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## COMMUNITIES OF FILAMENTOUS FUNGI AND YEAST IN DECOMPOSING LOGS OF *PSEUDOTSUGA MENZIESII*

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### ABSTRACT

We investigated the communities of filamentous fungi and yeasts in logs in advanced stages of decay. Decay stages are generally defined from class I–V, with class I being the least decayed and class V being the most decayed. Fungi were isolated from cross-sections approximately 15 cm thick of *Pseudotsuga menziesii* logs in decay classes III and IV. Cross sections included portions of logs with and without conifer seedlings. Samples were removed from three vertical positions (top, middle, and bottom) of each cross-section. Comparisons of coefficient of community and detrended correspondence analysis ordinations indicated differences in community structure between class III and class IV logs. No community differences were found between samples with and without conifer seedlings. A total of 18 genera and 36 species of fungi were recovered from samples; more than 50% of recovered genera were dematiaceous hyphomycetes.

**Key Words:** Ecology, wood decay, fungus communities, *Pseudotsuga*

Most coniferous forests in the Pacific Northwest (PNW) are harvested for timber, and post-harvest treatments often include removal of large coarse woody debris (> 2.5 cm diam). Decomposing coarse woody debris (CWD) is important to nutrient cycling and biotic habitat (Harmon *et al.* 1986; Maser and Trappe, 1984), and its removal following harvest may negatively affect long-term site productivity.

The above-ground volume of CWD in *Pseudotsuga-Tsuga* forests of the Pacific Northwest is much greater than that found in comparable temperate deciduous forests (Harmon *et al.*, 1986). The volume of logs in a 250-year-old *Pseudotsuga-Tsuga* forest is 488 m<sup>3</sup>/ha, whereas a similarly aged *Quercus* stand has a log volume of 46 m<sup>3</sup>/ha (Harmon *et al.*, 1986). Sollins (1982) found that CWD comprises about 50% of the

above-ground detrital input of coniferous forests in the Pacific Northwest. Grier and Logan (1977) report that on average 1.2 trees died/ha<sup>-1</sup>/year<sup>-1</sup> in an undisturbed 470-year-old *Pseudotsuga* stand.

During decomposition, logs undergo structural and biological changes and have been categorized into five decay classes, with class I the least and class V the most decomposed (Fogel *et al.*, 1973; Maser *et al.*, 1979; Sollins, 1982; Triska and Cromack, 1980). The decay classes and their characteristics are shown in TABLE I. Maser and Trappe (1984) determined that residence time of a log is positively correlated with decay class and that the relation is logarithmic. The more decayed a log, the more difficult it is to determine its residence time on the ground. Regardless of residence time, decay classes support unique communities of plants and animals.

The transition of logs from decay class III to decay class IV involves several important biological and structural changes. During this pe-

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TABLE I  
CHARACTERISTICS OF FALLEN DOUGLAS-FIR TREES IN FIVE DECAY CLASSES

Characteristics	Decay class				
	I	II	III	IV	V
Bark	intact	intact	trace	absent	absent
Twigs, 0.3 cm	present	absent	absent	absent	absent
Texture	intact	intact to partly soft	hard, large pieces	small, soft, blocky pieces	soft, powdery
Shape	round	round	round	round to oval	oval
Wood color	original	original	original to faded	light brown to reddish brown	red brown to dark brown
Invasive roots	none	none	sapwood	heartwood	heartwood
Portion on ground	elevated	elevated	sagging near ground	on ground	on ground

\* Adapted from Maser and Trappe (1984).

riod, for example, *Pseudotsuga* logs lose about 50% of their volume (Maser and Trappe, 1984) from the sloughing of partially decomposed bark and sapwood (Graham, 1982). Tree seedlings, especially *Tsuga heterophylla* (Raf.) Sarg. commonly become established on logs of decay class III-IV (McKee *et al.*, 1982; Christy and Mack, 1984). The high water-retention capacities of *Pseudotsuga menziesii* (Mirb.) Franco logs in decay classes III and IV make them an excellent habitat for a wide range of small vertebrates, invertebrates, plants, and microorganisms, especially during summer drought (Maser and Trappe, 1984). However, not all organisms are favored by these conditions. The high moisture content of logs in these decay classes (150% in class III and >250% in class IV) and advanced exploration by early colonizers may restrict the activity of basidiomycetes and favor ascomycetes (Kaarak, 1974).

Although the role of fungi in early wood decomposition has been well-documented (Kaarak, 1974; Rayner and Todd, 1979; Frankland *et al.*, 1982; Cooke and Rayner, 1984), their role in the later stages of wood decomposition has received little attention. Fungal communities in CWD may possibly be affected by decay class, presence or absence of *Tsuga* seedlings, and slope orientation. The purpose of this study was to focus on the genera/species of hyphomycetes and yeast present in wood of two advanced decay classes.

We addressed three questions related to community structure of these fungi: 1) do community patterns differ between decay classes III and IV; 2) do community patterns differ in logs with and

without *Tsuga* seedlings; and 3) are the fungal communities similar in the top, center, and bottom of decomposing logs?

This study does not encompass white rot fungi, brown rot fungi, mycorrhizal fungi and bacteria. Their presence in wood may be common, but time and fiscal constraints prohibited their identification. Nonetheless, exclusion of these organisms was not based on the assumption that they were unimportant in wood decomposition.

#### MATERIALS AND METHODS

**Study sites.**—Two study sites were selected at 400-m elevation near Marys Peak in the Coast Range of Oregon (latitude 44°N, longitude 123°W). Rainfall in the area averages 15.84 cm/month from September through May and 1.24 cm/month from June through August. Average day-time temperatures from September through May range from 20°C to -2.2°C, and from June through August the range is 32°C to 7.7°C. The sites are characterized by 60–80-year-old mixed stands of *Tsuga heterophylla* and *Pseudotsuga menziesii*. A sparse understory of *Acer circinatum* Pursh and *Vaccinium* spp. is present, and bryophytes carpet the forest floor. The canopy affords about 50–70% shade at both sites. Each site was logged 80–100 years ago and left to regenerate naturally.

**Sampling of logs.**—Three logs of decay classes III and IV were sampled at each site in October, 1984. Logs were selected by using the following criteria: 1) each log was horizontal across sloping aspects; 2) sampled logs were not closer than 50

m; 3) logs were unbroken along a minimum length of 3 m; 4) minimum log diameter was 0.5 m; and 5) *T. heterophylla* seedlings were present on logs.

Two disks including the entire diameter were removed from each log. The average disk diameter was 32 cm with an average thickness of 15 cm. From each log, we selected one cross-sectional disk containing roots of a *T. heterophylla* seedling and one without. The disks were cut at least 3 m from the end of the log with a chainsaw. The average distance between disks was 1.5 m. The vertical orientation of each disk was marked for reference. Each disk was placed in a separate large plastic bag and transported to the laboratory within 1 hr of removal from the log. Disks were stored in the bags up to 18 hr at 4°C before processing.

*Processing of samples.*—In the laboratory, subsamples from each disk were taken to determine moisture content and for fungal recovery. Three samples, representing top, center, and bottom of each log were taken from the interior of each disk by using ethanol-rinsed, flamed chisels and forceps. Top and bottom samples were taken 5 cm inside the log surface, and the center sample was taken along the midpoint of the vertical diameter. Sample fresh weight was 5–10 g. Surfaces exposed by cutting with the chainsaw were avoided to reduce the possibility of contamination.

A modified dilution-plate method was used to recover fungi from the wood. Samples were placed in a sterile, stainless steel blender with 500 ml of sterile distilled water. All samples were blended at high speed for 45 s or until the samples were broken into very small pieces (*i.e.*, <1 mm<sup>3</sup>). The woody material was decanted and subsequently diluted by using wide-mouthed pipettes. Concentrations of about 1/100, 1/1000, and 1/10,000 were prepared. Each dilution was used at the rate of 1 ml per sterile plastic Petri dish; agar at 45°C was then poured into the plates and swirled for 60 s to distribute wood chips throughout the medium. Three media were used: potato-dextrose agar, water agar (15%), and rose-bengal agar. Rose-bengal plates were wrapped in aluminum foil to prevent breakdown of the medium by incidental light. Streptomycin-sulfate was added to all three media at a rate of 100 ppm to retard bacterial growth. Two plates for each dilution and medium were prepared for each sam-

ple. Plates were incubated at 15°C in an unlighted incubator and examined daily for fungal growth for 1 month or until they were overgrown. Fungi were subcultured from plates and transferred to PDA slant tubes for subsequent identification and storage.

*Statistical analyses.*—Presence or absence of a species was noted for each sample. Species were given a score of 1 if they occurred in any of the 18 plates prepared for a sample. The frequency of occurrence of a species was calculated as the number of samples ( $n = 36$ ) with the species present divided by the total number of samples cultured.

Differences in species composition among classes, sites, positions, and cross-sections with and without *Tsuga* seedlings were compared by using coefficient of community (Gauch, 1982). This statistic was calculated from the presence and absence of species and genera in the samples of a category of log (*e.g.*, class III versus class IV). The coefficient of community ranges from 0 (no species or genera in common) to 1.0 (the same species or genera in each class).

Detrended correspondence analysis (DECORANA) was used to ordinate the samples based on presence or absence of species. This method arranges both species and samples along axes so that those that are most similar are closest (Hill, 1979). Ordinations were performed on the individual samples (the sum of the 18 plates). The importance of species occurring in <10 samples was downweighted by using Hill's (1979) method.

#### RESULTS

A total of 18 genera and 36 species were recovered from the logs (TABLE II). The majority of the fungal genera were dematiaceous hyphomycetes.

Species composition overlapped between decay classes (FIG. 1). The most commonly recovered fungi in both classes of logs were *Penicillium* spp., *Pichia burtonii*, *Sistotrema brinkmannii*, *Torulomyces lagena*, *Humicola* spp., and *Trichoderma* sp. *Penicillium* was recovered in twice as many class III samples as in class IV samples. All 18 species of *Penicillium* were recovered from class III logs, whereas only 5 species were recovered from class IV logs. *Penicillium lividum* was the second most frequently found species (14%) in class III logs and *Penicillium janthinellum*

TABLE II  
LIST OF FUNGI ISOLATED FROM CLASS III AND IV LOGS

Species	Abbreviation <sup>a</sup>
<i>Aureobasidium pullulans</i> (de Bary) Arnaud	AP
Basidiomycete unidentified	B
<i>Chalara</i> sp.	CS <sup>b</sup>
<i>Chalara thieliaviooides</i> (Peyr.) Nag Raj & Kendrick	CS <sup>b</sup>
<i>Chloridium chlamydosporis</i> (van Beyma) Hughes	CC
<i>Chrysosporium pannorum</i> (Link) Hughes	CP
<i>Humicola fuscoatra</i> Traaen	HS <sup>b</sup>
<i>Humicola grisea</i> Traaen	HS <sup>b</sup>
<i>Leptodontidium elatius</i> (Mangenot) Linnemann	LE
<i>Mortierella ramanniana</i> (Moeller) Linnemann	MR
<i>Oidiodendron echinulatum</i> Barron	OE
<i>Penicillium</i> spp.	PS <sup>b</sup>
<i>Penicillium charlesii</i> Smith	PS <sup>b</sup>
<i>Penicillium citrinum</i> Thom	PS <sup>b</sup>
<i>Penicillium corylophilum</i> Dierckx	PS <sup>b</sup>
<i>Penicillium fellutanum</i> Biourge	PS <sup>b</sup>
<i>Penicillium frequentans</i> Westling	PS <sup>b</sup>
<i>Penicillium implicatum</i> Biourge	PS <sup>b</sup>
<i>Penicillium janthinellum</i> Biourge	PS <sup>b</sup>
<i>Penicillium lanosum</i> Westling	PS <sup>b</sup>
<i>Penicillium lividum</i> Westling	PS <sup>b</sup>
<i>Penicillium purpurogenum</i> Stoll	PS <sup>b</sup>
<i>Penicillium raperi</i> G. Smith	PS <sup>b</sup>
<i>Penicillium restrictum</i> Gilman & Abbott	PS <sup>b</sup>
<i>Penicillium rubrum</i> Stoll	PS <sup>b</sup>
<i>Penicillium simplicissimum</i> (Oudemans) Thom	PS <sup>b</sup>
<i>Penicillium spinulosum</i> Thom	PS <sup>b</sup>
<i>Penicillium steckii</i> Zaleski	PS <sup>b</sup>
<i>Penicillium stoloniferum</i> Thom	PS <sup>b</sup>
<i>Phialophora</i> sp.	PS <sup>b</sup>
<i>Pichia burtonii</i> (Boidin et al.) Kreger van Rij	PB
<i>Sistotrema brinkmannii</i> (Bres.) J. Erikss.	SB
<i>Spiniger</i> sp.	SS
<i>Thermomyces lanuginosus</i> Tsiklinsky	TL <sup>b</sup>
<i>Thysanophora penicillioides</i> (Roum.) Kendrick	TP
<i>Torula herbarum</i> Pers.	TH
<i>Torulomyces lagena</i> Delitsch	TL
<i>Trichoderma</i> sp.	TS

<sup>a</sup> Abbreviations used in FIG. I.

<sup>b</sup> These were combined by genus for FIG. I.

was the second most frequently found species (13%) in class IV logs. *Sistotrema brinkmannii*, *Torulomyces*, *Humicola*, and *Trichoderma* were recovered two to three times more frequently from class IV logs than from class III logs. However, the yeast *P. burtonii* was recovered at a very high rate in class IV logs and to a lesser extent in class III logs regardless of medium used.

Comparing communities by using the coefficient of community indicated class III and IV logs were less similar to each other than they were in community comparisons based on sites, positions, or the presence of seedlings. The coefficient of community for class III and class IV logs was 54%, whereas that for sections with and without tree seedlings was 60%. The same pattern was observed when the presence or absence of genera was used to calculate the coefficient of community.

DECORANA ordination indicated that there was considerable overlap in the species composition of logs in classes III and IV (FIG. 2). Class III logs composed 70% of the samples with first-axis scores >150, and 27% of the samples with first-axis scores of <150. The first DECORANA axis therefore seems to weakly correspond to a time or succession gradient. The ecological interpretation of the second axis was not apparent; it was included in FIG. 2 to display the results more clearly. In contrast to decay class, samples from different positions within the cross-section did not occur in discrete areas of the ordination. The same pattern occurred for cross-sections with or without seedlings. This indicated that species composition for these factors had even more overlap than decay classes. Samples from site 1 tended to have lower scores than those from site 2. This may reflect the greater degree of decomposition in the logs at site 1.

#### DISCUSSION

Fungal community composition differed most between logs of decay classes III and IV. Differences between categories tested such as the presence or absence of *T. heterophylla* seedlings were not evident in comparisons. Our conclusions about differences in community composition made at the species level remained unchanged when the differences were analyzed at the genus level. Our data suggest that it may be possible to separate fungal communities at the genus level without losing information. We are not, however, advocating an abandonment of species identification in such studies. Each ecological case is different and requires an initial analysis of species/genus community relations before a decision is made to identify fungi only to genus. The frequencies of *Penicillium* and the yeast *Pichia* in these logs is of interest. Our data support the possibility of using relative frequencies of *Pichia* and *Penicillium* to determine the decay class of

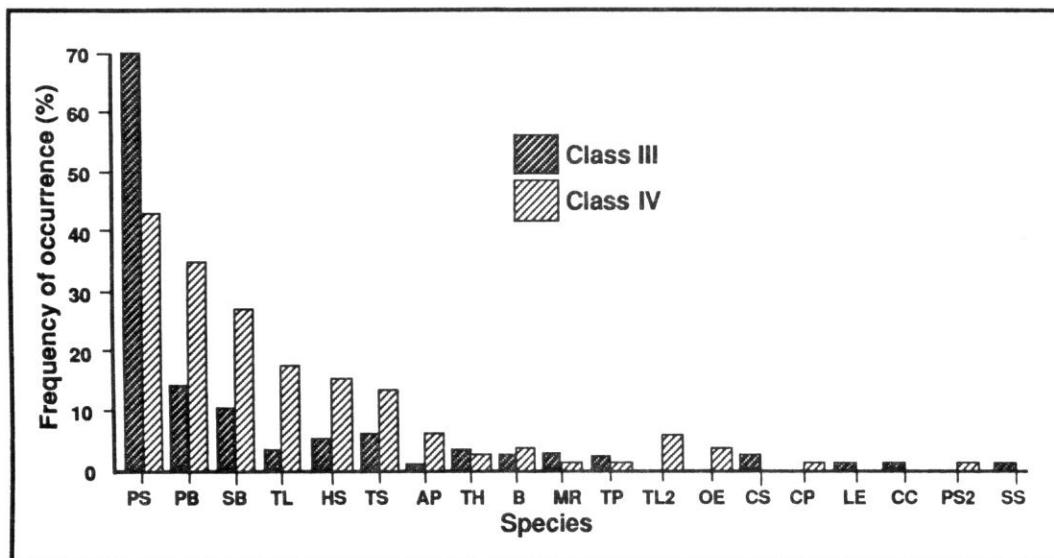


FIG. 1. Frequency of occurrence of fungi isolated from logs in decay classes III and IV. Species abbreviations are given in TABLE II. Although *Penicillium* spp. were combined in this figure, the community analysis was based on individual species.

logs. *Penicillium* was more frequent than *Pichia* in class III logs, whereas in class IV logs the frequencies of these two genera were roughly equal.

DECORANA analysis indicated a good deal of overlap between the two decay classes in terms of fungal species isolated. This result is reasonable because logs are not uniform but contain pockets of wood in various stages of decay. The first DECORANA axis seemed to correspond to species succession over time. The temporal pattern of species might have been more dramatic if a wider range of decay classes had been examined.

Rayner and Todd (1979) discuss the problem of delimiting the fungus individual in wood. When a piece of mycelium is broken, an individual mycelium potentially becomes two mycelia in an instant; additionally, some recovered species are prolific sporulators. With no reliable way to count individuals for statistical analyses, we decided to rely on the presence/absence data for these organisms. Community analysis procedures, such as DECORANA, can reveal community patterns with presence/absence data. Our study design with six samples/log may have limited the number of species recovered from logs. Further work is needed on the number of samples required to make a more complete species list.

One of the more interesting results of this research is that basidiomycetes were not recovered as major fungal components of highly decayed logs, in contrast to logs in early decay states (Rayner and Todd, 1979; Cooke and Rayner, 1984; Kaarik, 1974; Frankland *et al.*, 1982). These results may have been influenced by media and material processing method. The most prevalent fungi recovered from logs were hyphomycetes. Because we cultured from small pieces of wood, our sampling methods may have excluded some basidiomycetes. Whether a larger piece of wood, and therefore a larger potential volume of hyphae, is required for successful culture of basidiomycetes is not known, but species of basidiomycetes were isolated, leading us to believe that inoculum size was not a totally limiting factor.

Our results suggest that hyphomycetes are highly active in advanced decay stages of *P. menziesii*. The dominance of this group may in part be related to physical and chemical changes associated with decomposition (Maser and Trappe, 1984). High moisture content throughout much of the year may favor hyphomycetes and ascomycetes over basidiomycetes. The wood chemistry of *P. menziesii* changes markedly during decomposition with an enrichment of lignin and depletion of cellulose and hemicellulose (Means *et al.*, 1985). Carbon quality therefore decreases

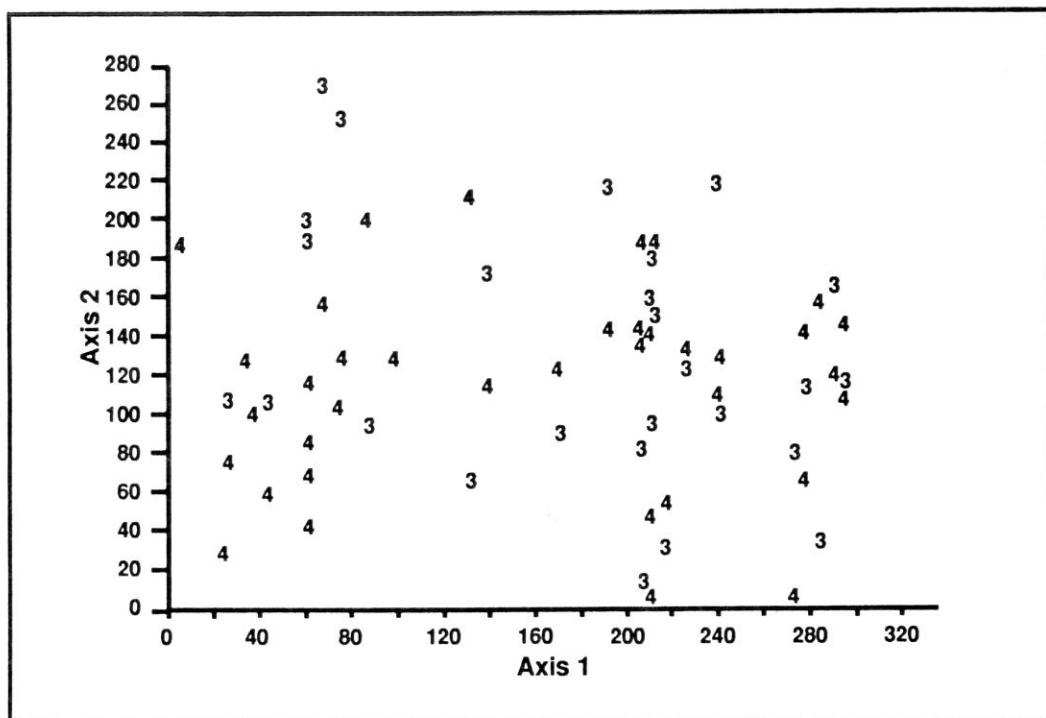


FIG. 2. DECORANA ordination of the 72 samples from which fungi were isolated. A 3 indicates class III log, and a 4 indicates a class IV log sample.

during decomposition and the activity of wood-degrading basidiomycetes is likely to decrease. In contrast, ascomycetes and hyphomycetes may decompose metabolites produced from plant, animal, fungal, or prokaryote activity in the log. Some ascomycetes, however, have been shown to have cellulolytic activity *in vivo* (Merrill and French, 1966). Further study is needed on the chemistry of logs in the later stages of decomposition and the effect on microbial activity.

We originally expected to find some differences between fungal communities around roots of *Tsuga* seedlings and in wood without seedlings, but our results indicated no significant differences in community structure. We think that biochemical effects of the rhizosphere on saprophytic fungi in rotten wood may: 1) extend far beyond the immediate vicinity of the roots themselves, thus equally affecting the fungal community in portions of the logs uncolonized by roots; 2) not extend far enough beyond the root surface to affect the surrounding microbial community; or 3) not affect the fungal community.

Closer investigation is needed of rhizosphere relations in the environment of the rotten log.

The importance of the various mechanisms responsible for dispersing fungi between and within logs is not clearly understood. Since fungi lacking wind-dispersal mechanisms are widespread in highly decayed conifer wood, we speculate that they move from log to log by: 1) active growth; 2) dispersal of propagules by water percolation; and 3) dispersal by animals. The spores of *Pichia burtonii*, for example, are not adapted for wind dispersal, and their spread is likely due to insect dispersal. Propagules of many ascomycetes can be carried in litter and soil by microarthropods (Visser *et al.*, 1987). Additionally, propagules of many ascomycetes may be introduced to the surface of logs by canopy throughfall. *Pichia* grows very slowly in culture, producing minute hyphae with multitudes of spores along the hyphae: its movement in logs is more likely due to the spread of its conidia than to rapid penetration by hyphae. Although spores of some genera, such as *Penicillium*, are easily dis-

persed to new logs by wind, this mechanism is not active deep in wood; again, active growth, dissemination of propagules by water percolation, and the action of animals are the likely mechanisms for within-log movement of such fungi.

The fungal community present in logs determines, in part, the rate and type of decomposition and nutrient cycling processes. Although our results indicate fungal communities in logs of decay classes III and IV are similar, they seem to be different from those found in prior studies of early stages of decay (Kaarik, 1974; Rayner and Todd, 1979; Frankland et al., 1982; Cooke and Rayner, 1984). Our study suggests that basidiomycetes may be less active than ascomycetes and hyphomycetes, but more work is required before this question is completely addressed.

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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 ( $\text{Al(OH)}_3(\text{s})$ ); and (iii) outflow of the soil solution. The chemical species in the system include all of the products of reactions of  $\text{H}_2\text{SO}_4$ ,  $\text{Al(OH)}_3(\text{s})$ , 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  $\text{H}_2\text{SO}_4$  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. <u>Species:</u>	
mobile:	$\text{H}^+$ , $\text{OH}^-$ , $\text{SO}_4^{2-}$ , $\text{Al}^{3+}$ , $\text{AlOH}^{2+}$ , $\text{Al}(\text{OH})_2^+$ , $\text{Al}(\text{OH})_3^0$ , $\text{Al}(\text{OH})_4^-$ , $\text{AlSO}_4^-$
immobile:	$\text{XOH}_2^+$ , $\text{XOH}$ , $\text{XSO}_4^-$
b. <u>Components:</u>	
mobile:	$\text{H}^+$ , $\text{SO}_4^{2-}$ , $\text{Al}^{3+}$
immobile:	$\text{XOH}_2^+$
c. <u>Mass-action equations<sup>a</sup></u>	
(1)	$[\text{OH}^-] = K_w [\text{H}^+]^{-1}$
(2)	$[\text{AlOH}^{2+}] = K_1 [\text{Al}^{3+}] [\text{H}^+]^{-1}$
(3)	$[\text{Al}(\text{OH})_2^+] = K_2 [\text{Al}^{3+}] [\text{H}^+]^{-2}$
(4)	$[\text{Al}(\text{OH})_3^0] = K_3 [\text{Al}^{3+}] [\text{H}^+]^{-3}$
(5)	$[\text{Al}(\text{OH})_4^-] = K_4 [\text{Al}^{3+}] [\text{H}^+]^{-4}$
(6)	$[\text{AlSO}_4^-] = K_5 [\text{Al}^{3+}] [\text{SO}_4^{2-}]$
(7)	$[\text{XOH}] = K_6 [\text{XOH}_2^+] [\text{H}^+]^{-1}$
(8)	$[\text{XSO}_4^-] = K_7 [\text{XOH}_2^+] [\text{SO}_4^{2-}]$
d. <u>Fluxes of the components through inflow and dissolution</u>	
(9)	$J(\text{in}, \text{H}^+) = 2 v c$
(10)	$J(\text{in}, \text{SO}_4^{2-}) = v c$
(11)	$J(\text{diss}, \text{H}^+) = -3 k [\text{H}^+]^{0.4}$
(12)	$J(\text{diss}, \text{Al}^{3+}) = k [\text{H}^+]^{0.4}$
e. <u>Fluxes of the components through outflow</u>	
(13)	$J(\text{out}, \text{H}^+) = -v ([\text{H}^+] - [\text{OH}^-] - [\text{AlOH}^{2+}] - 2 [\text{Al}(\text{OH})_2^+] - 3 [\text{Al}(\text{OH})_3^0] - 4 [\text{Al}(\text{OH})_4^-])$
(14)	$J(\text{out}, \text{SO}_4^{2-}) = -v ([\text{SO}_4^{2-}] + [\text{AlSO}_4^-])$
(15)	$J(\text{out}, \text{Al}^{3+}) = -v ([\text{Al}^{3+}] + [\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}(\text{OH})_3^0] + [\text{Al}(\text{OH})_4^-] + [\text{AlSO}_4^-])$
f. <u>Mole-balance equation for the immobile component</u>	
(16)	$[\text{XOH}_2^+] + [\text{XOH}] + [\text{XSO}_4^-] - T_{\text{XOH}_2^+} = 0$
g. <u>Flux-balance equations for the mobile components</u>	
(17)	$J(\text{out}, \text{H}^+) + J(\text{in}, \text{H}^+) + J(\text{diss}, \text{H}^+) = 0$
(18)	$J(\text{out}, \text{SO}_4^{2-}) + J(\text{in}, \text{SO}_4^{2-}) = 0$
(19)	$J(\text{out}, \text{Al}^{3+}) + J(\text{diss}, \text{Al}^{3+}) = 0$

<sup>a</sup> 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  $\text{H}_2\text{SO}_4$ , (ii) the dissolution of gibbsite,  $\text{Al}(\text{OH})_3(\text{s})$ , 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  $J$  [ $\text{mol dm}^{-2} \text{s}^{-1}$ ].

The fluxes of the components  $\text{H}^+$  and  $\text{SO}_4^{2-}$  that result from the inflow process are given by Eqns. (9) and (10) in Table 1d, where  $v$  is the flow velocity [ $\text{dm s}^{-1}$ ] and  $c$  is the concentration of sulfuric acid in the inflow [ $\text{mol dm}^{-3}$ ]. Note that the hydrogen ion flux is twice as large as the sulfate flux, on account of the stoichiometry of sulfuric acid.

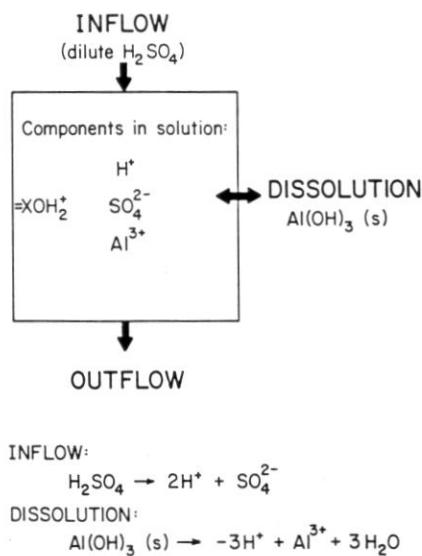


FIG. 1. A simple box model of a compartment of soil and soil water. The chemical components are  $H^+$ ,  $SO_4^{2-}$ ,  $Al^{3+}$ ,  $H_2O$  and the surface hydroxyl group,  $XOH_2^+$ . The processes resulting in fluxes of these components into and out of the box are inflow, dissolution, and outflow. 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



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

$$R = k[H^+]^{0.4} \quad (2)$$

where  $R$  is the area-specific rate [ $\text{mol dm}^{-2} \text{ s}^{-1}$ ] and  $k$  is the reaction rate constant when  $[H^+]$  is expressed in  $\text{mol dm}^{-3}$ . 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 ( $\text{mol dm}^{-3}$ ). 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  $v$ ,  $c_s$ ,  $k$ , 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

$$Q_{i,m} = \frac{\partial \ln C_i}{\partial \ln P_m} \quad (3)$$

## **University of Virginia Subcontract - Work statement and budget justification**

### **Work Statement:**

Investigators at the University of Virginia will participate in objectives 1, 2 and 3 of the overall proposal.

### **Budget Justification**

The budget includes funding for a post-doctoral research associate who will have primary responsibilities Prof. William D. Williams. The post-doc will be assisted by a graduate student who is supported full-time for one academic semester and during the summer when the most intensive field work is required. Dept. Zoology Field efforts will be supplemented by undergraduate students during the summer months. Equipment University of Adelaide includes computers and software required for the fieldwork, modeling and analysis. Travel includes money Adelaide, South Australia 5005 for room and board for students conducting fieldwork, for travel between Charlottesville VA and the field Australia. Site on Parramore Island on the Eastern Shore of Virginia, gas for a boat and for travel to national scientific meeting per year for the Post-doc.

FAX: 61 8303 4364

Professor Williams,

I am the first author on a paper presented at SIL - Summer 1995 - entitled:

"Do seasonality and disturbance influence reproduction in freshwater atyid shrimp in headwater streams, Puerto Rico?" Authors are Sherri Johnson, Alan Covich, Todd Crowl, Alejo Estrada, John Bithorn, and Wayne Wurtzbaugh.

I am writing to inform you that galley proofs should be sent to my new address below (for rapid turnaround).

Please contact me if there are problems.

Thank you,

Dr. Sherri Johnson  
Forestry Sciences Lab  
3200 SW Jefferson Way  
Corvallis, OR 97331  
USA

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):

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

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		
$K_w = 10^{-14.0}$	$v = 3.17 \times 10^{-7} \text{ dm s}^{-1}$	
$K_1 = 10^{-5.4}$	$c = 5.00 \times 10^{-5} \text{ mol dm}^{-3}$	
$K_2 = 10^{-10.0}$	$k = 1.40 \times 10^{-10} \text{ (*)}$	
$K_3 = 10^{-15.7}$		
$K_4 = 10^{-23.5}$		
$K_5 = 10^{3.2}$	$T_{XOH_2^+} = 1.00 \times 10^{-6} \text{ mol dm}^{-3}$	
$K_6 = 10^{-7.5}$		
$K_7 = 10^{4.5}$		

b. Speciation		
Species	$C(i)^b$ (mol/L)	$\log C(i)$
$H^+$	$7.21 \times 10^{-5}$	-4.14
$OH^-$	$1.39 \times 10^{-10}$	-9.86
$SO_4^{2-}$	$4.94 \times 10^{-5}$	-4.31
$Al^{3+}$	$7.90 \times 10^{-6}$	-5.10
$AlOH_2^+$	$1.10 \times 10^{-6}$	-5.96
$Al(OH)_2^+$	$1.21 \times 10^{-7}$	-6.92
$Al(OH)_3$	$2.10 \times 10^{-9}$	-8.68
$Al(OH)_4^-$	$2.92 \times 10^{-12}$	-11.54
$AlSO_4^+$	$6.18 \times 10^{-7}$	-6.21
$XOH_2^+$	$3.90 \times 10^{-5}$	-4.41
$XOH$	$1.71 \times 10^{-8}$	-7.77
$XSO_4^-$	$6.10 \times 10^{-5}$	-4.22

c. Composition		
Component	$X(j)^c$ (mol/L)	$\log X(j)$
$XOH_2^+$	$3.90 \times 10^{-5}$	-4.41
$H^+$	$7.21 \times 10^{-5}$	-4.14
$SO_4^{2-}$	$4.94 \times 10^{-5}$	-4.31
$Al^{3+}$	$7.90 \times 10^{-6}$	-5.10

d. Normalized Sensitivity Coefficients* $\delta \ln C_i / \delta \ln P_m$			
Species i	$v$	Parameter $m$	
$H^+$	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

\* 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  $\mu\text{mol/L}$  sulfuric acid in the inflow corresponds to pH = 4.0. The reaction constant  $k$  is calculated for approximately 2  $\text{m}^2$  of gibbsite surface per  $\text{dm}^2$  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.

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.

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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.

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$K_2 = 10^{-10.0}$	$k = 1.40 \times 10^{-10} (*)$	
$K_3 = 10^{-15.7}$		
$K_4 = 10^{-23.5}$	$T_{XOH_2^+} = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$	
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c. Composition		
Component	$X(j)^c (\text{mol L}^{-1})$	$\log X(j)$
	$T(j)^d (\text{mol L}^{-1})$	
$XOH_2^+$	$3.90 \times 10^{-5}$	-4.41
$H^+$	$7.21 \times 10^{-5}$	-4.14
$SO_4^{2-}$	$4.94 \times 10^{-5}$	-4.31
$Al^{3+}$	$7.90 \times 10^{-6}$	-5.10
		$9.74 \times 10^{-6}$

d. Normalized Sensitivity Coefficients* $\partial \ln C_i / \partial \ln P_m$			
Species i	v	c	k
$H^+$	0.319	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
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## 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  $\mu\text{mol/L}$  sulfuric acid in the inflow corresponds to pH = 4.0. The reaction constant  $k$  is calculated for approximately 2  $\text{m}^{-2}$  of gibbsite surface per  $\text{dm}^2$  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 consumed in the dissolution process. The corresponding flux of aluminum into solution is one third of the  $H^+$  flux, 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 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; 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 mainly 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 on 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 at-

## FLUXES OF MOBILE COMPONENTS

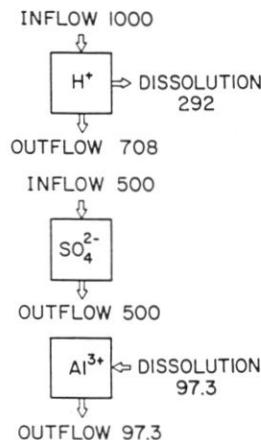


FIG. 2. The fluxes of the components through the system at steady state, as defined by Table 1, Eqns. (1-19) and the numerical values in Table 2a. The units are mol ha<sup>-1</sup> yr<sup>-1</sup> (1 hectare (ha) = 10<sup>4</sup> m<sup>2</sup>).

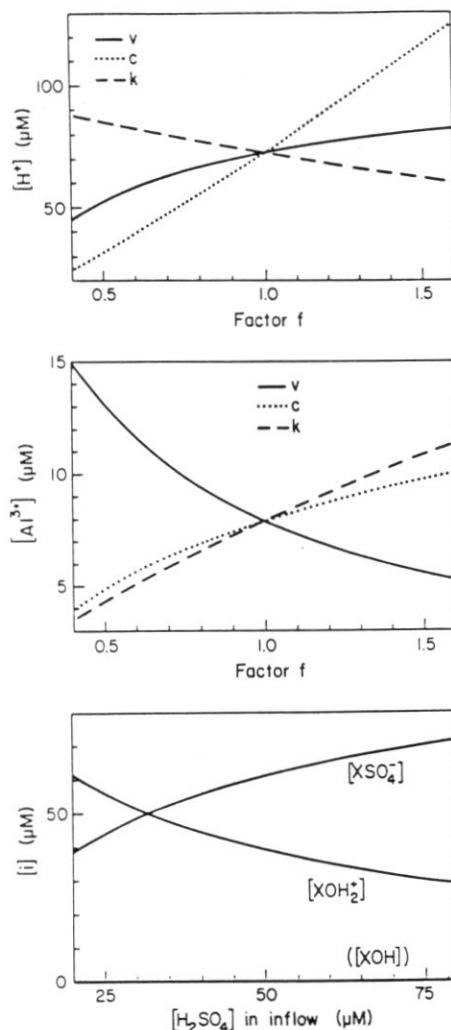


FIG. 3. Sensitivity of the steady-state solution to changes in values of the parameters controlling the system. The lines in panels 3A and 3B show the steady-state concentrations of  $H^+$  and  $Al^{3+}$ , respectively, as the designated parameter  $P$  is varied about its standard value by the factor  $f$  (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,  $v = 1 \text{ m yr}^{-1}$ ; concentration of sulfuric acid in the inflowing water,  $c = 50 \mu\text{mol dm}^{-3}$ ; 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.

tention 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.

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:

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

where  $C(i)$  is the concentration of species  $i$  [ $\text{mol dm}^{-3}$ ],  $K(i)$  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

Table A1. Matrix representation of problem.

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

Species	A Matrix Components			K Vector <sup>a</sup>
	XOH <sub>2+</sub>	H <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	
1 H <sup>+</sup>	0	1	0	0
2 OH <sup>-</sup>	0	-1	0	0
3 SO <sub>4</sub> <sup>2-</sup>	0	0	1	0
4 Al <sup>3+</sup>	0	0	0	1
5 AlOH <sup>2+</sup>	0	-1	0	1
6 Al(OH) <sub>2</sub> <sup>+</sup>	0	-2	0	1
7 Al(OH) <sub>3</sub>	0	-3	0	1
8 Al(OH) <sub>4</sub> <sup>-</sup>	0	-4	0	1
9 AlSO <sub>4</sub> <sup>+</sup>	0	0	1	1
10 XOH <sub>2+</sub>	1	0	0	0
11 XOH	1	-1	0	0
12 XSO <sub>4</sub> <sup>-</sup>	1	0	1	0

b. T vector<sup>a</sup>:  $T(j)$  is the total concentration of an immobile component.

$$\text{T}_{\text{XOH}_2^+} \quad \text{total concentration of XOH}_2^+$$

c. P vector<sup>a</sup>:  $P(m)$  is a parameter used in the rate expressions for slow processes.

Parameter m	Description
v	flow velocity
c	concentration of H <sub>2</sub> SO <sub>4</sub> 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  $l$ .

Process l	Parameter m
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.

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  $l$ .

Process l	Component j
inflow	2
dissolution	-3

\* Numerical values are given in Table 2a.

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.

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

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

where  $R(l)$  is the rate of process  $l$  [ $\text{mol dm}^{-2} \text{s}^{-1}$ ],  $P(m)$  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:

$$J(l, j) = R(l)s(l, j) \quad (A3)$$

where  $J(l, j)$  is the flux of component  $j$  in process  $l$  [mol dm<sup>-2</sup> s<sup>-1</sup>], 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):

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

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:

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

where  $v$  is the outflow velocity [dm s<sup>-1</sup>] 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

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

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:

$$Y(j') = \sum_l J(l, j') = 0 \quad (A5)$$

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,  $P(m)$ :

$$Y_{j'} = Y_{j'}(X_k \cdot (P_m), P_m). \quad (A6)$$

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,  $X(k')$ :

$$Y_{j''} = Y_{j''}(X_k \cdot (P_m), X_k \cdot (P_m)). \quad (A7)$$

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):

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

For a set of  $n'$  mobile components, there are  $j' = 1, \dots, n'$  equations of the form of Eqn. (A8), and  $k' = 1, \dots, n'$  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):

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

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  $n'' \times n''$  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:

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

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.