values of the parameters v, c and k are illustrated graphically in Fig. 3 and numerically in Table 2d. In the figure, the steady-state concentrations of H^+, Al^{3+}, and surface species are shown as functions of the parameters k, v, and c. For each line in the figure, one of the parameters was multiplied by the factor f to vary it about the reference value (Table 2a), while the other two parameters were maintained at their reference values.

Figure 3a shows that the steady-state hydrogen ion concentration is most sensitive to the concentration of sulfuric acid in the inflow, c. The sensitivity of the hydrogen ion concentration is positive with respect to the flow velocity, v, (due to a decrease in neutralization by the dissolution reaction as the residence time is reduced) and negative with respect to the reaction constant, k, of the gibbsite dissolution process.

For the parameters v and k, the signs of the sensitivity coefficients for Al^{3+} are opposite to those for H^+ (Fig. 3b). This condition results from the stoichiometry of the dissolution reaction.

The concentrations of the immobile species depend primarily on the inflow concentration of H_2SO_4 (Fig. 3c). For example, an increase in the concentration of sulfuric acid results in an increase in the total amount of adsorbed sulfate. The concentration of the uncharged species XOH is negligible; in effect, XOH_2^+ and XSO_4^- share the available sites at the mineral surface.

While graphs such as those presented in Fig. 3 show in a detailed way the sensitivity of the concentration of species to particular parameters, an overview of the sensitivity of the system at any point in parameter space can be obtained quickly from the normalized sensitivity coefficients, defined by Eqn. (3). For the parameter values given in Table 2a, the normalized sensitivity coefficients are presented in Table 2d. These coefficients are related to the slopes of the lines presented in Fig. 3, at the reference points. From this table it is seen that most sensitivities are of approximately the same order of magnitude for this very simple example. However, as noted above, H^+ is most sensitive to the parameter c, while Al^{3+} is most sensitive to v and k.

DISCUSSION

The value of a matrix-oriented, steady-state approach lies in its speed and flexibility. It is systematic and general, and the matrix implementation allows the algorithm to be coded compactly and to run quickly on even small computers. Very large problems can be handled almost as easily as the simple one presented here. For ecological (environmental) problems, the need to deal with large sets of species, processes, and components is critical. Soil solution speciation, for example, is controlled by complex interactions involving chemical equilibrium reactions, microbial and plant processes, and kinetically controlled chemical and physical processes such as weathering and degassing. Most modeling attempts to date have focused on only a subset of these processes (*e.g.*, SCHNOOR *et al.*, 1984; COSBY *et al.*, 1986) and thus provide limited insight into how the overall system functions. The ILWAS model (GOLDSTEIN *et al.*, 1984; DAVIS *et al.*, 1987) does attempt to consider all relevant processes, but the non-matrix oriented approach resulted in a large, complex Fortran program that has proven very difficult to use or to modify. Moreover, the product is the computer code; abstracting the chemical/mathematical model from that code is difficult.

The steady-state approach has a major limitation, of course, in that real systems never reach steady-state, thus comparison of model predictions with observed behavior is, strictly speaking, impossible. Nonetheless, with some thoughtful attention to the reasons why the real system is not at steady state, comparison of observed and predicted speciation is practical. The steady-state solution also provides a well-defined reference state against which transient behavior can be judged. Moreover, sensitivity analysis based on the steady-state model can (i) indicate the direction of change in the state of the system induced by short- and long-term variations, such as daily or yearly temperature variations, and (ii) guide research by helping to set priorities and design experiments.

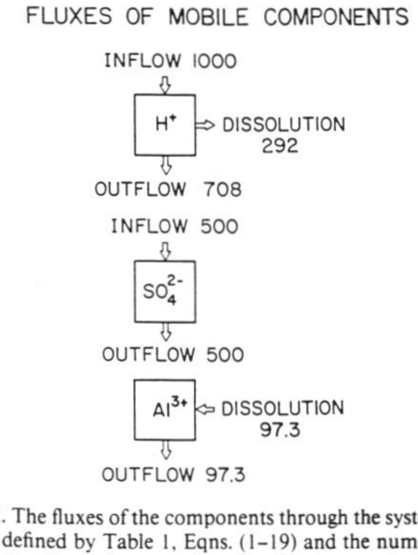

FIG. 2. The fluxes of the components through the system at steady state, as defined by Table 1, Eqns. (1–19) and the numerical values in Table 2a. The units are mol ha^{-1} yr^{-1} (1 hectare (ha) = 10^4 m^2).

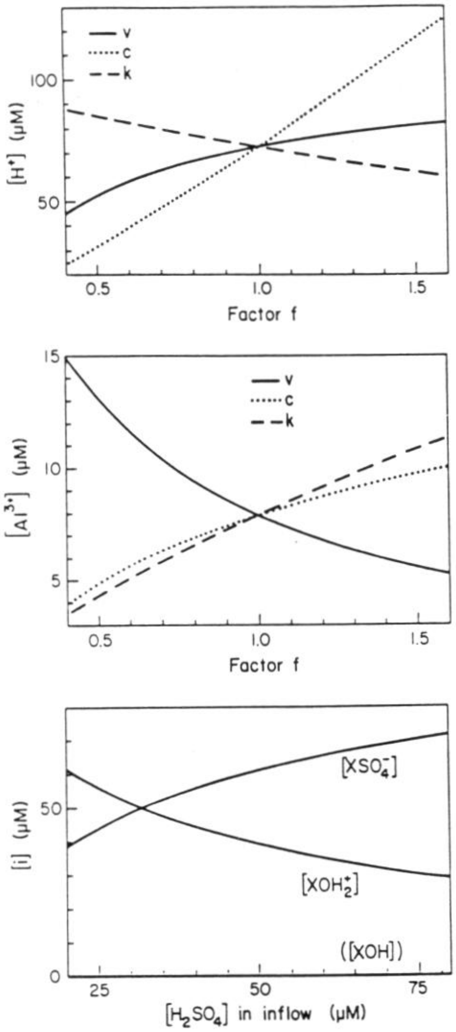

FIG. 3. Sensitivity of the steady-state solution to changes in values of the parameters controlling the system. The lines in panels 3A and 3B show the steady-state concentrations of H^+ and Al^{3+}, respectively, as the designated parameter P is varied about its standard value by the factor f (*i.e.*, $P' = fP$), while the other two parameters are held at their standard values. The standard ($f = 1$) values of the parameters are those in Table 2a: inflow velocity, $v = 1$ m yr^{-1}; concentration of sulfuric acid in the inflowing water, $c = 50$ μmol dm^{-3}; and dissolution rate constant, $k = 1.4 \cdot 10^{-10}$ (with units as defined by Eqn. 2). In panel 3C the steady-state concentrations of the surface species are shown as a function of the concentration of sulfuric acid in the inflow.

The greatest value of the approach is simply that it can help us come to grips with the behavior of complex systems. In a sequel to this paper, we explore the utility of this approach in studying the effects of the biota and mineralogy on soil solution speciation and soil acidification.

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APPENDIX 1

Formulation of the General Case

The equations in Table 1 define completely a simple system at steady state. It is convenient to express these equations in a more general form to facilitate solution of the problem and to allow virtually any problem to be expressed in the same general format, with few constraints on the choice of components, species, and expressions for fluxes and reaction rates.

The objectives of this appendix are to illustrate how a specific problem (Table 1) is represented in general notation (Table A1) and to provide a formal algebraic definition of the problem that was presented descriptively in the text.

Mass action equations. The mass action equation for any reaction at equilibrium can be written in a general algebraic form as:

$$C(i) = K(i) \prod_j X(j)^{a(i,j)} \qquad \text{(A1)}$$

where $C(i)$ is the concentration of species i [mol dm^{-3}], $K(i)$ is the conditional stability constant of species i, $X(j)$ is the free concentration of the component j, $a(i, j)$ is the stoichiometric coefficient of component j in species i, and the product is taken over all components j.

For the reactions in the example, the stoichiometric coefficients $a(i, j)$ are shown in matrix format in Table A1.a. For each component there is a column and for each species a row. The correspondence between the exponents in Table 1c and the matrix in Table A1.a can be seen. The mass action equations for the species composed of only one component are trivial, but their inclusion makes it possible to write all of the equations for the chemical equilibrium in a general and comprehensive form.

Table A1. Matrix representation of problem.

a. A matrix and K vector. Stoichiometry and stability constants for the equilibrium reactions.

		A Matrix	Components			K Vector[a]
	Species	XOH_2^+	H^+	SO_4^{2-}	Al^{3+}	
1	H^+	0	1	0	0	1
2	OH^-	0	-1	0	0	K_w
3	SO_4^{2-}	0	0	1	0	1
4	Al^{3+}	0	0	0	1	1
5	$AlOH^{2+}$	0	-1	0	1	K_1
6	$Al(OH)_2^+$	0	-2	0	1	K_2
7	$Al(OH)_3$	0	-3	0	1	K_3
8	$Al(OH)_4^-$	0	-4	0	1	K_4
9	$AlSO_4^+$	0	0	1	1	K_5
10	XOH_2^+	1	0	0	0	1
11	XOH	1	-1	0	0	K_6
12	XSO_4^-	1	0	1	0	K_7

b. T vector[a]: T(j) is the total concentration of an immobile component.

$T_{XOH_2^+}$	total concentration of XOH_2^+

c. P vector[a]: P(m) is a parameter used in the rate expressions for slow processes.

Parameter m	Description
v	flow velocity
c	concentration of H_2SO_4 in the inflow
k	rate constant for dissolution reaction

d. W Matrix: w(l,m) is the exponent of parameter m in the rate expression for process l.

	Parameter m		
Process l	v	c	k
inflow	1	1	0
dissolution	0	0	1

e. N matrix: n(l,i) is the exponent of species i in the rate expression for process l. The species can be identified through the species identification numbers in Table A1a.

	Species i											
Process l	1	2	3	4	5	6	7	8	9	10	11	12
inflow	0	0	0	0	0	0	0	0	0	0	0	0
dissolution	0.4	0	0	0	0	0	0	0	0	0	0	0

f. S matrix: s(l,j) is the stoichiometric coefficient of component j in process l.

		Component j		
Process l	XOH_2^+	H^+	SO_4^{2-}	Al^{3+}
inflow	0	2	1	0
dissolution	0	-3	0	1

[a] Numerical values are given in Table 2a.

Rates of slow processes and fluxes. The rate of any slow process is expressed as:

$$R(l) = \prod_m P(m)^{w(l,m)} \prod_i C(i)^{n(l,i)} \qquad \text{(A2)}$$

where $R(l)$ is the rate of process l [mol dm^{-2} s^{-1}], $P(m)$ is the value of parameter m, $w(l, m)$ is the exponent of parameter m in process l, and $n(l, i)$ is the exponent of the concentration of species i in the rate of process l. The products are taken over all parameters m and all species i. Thus the rate of any of the slow processes is formulated as a power function of the parameters P and the concentrations of species C.

The flux of a component due to a process is the rate of the process multiplied by the stoichiometric coefficient of the component in the process:

$$J(l, j) = R(l)s(l, j) \tag{A3}$$

where $J(l, j)$ is the flux of component j in process l [mol dm^{-2} s^{-1}], and $s(l, j)$ is the stoichiometric coefficient of component j in process l.

Equation (A3) is valid for fluxes due to all slow processes. In the practical formulation of a problem, it is convenient to separate fluxes due to outflow from fluxes due to all other slow processes. For processes other than outflow, the flux is expressed by an equation similar in form to (A2) and (A3):

$$J(l^0, j) = s(l^0, j) \prod_m P(m)^{w(l,m)} \prod_i C(i)^{n(l,i)} \tag{A3.a}$$

where l^0 represents any process other than outflow.

In this example, the only two slow processes other than outflow are inflow and dissolution. The equations for the flux of the components due to these processes are given in Table 1d. These equations can be expressed in the form of Eqn. (A3.a) using the matrices of coefficients given in Table A1.c–f. The parameters in the flux equation are the flow velocity, v, the concentration of sulfuric acid in the inflow, c, and the rate constant of dissolution, k. These parameters are represented as the P vector in Table A1.c. The exponents of the parameters are shown as the W matrix in Table A1.d, and the exponents of the concentrations are shown as the N matrix in Table A1.e. The stoichiometric coefficients $s(l^0, j)$ of the components in the flux equation are shown in Table A1.f. The correspondence between the matrices in Table A1.c–f, Eqn. (A3.a), and the explicit equations of Table 1d in the text can easily be verified.

The flux due to outflow, for any mobile component j', is:

$$J(\text{out}, j') = -v \sum_{i'} a(i', j')C(i') \tag{A3.b}$$

where v is the outflow velocity [dm s^{-1}] and the summation is taken over all mobile species i'. The correspondence between Eqn. (A3.b) and the equations in Table 1e of the example can be seen.

Flux balance and mole balance. The flux-balance and mole-balance equations are formulated as difference functions, which must equal zero when these conservation conditions are satisfied.

For the immobile components, the simple mole-balance equation is

$$Y(j'') = \sum_{i''} a(i'', j'')C(i'') - T(j'') = 0 \tag{A4}$$

where $Y(j'')$ is the difference function for any immobile component j'', $T(j'')$ is the total concentration of the component, and the summation is taken over all immobile species i''. Equation (A4) corresponds to the equation in Table 1f for the example.

For any mobile component, the sum of all fluxes must be zero at steady state:

$$Y(j') = \sum_{l} J(l, j') = 0 \tag{A5}$$

where $Y(j')$ is the difference function for any mobile component j', and the summation is taken over all processes l. The correspondence between Eqn. (A5) and the equations in Table 1g is easily verified.

Summary. The example defined in Table 1 has been re-expressed in terms of the A, K, T, P, W, N, and S matrices in Table A1. These matrices along with Equations A1–A5 define the steady-state soil chemistry model in a completely general way.

APPENDIX 2

Sensitivity analysis

To determine sensitivity coefficients, it is necessary first to distinguish between the dependent and independent variables in Eqns. (A1–A5). The difference function for any *mobile* component j' is an explicit function of the concentrations of all mobile components, $X(k')$, and all parameters, $P(m)$:

$$Y_{j'} = Y_{j'}(X_{k'}(P_m), P_m). \tag{A6}$$

The concentrations of the mobile components $X(k')$ are implicit functions of the parameters $P(m)$. (A complete definition of $Y(j')$ in Eqn. (A6) would include the coefficients A, K, W, N, and S as independent variables.) It is noteworthy that the difference function for a mobile component is independent of the concentrations of the immobile components. Thus the steady-state solution for mobile components is independent of the presence of immobile species.

For any *immobile* component j'', the difference function is an explicit function of the concentrations of the immobile components, $X(k'')$, and the mobile components, $X(k')$:

$$Y_{j''} = Y_{j''}(X_{k''}(P_m), X_{k'}(P_m)). \tag{A7}$$

The concentrations of the immobile components $X(k'')$ and the mobile components $X(k')$ are implicit functions of the parameters $P(m)$. (Again a complete definition of $Y(j'')$ in Eqn. (A7) would include the coefficients A, K, T, W, N, and S as independent variables.) Note that the difference function for immobile components does not depend explicitly on the parameters $P(m)$; the dependence is implicit, through the concentrations of the components.

Sensitivity coefficients for the components. The goal is to find the partial derivatives $\partial X(j)/\partial P(m)$, subject to the constraints of flux and mole balance. As can be seen in Eqns. (A6) and (A7), both of the difference functions depend ultimately on the parameters $P(m)$. If the value of a parameter is changed infinitesimally, the system will readjust itself and reach a new steady state, such that the flux-balance equations (Eqn. A6) and the mole-balance equations (Eqn. A7) are satisfied. Therefore, the partial derivatives of all difference functions $Y(j)$ with respect to all parameters $P(m)$ must be equal to zero. These partial derivatives provide the basis for calculating the sensitivity coefficients.

The partial derivative of the function in Eqn. (A6), with respect to a parameter $P(m)$, is found by application of the chain rule to (A6):

$$\frac{\partial Y(j')}{\partial P(m)} = \sum_{k'} \frac{\partial Y(j')}{\partial X(k')} \frac{\partial X(k')}{\partial P(m)} + \frac{\partial Y(j')}{\partial P(m)} = 0. \tag{A8}$$

For a set of n' mobile components, there are $j' = 1, \cdots n'$ equations of the form of Eqn. (A8), and $k' = 1, \cdots n'$ unknown derivatives $\partial X(k')/\partial P(m)$. The other partial derivatives in the equation, $\partial Y(j')/\partial X(k')$ and $\partial Y(j')/\partial P(m)$, are found explicitly by taking the derivatives of the function $Y(j')$ (Eqn. A6). Then the set of n' equations in n' unknowns can be solved for the derivatives that are sought, $\partial X(k')/\partial P(m)$. The entire procedure is repeated for each parameter $P(m)$.

For an immobile component, the partial derivative of the function in Eqns. (A7), with respect to the parameter $P(m)$, is found by application of the chain rule to (A7):

$$\frac{\partial Y(j'')}{\partial P(m)} = \sum_{k''} \frac{\partial Y(j'')}{\partial X(k'')} \frac{\partial X(k'')}{\partial P(m)} + \sum_{k'} \frac{\partial Y(j'')}{\partial X(k')} \frac{\partial X(k')}{\partial P(m)} = 0. \tag{A9}$$

There are n'' equations of this form in the n'' unknown partial derivatives $\partial X(k'')/\partial P(m)$. In these equations the partial derivatives $\partial Y(j'')/\partial X(k'')$ and $\partial Y(j'')/\partial X(k')$ are found explicitly by taking the derivatives of Eqn. (A7), and the partial derivatives $\partial X(k')/\partial P(m)$ are found from the solution to Eqn. (A8). Then the n'' x n'' equations can be solved for the unknown partial derivatives $\partial X(k'')/\partial P(m)$. The entire procedure must be repeated for each parameter $P(m)$.

Sensitivity coefficients for the species. The sensitivity coefficients of any species can be found through application of the chain rule to Eqn. (A1), in which the concentration of a species is defined as an explicit function of the concentration of the components:

$$\frac{\partial C(i)}{\partial P(m)} = \sum_{k} \frac{\partial C(i)}{\partial X(k)} \frac{\partial X(k)}{\partial P(m)} \tag{A10}$$

where the summation is taken over all components k, and the partial derivatives $\partial X(k)/\partial P(m)$, subject to the mole- and flux-balance conditions, are determined from the solution of Eqns. (A8) and (A9). The value of $\partial C(i)/\partial P(m)$ found from Eqn. (A10) is used to calculate the normalized sensitivity coefficients as defined by Eqn. (4) in the text.