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Research and Development

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Effects of Acid Precipitation on Soil Leachate Quality

Computer Calculations

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EFFECTS OF ACID PRECIPITATION ON SOIL LEACHATE QUALITY

Computer Calculations

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DISCLAIMER

One of the principal reasons for the preparation of this report for the Environmental Protection Agency was to supply scientifically valid information which could be incorporated into the EPA SO_2-Particulate Matter criteria document, presently in the final stages of preparation. A strict requirement pertaining to that document is that any scientific information used there must be published (or at least in press) by January 1, 1980. Because of this demanding time constraint, it was necessary that the contractor prepare this report in a shorter time than would ordinarily be attempted, and that it be published by EPA without undergoing peer review. We feel that early publication of these results in order to stimulate the broadest scientific discussion prior to completion of the criteria document justified waiving our normally more rigorous prepublication review requirements. Publication, however, does not signifiy that the the contents necessarily reflect the views and policies of EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its 15 major field installations, one of which is the Corvallis Environmental Research Laboratory.

The primary mission of the Corvallis Laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects and control of pollutants in lakes and streams; and the development of predictive models on the movement of pollutants in the biosphere.

In the investigation reported here, a chemical thermodynamic model has been used to predict the chemical species in solutions of soils, from three northeastern states, affected by acid precipitation. This kind of information is basic to the prediction of acid precipitation effects on soil fertility, ecosystem productivity, and toxicity effects on aquatic species.

Thomas A. Murphy, Director
Corvallis Environmental Research Laboratory

ABSTRACT

The multipurpose computer program GEOCHEM was employed to calculate the equilibrium speciation in 23 examples of acid precipitation from New Hampshire, New York, and Maine, and in the same number of mixtures of acid precipitation with minerals characteristic of soils in the three states mentioned. Between 100 and 200 soluble inorganic and organic complexes were taken into account in each speciation calculation. The calculations performed on the acid precipitation samples showed that the metals (including heavy metals) and the sulfate, chloride, and nitrate ligands would be almost entirely in their free ionic forms, while the phosphate, carbonate, ammonia, and organic ligands would be in their protonated forms. This result was independent of the geographic location of the acid precipitation and the month of the year in which the sample was collected.

The speciation calculations on the precipitation-soil mineral mixtures showed that aluminum and iron levels in a soil solution affected by acid precipitation would be significantly higher than in one whose chemistry is dominated by carbonic acid. The higher levels found were caused by the lower pH value of acid precipitation as well as by complexes formed with inorganic and organic ligands. It was also shown that soil cation exchangers would adsorb preferentially heavy metals, such as Cd and Pb, which are found in acid precipitation.

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CONTENTS

Foreword iii

Abstract iv

Figures vi

Tables vi

Acknowledgements viii

1. Introduction 1

2. Conclusions 2

3. Recommendations 3

4. The Computer Program GEOCHEM 4

Development of the program 4

General features of the program 4

Input data required by the program 8

5. Scenario for the Mixing of Acid Precipitation with Surface Soils 8

Composition data and speciation for acid precipitation 9

Interaction of acid precipitation with soil minerals 24

6. Soil Response to Acid Precipitation 27

New Hampshire soils 27

New York and Maine soils 33

References 36

FIGURES

Number		Page
1	GEOCHEM computer program model	6

TABLES

Number		Page
1	Code numbers and symbols for the metals and ligands considered by GEOCHEM	10
2	Speciation in the mean annual precipitation at Hubbard Brook	11
3	Speciation in the mean January precipitation at Hubbard Brook	13
4	Speciation in the mean February precipitation at Hubbard Brook	13
5	Speciation in the mean March precipitation at Hubbard Brook	14
6	Speciation in the mean April precipitation at Hubbard Brook	14
7	Speciation in the mean May precipitation at Hubbard Brook	15
8	Speciation in the mean June precipitation at Hubbard Brook	15
9	Speciation in the mean July precipitation at Hubbard Brook	16
10	Speciation in the mean August precipitation at Hubbard Brook	16
11	Speciation in the mean September precipitation at Hubbard Brook	17
12	Speciation in the mean October precipitation at Hubbard Brook	17

TABLES (cont'd)

Number		Page
13	Speciation in the mean November precipitation at Hubbard Brook	18
14	Speciation in the mean December precipitation at Hubbard Brook	18
15	Speciation in the mean annual precipitation at Mt. Moosilauke	19
16	Speciation in throughfall at Hubbard Brook (June and October mean)	20
17	Speciation in throughfall at Mt. Moosilauke (mean annual)	21
18	Speciation in precipitation at Ithaca, New York	22
19	Speciation in precipitation at Caribou, Maine	23
20	Total "baseline" soluble aluminum and iron in representative soils from three precipitation study areas	25
21	Speciation in the mean annual precipitation/soil mixture at Hubbard Brook	28
22	Speciation in the mean January precipitation/soil mixture at Hubbard Brook	29
23	Speciation in the mean July precipitation/soil mixture at Hubbard Brook	30
24	Speciation in the mean annual precipitation/soil mixture at Mt. Moosilauke	31
25	Speciation in the throughfall/soil mixture at Mt. Moosilauke	32
26	Speciation in the precipitation/soil mixture at Ithaca, New York	34
27	Speciation in the precipitation/soil mixture at Caribou, Maine	35

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The acquisition of experimental data on the chemical composition of acid precipitation was made possible through the splendid assistance of Mr. Danny Rambo, USEPA-Corvallis Environmental Research Laboratory. Gratitude is expressed also to Dr. Christopher S. Cronan of the Department of Biological Sciences at Dartmouth College for sending reprints and a preprint containing data on the composition of acid precipitation, throughfall, and soil percolate.

INTRODUCTION

Much evidence has accumulated during the past several years concerning the phenomenon of acid precipitation in the northeastern United States. A general consensus appears to be developing in regard to the importance of obtaining a thorough understanding of the chemistry of the soil solution in ecosystems affected by acid precipitation. It is appreciated now that predictions about soil fertility, ecosystem productivity, and toxicity effects on aquatic species cannot be made unless information is available to permit a detailed consideration of the chemical species which appear in soils receiving meteoric waters containing excess strong inorganic acids.

One observation that has emerged in recent biogeochemical studies on acid precipitation effects is that the replacement of a soil solution dominated by carbonic and organic acids by one whose pH value is controlled by strong inorganic acids, such as nitric and sulfuric acids, may produce increased levels of soluble aluminum in the soil. This increase in aluminum solubility is proposed to occur because of the enhanced dissolution of soil minerals. The resultant high levels of aluminum in the soil solution are easily transferred to the channel system, if the pH value of the subsurface water remains low, and thereby can disturb seriously the ecological balance among aquatic species through toxicity.

In the present investigation, an attempt has been made to predict the chemical species in a soil solution affected by acid precipitation. The method is a calculation, based on chemical thermodynamic principles, performed by the computer program GEOCHEM. GEOCHEM can compute the equilibrium speciation in an aqueous solution where several hundred soluble complexes and solids can form among as many as 36 metals and 66 inorganic and organic ligands. It is, therefore, capable of accurate estimation of metal solubility characteristics in a soil solution, despite the chemical heterogeneity expected in this system.

CONCLUSIONS

An application of the computer program GEOCHEM to the calculation of the chemical species in acid precipitation collected in New Hampshire, New York, and Maine has shown that the metals in precipitation are in their free ionic forms, as are the ligands SO_4, Cl, and NO_3, while the ligands CO_3, PO_4, NH_3, and organic ligands are in their protonated forms. This result is based on the consideration of about 140 possible complexes by the program and is in agreement with the generally accepted view of acid precipitation as a solution of salts mixed with sulfuric, hydrochloric, and nitric acids. The speciation calculation produced virtually identical results regardless of the location of collection of the acid precipitation or the time of year it was collected.

The interaction between acid precipitation and soil, simulated in speciation calculations on a system comprising the precipitation, amorphous $Al(OH)_3(s)$ and $Fe(OH)_3(s)$, and a cation exchange surface, was shown to produce levels of Al and Fe in the soil solution which were orders of magnitude larger than the levels predicted for a soil solution dominated by carbonic acid and in equilibrium with amorphous Al and Fe hydrous oxides. These higher levels were the result both of lower pH value in the acid precipitation and of the presence of metal-complexing ligands. The cation exchanger in the soil was found to adsorb preferentially the heavy metals in acid precipitation, such as Cd and Pb. All of these effects occurred regardless of the geographical location or month of collection of the acid precipitation data.

The calculations performed by GEOCHEM corroborated the recent suggestions of ecologists and earth scientists, that percolation of acid precipitation through the soil tends to dissolve the least stable soil minerals and raise the levels of aluminum significantly in the subsurface runoff which ultimately finds its way into the channel system of a watershed.

RECOMMENDATIONS

Much more detailed chemical information about the interaction between acid precipitation and northeastern U.S. soils could be obtained through further simulation studies using GEOCHEM. In the present investigation, only a portion of the aluminum-containing soil minerals was included and a very simple set of soil solution organic ligands was employed. There is a need to involve complex aluminosilicates which are known to exist in the soils of interest, such as muscovite and vermiculite, in the simulations to obtain a complete picture of the effect of acid precipitation on the dissolution of aluminum-bearing soil minerals. There is also a need to consider a broad range of organic acids which better represents the actual water-soluble organic matter in the soil solution. These extensions are both possible with the current level of development of GEOCHEM.

This study of the effect of acid precipitation on soils was made somewhat more difficult than need be by the lack of available data on the complete chemical composition and mineralogy of the pertinent surface soils. Every effort should be made in the future to characterize the soils in the watersheds of interest with respect to their chemical properties just as completely as the acid precipitation which infiltrates them has been characterized in the past.

THE COMPUTER PROGRAM GEOCHEM

DEVELOPMENT OF THE PROGRAM

GEOCHEM is a multipurpose computer program for calculating the equilibrium speciation of the chemical elements in the soil solution (Mattigod and Sposito, 1979; Sposito and Mattigod, 1979). The method of calculation employed in the program is based in chemical thermodynamics. For each component of a soil solution, a mole balance equation is set up and thermodynamic equilibrium constants corrected for ionic strength are incorporated into the various terms of this equation according to the law of mass action. The solution of the set of non-linear algebraic equations which results from mole balance applied to all the components simultaneously ultimately provides the concentration of each dissolved, solid, and adsorbed species in the soil system under consideration. Some typical applications of GEOCHEM would include: (1) prediction of the concentrations of inorganic and organic complexes of a metal cation in a soil solution; (2) calculation of the concentration of a particular chemical form of a nutrient element in a solution bathing plant roots so as to correlate that form with nutrient uptake; (3) prediction of the fate of a pollutant metal added to a soil solution of known characteristics; and (4) estimation of the effect of changing pH, ionic strength redox potential, water content, or the concentration of some element on the solubility of a chosen chemical element in a soil solution.

GEOCHEM is a modified version of the computer program REDEQL2, which was developed at the California Institute of Technology by F. M. M. Morel, R. E. McDuff, and J. J. Morgan. The detailed structure of REDEQL2 has been described in several published articles (Morel and Morgan, 1972; Morel et al., 1973; Morel and Yeasted, 1977) and in two reports (McDuff and Morel, 1973; Ingle et al., 1978). The methods of numerical analysis employed in the program are discussed by Morel and Morgan (1972) and are compared with the methods used in other computer programs by Leggett (1977). GEOCHEM differs from REDEQL2 principally in containing more than twice as much thermodynamic data; in utilizing thermodynamic data which have been selected critically especially for soil systems; in containing a method for describing cation exchange (Mattigod and Sposito, 1979), and in employing a different subroutine for correcting thermodynamic equilibrium constants for the effect of nonzero ionic strength.

GENERAL FEATURES OF THE PROGRAM

GEOCHEM is written in IBM 370 FORTRAN IV and is compatible with the G compiler, level 21.7. The program requires about 200K of core. For any soil

solution data to be analyzed by the program, the chemical components are identified as metals and unprotonated ligands instead of, for example, complexes and solids containing metals and ligands. The principal variables considered by the program are the free ionic concentrations of the metals and ligands. Accordingly, the mole balance equation for a metal M is written in the form:

$$M_T = [Mn^+] + \Sigma\ \alpha {}^cK_{\alpha\gamma\beta}\ [M^{n+}]^\alpha\ [H^+]^\gamma\ [L^{p-}]^\beta \qquad (1)$$

where M_T is the total molar concentration of the metal ${}^cK_{\alpha\gamma\beta}$ is the conditional stability or formation constant for the compound, $M_\alpha H_\gamma L_\beta$, H refers to the proton, and L refers to a ligand. The conditional stability and formation constant, ${}^cK_{\alpha\gamma\beta}$, and the notation employed for a compound are discussed by Sposito and Mattigod (1979). The point to be made here is that Eq. (1) and the analogous expression for the total molar concentration of a ligand, L_T, are nonlinear algebraic equations in the free ionic concentrations. The numerical analysis problem solved by GEOCHEM is to calculate the set of free ionic concentrations that satisfies a given set of mole balance equations (one equation for each metal and each ligand in the system being investigated), subject to input values of the M_T and L_T along with the thermodynamic equilibrium $K_{\alpha\gamma\beta}$ which are stored in the program. During the computation, the ionic strength is calculated using the current values of the concentrations of all charged species that are possible and the ${}^cK_{\alpha\gamma\beta}$ are computed in the usual way with the values of the $K_{\alpha\gamma\beta}$ and with single-ion activity coefficients (see, e.g., Stumm and Morgan, 1970). Thus the computer calculation is done self-consistently, with the total analytical concentrations and the thermodynamic equilibrium constants corrected for ionic strength related through mole balance (see Figure 1).

GEOCHEM currently stores thermodynamic data for 36 metals and 66 ligands which form more than 2,000 compounds. These metals and ligands are listed in Table 1 along with their code numbers and code symbols. For a given metal-ligand combination, up to six soluble complexes and up to three solids can be considered by the program. In addition to the three solids per metal-ligand combination, mixed solids containing more than one metal or ligand are included in the program. Formation constants for up to 20 mixed solids may be incorporated into GEOCHEM; at present there are 18 mixed solids, including illite, muscovite, chlorite, vermiculite, and several montmorillomites.

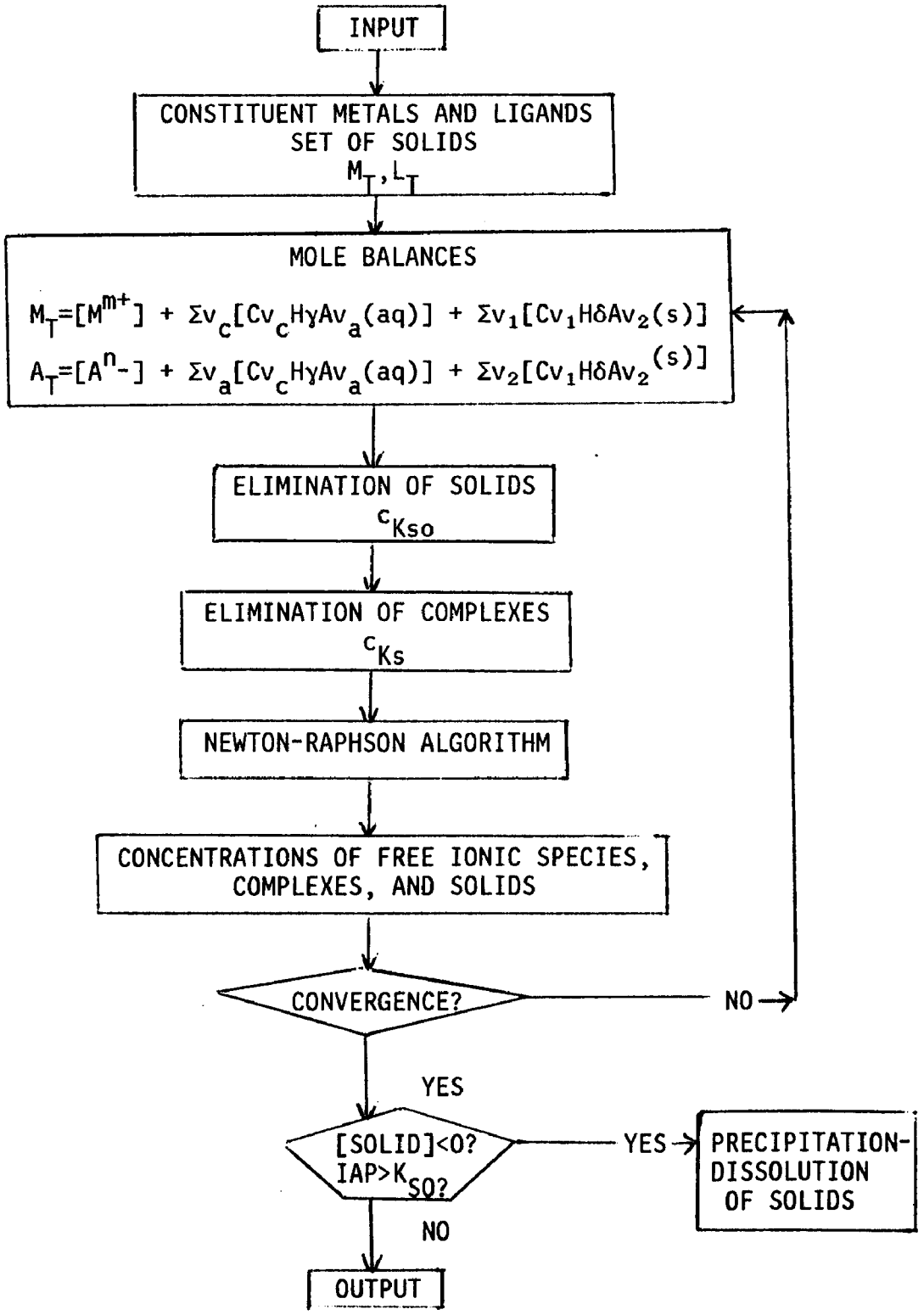
INPUT
CONSTITUENT METALS AND LIGANDS
SET OF SOLIDS
M_T, L_T
MOLE BALANCES
$M_T=[M^{m+}] + \Sigma v_c[Cv_c H\gamma Av_a(aq)] + \Sigma v_1[Cv_1 H\delta Av_2(s)]$
$A_T=[A^{n-}] + \Sigma v_a[Cv_c H\gamma Av_a(aq)] + \Sigma v_2[Cv_1 H\delta Av_2(s)]$
ELIMINATION OF SOLIDS
c_{Kso}
ELIMINATION OF COMPLEXES
c_{Ks}
NEWTON-RAPHSON ALGORITHM
CONCENTRATIONS OF FREE IONIC SPECIES,
COMPLEXES, AND SOLIDS
CONVERGENCE?
NO
YES
[SOLID]<0?
IAP>K_{SO}?
YES
PRECIPITATION-
DISSOLUTION
OF SOLIDS
NO
OUTPUT

Figure 1.

GEOCHEM can describe soil solution equilibria in which the partial pressures of N_2, O_2, and CO_2 are permitted to vary. The variation in O_2 pressure is treated as an oxidation-reduction phenomenon through the inclusion of 24 redox equations in the program. These redox equations are discussed fully by Sposito and Mattigod (1979).

There are several specific characteristics of GEOCHEM that should be kept in mind as the results of this report are read. These characteristics are most conveniently emphasized by the following list.

(1) The data bank of GEOCHEM consists of thermodynamic data at 25°C and 1 atmosphere. Therefore, all equilibrium calculations are performed at this fixed temperature and pressure. It is possible for a user to run equilibrium computations on GEOCHEM at temperatures and pressures other than 25°C and 1 atmosphere provided that a separate data bank is compiled by the user for the temperature and pressure of interest.

(2) An accounting for metastable species and species that are not favored kinetically can be incorporated into the computation by methods which are described by Sposito and Mattigod (1979). It is not necessary to assume complete thermodynamic equilibrium in order to do a calculation.

(3) The condition of electroneutrality is <u>not</u> imposed during a computation performed by GEOCHEM. The only constraint imposed is that of mole balance (i.e., mass conservation), as discussed above. The fact that charge conservation is not considered by the program has the advantage that analytical data in which, for reasons of experimental error or omission, the equivalents of metals do not equal the equivalents of ligands may still be analyzed for speciation. On the other hand, there is no guarantee that the weighted sum of positively-charged species will equal the weighted sum of negatively-charged species according to the electroneutrality principle. This condition may be useful when examining the speciation results for a complete and accurate set of analytical data to see if the computer results are self-consistent. If electrical neutrality is violated, the thermodynamic data that were used may need revision or augmentation.

(4) Ionic strength corrections are made in the program through the use of single-ion or single-molecule activity coefficients. The equation employed to compute the activity coefficients (at 25°C) is:

$$\mathrm{Log}\gamma = \frac{AZ^2\sqrt{I}}{1+aB\sqrt{I}} + B^0 I \qquad (2)$$

where $A = 0.5116\ dm^{3/2}\ mol^{-1/2}$, $B = 0.3292 \times 10^8\ dm^{3/2}\ cm\ mol^{-1/2}$, Z is the valence of the chemical species, and I is the true ionic strength in mol dm^{-3} ($1\ dm^3 = 10^3\ cm^3$). The values of the parameters <u>a</u> and B^0 in turn depend on the value of I:

(a) If $I \leq 0.5$ mol dm^{-3}, $a = I/B$ and $B^0 = 0.3AZ^2$. Thus Eq. (2) reduces to the Davies equation.

(b) If $I > 0.5$ mol dm^{-3}, $B^0 = 0.041$ dm^3 mol^{-1} and $\underline{a} = 4 \times 10^{-8}$ cm, 5×10^{-8} cm, and 6×10^{-8} cm for monovalent, bivalent, and trivalent ions, respectively. In this case, Eq. (2) becomes the Helgeson (1969) equation as modified by Truesdell and Jones (1973).

(c) For neutral species, at all values of I, $B^0 = 0.1$ dm^3 mol^{-1} (see, e.g., Helgeson, 1969). Since $Z = 0$ in this case, the first term in Eq. (2) does not contribute to the calculation of Υ.

INPUT DATA REQUIRED BY THE PROGRAM

To some extent the data which must be input to GEOCHEM in order for the program to do a speciation analysis depend on the type of problem to be considered. Some of the general requirements are as follows:

(1) Total molar concentrations of each metal and each ligand chosen from Table 1.

(2) Either the pH value or the total net proton concentration in mol dm^{-3}. If the pH value is available, it should be used.

(3) If solids are to be considered, a choice must be made as to which solid phases will be permitted to precipitate during the computation.

(4) If the soil solution is to be regarded as open with respect to CO_2, the partial pressure of this gas must be imposed.

SCENARIO FOR MIXING OF ACID PRECIPITATION WITH SURFACE SOILS

COMPOSITION DATA AND SPECIATION FOR ACID PRECIPITATION

A diligent review of the available data on the chemical composition of acid precipitation in the northeastern United States produced several sets of total concentration values which could be employed in the present study. These sets of data referred to three localities of current interest in acid precipitation research: the area in or near the Hubbard Brook Experimental Forest in New Hampshire, the area near Ithaca, New York, and the area near Caribou, Maine. The composition data for New Hampshire were obtained from four sources. Data on the major constituents of acid precipitation were taken from tables compiled by Likens et al., (1977) and by Cronon (1979). In the case of Cronan's data, it was necessary to compute Al_T with the help of Eq. (1) and the assumption that the only species to be included on the right-hand side of the equation are Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^+$. These basic data were augmented by the inclusion of organic acid and heavy metal components. The added organic acid was citric acid, at a total concentration of $10^{-5.28}$M (1.1 x 10^{-6} kg dm^{-3}) as suggested by Likens (1975). The added heavy metals were Cd at $10^{-8.28}$M and Pb(II) at $10^{-7.19}$M, based on the data presented by Schlesinger et al. (1974). These additional data were included so as to obtain the most complete overall chemical picture of the New Hampshire acid precipitation in the present modeling effort. The composition data for New York were obtained from Tables 1 and 2 in Likens (1972) and Table 2 in Likens (1975). In this case, the organic acid component was taken to be acetic acid at three times the molarity of the citric acid employed in the New Hampshire data. This change was necessitated here and in certain cases reported in Section 6 by the fact that convergence of the speciation calculation was improved when citric acid was replaced. The composition data for Maine were obtained from maps presented in Lodge et al., (1968) and, for the trace metal components, Cd, Cu, Fe, Mn, Ni, Pb, and Zn, from data provided by D. Rambo (personal communication, 1979). In all, 21 sets of composition data were generated for New Hampshire acid precipitation, with one set each for New York and Maine. The data gathered correspond to both different years and different months of the year averaged over several seasons of data collection. It is expected that the total concentration values obtained and analyzed will be representative of the general chemical features of acid precipitation.

Table 2 lists the results of a speciation calculation for the mean annual acid precipitation (1963-1974) at Hubbard Brook (Table 4 in Likens et al., 1977). The second column in the table gives the negative common logarithm of the total molar concentration of each component, the third column gives the negative common logarithm of the molar concentration of the free ionic species of the component (e.g., Ca^{2+} in the case of Ca and NO_3^- in the case of NO_3),

TABLE 1. CODE NUMBERS AND SYMBOLS FOR THE METALS AND LIGANDS CONSIDERED BY GEOCHEM

Metals

1.	Ca^{2+}	8.	Mn^{2+}	15.	Pb^{2+}	22.	Li^{+}	29.	Ce^{3+}
2.	Mg^{2+}	9.	Cu^{2+}	16.	Co^{2+}	23.	Be^{2+}	30.	Au^{+}
3.	Sr^{2+}	10.	Ba^{2+}	17.	Co^{3+}	24.	Sc^{3+}	31.	Th^{4+}
4.	K^{+}	11.	Cd^{2+}	18.	Ag^{+}	25.	TiO^{2+}	32.	UO_2^{2+}
5.	Na^{+}	12.	Zn^{2+}	19.	Cr^{3+}	26.	Sn^{2+}	33.	Cu^{+}
6.	Fe^{3+}	13.	Ni^{2+}	20.	Al^{3+}	27.	Sn^{4+}	34.	CH^3Hg^{+}
7.	Fe^{2+}	14.	Hg^{2+}	21.	Cs^{+}	28.	La^{3+}	35.	Rb^{+}
								50.	H^{+}

Ligands*

1.	CO_3^{2-}	13.	$S_2O_3^{2-}$	25.	$GLUT^{2-}$	37.	ASP^{-}	49.	SO_3^{2-}	61.	BES^{-}
2.	SO_4^{2-}	14.	CN^{-}	26.	PIC^{-}	38.	SER^{-}	50.	SCN^{-}	62.	ClO_4^{-}
3.	Cl^{-}	15.	AC^{-}	27.	NTA^{3-}	39.	ALA^{-}	51.	NH^2OH	63.	$CBER^{-}$
4.	F^{-}	16.	$ACAC^{-}$	28.	$EDTA^{4-}$	40.	TYR^{2-}	52.	MoO_4^{2-}	64.	$CHAM^{-}$
5.	Br^{-}	17.	CIT^{3-}	29.	$DCTA^{4-}$	41.	MET^{-}	53.	WO_4^{2-}	65.	FOR^{-}
6.	I^{-}	18.	OX^{2-}	30.	$CYST^{2-}$	42.	VAL^{-}	54.	AsO_4^{3-}	90.	ADS1
7.	NH_3^0	19.	SAL^{2-}	31.	NOC^{3-}	43.	THR^{-}	55.	HVO_4^{2-}	91.	ADS2
8.	S^{2-}	20.	$TART^{2-}$	32.	$PHTH^{2-}$	44.	PHE^{-}	56.	SeO_3^{2-}	92.	ADS3
9.	PO_4^{3-}	21.	EN^0	33.	ARG^{-}	45.	ISO^{-}	57.	NO_3^{-}	93.	ADS4
10.	$P_2O_7^{4-}$	22.	DIP^0	34.	ORN^{-}	46.	LEU^{-}	58.	$DTPA^{5-}$	94.	ADS5
11.	$P_3O_{10}^{5-}$	23.	$SUSAL^{3-}$	35.	LYS^{-}	47.	PRO^{-}	59.	SeO_4^{2-}	99.	OH^{-}
12.	$SiO_2(OH)_2^{2-}$	24.	GLY^{-}	36.	HIS^{-}	48.	$B(OH)_4^{-}$	60.	MAL^{2-}		

*AC = acetate
ACAC = acetylactate
CIT = citrate
OX = oxalate
SAL = salicylate
TART = tartrate
EN = enthylenediamine
DIP = dipyridyl
SUSAL = sulfosalicylate
GLY = glycine
GLU = glutamate
PIC = picolinate
NTA = nitrilotriacetate
EDTA = ethylenediaminetatraacetate
DCTA = 1,2-diaminocclohexane-tetracetate
CYST = cysteine
NOC = nocardamine (desferri-ferrioxamine)
PHTH = phthalate
ADG = arginine
ORN = ornithine
LYS = lysine
HIS = histidine
DTPA = diethylenetriaminepentaacetate
ASP = aspartate
SER = serine
ALA = alanine
TYR = tyrosine
MET = methionine
VAL = valine
THR = threonine
PHE = phenylalanine
ISO = isoleucine
LEU = leucine
PRO = proline
MAL = maleate
BES = benzylsulfonate
CBER = Camp Berteau montmorillonite
CHAM = Chambers bentonite
FOR = fornmate
ADS1-ADS5 = adsorption surfaces

and the fourth column lists any species whose mole percentage of C_T is ten or greater. The actual mole percentages are given in parentheses.

TABLE 2. SPECIATION IN THE MEAN ANNUAL PRECIPITATION AT HUBBARD BROOK

Component	C_T	Free Ion	Principal Species
Ca	5.37	5.37	Ca^{2+} (99.3)
Mg	5.69	5.69	Mg^{2+} (99.6)
K	5.75	5.75	K^{+} (100.0)
Na	5.28	5.28	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.3)
Pb(II)	7.19	7.20	Pb^{2+} (98.8)
CO_3	7.00	15.40	H (100.0)
SO_4	4.52	4.52	SO_4^{-2} (99.2)
Cl	4.84	4.84	Cl^{-1} (100.0)
NH_3	4.91	9.77	NH_4^{+} (100.0)
PO_4	7.07	18.26	H (100.0)
CIT	5.28	8.28	H (99.8)
NO_3	4.64	4.64	NO_3^{-1} (100.0)
H		4.13	H^{+} (100.0)

A glance at Table 2 shows that all of the metals are free ionic species, as are NO_3, Cl, and SO_4, while CO_3, PO_4, NH_3, and citrate are in their protonated forms. This result is in complete agreement with the accepted characterization of acid precipitation as a solution of sulfuric, hydrochloric, and nitric acid. It should be mentioned that the speciation calculation performed by GEOCHEM which led to Table 2 and the subsequent tables in this section took into account the formation of 137 soluble inorganic and organic complexes. Thus the resultant characterization of the acid precipitation data is based on a calculation which is considerably more sophisticated than that indicated by Likens (1975), which led to the same conclusion.

In Tables 3 to 14 the speciation of acid precipitation at Hubbard Brook by month of the year is given. The values of C_T represent 12-year averages as presented in Table 14 of Likens et al. (1977).

An examination of each component listed in Tables 3 to 14 shows that there are no changes in speciation in the acid precipitation throughout the year. Thus, despite the seasonal trends in C_T-values noted by Likens et al. (1977), no trends appear in the species of the components. The largest changes are seen in the trace metals such as Pb, which are expected to be the most sensitive to any changes in pH and total ligand concentrations. However, even these changes amount to only a few tenths of a percent (e.g., Pb^{2+} is at a high of 99.3% of Pb_T in February and is at a low of 98.4% of Pb_T in June and July).

Table 15 shows the results of a speciation calculation for acid precipitation at Mt. Moosilauke (Cronan, 1979), which is about 13 km west of the Hubbard Brook Experimental Forest. Although the total concentration data in Table 15 are different from those in Table 2, the speciation of the components which are common to both tables is not different. The speciation calculation summarized in Table 15 took into account 102 inorganic complexes between the seven metals plus H^+ and the four ligands plus OH^-.

TABLE 3. SPECIATION IN THE MEAN JANUARY PRECIPITATION AT HUBBARD BROOK

Component	C_T	Free Ion	Principal Species
Ca	5.60	5.60	Ca^{2+} (99.4)
Mg	6.08	6.08	Mg^{2+} (99.7)
K	5.99	5.99	K^{+} (100.0)
Na	5.25	5.25	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.5)
Pb	7.19	7.19	Pb^{2+} (99.0)
SO_4	4.66	4.66	SO_4^{-2} (99.5)
Cl	5.09	5.09	Cl^{-1} (100.0)
NH_3	4.89	9.60	NH_4^{+} (100.0)
PO_4	7.28	18.16	H (100.0)
CIT	5.28	8.00	H (99.7)
NO_3	4.52	4.52	NO_3^{-1}(100.0)
H		4.28	H^{+} (100.0)

TABLE 4. SPECIATION IN THE MEAN FEBRUARY PRECIPITATION AT HUBBARD BROOK

Component	C_T	Free Ion	Principal Species
Ca	5.43	5.43	Ca^{2+} (99.5)
Mg	5.78	5.78	Mg^{2+} (99.8)
K	6.12	6.12	K^{+} (100.0)
Na	5.22	5.22	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.6)
Pb	7.19	7.19	Pb^{2+} (99.3)
SO_4	4.84	4.84	SO_4^{-2} (99.5)
Cl	5.04	5.04	Cl^{-1}(100.0)
NH_3	5.08	9.68	NH_4^{+} (100.0)
PO_4	7.98	18.66	H (100.0)
CIT	5.28	7.82	H (99.5)
NO_3	4.66	4.66	NO_3^{-1}(100.0)
H		4.38	H^{+} (100.0)

TABLE 5. SPECIATION IN THE MEAN MARCH PRECIPITATION AT HUBBARD BROOK

Component	C_T	Free Ion	Principal Species
Ca	5.30	5.30	Ca^{2+} (99.4)
Mg	5.78	5.78	Mg^{2+} (99.6)
K	5.99	5.99	K^{+} (100.0)
Na	5.28	5.28	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.4)
Pb	7.19	7.19	Pb^{2+} (98.9)
SO_4	4.58	4.58	SO_4^{-2} (99.3)
CI	5.03	5.03	CI^{-1} (100.0)
NH_3	4.93	9.71	NH_4^{+} (100.0)
PO_4	7.50	18.54	H (100.0)
CIT	5.28	8.14	H (99.7)
NO_3	4.50	4.50	NO_3^{-1}(100.0)
H		4.20	H^{+} (100.0)

TABLE 6. SPECIATION IN THE MEAN APRIL PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.17	5.17	Ca^{2+} (99.3)
Mg	5.61	5.61	Mg^{2+} (99.6)
K	5.81	5.81	K^{+} (100.0)
Na	5.32	5.32	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.4)
Pb	7.19	7.20	Pb^{2+} (98.8)
SO_4	4.49	4.49	SO_4^{-2} (99.2)
Cl	5.06	5.06	Cl^{-1} (100.0)
NH_3	4.76	9.63	NH_4^{+} (100.0)
PO_4	6.86	18.07	H (100.0)
CIT	5.28	8.30	H (99.7)
NO_3	4.52	4.52	NO_3^{-1}(100.0)
H		4.11	H^{+} (100.0)

TABLE 7. SPECIATION IN THE MEAN MAY PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.20	5.20	Ca^{2+} (99.2)
Mg	5.69	5.69	Mg^{2+} (99.5)
K	5.59	5.59	K^{+} (100.0)
Na	5.32	5.32	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.2)
Pb	7.19	7.20	Pb^{2+} (98.6)
SO_4	4.39	4.39	SO_4^{-2} (99.1)
Cl	4.93	4.93	Cl^{-1} (100.0)
NH_3	4.78	9.73	H (100.0)
PO_4	6.86	18.22	H (100.0)
CIT	5.28	8.44	H (99.8)
NO_3	4.52	4.52	NO_3^{-1}(100.0)
H		4.03	H^{+} (100.0)

TABLE 8. SPECIATION IN THE MEAN JUNE PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.43	5.43	Ca^{2+} (99.2)
Mg	5.69	5.69	Mg^{2+} (99.4)
K	5.59	5.59	K^{+} (100.0)
Na	5.25	5.25	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.1)
Pb	7.19	7.20	Pb^{2+} (98.4)
SO_4	4.40	4.40	SO_4^{-2} (99.2)
Cl	4.63	4.63	Cl^{-1} (100.0)
NH_3	4.89	9.77	NH_4^{+} (100.0)
PO_4	7.13	18.35	H (100.0)
CIT	5.28	8.31	H (99.8)
NO_3	4.63	4.63	NO_3^{-1}(100.0)
H		4.11	H^{+} (100.0)

TABLE 9. SPECIATION IN THE MEAN JULY PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.37	5.37	Ca^{2+} (99.1)
Mg	5.69	5.69	Mg^{2+} (99.4)
K	5.75	5.75	K^{+} (100.0)
Na	5.52	5.52	Na^{+} (99.9)
Cd	8.28	8.28	Cd^{2+} (99.2)
Pb	7.19	7.20	Pb^{2+} (98.4)
SO_4	4.34	4.34	SO_4^{-2} (99.0)
Cl	5.15	5.15	Cl^{-1} (100.0)
NH_3	4.82	9.83	NH_4^{+} (100.0)
PO_4	6.98	18.45	H (100.0)
CIT	5.28	8.55	H (99.9)
NO_3	4.63	4.63	NO_3^{-1}(100.0)
H		3.98	H^{+} (100.0)

TABLE 10. SPECIATION IN THE MEAN AUGUST PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.49	5.49	Ca^{2+} (99.3)
Mg	5.91	5.91	Mg^{2+} (99.5)
K	5.99	5.99	K^{+} (100.0)
Na	5.58	5.58	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.3)
Pb	7.19	7.20	Pb^{2+} (98.7)
SO_4	4.48	4.48	SO_4^{-2} (99.3)
Cl	4.96	4.96	Cl^{-1} (100.0)
NH_3	4.89	9.74	NH_4^{+} (100.0)
PO_4	6.90	18.06	H (100.0)
CIT	5.28	8.26	H (99.8)
NO_3	4.70	4.70	NO_3^{-1}(100.0)
H		4.13	H^{+} (100.0)

TABLE 11. SPECIATION IN THE MEAN SEPTEMBER PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.52	5.52	Ca^{2+} (99.3)
Mg	5.78	5.78	Mg^{2+} (99.5)
K	5.81	5.81	K^{+} (100.0)
Na	5.46	5.46	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.3)
Pb	7.19	7.20	Pb^{2+} (98.7)
SO_4	4.44	4.44	SO_4^{-2} (99.0)
Cl	4.91	4.91	Cl^{-1} (100.0)
NH_3	4.89	9.88	NH_4^{+} (100.0)
PO_4	7.13	18.57	H (100.0)
CIT	5.28	8.52	H (99.9)
NO_3	4.61	4.61	NO_3^{-1}(100.0)
H		3.99	H^{+} (100.0)

TABLE 12. SPECIATION IN THE MEAN OCTOBER PRECIPITATION AT HUBBARD BROOK

Component			
Ca	5.20	5.20	Ca^{2+} (99.4)
Mg	5.48	5.48	Mg^{2+} (99.6)
K	5.48	5.48	K^{+} (100.0)
Na	5.00	5.00	Na^{+} (100.0)
Cd	8.28	8.28	Cd^{2+} (99.3)
Pb	7.19	7.19	Pb^{2+} (98.9)
SO_4	4.57	4.57	SO_4^{-2} (99.2)
Cl	4.55	4.55	Cl^{-1} (100.0)
NH_3	4.89	9.75	NH_4^{+} (100.0)
PO_4	6.86	18.06	H (100.0)
CIT	5.28	8.29	H (99.7)
NO_3	4.56	4.56	NO_3^{-1}(100.0)
H		4.11	H^{+} (100.0)

TABLE 13. SPECIATION IN THE MEAN NOVEMBER PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.46	5.46	Ca^{2+} (99.5)
Mg	5.54	5.54	Mg^{2+} (99.7)
K	5.64	5.64	K^+ (100.0)
Na	5.13	5.13	Na^+ (100.0)
Cd	8.28	8.28	Cd^{2+} (99.3)
Pb	7.19	7.19	Pb^{2+} (99.0)
SO_4	4.64	4.64	SO_4^{-2} (99.3)
Cl	4.52	4.52	Cl^{-1} (100.0)
NH_3	5.05	9.82	NH_4^+ (100.0)
PO_4	7.28	18.32	H (100.0)
CIT	5.28	8.14	H (99.8)
NO_3	4.60	4.60	NO_3^{-1}(100.0)
H		4.19	H^+ (100.0)

TABLE 14. SPECIATION IN THE MEAN DECEMBER PRECIPITATION AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	5.65	5.65	Ca^{2+} (99.5)
Mg	5.91	5.91	Mg^{2+} (99.7)
K	5.89	5.89	K^+ (100.0)
Na	5.41	5.41	Na^+ (100.0)
Cd	8.28	8.28	Cd^{2+} (99.6)
Pb	7.19	7.19	Pb^{2+} (98.2)
SO_4	4.78	4.78	SO_4^{-2} (99.5)
Cl	5.07	5.07	Cl^{-1} (100.0)
NH_3	5.21	9.83	NH_4^+ (100.0)
PO_4	7.28	17.99	H (100.0)
CIT	5.28	7.85	H (99.6)
NO_3	4.66	4.66	NO_3^{-1}(100.0)
H		4.37	H^+ (100.0)

TABLE 15. SPECIATION IN THE MEAN ANNUAL PRECIPITATION AT MT. MOOSILAUKE

Component	CH_T	Free Ion	Principal Species
Ca	5.35	5.35	Ca^{2+} (99.4)
Mg	5.82	5.82	Mg^{2+} (99.5)
K	5.52	5.52	K^{+} (100.0)
Na	5.40	5.40	Na^{+} (100.0)
Fe(II)	6.30	6.30	Fe^{2+} (99.5)
Cd	8.28	8.28	Cd^{2+} (99.3)
Pb	7.19	7.20	Pb^{2+} (98.7)
Al	6.14	6.23	Al^{3+} (80.9), OH (15.1)
SO_4	4.43	4.43	SO_4^{-2} (99.0)
Cl	5.15	5.15	Cl^{-1} (100.0)
NH_3	4.89	9.80	NH_4^{+} (100.0)
NO_3	4.68	4.68	NO_3^{-1}(100.0)
H		4.08	H^{+} (100.0)

Tables 16 and 17 give the results of two speciation calculations for throughfall, one for Hubbard Brook (Likens et al., 1977) and one for Mt. Moosilauke (Cronan, 1979). For these calculations, the organic carbon concentrations were assumed to be divided equally between acetic and formic acids on a molar basis. These two metal-complexing organic acids are common in soil-plant systems and have been identified in soil leachates at Mt. Moosilauke (Cronan et al., 1978; Cronan, 1979). They serve in the present case as model organic ligands. The total number of inorganic and organic complexes considered in the speciation calculations was 92.

TABLE 16. SPECIATION IN THROUGHFALL AT HUBBARD BROOK (JUNE-OCTOBER MEAN)

Component	CH_T	Free Ion	Principal Species
Ca	4.40	4.41	Ca^{2+} (98.7)
Mg	4.73	4.73	Mg^{2+} (98.9)
K	3.79	3.79	K^+ (100.0)
Na	5.22	5.22	Na^+ (99.9)
SO_4	4.25	4.25	SO_4^{-2} (98.9)
Cl	4.39	4.39	Cl^{-1} (100.0)
NH_3	4.17	8.16	NH_4^+ (100.0)
PO_4	5.80	15.20	H (99.8)
AC	3.94	4.15	AC^{-1} (62.4), H (37.6)
NO_3	4.97	4.97	NO_3^{-1}(100.0)
FOR	3.94	3.96	FOR^{-1} (95.3)
H		5.00	H^+ (100.0)

TABLE 17. SPECIATION IN THROUGHFALL AT MT. MOOSILAUKE (MEAN ANNUAL)

Component	CH_T	Free Ion	Principal Species
Ca	4.74	4.75	Ca^{2+} (98.8)
Mg	5.15	5.15	Mg^{2+} (99.1)
K	4.43	4.43	K^{+} (99.9)
Na	5.52	5.52	Na^{+} (99.9)
Fe(II)	6.30	6.30	Fe^{2+} (99.1)
Mn(II)	5.70	5.71	Mn^{2+} (98.8)
Al	5.75	5.84	Al^{3+} (80.9), OH (12.0)
SO_4	4.15	4.16	SO_4^{-2} (98.5)
Cl	4.89	4.89	Cl^{-1} (100.0)
NH_3	5.22	10.19	NH_4^{+} (100.0)
AC	4.78	5.61	H (85.2), AC^{-1} (14.8)
NO_3	4.92	4.92	NO_3^{-1}(100.0)
FOR	4.78	4.94	FOR^{-1} (68.6), H (31.4)
H		4.02	H^{+} (100.0)

Once again, despite major increases in the total concentrations of all components (except H^+) in the throughfall relative to the corresponding precipitation, the data in Tables 16 and 17 show that there is very little difference in the speciation. The overall trend is toward a slight decrease in the free ionic percentages for the metals in going from precipitation to throughfall.

Tables 18 and 19 give the results of speciation calculations for acid precipitation at Ithaca, New York and Caribou, Maine, respectively. The calculations performed by GEOCHEM took into account 129 soluble complexes for the New York data and 141 soluble complexes for the Maine data. Both precipitation solutions were found to be supersaturated with respect to amorphous $Fe(OH)_3(s)$. This result may be caused by the presence of colloidal $Fe(OH)_3(s)$ or by disequilibrium with respect to the solid. Other than this special characteristic, the data in Tables 18 and 19 show no significant differences from the data in Table 2.

TABLE 18. SPECIATION IN PRECIPITATION AT ITHACA, NEW YORK

Component	CH_T	Free Ion	Principal Species
Ca	4.77	4.77	Ca^{2+} (99.3)
Mg	5.18	5.18	Mg^{2+} (99.4)
K	5.81	5.81	K^+ (100.0)
Na	5.22	5.22	Na^+ (99.9)
Fe(III)	6.14	8.66	OH (99.2)*
Mn(II)	7.04	7.04	Mn^{2+} (99.3)
Al	5.73	5.82	Al^{3+} (80.9), OH (14.6)
CO_3	4.99	13.50	H (100.0)
SO_4	4.37	4.38	SO_4^{-2} (98.7)
Cl	4.54	4.54	Cl^{-1} (100.0)
NH_3	4.62	9.53	NH_4^+ (100.0)
PO_4	6.82	18.11	H (98.5)
AC	4.25	5.04	H (83.7), AC^{-1} (16.3)
NO_3	4.50	4.50	NO_3^{-1}(100.0)
H		4.07	H^+ (100.0)

* Supersaturation with respect to amorphous $Fe(OH)_3(s)$.

TABLE 19. SPECIATION IN PRECIPITATION AT CARIBOU, MAINE

Component	CH_T	Free Ion	Principal Species
Ca	5.01	5.01	Ca^{2+} (99.4)
Mg	5.13	5.13	Mg^{2+} (99.5)
K	5.45	5.45	K^{+} (100.0)
Na	5.00	5.00	Na^{+} (100.0)
Fe(III)	5.89	9.04	OH (99.9)*
Mn(II)	6.79	6.79	Mn^{2+} (99.4)
Cu	6.66	6.66	Cu^{2+} (99.2)
Cd	7.75	7.75	Cd^{2+} (99.3)
Zn	5.97	5.97	Zn^{2+} (99.2)
Ni	6.77	6.77	Ni^{2+} (99.4)
Pb(II)	6.47	6.48	Pb^{2+} (98.7)
SO_4	4.44	4.44	SO_4^{-2} (99.3)
Cl	5.13	5.13	Cl^{-1} (100.0)
NO_3	5.21	5.21	NO_3^{-1} (100.0)
H		4.41	H^{+} (100.0)

* Supersaturation with respect to amorphous $Fe(OH)_3(s)$.

INTERACTION OF ACID PRECIPITATION WITH SOIL MINERALS

According to Likens et al. (1977), rainwater impinging on the soils at Hubbard Brook infiltrates directly and produces no significant overland flow. Since vertical movement of the water tends to be impeded by the near-surface occurrence of either bedrock or clayey layers, it may be concluded that interflow is the principal mechanism of runoff at Hubbard Brook. This conclusion is in agreement with the accepted picture of the runoff cycle in forested areas (Ward, 1975).

Given that interflow is the principal means by which acid precipitation is transported to the channel system in a watershed, it follows that the chemical properties of the precipitation may be altered by interaction with the more soluble soil minerals. In particular, as has been proposed by Cronan et al. (1978), Cronan (1979), Cronan and Schofield (1979), and Johnson (1979) in recent papers, acid precipitation may interact with iron and aluminum hydrous oxides to dissolve these minerals and release the metals they contain into subsurface runoff. It was decided to check this hypothesis chemically through a simulation using GEOCHEM.

For each of the three areas represented by the data in Tables 2 to 19, soil surveys were consulted to identify the principal great groups (Likens et al., 1977; Soil Survey, Tompkins County, New York, 1965; Soil Survey, Aroostook County, Maine, 1964). This accomplished, the chemical properties of representative soil profiles in these great groups were obtained from soil survey data presented in Appendix IV of Soil Taxonomy (Soil Survey Staff, 1975). Although the soils under consideration contain vermiculite, illite, montmorillonite, muscovite, and other crystalline aluminosilicates (Johnson et al., 1968), it is expected that amorphous aluminum and iron hydrous oxides, which typically coat mineral surfaces, will be the most reactive with acid precipitation (Johnson, 1979). Therefore, only these minerals were considered in the simulation.

In order to establish a "baseline value" for Al and Fe in the soil solutions prior to the intrusion of acid precipitation, the following calculation was performed. Let W be the weight percent of $Al(OH)_3(s)$ or $Fe(OH)_3(s)$ in a surface soil horizon and let M be the molecular weight of the hydroxide. Then the molar concentration of the hydroxide in toto in a water-saturated soil is given by the equation:

$$C_{Hy} = W/MV \tag{3}$$

where V is the volume of pore space per 100 g of soil. The parameter C_{Hy} is the molar concentration of Al or Fe that would be found in the soil solution if the soil were water-saturated and all of the hydroxide had dissolved. If this total concentration is input to GEOCHEM, the program will predict how much of it actually will form the solid hydroxide phase and how much will remain in aqueous solution. The results of such a calculation for the three acid precipitation study areas are given in Table 20.

TABLE 20. TOTAL "BASELINE" SOLUBLE ALUMINUM AND IRON IN REPRESENTATIVE SOILS FROM THE THREE PRECIPITATION STUDY AREAS

Area	% Al	% Fe	V (cm^3/100 g)	pH	Al_{TS}	Fe_{TS}
New Hampshire	1.09	1.90	37	5.65	4.26	8.36
New York	0.20	0.60	21	5.60	4.23	8.32
Maine	0.47	1.50	18	4.80	3.38	7.57

The second and third columns in Table 20 give the weight of amorphous Al and Fe hydrous oxides per 100 g soil as obtained from soil survey data. The fourth and fifth columns give the pore space volume and the soil pH value, respectively, also obtained from soil survey data. The last two columns give the negative common logarithm of the total molar concentration of Al and Fe in the soil solution after the precipitation of $Al(OH)_3(am)$ and $Fe(OH)_3(am)$. These latter figures were estimated by GEOCHEM in a speciation calculation which included all known soluble hydrolytic species of Al and Fe, as well as complexes of these metals with CO_3. The total concentration of CO_3 included in each calculation was computed as that CO_{3T} which is expected in a solution, at the appropriate pH value given in Table 20, which is in equilibrium with atmospheric CO_2 at a pressure of $10^{-3.52}$ atm. No other ligands than CO_3 and OH were considered. Thus the results in Table 20 refer to a soil solution whose chemistry is dominated by carbonic acid.

With the "baseline" estimates in Table 20 in hand, a computer simulation of the interaction between acid precipitation and amorphous Al and Fe hydroxides in soil may be carried out quite easily. The simulation consists of a speciation calculation on a system whose input total concentrations are those of the acid precipitation under study plus the total concentrations of Al and Fe corresponding to C_{Hy} as calculated in Eq. (3). The program then can predict the total soluble Al and Fe remaining in solution after $Al(OH)_3(am)$ and $Fe(OH)_3(am)$ have precipitated in the system.

Because of the presence of trace metals, such as Pb and Cd, in the acid precipitation, it was decided to include the possibility of cation adsorption by clay minerals in the simulation. Adsorption often is observed to be an effective mechanism for immobilizing trace metals. The degree to which this mechanism may apply in the soils in this investigation was assessed by including data on exchangeable cations in the simulation, following the procedures outlined by Sposito and Mattigod (1979) for handling cation exchange phenomena in GEOCHEM. The data on the distribution of exchangeable cations were taken from soil surveys. The exchanger was assumed to be montmorillonite (as modeled by Chambers bentonite).

To simulate the effect of organic acids in the soil solution, acetic and formic acids were included in all of the mixtures except for Maine at $10^{-4.54}$M each in total concentration. This level was suggested by the leachate data of Cronan *et al*. (1978).

SOIL RESPONSE TO ACID PRECIPITATION

NEW HAMPSHIRE SOILS

The speciation of a mixture of acid precipitation and soil in New Hampshire is illustrated in Tables 21 to 23. Table 21 gives the results of a speciation calculation for the acid precipitation described in Table 2. The principal effects on the soil are: (1) the solubilization of Al and Fe, and (2) the adsorption of Cd and Pb. It may be noted that Al_T in Table 21 is more than two orders of magnitude larger than the "baseline" value in Table 20 and that Fe_T in Table 21 is about two orders of magnitude larger than the "baseline" value. Hydrolytic species are in part responsible for this increase in solubility, although the model organic acids, acetic and formic, and the inorganic ligands, SO_4 and Cl did complex Al significantly.

An examination of Tables 22 to 24 reveals that the same trends seen in Table 21 prevail. Therefore, the behavior of Al, Fe, Cd, and Pb does not depend on time of year (Tables 22 and 23) or the (nearby) location of the acid precipitation (Table 24). It may be noted that the predicted lack of dominant organic complexation of Al and Fe (Table 24) did not preclude increased solubility levels for these metals. The speciation calculations summarized in Tables 21 to 24 took into account about 200 inorganic and organic complexes.

Table 25 illustrates the speciation in a mixture of throughfall and soil. The trends shown in the table are identical with those in Tables 21 to 24, with respect to Al and Fe solubilities.

TABLE 21. SPECIATION IN THE MEAN ANNUAL PRECIPITATION/SOIL MIXTURE AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	1.49	1.49	Ca^{2+} (99.9)
Mg	2.39	2.39	Mg^{2+} (99.9)
K	5.75	5.75	K^+ (100.0)
Na	5.28	5.28	Na^+ (100.0)
Fe(III)	6.83	9.45	OH (100.0)
Cd	8.28	9.69	CHAM(s)(96.1)
Pb(II)	7.19	19.69	CHAM(s)(100.0)
Al	1.83	1.95	Al^{3+} (75.9), OH (23.4)
CO_3	4.91	13.33	H (98.4)
SO_4	4.52	5.87	Al (67.4), Ca (25.6)
Cl	4.84	4.97	Cl^{-1} (74.8), Al (15.3)
NH_3	4.91	9.78	NH_4^+ (100.0)
PO_4	7.07	18.58	H (47.5), Ca (46.4)
AC	4.35	5.22	H (61.7), Al (17.4), AC^{-1} (13.5)
NO_3	4.64	4.70	NO_3^{-1} (86.6), Ca (13.1)
CHAM	1.14	1.14	$CHAM^{-1}$(100.0)
FOR	4.54	5.05	Al (31.6), FOR^{-1} (30.9) Ca (23.4), H (11.2)
H		4.13	H^+ (100.0)

TABLE 22. SPECIATION IN THE MEAN JANUARY PRECIPITATION/SOIL MIXTURE AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	1.49	1.49	Ca^{2+} (99.9)
Mg	2.39	2.39	Mg^{2+} (99.9)
K	5.99	5.99	K^+ (100.0)
Na	5.25	5.25	Na^+ (100.0)
Fe(III)	7.01	9.91	OH (100.0)
Cd	8.28	9.70	CHAM(s)(96.2)
Pb(II)	7.19	19.70	CHAM(s)(100.0)
Al	2.26	2.41	Al^{3+} (70.8), OH (29.5)
CO_3	4.91	13.03	H (99.0)
SO_4	4.66	5.76	Ca (45.7), Al (41.7)
Cl	5.09	5.17	Cl^{-1} (83.1), Ca (10.0)
NH_3	4.89	9.61	NH_4^+ (100.0)
PO_4	7.28	18.50	H (47.3), Ca (46.7)
AC	4.54	5.26	H (61.8), Ac^{-1} (19.1), AC^{-1} (13.5)
CIT	5.28	26.51	Al (100.0)
NO_3	4.52	4.58	NO_3^{-1} (86.6), Ca (13.1)
CHAM	1.14	1.14	$CHAM^{-1}$(100.0)
FOR	4.54	4.93	FOR^{-1} (40.6), Ca (30.7), Al (14.4), H (10.4)
H		4.28	H^+ (100.0)

TABLE 23. SPECIATION IN THE MEAN JULY PRECIPITATION/SOIL MIXTURE AT HUBBARD BROOK

Component	CH_T	Free Ion	Principal Species
Ca	1.49	1.49	Ca^{2+} (100.0)
Mg	2.39	2.39	Mg^{2+} (1000.0)
K	5.75	5.75	K^+ (100.0)
Na	5.52	5.52	Na^+ (100.0)
Fe(III)	6.65	9.00	OH (100.0)
Cd	8.28	9.69	CHAM(s)(96.1)
Pb(II)	7.19	19.69	CHAM(s)(100.0)
Al	1.39	1.50	Al^{3+} (77.6), OH (22.9)
CO_3	4.91	13.62	H (97.1)
SO_4	4.34	6.03	Al (85.3), Ca (11.5)
Cl	5.15	5.38	Cl^{-1} (58.)6, Al (33.7)
NH_3	4.82	9.84	NH_4^+ (100.0)
PO_4	6.98	18.79	H (48.3), Ca (45.6)
AC	4.54	5.42	H (55.5), Al (31.2),
NO_3	4.63	4.69	NO_3^{-1} (86.6), Ca (13.1)
CHAM	1.14	1.14	$CHAM^{-1}$(100.0)
FOR	4.54	5.26	Al (54.9), FOR^{-1} (19.0) Ca (14.4)
H		3.98	H^+ (100.0)

TABLE 24. SPECIATION IN THE MEAN ANNUAL PRECIPITATION/SOIL MIXTURE AT MT. MOOSILAUKE

Component	CH_T	Free Ion	Principal Species
Ca	1.49	1.49	Ca^{2+} (99.9)
Mg	2.39	2.39	Mg^{2+} (100.0)
K	5.52	5.52	K^{+} (100.0)
Na	5.40	5.40	Na^{+} (100.0)
Fe(III)	6.77	9.30	OH (100.0)
Fe(II)	6.30	6.30	Fe^{2+} (100.0)
Cd	8.28	9.69	CHAM(s)(96.1)
Pb(II)	7.19	19.69	CHAM(s)(100.0)
Al	1.67	1.80	Al^{3+} (74.1), OH (25.2)
CO_3	4.91	13.42	H (98.0)
SO_4	4.43	5.88	Al (74.0), Ca (20.4)
Cl	5.15	5.30	Cl^{-1} (70.4), Al (20.3)
NH_3	4.89	9.81	NH_4^{+} (100.0)
AC	4.54	5.47	H (60.3), Al (21.4), AC^{-1} (11.8)
NO_3	4.68	4.74	NO_3^{-1} (86.6), Ca (13.1)
CHAM	1.14	1.14	$CHAM^{-1}$(100.0)
FOR	4.54	5.11	Al (39.0), FOR^{-1} (27.0) Ca (20.5), H (11.0)
H		4.08	H^{+} (100.0)

TABLE 25. SPECIATION IN THE MEAN THROUGHFALL/SOIL MIXTURE AT Mt. MOOSILAUKE

Component	CH_T	Free Ion	Principal Species
Ca	1.49	1.49	Ca^{2+} (99.9)
Mg	2.39	2.39	Mg^{2+} (99.9)
K	4.43	4.43	K^+ (100.0)
Na	5.52	5.52	Na^+ (100.0)
Fe(III)	6.69	9.10	OH (100.0)
Fe(II)	6.30	6.30	Fe^{2+} (100.0)
Mn	5.70	5.70	Mn^{2+} (100.0)
Al	1.48	1.60	Al^{3+} (75.9), OH (22.9)
CO_3	4.91	13.53	H (97.5)
SO_4	4.15	5.73	Al (81.4), Ca (14.5)
Cl	4.89	5.08	Cl^{-1} (63.9), Al (27.9)
NH_3	5.22	10.20	H (100.0)
AC	4.34	5.34	H (57.3), Al (27.4), AC^{-1} (10.0)
NO_3	4.92	4.98	NO_3^{-1} (86.8), Ca (12.8)
CHAM	1.14	1.14	$CHAM^{-1}$(100.0)
FOR	4.34	4.99	Al (48.8), FOR^{-1} (22.3) Ca (16.5), H (10.2)
H		4.02	H^+ (100.0)

NEW YORK AND MAINE SOILS

Tables 26 and 27 give the results of speciation calculations for mixtures of acid precipitation and soil in the areas near Ithaca, New York, and Caribou, Maine. These calculations involved the consideration of 139 and 191 soluble complexes, respectively. Both tables show significant increases in the solubility of Al and Fe (see Table 20) and adsorption of trace metals by clays (Table 27). The solubility increases for Al and Fe are about the same as were found for the precipitation/soil mixtures in New Hampshire.

TABLE 26. SPECIATION IN THE PRECIPITATION/SOIL MIXTURE AT ITHACA, NEW YORK

Component	CH_T	Free Ion	Principal Species
Ca	1.15	1.49	CHAM(s)(53.9), Ca^{2+} (46.1)
Mg	1.62	1.62	Mg^{2+} (100.0)
K	5.81	5.81	K^+ (100.0)
Na	5.22	5.22	Na^+ (100.0)
Fe(III)	6.76	9.26	OH (100.0)
Mn(II)	7.04	7.04	Mn^{2+} (100.0)
Al	1.65	1.76	Al^{3+} (77.6), OH (22.9)
CO_3	4.99	13.51	H (97.9)
SO_4	4.37	5.88	Al (69.1), Ca (17.5) Mg (10.2)
Cl	4.54	4.72	Cl^{-1} (66.6), Al (20.6)
NH_3	4.62	9.55	NH_4^+ (100.0)
PO_4	6.82	18.55	H (37.4), Ca (35.9) Mg (26.6)
AC	4.25	5.20	H (56.9), Al (21.6), AC^{-1} (11.1)
NO_3	4.50	4.57	NO_3^{-1} (85.1), Ca (13.0)
CHAM	0.72	0.94	$CHAM^{-1}$ (60.0), Ca(s) (40.0)
H		4.07	H^+ (100.0)

TABLE 27. SPECIATION IN THE PRECIPITATION/SOIL MIXTURE AT CARIBOU, MAINE

Component	CH_T	Free Ion	Principal Species
Ca	0.47	1.50	CHAM(s)(90.7), Ca^{2+}(99.9)
Mg	1.25	1.60	CHAM(s)(55.7), Mg^{2+}(44.3)
K	5.45	5.45	K^+ (100.0)
Na	5.00	5.00	Na^+ (100.0)
Fe(III)	7.15	10.29	OH (100.0)
Mn(II)	6.79	6.79	Mn^{2+} (99.9)
Cu	6.66	11.40	CHAM(s)(100.0)
Cd	7.75	10.10	CHAM(s)(99.6)
Zn	5.97	8.00	CHAM(s)(99.1)
Ni	6.77	6.77	Ni^{2+} (99.9)
Pb(II)	6.47	20.10	CHAM(s)(100.0)
Al	2.58	2.79	Al^{3+} (61.7), OH (37.2)
CO_3	5.00	12.86	H (99.0)
SO_4	4.44	5.53	Ca (45.6), Mg (28.7), Al (17.5)
Cl	5.13	5.22	Cl^{-1} (82.0), Ca (9.5)
NO_3	5.21	5.28	NO_3^{-1} (85.4), Ca (12.5)
CHAM	0.10	0.93	Ca (77.4), $CHAM^{-1}$(14.7)
H		4.41	H^+ (100.0)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The multipurpose computer program GEOCHEM was employed to calculate the equilibrium speciation in twenty-three examples of acid precipitation from New Hampshire, New York, and Maine, and in the same number of mixtures of acid precipitation with minerals characteristic of soils in the three states mentioned. Between 100 and 200 soluble inorganic and organic complexes were taken into account in each speciation calculation. The calculations performed on the acid precipitation samples showed that the metals (including heavy metals) and the sulfate, chloride, and nitrate ligands would be almost entirely in their free ionic forms, while the phosphate, carbonate, ammonia, and organic ligands would be in their protonated forms. This result was independent of the geographic location of the acid precipitation and the month of the year in which it was collected.

The speciation calculations on the precipitation-soil mineral mixtures showed that aluminum and iron levels in a soil solution affected by acid precipitation would be significantly higher than in one whose chemistry is dominated by carbonic acid. The higher levels found were caused by the lower pH value of acid precipitation as well as by complexes formed with inorganic and organic ligands. It was also shown that soil cation exchangers would adsorb preferentially heavy metals, such as Cd and Pb, which are found in acid precipitation.

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