SOIL PROCESSES AT EMERALD LAKE WATERSHED

FINAL REPORT

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Lanny J. Lund
Aaron D. Brown
Mary A. Lueking
Stephen C. Nodvin
Albert L. Page
Garrison Sposito

Department of Soil and Environmental Sciences
University of California
Riverside, CA 92521

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ABSTRACT

The objectives of the Soils Processes research at Emerald Lake Watershed were to assess physical, chemical and biological processes contributing to the production or consumption of acidity in soils and to assess the net effect of soil processes on surface water quality in an alpine watershed. The ELW consists of a high elevation lake in a subalpine to alpine Sierra Nevada landscape. The soils found in ELW are typical of those found throughout the Sierra Nevada and are shallow and rocky. However, these soils do support subalpine to alpine vegetation.

Most of the N and S in ELW soils is stored in organic forms. Most of the soil P is present in nearly insoluble mineral forms. The ELW soils can adsorb only small quantities of sulfate thus, their capacity for buffering acid additions by sulfate adsorption is also fairly low. Concentrations of Al, Ca, Mg, K, and Na in both soil solution and stream samples reflected patterns of mineral weathering in the watershed. Calculations showed that bicarbonate alkalinity resulted from mineral weathering in that the major basic cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) were primarily in their free ionic form. Rainfall and throughfall collected during four precipitation events in 1985 showed that evergreens (pine and chinquapin) tended to contribute many substances to throughfall including Al while willows apparently removed N compounds. Organic acids were a very important part of throughfall solution chemistry. Organic acids in water extracts of leaf litter from pine, chinquapin and willow were characterized and the results were used in the analysis of throughfall solution chemistry. Litter from three vegetative types was collected and returned to ELW for incubation to monitor decomposition. Most of the weight loss from decomposition during the initial year of the study occurred during the winter. Mineralization was very slow during the summer due to very dry soil conditions. Mineralization is very sensitive to acid additions. Summer CO_2 concentrations in the soils were high enough to increase soil solution acidity and influence the speciation of dissolved elements. Lysimeters were installed at four sites in the watershed to extract soil water. Concentrations of N compounds found in surface waters appear

to be directly related to concentrations found in soil solutions. Three small streams were sampled in the watershed to observe differences in water quality along their lengths. Aluminum concentrations appeared to be related to the solubility of an aluminum hydroxide mineral. Nitrate was highest during the spring and fall, but NH_4^+ was highest during the summer. This could be due to plant and microbial assimilation of NO_3^- in mid-summer. Sulfate concentrations declined downstream apparently due to adsorption by soils. The overall chemistry of stream waters reflects the mineral composition of soils and rocks at ELW. Mineral weathering exerts a major influence on Ca, Na, Mg and K concentrations in surface waters at ELW.

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DISCLAIMER

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SUMMARY

The Emerald Lake Watershed (ELW) is the site of an integrated watershed study of which this investigation of soil chemical and microbial processes and their interactions with vegetation and surface waters is a part. Emerald Lake is a high elevation (2,804 m) lake in a subalpine to alpine landscape. Like most of the Sierra Nevada, the bedrock is granitic and the primary source of water is snow which is present nearly year-round. The soils which have developed under these conditions are shallow and rocky, but do support growth of alpine and subalpine vegetation. The processes which occur in these soils interact with anthropogenic acidic deposition and may either enhance or ameliorate its effects on ecosystem components.

Many soil processes at ELW that either consume or produce acidity are related to the elemental budgets for N, S, P and Al. The approach taken here has been to gather data necessary to guide us in developing nutrient budgets and fluxes. In any future effort to model the effects of anthropogenic inputs on surface waters in ELW it will be necessary to relate these parameters to a soils map and to determine the permeability of the soils to water.

The objectives of this investigation were to:

Objective 1: Assess physical-chemical processes contributing to the production or consumption of acidity and nutrients in alpine soils.

a. Nutrient Pools

Most of the N and S in ELW soils is stored in organic forms. Most of the soil P is present in nearly insoluble mineral forms. The quantity and quality of the stored nutrients is related to other soil physical and chemical parameters such as texture and pH.

b. Sulfate Adsorption

Sulfate adsorption by soils is a major mechanism by which soils may neutralize acidic deposition. The sulfate adsorption characteristics of two major soils from ELW were determined. Soil samples were treated with solution containing nitrate and sulfate under acidic conditions much like those of anthropogenic acidic deposition. The ELW soils can adsorb only small quantities of sulfate thus, their capacity

for buffering acid additions by sulfate adsorption is also fairly low.

c. Mineral Weathering

The ultimate source of acid neutralization in soil is mineral weathering. The breakdown of primary and secondary minerals released substantial quantities of cations into the soil solution. Concentrations of Al, Ca, Mg, K, and Na in both soil solution and stream samples reflected patterns of mineral weathering in the watershed. Calculations showed that bicarbonate alkalinity resulted from mineral weathering in that the major basic cations (Ca, Mg, K, Na) were primarily in their free ionic form.

Objective 2: Assess biological processes contributing to the production or consumption of acidity and nutrients in alpine soils.

a. Throughfall

Bulk collectors were placed under three types of vegetation in ELW. Rainfall and throughfall were collected during four precipitation events in 1985. The evergreens (pine and chinquapin) tended to contribute many substances to throughfall including Al while willows apparently removed N compounds. Organic acids were a very important part of throughfall solution chemistry. Phosphorus was contributed to throughfall by willows and to a lesser extent by pines and chinquapin.

b. Organic Acids in Leaf Litter Extracts

One of the major ways in which Al is mobilized in soil is through the interaction between organic acids from leaf litter and soil minerals. Water extracts of litter form pine, chinquapin and willow were characterized and the results were used in the analysis of throughfall solution chemistry.

c. Litter Decomposition and Collection

Leaves and branches from vegetation contribute N, S, P and Al to the soil surface as they decay. Litter from three vegetative types was collected and returned to ELW for incubation to monitor decomposition. Most of the weight loss from decomposition during the initial year of the study occurred during the winter. Willow leaves decomposed faster than pine or chinquapin in the first year. Collection of leaf fall on litter screens was initiated in cooperation with the NPS.

d. Mineralization of N, S and P

Mineralization is the breakdown of organic matter by microbes releasing N and S in soluble inorganic forms. The overall effect of mineralization is the production of acidity. The potential for N and S mineralization in ELW soils was found to be the highest in the wet meadow soil. Mineralization in the field in July and August (1985) was found to be related to soil moisture and temperature as well as the quality and quantity of organic matter present. In some cases, N and S mineralization in the field were very low or negative indicating microbial assimilation was tying up inorganic N and S in these soils. Phosphorus mineralization was undetectable even under laboratory conditions. Nitrification (conversion of NH_4^+ to NO_3^-) of the mineralized N ranged from 7 to 100% in the field.

e. Soil Respiration

The respiration of microbes and plant roots in the soil produces carbon dioxide (CO_2). This is important as a control of solution acidity since CO_2 reacts with water to form carbonic acid. Tubes were inserted in the soil at the lysimeter sampling sites to allow samples of air to be extracted directly from the pore space in the soil. It was calculated that summer CO_2 concentrations in the soils were high enough to have a significant effect on soil solution acidity and the speciation of dissolved elements.

Objective 3: Assess the net effect of soil processes on surface water quality in an alpine watershed.

a. Soil Solution Sampling

Biological and chemical processes in soils affect soil solution composition and the mobilization of N, S and Al. Lysimeters were installed at four sites in the watershed to extract soil water directly from the soil. Concentrations of Al (total), SO_4^{2-}, NO_3^- and PO_4^{3-} were measured along with alkalinity and other major ions. Dissolved Al was more concentrated in soil waters than in surface waters. This may be related to interactions with dissolved organic compounds which were also more concentrated. Concentrations of N compounds found in surface waters appear to be directly related to concentrations found in soil solutions. Overall, concentrations were related to the moisture

content of the soil. Phosphorus was practically undetectable in soil solutions.

b. Stream Sampling

Soils adjacent to streams affect the composition of the stream waters and transport of N, S and Al. Three small streams were sampled in the watershed to observe differences in water quality along their lengths. Samples were analyzed for the same dissolved elements and compounds found in lysimeters. Overall concentrations of dissolved solids were higher during the summer due to low flow conditions and longer soil-water contact times. Aluminum was highest during the spring and early summer while snow was melting. This is apparently related to solubility of an aluminum hydroxide mineral (like gibbsite [$Al(OH)_3$]), pH and organic-Al complexation. Nitrate was highest during the spring and fall, but NH_4^+ was highest during the summer. This could be due to plant and microbial assimilation of NO_3^- in mid-summer. Sulfate concentrations declined downstream apparently due to adsorption by soils. Phosphate was practically undetectable in surface waters. The overall chemistry of stream waters reflects the mineral composition of soils and rocks at ELW. Mineral weathering exerts a major influence on total concentrations of Ca, Na, Mg and K in surface waters at ELW.

CONCLUSIONS

Our research has shown that the soils of ELW may be sensitive to anthropogenic acidic deposition and that the soils have an influence on surface water quality. These conclusions are based on both laboratory and field data but are limited to characteristic soils believed to represent the watershed. Measurements of the spatial distribution and variability of soil chemical and physical parameters are needed to project these results over the entire watershed in a quantitative manner.

The soils of ELW are naturally acidic. This is reflected in the pH's of the water and $CaCl_2$ soil extracts, and the low percent base saturation (PBS) of the characteristic soils. The accumulation of organic matter is the most likely cause of low pH. Organic acids were found in throughfall. Carbon dioxide (CO_2) concentrations in the soil air are also high enough to influence soil pH.

The cation exchange capacities (CEC) of the soils indicate that the size of the exchangeable cation pool is limited, therefore, they are potentially sensitive to acidic deposition. Similarly, the sulfate adsorption data show that the sulfate adsorption capacity of ELW soils is low.

Weathering rates for ELW soils were found to be relatively high in laboratory studies compared to soils of the Northeastern U.S. Decreases in pH resulted in higher rates. If the rates of soil mineral weathering are high enough, this may be a very important long-term mechanism for the mitigation of the effects of acidic deposition.

The organic forms of the nutrients N and S dominate in ELW soils. One of the major implications is that the biological processes that mediate the transformations of these compounds may control their concentrations in the soil solution. Immobilization of N and S occurred in the field during the summer, in spite of the substantial potential for mineralization measured in the laboratory. This was due to dry soil conditions. Measurements of leaf litter decomposition indicate that most of the decomposition occurs in the winter and spring. This suggests that most of the mineralization may also be occurring in

these seasons.

Nitrate concentrations in surface waters are higher in the spring and fall. This is consistent with higher nitrification and lower plant uptake during those seasons. If ELW soils are retaining N and S through immobilization or other biological processes, this may be an important sink for neutralization of acidic deposition. More measurements of these soil processes need to be made during the winter and spring.

Acid additions reduced mineralization rates in laboratory studies of ELW soils. A direct effect of the acid could not be determined. One implication is that acidic deposition could lead to organic matter accumulation in ELW soils.

The concentrations of Al and other cations in soil solutions and surface waters reflect the mineralogy of the soils of ELW. Solution concentrations of Al appear to be controlled by equilibrium with microcrystalline gibbsite or a mineral with a similar solubility. Observed concentrations of Al in surface waters were much lower than those expected to have toxic effects on fish.

The distribution of cations and bicarbonate in soil solution and surface waters are proportional to the fractions of those cations in the minerals found in the area. Differences in the distribution of cations during the season are not readily explained. Differences in the rates of weathering of individual minerals are implied.

RECOMMENDATIONS

The soils of ELW have an influence on surface water quality. Biological and chemical processes in these soils may be affected by changes in the rates of anthropogenic acidic deposition. The following recommendations are suggested for future research at ELW.

1. Construct elemental budgets for N, S, Al and P.

It will be necessary to obtain information on soil volumes (i.e. a map) and spatial variability of soil characteristics of ELW. Soil temperature and moisture affect the rates of all biological, chemical and physical soil processes and thus need to be monitored to determine their impact on elemental fluxes within ELW. Large seasonal variations in climatic conditions need to be taken into account in nutrient budgets. It will be necessary to integrate the soil processes work with the vegetation studies on productivity and nutrient uptake.

2. Identify mechanisms (flow paths) of solute transport through soils of ELW.

To gain a full understanding of the relationship between soil processes and surface water chemistry, mechanisms (flow paths) of solute transport must be identified. Soil biological and chemical processes, including cation exchange and mineral weathering, are important elements of the solute transport mechanism. Also, the rates of water movement through the soil need to be quantified.

3. Construct a biogeochemical mass balance for ELW

In order to determine the sensitivity of Sierra Nevada ecosystems to acidic deposition, soil process data need to be integrated with atmospheric, hydrologic, vegetation (productivity) and limnological data. This will require data on pools and fluxes of elements in addition to N, S, P and Al.

PART I

PHYSICAL-CHEMICAL CHARACTERIZATION OF EMERALD LAKE WATERSHED SOILS

The ability of soils to interact with acidic deposition depends both on the quantity (pool) of acid-forming and acid-neutralizing substances in a unit of soil and the rate (flux) at which these are made available to the soil solution. Soils contain large pools of acid and acid-neutralizing materials. Acid-forming substances include reduced and organic forms of nitrogen (N), sulfur (S) and phosphorus (P). Acid-neutralizing materials include the exchangeable cation pool, sulfate (SO_4^{2-}) adsorption and weatherable soil minerals. The net effect of acidification on soils depends on how fast these components are transformed. Cation exchange and SO_4^{2-} adsorption are essentially instantaneous while mineral weathering is a long-term source of acid neutralization. The transformations of the nutrients N, S and P and the decomposition of organic matter are biologically mediated and will be discussed in detail in Part II.

The nutrients N, S, and P are found in a variety of inorganic and organic forms which affect their availability to organisms, their mobility and their susceptibility to transformations among forms. The forms of these nutrients, as well as their total quantities, together with other physical and chemical characteristics of soils are important in determining the relative capacities of soils to enhance or ameliorate surface water acidification.

Organic matter content, pH, exchangeable ions, and ions present in solution are highly correlated with a soil's ability to produce and/or consume natural acidity and also affect acidification of receiving waters (Tabatabai, 1985; Krug and Frink, 1983; Reuss and Johnson, 1985). Cation exchange buffers the soil against drastic changes in the chemistry of the soil system resulting from changes in

inputs of acidity. Soil texture is a physical property which affects water-holding capacity, infiltration, and hydraulic conductivity and thereby is important in evaluating transformations and mobility of soil solution constituents.

Sulfate adsorption is one process by which soils may ameliorate the effects of acidic deposition on surface waters. A consistent characteristic of the acidification of freshwater in northern Europe and eastern North America has been the partial replacement of the bicarbonate (HCO_3^-) by SO_4^{2-} (Henricksen, 1980; Christophersen and Wright, 1981). Increased SO_4^{2-} loading contributes to the mobilization and subsequent transport of aluminum (Al^{3+}) and other cations from soils to aquatic systems (Gorham, 1958; Johnson and Cole, 1980; Cronan et al., 1978; Johnson, 1977). Because most of the exchangeable cations in extremely acid soils (pH <4.5) are hydrogen (H^+) and Al^{3+}, increased SO_4^{2-} inputs cause increased output of the acidic cations (H^+ and Al^{3+}) via cation exchange processes (Seip, 1980).

Galloway et al. (1983) and Cosby et al. (1985) have proposed that the introduction of acidic deposition to a region will produce a sequence of changes in lake chemistry based upon the SO_4^{2-} status of soils of the drainage basin (Fig. 1). Initially, the soils are presumed to be non-acid and to have a high "SO_4^{2-} adsorption capacity". Increases in proton (H^+) and SO_4^{2-} deposition lead to an increased output of basic cations (calcium, Ca^{2+}; magnesium, Mg^{2+}; sodium, Na^+; potassium, K^+) and HCO_3^- from the watershed with consequent increases in lake alkalinity. Once the capacity of the soil to adsorb SO_4^{2-} is reached, this anion becomes the predominant counter ion in soil solution waters and allows increased H^+ and Al^{3+} leaching to the lake ecosystem. The net result is a reduction of alkalinity and an increase in SO_4^{2-} and acidity of lakewater.

The ultimate source of acid neutralization within soils is the dissolution of minerals to release the basic cations Ca, Mg, Na and K. The ratios among cations released and between cations and silicon (Si) released depends on the presence of soil minerals and other reactive geological materials (Garrels and MacKenzie, 1967). Quantities of cations released from minerals and associated acid neutralization rates are determined by the relative reactivities of minerals and acidity of the

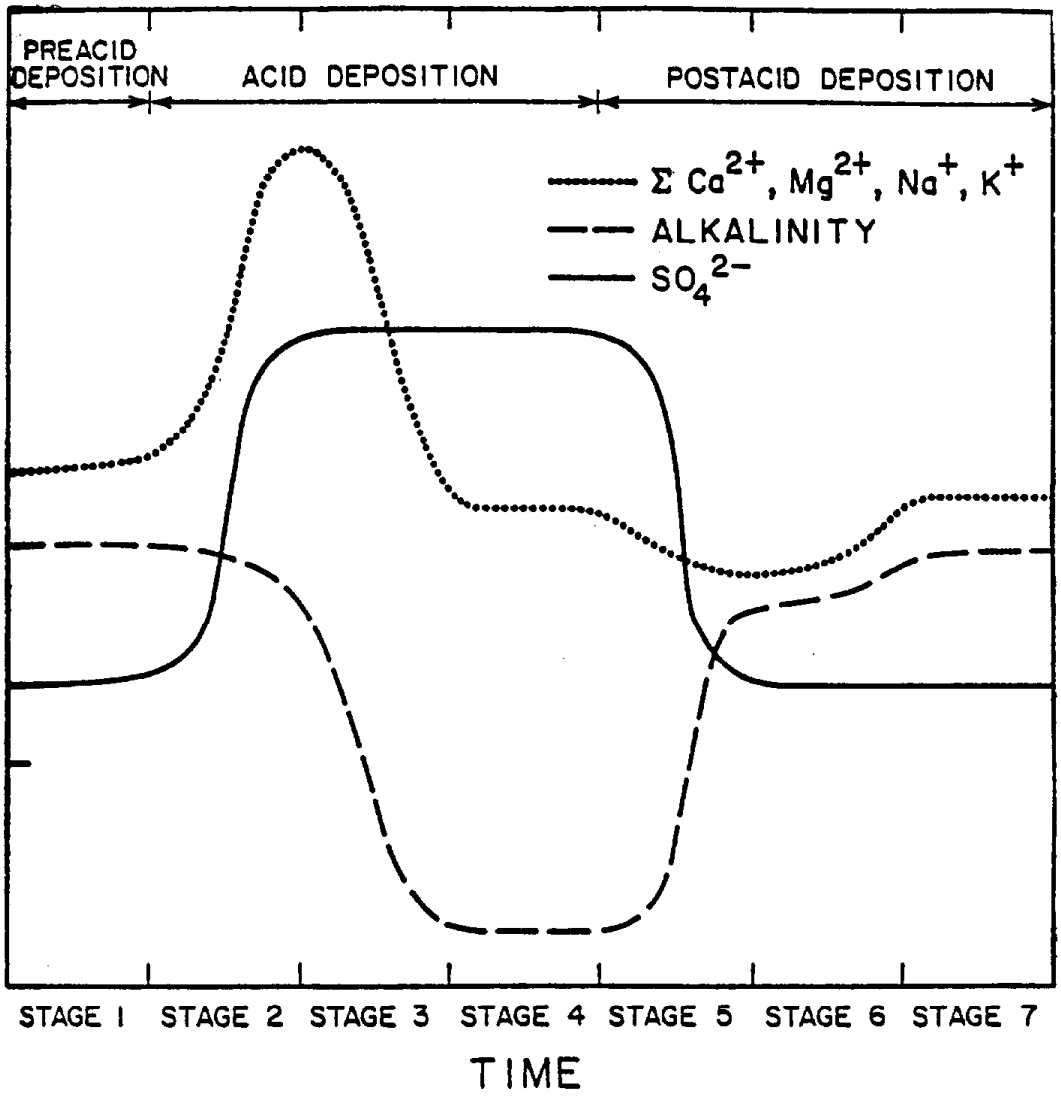

Fig. 1. A conceptual model of freshwater acidification (after Galloway et al., 1983). Stage 1: preacidification; Stage 2: soil sulfate adsorption undersaturated; Stage 3: soil sulfate adsorption saturated; Stage 4: steady state lake acidification; Stage 5: soil sulfate adsorption supersaturated; Stage 6: recovery of soil percent base saturation; Stage 7: stable period of lake recovery.

contact solutions. Weathering rates for a Spodosol (Beckett series) found at Woods Lake Watershed, New York and Hubbard Brook Experimental Forest, New Hampshire, are on the order of 1.5 to 2.0 $kEq \cdot ha^{-1} \cdot yr^{-1}$ (Cronan, 1985). A high elevation granitic watershed (Silver Creek study area) containing Cryumbrepts and Cryorthents in central Idaho, exhibits weathering rates of 2.4 to 4 $kEq \cdot ha^{-1} \cdot yr^{-1}$ (J. L. Clayton, US Forest Service, Boise, 1986, personal communication). These weathering rates were obtained using a mass balance approach (Likens et al., 1977).

Soil mineral weathering rates have been observed to increase with increased acid additions (Cronan, 1985) because of the pH-dependence of weathering rates for many individual minerals. Rates of dissolution may also be influenced by changes in concentrations of total dissolved salts (Lasaga, 1981). Salt (ionic strength) effects are related to the mechanism of the acid attack in the weathering reaction.

To assess the relative potentials of several soils in the Emerald Lake Watershed (ELW) to enhance or ameliorate the effects of acidic deposition on surface water acidification, several physical chemical parameters were measured. Pools of N, S and P were evaluated for four representative soils. Buffering and SO_4^{2-} adsorption characteristics were studied in two soils. Soil mineral weathering rates were also determined.

A. SOIL NUTRIENT POOLS: RELATIVE CONTRIBUTIONS

Methods

Four soils representative of ELW were selected for sampling in August 1984 (Huntington and Akeson, UCD, 1984, personal communication). Samples were collected from the major horizons in each soil. Particle size distribution was determined using the pipette method, pH in a 1:1 soil:H_2O suspension using a glass electrode and organic carbon (C) by wet oxidation using dichromate (Day, 1965; McLean, 1982; Nelson and Sommers, 1982, respectively). Total soil N was determined by Kjeldahl digestion (Bremner and Mulvaney, 1982). Inorganic soil N was determined colorimetrically in 1 M potassium chloride (KCl) extracts (Keeney and Nelson, 1982); whereas, soluble SO_4^{2-} was extracted in 0.1 M lithium chloride (LiCl) and determined by liquid

chromatography (Tabatabai, 1982). Reserve S (organic S plus reduced inorganic S) was determined turbidimetrically after fusion with sodium bicarbonate ($NaHCO_3$) and extraction of the resultant SO_4^{2-} with acid (Bardsley and Lancaster, 1960). Total soil P was determined by digestion in perchloric acid and colorimetric analysis of phosphate (PO_4^{3-}) (Olsen and Sommers, 1982). Inorganic PO_4^{3-} was determined colorimetrically after extraction with dilute acid fluoride (Bray extractant) (Olsen and Sommers, 1982). Electrical conductivity (EC) was determined for saturation extracts and major ions in the extracts were determined by atomic absorption spectrophotometry (cations) and colorimetric analysis (anions) (Rhoades, 1982). Cation exchange data for the four major soil types were obtained from Mark Akeson, University of California, Davis.

Results and Discussion

The Lithic Histic Cryaquept (inlet meadow) and Entic Cryumbrept (joint) have the highest clay contents (Table 1). This may be important because, given that other factors are equal (mineralogy, organic matter content, etc.), as the percentage of clay and silt in a soil increases, the water holding capacity increases. A higher moisture holding capacity will affect plant growth, organic matter decomposition and mineral weathering.

Soil pH values (Table 1) are not different among horizons or among the soils, ranging from 4.4 to 4.8 (1:1 in H_2O). These low pH values, which are considered very strongly acid, not only affect nutrient availability to plants but slow many microbial processes, including nitrification (Alexander, 1977). Soil pH values determined in $CaCl_2$ are different from values in H_2O because calcium replaces acidic cations (Al^{3+} and H^+) on the exchange complex, releasing them to solution. The decrease in pH in $CaCl_2$ compared to pH in H_2O is 0.2 to 0.5 units. This indicates that these soils have a significant exchange acidity, that is, they are naturally acidic and will buffer soil solution pH in the acidic range.

The cation exchange data further support these conclusions (Table 2). The cation exchange capacities (CEC) of all but the Lithic Histic Cryaquept are less than 15 mEq/100 g(soil). This is a low CEC

Table 1. Data for Emerald Lake Watershed soils.

Soil Subgroup classification	Location	Depth	Particle Size Distribution			Organic Carbon	pH (1:1)	EC
			Sand	Silt	Clay			
		cm	---------- % ----------					$dS \cdot m^{-1}$
Lithic Cryumbrept	Lake outlet	0-5	89	5	6	0.89	4.64	0.087
		5-23	83	11	6	0.92	4.79	0.073
Typic Cryorthent	Ridge	0-6	81	13	6	0.82	4.39	0.057
		6-44	78	17	5	0.29	4.52	0.041
		44-68	86	7	7	0.11	4.58	0.035
Lithic Histic Cryaquept	Inlet meadow	0-15	42	39	19	13.51	4.48	0.162
		15-30	58	26	16	8.84	4.53	0.052
		30-45	67	24	9	3.68	4.52	0.067
Entic Cryumbrept	NE joint	0-6	60	25	15	4.50	4.71	0.188
		6-28	64	24	12	2.66	4.47	0.130
		28-55	68	26	6	2.41	4.51	0.131
		55-70	69	21	10	2.64	4.64	0.098

Table 2. Cation exchange data for ELW soils (M. Akeson, UCD, 1985).

Soil subgroup	Depth	CEC	PBS
	cm	meq·100 g^{-1}	%
Lithic Cryumbrept	0-5	7.84	11.5
	5-23	11.26	7.1
Typic Cryorthent	0-6	7.93	8.1
	6-44	6.24	9.3
	44-68	6.37	6.0
Lithic Histic Cryaquept	0-15	52.06	15.3
	15-30	25.72	4.3
	30-45	15.54	4.8
Entic Cryumbrept	0-6	10.30	15.0
	6-28	11.15	9.5
	28-55	12.32	6.4
	55-70	9.72	7.8

range, characteristic of soils considered sensitive to acidic deposition (McFee, 1980). The CEC of the Lithic Histic Cryaquept is relatively high, characteristic of soils high in organic matter content. The percent base saturation (PBS) for all ELW soils is quite low, less than 15%. This is characteristic of soils which are naturally acidic. One implication of the low PBS is that exchangeable base cations will provide only a limited buffer for acidic inputs unless augmented by weathering.

The forms of nutrients (N, S and P) in soils can be divided into several fractions. Organic forms of these nutrients are largely immobile and unavailable to plants. These forms may be transformed to inorganic forms through decomposition and mineralization processes and thereby released to the soil solution. Exchangeable and water-extractable forms of N and S in soils are generally readily available to plants and other organisms. Exchangeable forms are adsorbed to clay mineral and organic surfaces; whereas, water-extractable forms are present as salts dissolved in the soil solution. Total P and acid-extractable P both represent mainly mineral fractions of P. Acid-extractable P is an index of P availability to plants.

Organic forms of C, N and S are the dominant fractions of these elements in the ELW soils (Table 1 and 3). The trend within the soil profiles is for organic C, N and S to decrease with depth. The Lithic Histic Cryaquept has the highest levels of organic C, N and S. This is primarily a result of the soil occurring in an accumulative landscape position where the high water table and cold conditions in this soil have resulted in slow decomposition rates for plant litter added to the soil. One implication of the dominance of organic forms of these nutrients in soils is that the biological processes affecting their transformations (e.g. immobilization, mineralization, nitrification, denitrification) will control their concentrations in the soil solution and availability to plants. Inorganic and mass transport processes such as exchange and deposition may have relatively minor effects.

Potassium chloride extractable N (exchangeable and soluble NH_4^+ and NO_3^-) tended to be higher than water-extractable N for all soils (Table 3). The highest N contents were found in the Lithic Histic Cryaquept and the Entic Cryumbrept soils, again probably a reflection

Table 3. Data for Emerald Lake Watershed soils.

Soil Subgroup classification	Location	Depth	Total Kjeldahl N	KCl Ext. Inorganic N (NO_3 + NH_4)	Saturation extract NO_3-N	Organic C:N ratio
		cm	----------mg·kg^{-1}----------			
Lithic Cryumbrept	Lake outlet	0-5	620	7.95	0.43	14.4
		5-23	560	7.39	0.36	16.4
Typic Cryorthent	Ridge	0-6	470	3.32	1.15	17.4
		6-44	310	1.03	0.21	9.4
		44-68	150	0.77	0.04	7.3
Lithic Histic Cryaquept	Inlet meadow	0-15	11300	15.32	0.45	12.0
		15-30	4680	5.02	0.00	18.9
		30-45	2590	3.09	0.46	14.2
Entic Cryumbrept	NE joint	0-6	4500	9.95	0.03	10.0
		6-28	2060	11.66	0.00	12.9
		28-55	1980	5.23	0.77	12.2
		55-70	1820	11.26	0.40	14.5

of the higher organic matter contents and greater exchange capacity. The highest extractable S contents were also found in the finer textured soils (Table 4). These higher exchangeable and soluble N and S contents may be a direct effect of higher substrate levels available to mineralizing bacteria.

Acid-extractable P was highest in the Lithic Cryumbrept and the Entic Cryumbrept. No explanation for this occurrence is readily available. Total P was highest in the surface horizon of the Lithic Histic Cryaquept, but acid-extractable levels were very low in the same soil. This may be due to the flooded conditions and high microbial activity which may effectively immobilize P.

B. SULFATE ADSORPTION

Methods

Two soils found at ELW were studied in this experiment: an Entic Cryumbrept and a Lithic Cryorthent. Samples of morphological horizons of these soils were collected at ELW and transported to the laboratory where they were air-dried and sieved using a 2mm sieve. Material larger than 2mm was discarded. For each adsorption experiment approximately 6g of soil and 60mL of an experimental solution were combined and shaken for 24hr at 20°C. After shaking, the suspensions were filtered using Whatman 42 filters and then Nucleopore (0.4um) filters. Equilibrium pH and SO_4^{2-} concentrations were then determined for the filtrates.

Each soil was treated with solutions containing one of four levels of SO_4^{2-} (0, 40, 100, or 140 $mEq \cdot L^{-1}$) in combination with one of four levels of nitric acid (HNO_3) (0, 1, 5, or 10 $mEq \cdot L^{-1}$). The methodology used in the study has been described by Nodvin et al. (1986a, b). The results obtained for the ELW soils were compared to those obtained for a B horizon of a Typic Haplorthod from the Hubbard Brook Experimental Forest (HB), New Hampshire (Nodvin et al., 1986b).

Results and Discussion

The ELW soils were found to be less effective in buffering against pH changes than the HB soil. This is indicated by the greater decreases in suspension pH with equal acid addition (Fig. 2). The

Table 4. Data for Emerald Lake Watershed soils.

Soil Subgroup classification	Location	Depth	Organic (reserve) S	Soluble S (SO_4^{2-})	Total P	Extract (Bray) P
		cm	----------	mg·kg^{-1}	----------	
Lithic Cryumbrept	Lake outlet	0-5	30	2.12	91	40
		5-23	37	0.00	142	61
Typic Cryorthent	Ridge	0-6	37	2.59	270	6
		6-44	32	5.00	192	3
		44-68	7	1.20	133	8
Lithic Histic Cryaquept	Inlet meadow	0-15	827	3.65	574	1
		15-30	362	1.64	175	1
		30-45	ND	0.00	180	0
Entic Cryumbrept	NE joint	0-6	238	2.47	223	44
		6-28	148	0.00	344	43
		28-55	156	0.00	384	9
		55-70	148	0.00	332	2

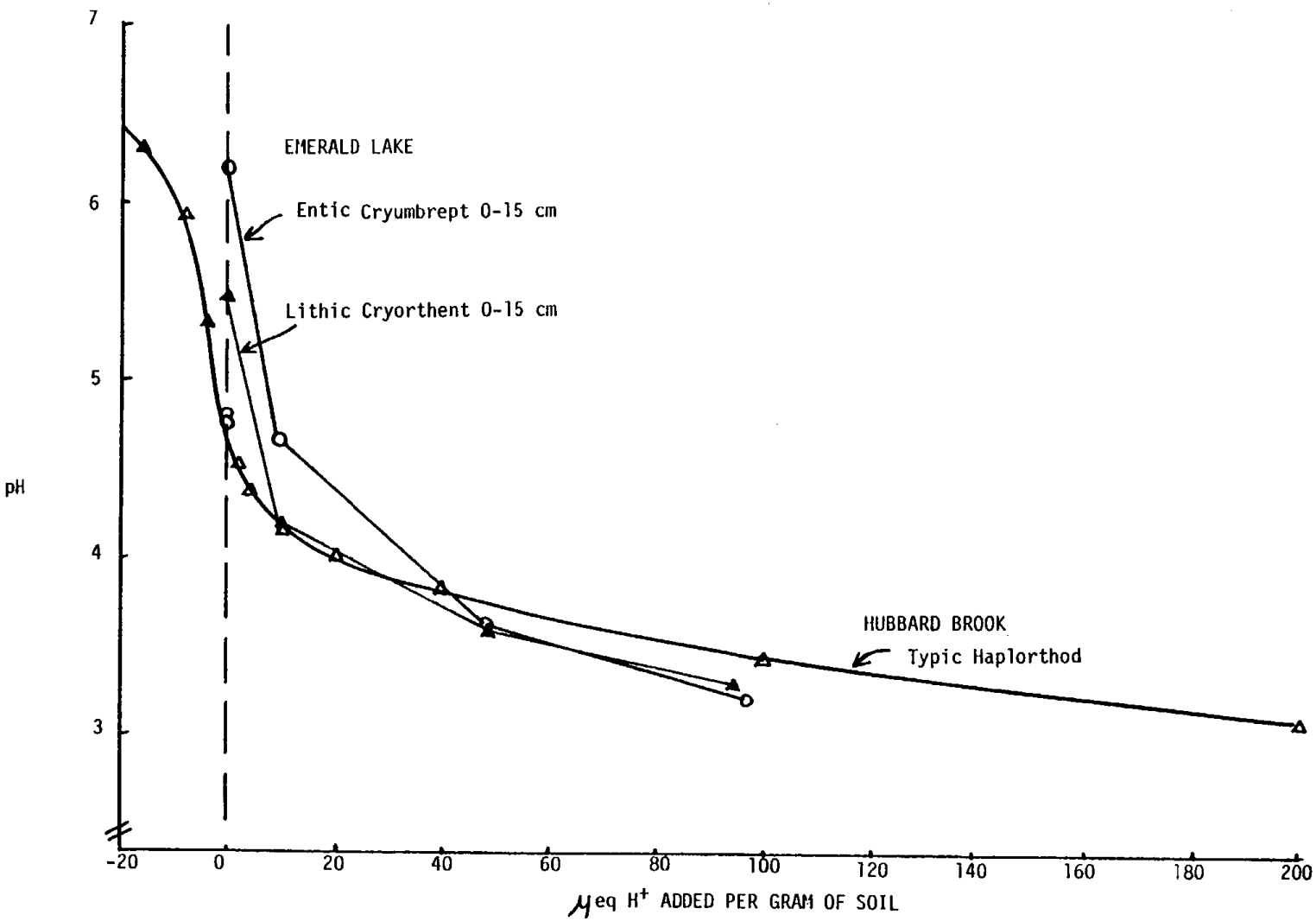

Fig. 2. Response of suspensions of Entic Cryumbrept and Lithic Cryorthent from ELW to additions of acid and base compared with Typic Haplorthod from Hubbard Brook.

initial pH values of surface horizons of the Entic Cryumbrept and the Lithic Cryorthent were 6.2 and 5.8, respectively, compared to 4.8 for the Typic Haplorthod. Nevertheless, additions of acid in amounts of 40 $uEq \cdot gm^{-1}$ were sufficient to lower the pH of all three soil equilibrium solutions to less than 4.0 (Fig. 2). Except for the first acid addition, the Entic Cryumbrept and the Lithic Cryorthent reacted quite similarly.

For all three soil types, the amount of SO_4^{2-} removed from or released to the equilibrium solution by the soil was linearly related to the initial amount added to the soil-water systems (Fig. 3). The Y-axis intercept represents the amount of SO_4^{2-} released from the soil to water in which no SO_4^{2-} was added. This value is related not only to the ability of the soil to retain SO_4^{2-} but also to the amount of labile SO_4^{2-} initially present in the soil. The slope of the relationship is an indicator of the SO_4^{2-} retaining ability with a greater slope indicating greater removal from solution (i.e. adsorrrrption). The slopes of the regression lines shown in Fig. 3 are 0.52, 0.11, 0.18 and 0.20 for the HB soil, Entic Cryumbrept, Lithic Cryorthent (0-15cm and 15-25 cm), respectively. This can be interpreted as evidence that the ELW soils have less ability to retain SO_4^{2-} compared to the HB soil. Also, no differences were found among the ELW soils.

Addition of acid to the equilibration solutions increased the SO_4^{2-} removal from solution by the ELW soils (Figs. 4 and 5). This is expected because of the increased positive surface charge of sesquioxides and variable charge clays at lower solution pH values (Nodvin et al., 1986b). This effect was found between ambient pH and about 4.2. By examining the change in slope of the isotherm as acid is added, one can evaluate the relative abilities of the soils to remove SO_4^{2-} from solution with respect to solution pH (Fig. 6). As can be seen in this figure, the HB and ELW soils have similar SO_4^{2-} removal abilities near pH 6. (NaOH was added to the HB soil to attain pH values above the natural pH of 4.8.) Decreasing solution pH by adding acid increased the slope of the isotherms. A slope maximum for the HB soil was reached slightly below pH 4 and for the Entic Cryumbrept near or below pH 4. Because of limited data points, it was not possible to locate a maximum for the Lithic Cryorthent. Below pH 5 the SO_4^{2-}

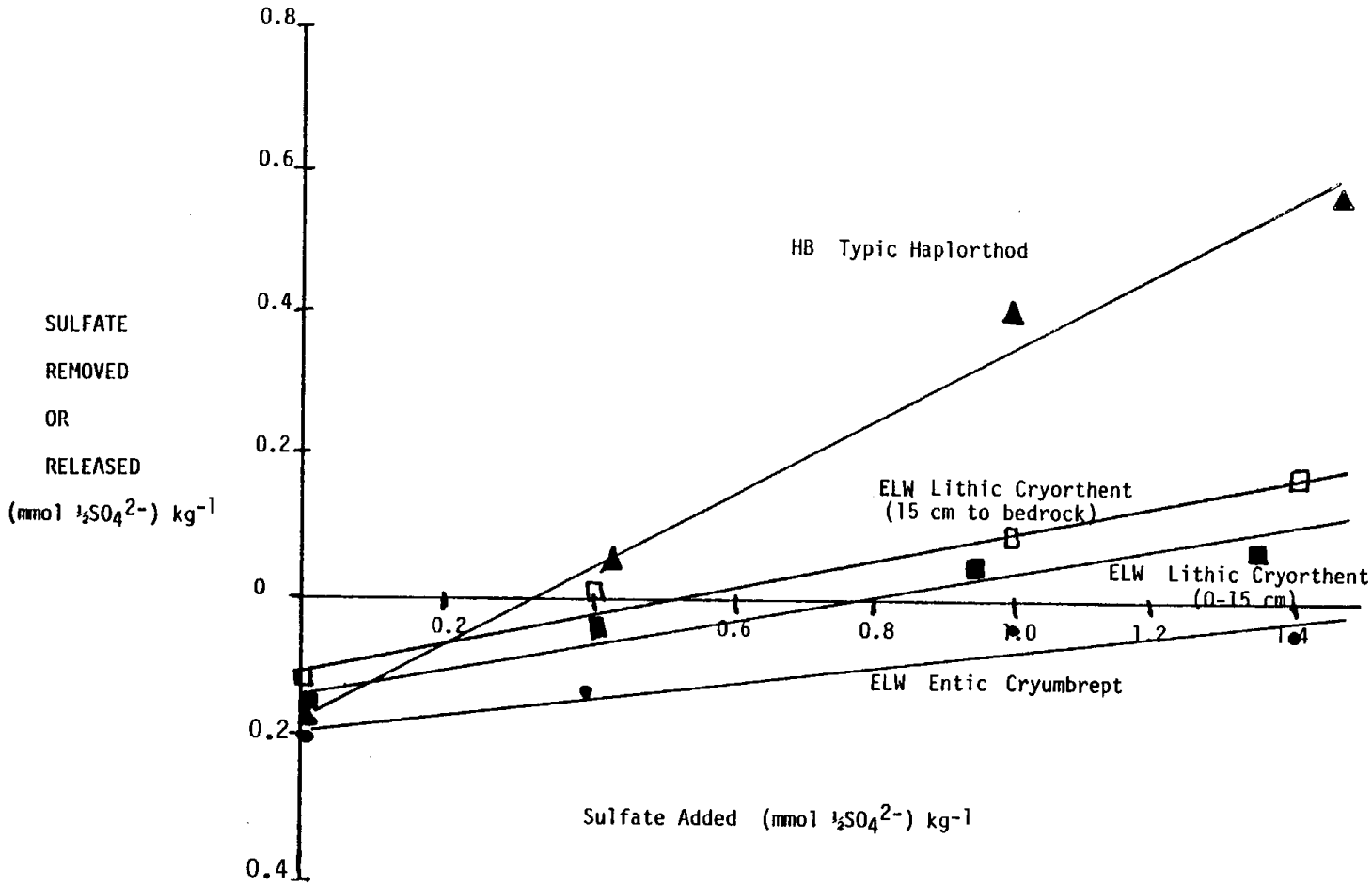

Fig. 3. Sulfate adsorption isotherms for ELW soils at ambient pH compared with a Hubbard Brook soil.

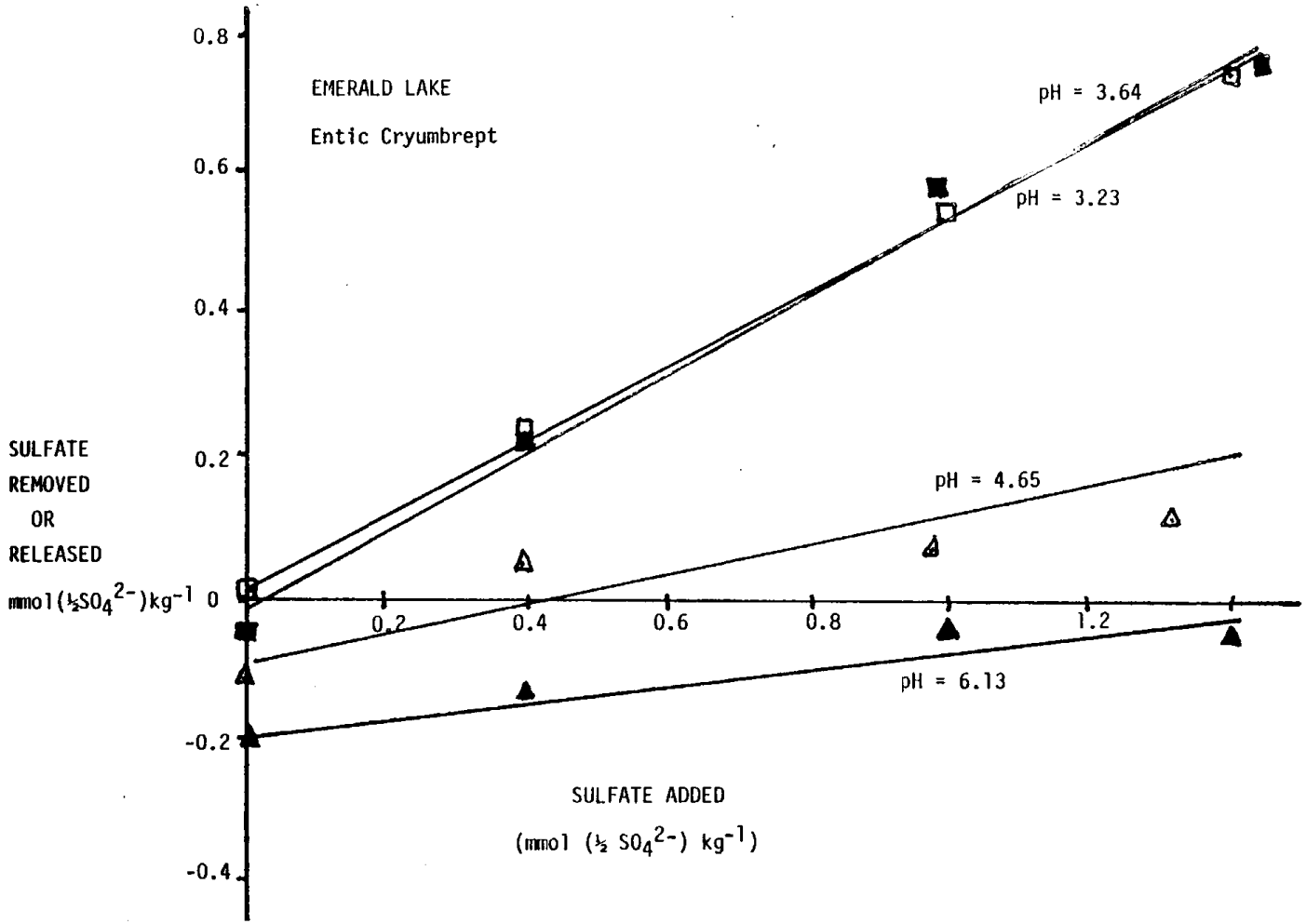

Fig. 4. Sulfate adsorption isotherm for Entic Cryumbrept from ELW at four pH intensities.

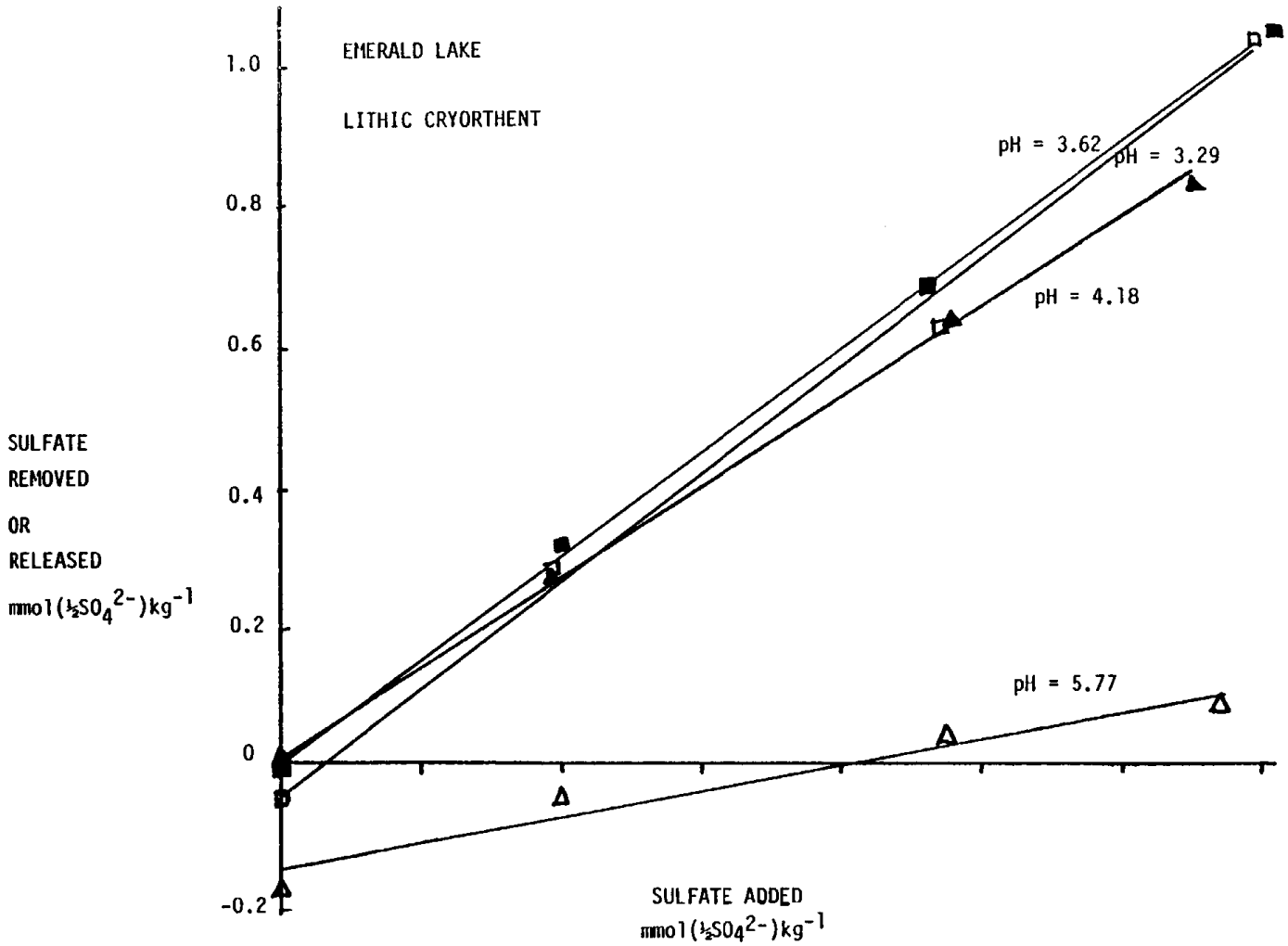

Fig. 5. Sulfate adsorption isotherms for Lithic Cryorthent from ELW at four pH intensities.

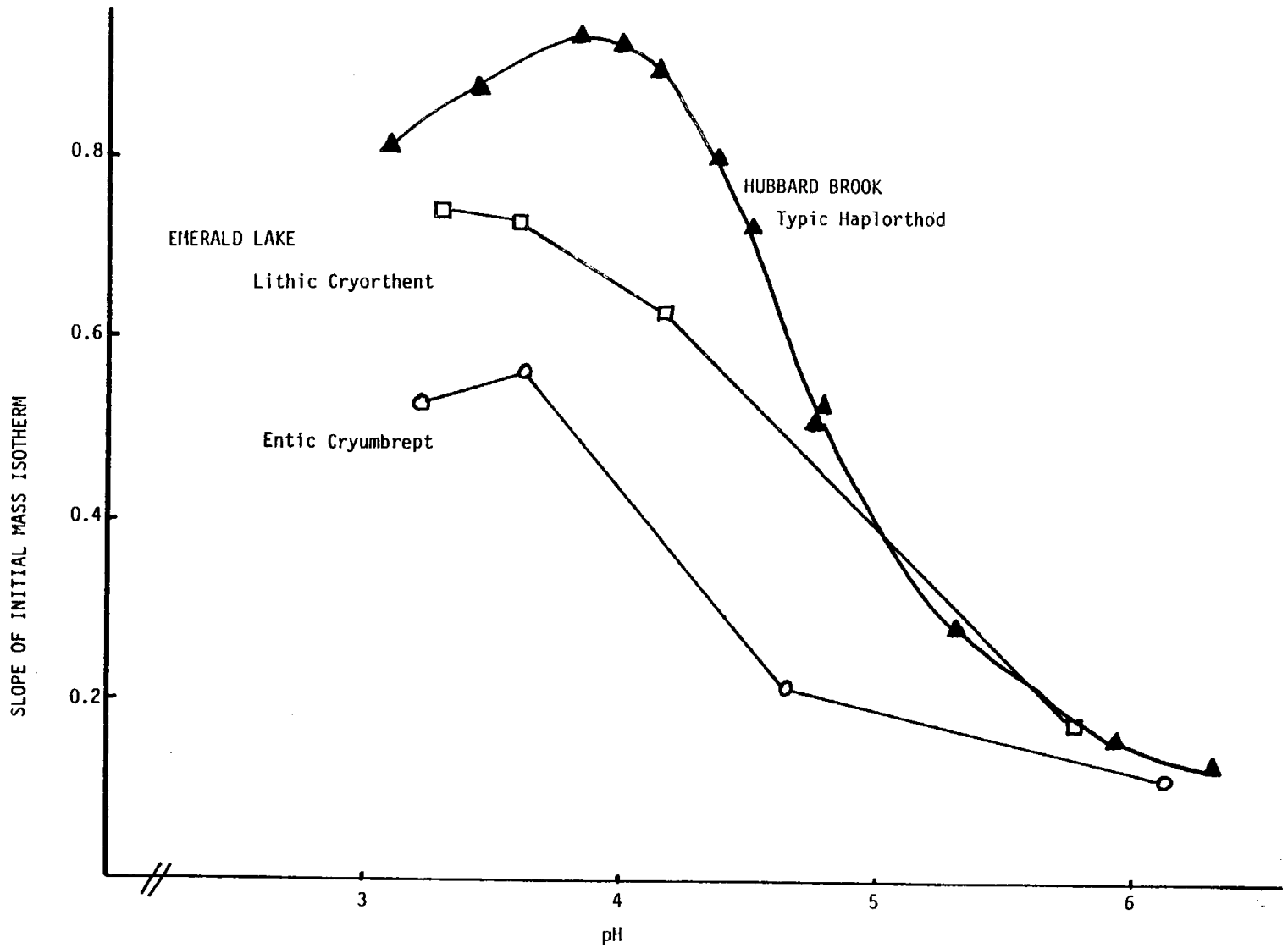

Fig. 6. The slopes of the sulfate adsorption isotherms at different pH intensities show a pH of maximum adsorption for the Entic Cryumbrept (ELW) and the Typic Haplorthod (Hubbard Brook).

retention ability of the ELW soils was less than that of the HB soil.

Chao et al. (1964) demonstrated the importance of the composition of soil surface coatings to SO_4^{2-} adsorption. When they coated less retentive soils with either Fe or Al oxides, SO_4^{2-} retention increased and there was a greater dependence of SO_4^{2-} adsorption on solution pH. Their Al oxide-coated soils showed a maximum adsorption around pH 4.0; whereas, Fe oxide-coated soils showed increasing adsorption with decreasing pH. Because a maximum adsorption pH appears to occur for the Entic Cryumbrept (near or below 4) but not for the Lithic Cryorthent, the findings of Chao et al. suggest that additional research is needed to determine if different adsorption sites may predominate in each of the two soils.

C. SOIL MINERAL WEATHERING

Methods

Samples of morphological horizons of four soils were collected from ELW and used in the weathering experiments. A Typic Cryorthent (44-68 cm horizon) and a Histic Lithic Cryaquept (30-45 cm horizon), which represent the extremes in the range of soil properties found at ELW, were selected for pH and ionic strength weathering studies. The remaining horizons of these soils were also used for less detailed, controlled pH weathering studies. Surface horizons of a Lithic Cryorthent and an Entic Cryumbrept were also included in the less detailed studies. All soils were prepared by washing five times with 0.1 M NaCl. To accomplish the washings, soils were suspended in the solution, shaken 10 minutes, then centrifuged at 3000 rpm. After the last washing, the soil samples were immediately freeze-dried to minimize weathering during storage.

Controlled pH weathering experiments were conducted in 0.1 M NaCl at pH 3, 4, 4.5, 5, 6, and 7. The pH was adjusted periodically by additions of 2 M HCl or 2 M NaOH. The ionic-strength weathering studies were conducted at pH 4.5 in 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 M NaCl. The remainder of the experiments were conducted at pH 4.5 in 0.1 M NaCl. The sample treatments were all duplicated in 50-mL polycarbonate centrifuge tubes containing 25 mL solution and 2.5 g soil. The tubes were shaken gently at room temperature (approxi-

mately 25°C).

Samples of the weathering solutions were obtained by filtration through 0.4um Nucleopore filters. In the pH experiment, pairs of tubes were sampled at regular intervals. The ionic strength and other experiments were all sampled at the end of the experiment, approximately four weeks. Samples were analyzed for Si, Ca, and Mg by argon plasma emission spectroscopy.

Weathering was calculated as an extent of reaction as moles product (Ca, Mg, Si) per kg of soil (or clay) per unit time (seconds). The controlled-pH data were plotted against time and a function was found to fit the data. The ionic strength-extent of reaction data were plotted against a transformed function of ionic strength (Lasaga, 1981). This function is based on the transition state theory. The slope of the function is the product of the charges of the determining reaction Z_aZ_b:

$$\log k = \log k_o + Z_aZ_b \, (I^{1/2})/(1 + I^{1/2})$$

where k is the rate constant and I is ionic strength.

Results and Discussion

The extent of weathering per unit time of the surface horizons at pH 4.5, 0.1 M NaCl increased in the order Histic Lithic Cryaquept, Typic Cryorthent, Lithic Cryorthent and Entic Cryumbrept. In this case weathering was evaluated in terms of Ca, Mg and Si produced (Table 5). Weathering rates also increased with depth in the Typic Cryorthent and the Histic Lithic Cryaquept profiles as measured in this study. These may be interpreted as showing greater amounts of weatherable minerals in the Cryumbrept and with increasing depth in the Typic Cryorthent and Cryaquept.

The extent of reaction versus time was plotted for Ca and Mg. Calcium release was an exponential function of time and Mg release was a linear function of time, as illustrated for the Typic Cryorthent in Fig. 7. Parameters for these functions were calculated and are included in Table 6. The rate of weathering as evidenced by Ca and Mg release increased as pH decreased.

The effect of salt concentration on the extent of reaction over the four week experiment is illustrated in Fig. 8 for the Typic Cryor-

Table 5. Weathering of soils by type and depth.

Soil	Depth	[Ca]	[Mg]	[Si]	Estimated weathering rates [Si]
	cm	pmol·kg^{-1}(soil)·s^{-1}			mmol·kg^{-1}·yr^{-1}
Typic Cryorthent	0-6	497	161	584	18
	6-44	534	238	556	17
	44-68	178	338	809	26
Histic Lithic Cryaquept	0-15	190	2.85	478	15
	15-30	248	171	587	19
	30-45	320	240	604	19
Lithic Cryorthent	0-15	513	232	705	22
Entic Cryumbrept	0-15	732	342	1073	34

a. Ca

b. Mg

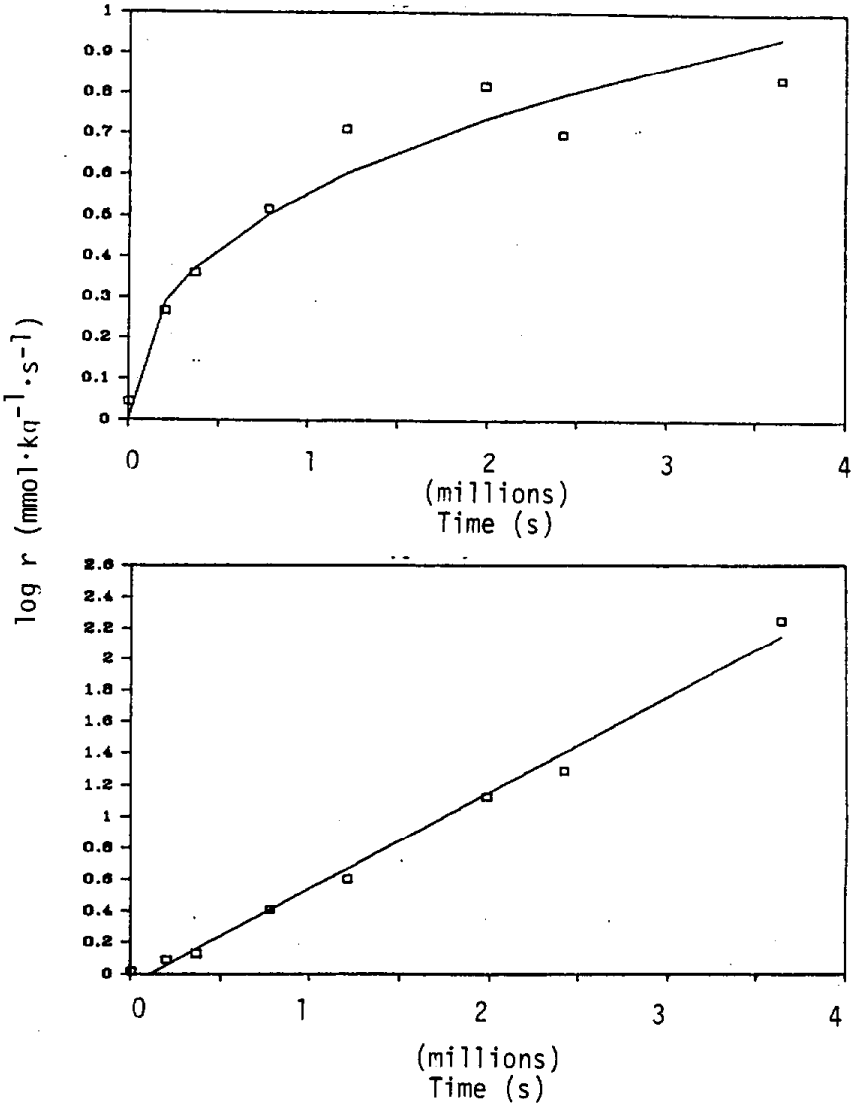

Fig. 7. Typic Cryorthent Ca release kinetics (a) and Mg release kinetics (b) at pH 4.0, 0.1 M NaCl.

Table 6. Parameters for Ca and Mg weathering as a function of pH.

	Ca ($m=k_1t^{n1}$)			Mg ($m=k_2t+a_2$)		
pH	n_1	k_1	r^2	k_2	a_2	r^2
	----$\mu mol \cdot k^{-1} \cdot s^{-n1}$----			($pmol \cdot kg^{-1}s^{-1}$)	($mmol \cdot kg^{-1}$)	
Histic Lithic Cryaqueptu						
3.0	0.43	8.1	0.93	370	0.14	0.89
4.0	0.10	450	0.92	150	0.10	0.85
4.2	0.13	180	0.89	120	0.09	0.90
5.0	-*	-	-	130	0.07	0.88
6.0	-	-	-	80	0.05	0.96
7.0	-	-	-	130	0.008	0.99
Typic Cryorthent						
3.0	0.33	7.26	0.88	260	0.40	0.91
4.0	0.41	2.07	0.93	610	-0.06	0.99
5.0	0.31	6.84	0.93	440	0.005	1.00
5.1	0.33	4.78	0.53	490	-0.06	1.00
6.0	0.23	19.05	0.97	360	0.02	0.93
7.0	0.14	63.68	0.94	370	0.03	0.99

*Rates below detection limit

a. Ca

b. Mg

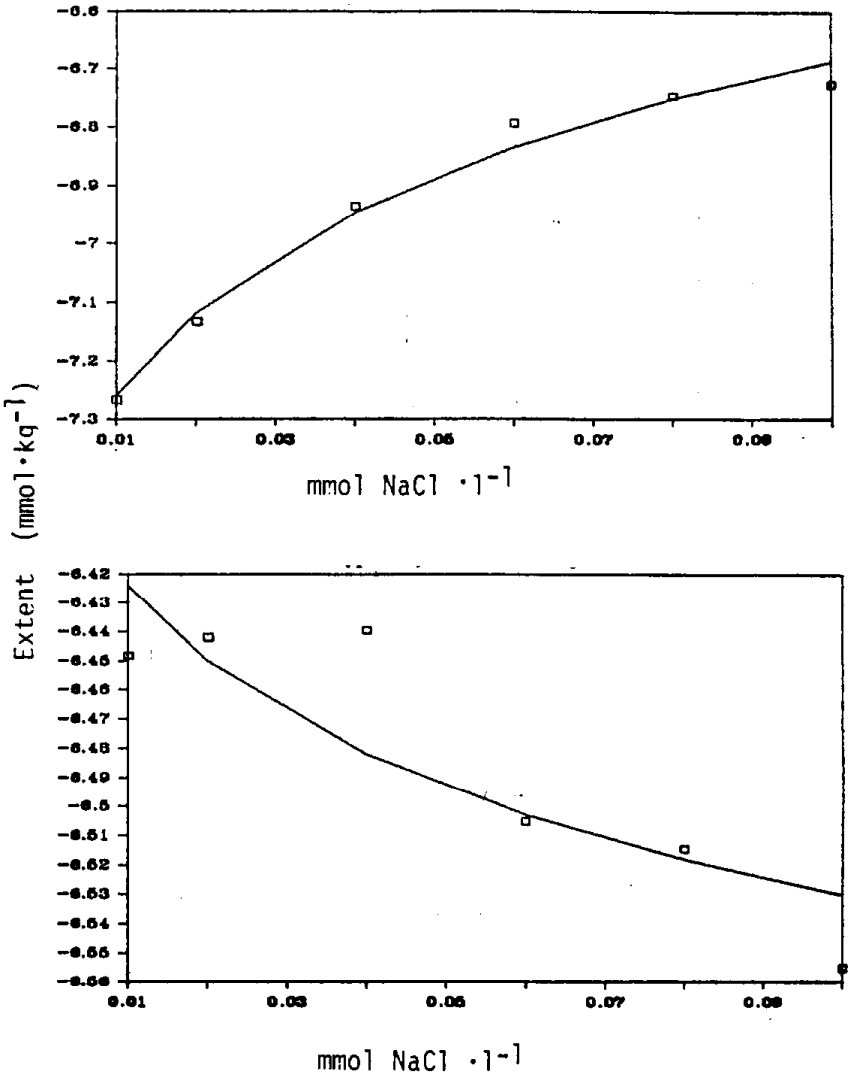

Fig. 8. The effect of solution salt concentration on weathering of Ca (a) and Mg (b) in Typic Cryorthent, pH 4.5.

thent. The rate of reaction increased with ionic strength for Ca release but decreased with ionic strength for Mg. The parameters for a linear function of ionic strength were determined for Ca and Mg (Table 7).

Weathering rates for the surface horizons of the four soils demonstrate that, at a constant pH, different soils will weather at different rates. The systems used simulate the effect of continuous deposition of pH 4.5 precipitation. The rates of weathering obtained under these conditions (as Si) are somewhat higher than equivalent rates calculated for soils found in New York and New Hampshire (Table 8). Weathering rates appear to decrease with depth in the eastern soils in contrast to the ELW soils (Table 5). Overall mineralogical differences must also be important since the pH's of the eastern soils were in the range 4-5 (Table 8). Using the Si release as an index of total mineral weathering, soils from ELW have higher rates of weathering than forest soils of the northeastern U.S.

The rate of Ca release increased and Mg release decreased with increased salt concentration for both the Typic Cryorthent and the Histic Lithic Cryaquept. This indicates that the mechanism of cation release from the Ca-silicate mineral is probably different from the Mg-silicate. Different minerals are likely to have slightly different cation release mechanism.

Table 7. Parameters for Ca and Mg weathering as a function of ionic strength.

	Ionic strength effect					
pH	Ca log k(0)	ZaZb	r^2	Mg log k(0)	ZaZb	r^2
Histic Lithic Cryaquept						
4.50	-7.21	3.28	0.99	-6.58	-0.17	0.15
Typic Cryorthent						
4.50	-7.67	4.68	0.99	-6.35	-0.87	0.73

Table 8. Normalized average weathering rates for some eastern U.S. soils (data of Cronan, 1985).

Series	Location	Suborder	Horizon	pH	Weathering rates
					$mmol \cdot kg^{-1} \cdot yr^{-1}$
Unadilla	New York	Typic Dystrochrept	O	3.76	31.5
			A	4.13	3.3
Beckett	Hubbard Brook (N.H.)	Typic Haplorthod	O	4.64	1.0
			A	3.62	6.4
			B	4.01	0.7
Adams	New Hampshire	Typic Haplorthod	O	4.15	0.2
			A	4.30	1.3
			B	4.55	0.2
				5.50	0.2

PART II

BIOLOGICAL INPUTS TO SOILS

Biological inputs to and transformations within soils may have substantial effects on a soils ability to alter acidic deposition. The vegetation contributes organic compounds to the soil which affect solubility of many soil components and provide C-rich substrates for soil microbes. Many microbially mediated soil processes either consume or produce acidity and thus may alter effects of acidic deposition (Tabatabai, 1985). Alternatively, reductions in soil microbial activity induced by acidic deposition have been widely reported (Francis, 1986).

As precipitation passes through a vegetative canopy, its chemistry is altered by washoff of leaf surfaces and the exchange of elements with the plant tissue (canopy exchange). Throughfall is water which drips off plant surfaces and falls on the soil. To study the movement of elements through the soil system and ultimately ELW as a whole, throughfall inputs must be quantified.

Canopy exchange rates are related to differences in canopy foliage such as nutrient content (Henderson et al., 1977) and shape, arrangement and surface roughness (Davidson and Elias, 1982). Differences in canopy morphology also influence the quantity of dry deposition on leaf surfaces and the eventual washoff of those leaves by precipitation (White and Turner, 1970). Thus, the major vegetative species of ELW would be expected to have different contributions to the soils on which they grow.

A major component of throughfall is water soluble organic matter. Dissolved organic matter derived from both vegetation and soils has been found to exert an important influence on soil solution and surface water acidity, and aluminum (Al) speciation in forested watersheds (Cronan and Aiken, 1985; McDowell, 1985). Organic complexes of Al are important species of soluble Al in acid soil solutions (James and Riha, 1984; Driscoll et al., 1983), in streams (Johnson et al., 1981) and in

lakes (Driscoll and Schafran, 1984). These water soluble Al-organic complexes are relatively stable and thus, contribute to the mobilization of Al during soil horizon development. Slowly reacting organic complexes of Al in a soil also may be responsible for controlling uncomplexed Al concentrations (Hooper and Schoemaker, 1985).

Dissolved organic matter in natural waters can contribute significantly to the anion budget. Oliver et al. (1983) have shown how an estimate of carboxylic acid concentrations based on a measurement of organic C may be used to achieve a cation-anion charge balance. These data demonstrated how dissolved organic matter has a total negative charge on the order of 10 $ueq(-)\cdot L^{-1}$ for a water sample containing 1 ppm dissolved organic carbon (DOC).

Litter fall and decomposition are critical factors in assessing nutrient cycles at ELW. The rate of accumulation vs. decomposition is a major component of maintenance of soil organic matter which in turn is a storehouse of nutrients required for both plant and microbial growth (Aber and Melillo, 1980). The nylon mesh litter bag has been used extensively in field decomposition studies (Weider and Lang, 1982). Weider and Lang (1982) found that the technique is statistically sound and that mathematical models can successfully be used to describe mass loss over time. Litter decomposition rates are dependent on numerous factors including litter quality, precipitation and throughfall (Gosz et al., 1973).

Both N and S are largely in the organic form in soils and are thus unavailable for plant use until decomposition occurs. Soil organic matter is very complex and consists of a wide variety of compounds. Some of these compounds such as simple sugars decompose readily while others like cellulose and lignin are very resistant to decomposition. Thus, the quantity of N and S released from organic matter via mineralization may be more important in assessing nutrient fluxes than is the total quantity of that nutrient present.

Potentially mineralizable N (PMN) is the quantity of N that is susceptible to mineralization under optimum conditions. It is generally highly correlated with N uptake by vegetation and sets the highest possible limit for N mineralization. In the field, however, conditions are not optimum and N mineralization will be controlled by environ-

mental factors such as temperature and moisture. Thus, in situ determinations are necessary to quantify actual contributions of N and S to the nutrient pool by mineralization.

Concern in recent years over effects of acid rain on terrestrial ecosystems has resulted in numerous studies addressing effects of acidic inputs on soil microbial processes. Many of these studies involve "time compression" or high levels of acidic inputs (Novick et al., 1984; Strayer et al., 1981). It is questionable whether these treatments actually reflect long-term effects of acid additions occurring in nature (Killham and Firestone, 1982).

Nitrogen mineralization and nitrification generally decrease upon addition of simulated acid rain (Strayer et al., 1981; Novick et al., 1984). However, these studies were conducted in the northeastern United States where soils and atmospheric pollutants are much different from in the western United States. Therefore, there is a need to look at effects of acid deposition on N mineralization in soils from the western U.S. The effects of acid deposition on the S mineralization process have not been addressed.

The ultimate fate of organic matter in soils is transformation to carbon dioxide (CO_2) and water through respiration. This CO_2 has been assumed to be a very important factor in chemical weathering of soils and rocks in the Sierra Nevada and, hence, the chemical composition of surface waters (Feth et al., 1964; Mankiewicz and Sweeney, 1977). The acidic properties of aqueous CO_2 are well known (eg. Stumm and Morgan, 1981). When CO_2 dissolves in water, much of it reacts with water molecules to form the diprotic carbonic acid (H_2CO_3). Carbonic acid dissociates in natural waters with neutral pH to release a proton (H^+) and form HCO_3^- the principal source of acid titratable alkalinity. These reactions are summarized as follows:

$$CO_2(g) = CO_2(aq)$$

$$CO_2(aq) + H_2 = H_2CO_3(aq)$$

$$H_2CO_3(aq) = H^+ + HCO_3^-$$

The extent of CO_2 dissolution in water is determined by the concentration (or pressure) of CO_2 in the adjacent air. The equilibrium concentration of aqueous CO_2 increases as the concentration in

air increases. The resulting shift in other chemical equilibria can also cause the solution pH to decrease by a fraction of a unit (eg. Reuss and Johnson, 1985).

Several conceptual models of the acidic behavior of the soil solution have been developed recently to help predict the interactions among anthropogenically derived acidic deposition, soil and surface water runoff (Cosby et al., 1985; Reuss and Johnson, 1985). In each case the three processes in soils which seem to best predict soil solution and surface water composition are the exchange of basic cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) with soil mineral surfaces, the dissolution of Al from soil minerals and the equilibrium between soil water CO_2 and soil air or atmospheric CO_2. Thus, it is very important to know what concentrations of CO_2 are present in Sierra Nevada soils and their fluctuations throughout the year.

Respiration by roots, fungi (including the micorrhyzae associated with roots) and free-living microbes produces the CO_2 found in soil air. The rate of respiration by these organisms is affected by both soil moisture and temperature. Concentrations of CO_2 found in soil air generally reflect microbial activity (Schlesinger, 1977). High soil moisture contents reduce gas permeability and may result in a buildup of CO_2 concentrations in the soil (de Jong and Schappert, 1972).

To assess the potential for biological inputs to soils of ELW to alter surface water acidification, several soil biological processes were studied. The quantity and quality of inputs to soils from throughfall, litterfall and litter decomposition were studied. Mineralization rates for organic N and S in soils were determined under both field and laboratory conditions and the potential effects of acidic deposition assessed. Patterns of soil respiration were observed and effects on soil solution composition inferred.

A. THROUGHFALL

Methods

Collection sites were under or near the three dominant vegetation types within the watershed: Castanopsis sempervirens, Salix sp., and

a mixed stand of Pinus monticola and Pinus contorta. There were two sites for each of the three vegetation types. Each site consisted of six collectors: three underneath the canopy and three away from the canopy.

The collectors consisted of 1-liter polyethylene bottles with 15 cm polyethylene funnels inserted in the bottle cap. A small amount of cotton was placed in the stems of the funnels to prevent leaves, insects and other macro-throughfall from falling into the bottles.

Throughfall collectors were surrounded by mesh hardware cloth to protect them from rodents. The bulk collectors were attached to redwood stakes by pipe clamps and stood approximately 70 cm above the ground. The collectors at each site were placed 2 to 5 m away from each other as the vegetation allowed. Samples were collected as soon as possible after each event and filtered with glass microfiber filters (Gelman GF/F) with an effective particle retention size of 0.7 microns.

The samples were analyzed for pH, electrical conductivity (EC), acid neutralizing capacity (ANC), anions, cations and DOC. An inductively coupled argon plasma emission spectroscope was used to determine cations. Anions were determined by liquid chromatography and the DOC determined by an automated persulfate-UV oxidation method.

Results and Discussion

Throughfall collected beneath Pinus contained the highest volume-weighted concentrations of NH_4^+-N, NO_3^--N, SO_4^{2-}-S, Al^{3+}, Ca^{2+}, and Mg^{2+} (Fig. 9 and 10). This may be due to higher rates of both canopy exchange and dry deposition on the Pinus surfaces. Levels of Na^+ and H^+ were nearly the same beneath Castanopsis and Pinus while K^+ was highest under Castanopsis (Figs. 9 and 10).

The Salix throughfall contained higher levels of Ca^{2+}, Mg^{2+}, Na^+,

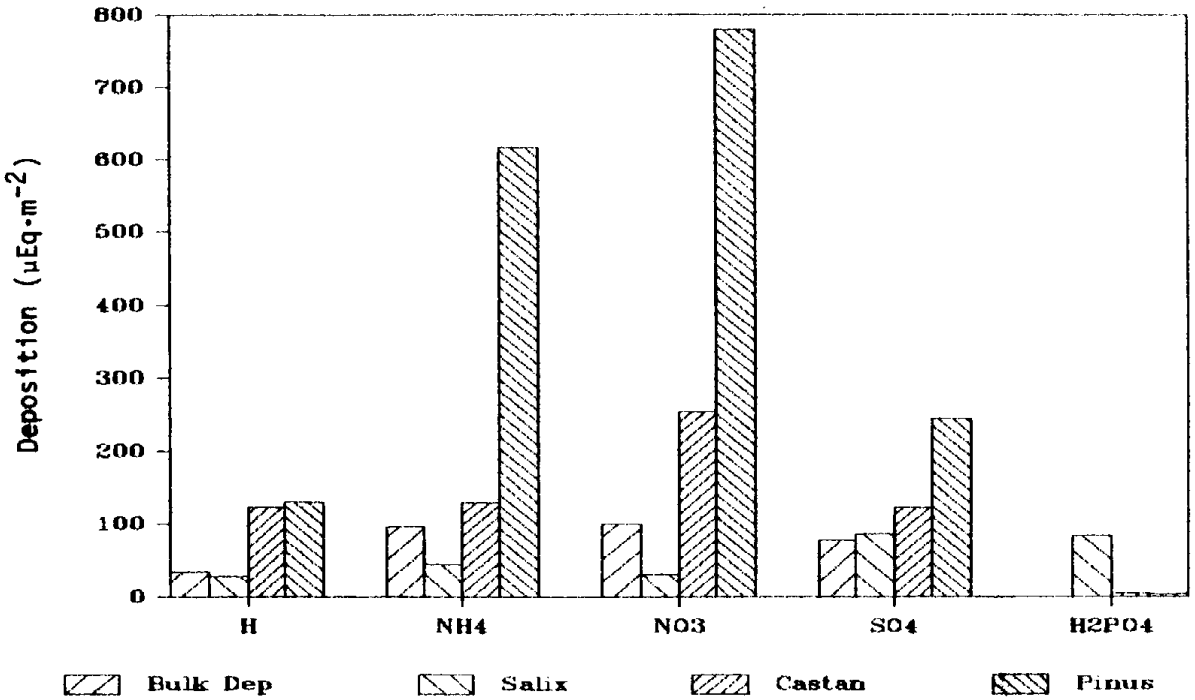

Fig. 9. Nutrient N, S, P and H^+ deposition and throughfall under Salix, Castanopsis, and Pinus species during four precipitation events at ELW in the 1985 season.

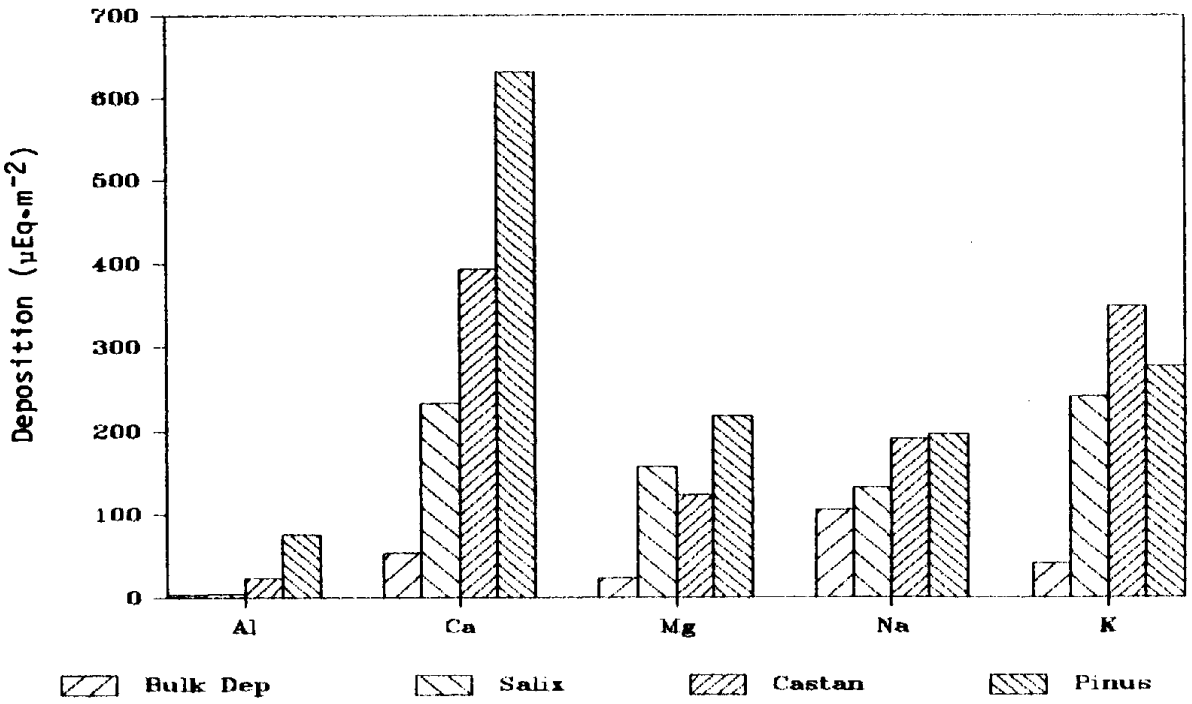

Fig. 10. Cation deposition and throughfall under Salix, Castanopsis, and Pinus species during four precipitation events at ELW in the 1985 season.

K^+, (Fig. 10) and PO_4^{3-}-P (Fig. 9) than bulk deposition. In addition, canopy exchange in Salix seems to have consumed NH_4^+-N and NO_3^--N while producing PO_4^{3-}-P. This may indicate that the Salix is preferentially absorbing N over P deposited on its leaves. If denitrification is taking place in the wet meadows where Salix grows, N may be lost from the soil before the plants have access to it. Thus, Salix may be satisfying its N requirement through foliar absorption.

Means of the 6 replications for throughfall cations and anions and 18 replications of the bulk deposition appear in Table 9 with standard error values. A charge balance (obtained by adding umoles·m^{-2} of anions and subtracting cations) indicates a net deficiency of anions (Table 9). The discrepancy may in part be due to functional groups on the dissolved organic matter. Organic C levels and functional groups are shown in Table 10. Depending on the pH of the solution, these functional groups will hydrolyze (release H^+ into solution) resulting in a negative charge on the organic particle. The characterization of the acidic components of throughfall organics is discussed further in Part VIII.

Data from the Mt. Moosilauke region in central New Hampshire have shown that differences in bulk throughfall chemistries under different canopy types are due to differences in the amounts of base cations and weak organic acids leached from leaves (Cronan and Reiners, 1983). Throughfall from a coniferous forest was found to exhibit a lower pH and higher organic anion content relative to hardwood (deciduous) forest and bulk precipitation. Bulk precipitation pH was 4.06, under the coniferous forest, 4.00, and under the hardwoods, 4.23. The same pattern is evident in ELW throughfall samples. The increased acidity of the coniferous throughfall relative to bulk precipitation may be due, in part, to the increased efficiency of evergreen leaves (needles) for scavenging dry deposition compared with bulk collectors (Lindberg et al., 1986). Sulfate deposition data (Table 9) confirm this, assuming no SO_4^{2-} is leached from the plant. Based on the net anion deficits for the ELW throughfall, a considerable portion of the acidity in throughfall must be associated with leaching of weak acids from leaves.

Table 9. Means and standard errors of cations, anions, and SiO_4 for throughfall collected after 4 precipitation events in 1985.

	Bulk deposition	Salix	Castanopsis	Pinus
	- - - - - - - - - - -µmoles·m^{-2}- - - - - - - - - - -			
Cations				
Al^{3+}	1.10±0.33	1.41±0.77	7.64±4.71	25.3±7.88
Fe^{2+}	0.24±0.05	0.32±0.14	3.94±1.22	5.08±1.79
Ca^{2+}	26.3±2.87	116±38.9	197±65.8	316±80.0
Mg^{2+}	11.6±2.52	78.9±26.8	61.5±25.2	109±30.9
Na^{+}	106±10.9	132±43.3	190±49.9	196±40.2
K^{+}	40.8±3.89	241±80.3	349±143	277±80.9
H^{+}	33.6±5.19	28.0±16.4	123±29.9	131±47.2
NH^{4+}	96.5±8.88	44.6±17.5	130±36.9	616±232
Anions				
F^{-}	8.26±5.42	12.3±5.43	113±24.5	70.7±18.7
Cl^{-}	58.9±17.3	126±46.5	142±50.6	100±31.1
NO_3^{-}	100±10.2	30.0±17.2	254±120	779±278
SO_4^{2-}	38.5±3.60	50.0±11.4	61.8±21.3	122±37.3
$H_2PO_4^{-}$	863±83.8	10.3±3.60	15.1±6.50	12.0±3.96
HCO_3^{-}	66.0±61.6	500±224	0±0	16.9±13.8
SiO_4	16.9±6.21	44.8±20.5	24.4±9.9	115±40.4
Charge balance				
Cations	357	841	1340	2160
Anions	245	400	650	1420
Net charge	-112	-441	-690	-740

Table 10. Means and standard errors of organic carbon and acid components of throughfall collected after four precipitation events in 1985.

	Bulk Deposition	Salix	Castanopsis	Pinus
	- - - - - - - - - - $\mu g \cdot m^{-2}$ - - - - - - - - - -			
Organic C	8.49 ± 1.01	69.3 ± 28.0	201 ± 61.0	199 ± 58.7
	- - - - - - - - - $\mu moles \cdot m^{-2}$ - - - - - - - - -			
Organic acids				
QP1 (carboxyl)	354 ± 41.9	59.7 ± 24.1	441 ± 134	734 ± 216
QP2 (amine)	0	70.7 ± 28.6	165 ± 5.04	22.5 ± 6.63
QP3 (phenols	0	67.1 ± 27.1	225 ± 68.3	57.3 ± 16.84

Table 11. Air-dried weights of leaf litter present in litter bags placed under the respective vegetation of three species in the Emerald Lake Watershed. Means of 8 replications are shown with the associated s.e.

Plant	Original weight October 1984	Spring weight June 1985	Fall weight October 1985
Salix sp.	7.06 ± 0.01	3.74 ± 0.08	3.93 ± 0.05
Castanopsis sempervirens	7.04 ± 0.01	5.59 ± 0.05	5.37 ± 0.07
Pinus monticola	7.17 ± 0.01	5.45 ± 0.11	5.23 ± 0.10

B. LITTER COLLECTION AND DECOMPOSITION

Methods

Litter from 3 tree and shrub species was selected for detailed laboratory analysis and manipulative field experiments: Pinus monticola (western white pine), Salix sp. (willow) and Castanopsis sempervirens (Chinquapin). Leaf litter decomposition studies for these 3 species were initiated in October, 1984.

Litter bags (15 x 15 cm) were constructed of nylon mesh screen. Leaf litter, collected by pulling senescent leaves or needles from branches, was placed in the bags and staked under the respective vegetation. Twice a year, 8 replicates of litter bags of each species are collected, dried and weighed to determine weight loss as a function of time. Sample collection will continue for 1 or 2 years. At that time, the collected samples will be ground and analyzed for total elemental content.

From preliminary results of this study, the wet meadow and the open subalpine forest vegetation plots were chosen for field studies. As part of its survey of the resources of Sequoia and Kings Canyon National Parks, the National Park Service (NPS) has established three 1-ha reference vegetation plots in ELW. These plots correspond to 3 different soil types and associated vegetation assemblages found in the watershed: wet meadow (Lithic Histic Cryaquept soil, Salix sp.), open subalpine forest (Typic Cryumbrept soil, Pinus monticola and Castanopsis sempervirens) and very sparsely vegetated alpine soils (Typic Cryorthent soil, Pinus sp. and forbs). To measure the accumulation of materials with respect to soil, litter screens were installed in September, 1985 to delineate areas and retain leaf litter for collection and analysis. The design used was similar to the one used in other areas in the park which will allow wider use of the data collected.

Leaf litter collected on each screen will be weighed for total biomass, sorted by species and reweighed. Acid digestion of the leaf litter in perchloric or sulfuric acid will be followed by measurement of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al^{3+}, Fe^{2+}) by standard flame emission (ICAP) methods and total N, P, and S by automated wet analysis

(Technicon AutoAnalyzer). By combining the litter biomass and analytical data, the flux of cations and elemental N, P and S to the soil surface will be calculated. These data can then be compared with similar data from other studies of atmospheric deposition and plant productivity.

Results and Discussion

After one year of litter bag collection, it appears that the Salix litter is decomposing more rapidly than the other species (Table 11). Nearly half of the Salix litter had disappeared in the first 8 months during the winter. Castanopsis and Pinus litter lost about 1/3 of their weights during the same 8-month period (Table 11). Very little change occurred in litter weights during the 4 months of summer, 1985. The same trend for more rapid litter decomposition under snow occurred at other study sites in the park (Tom Stolgren, NPS, personal communication). Bleak (1970) and Moore (1983) have both observed this phenomenon and suggest that freezing and thawing cycles, occurring before a permanent snowpack is established, physically break down the litter. Also, the constant temperature (above freezing) and high moisture content under the snowpack may be conducive to microbial decomposition processes. In contrast, Gosz, et al (1973) found that decomposition rates at Hubbard Brook Forest in New Hampshire were highest during the summer months. However, in that ecosystem, seasonal variations in temperature, moisture and length of time of snow cover are dramatically different than at ELW.

C. ACIDIC CHARACTERISTICS OF LEAF LITTER LEACHATES AND THROUGHFALL

Methods

Leaf litter of Castanopsis, Pinus and Salix from ELW were dried at 65°C, ground and extracted for 24 hours in distilled water (4 g per 100 mL). The leaf litter extracts were filtered promptly and subsamples were preserved by each of three methods: (1) samples for total elemental analysis and carboxyl contents were frozen; (2) samples for long-term reference and storage were freeze-dried; and (3) samples for the determination of acidity functions were preserved by

addition of 0.01% sodium azide and refrigeration under N_2 gas.

Dissolved organic C in the leaf litter extracts was determined by an automated persulfate-UV oxidation method. The EC and pH values of the extracts were determined using standard methods. Total elemental contents were determined for the extracts without any further preparation using ICAP emission spectroscopy. The carboxyl contents of the leaf litter extracts were determined using the modified Ca acetate method (Holtzclaw and Sposito, 1979). Total acidity and the proton formation function curve were determined by the constant concentration (of organic matter) back-titration (HCl) method (Sposito and Holtzclaw, 1977; Sposito et al., 1977; and Blaser et al., 1984). Precautions were taken to avoid contamination of the titration solution with CO_2 from the atmosphere and to maintain a constant ionic strength of 0.1 mole $(KCl) \cdot L^{-1}$. Several soils from the ELW were extracted and characterized in a manner similar to the leaf litter samples. Carboxyl contents were not determined.

The quasi-particle model of the proton formation function was assumed (Sposito et al., 1977) and the computer program FITEQL was used to calculate the conditional (ionic strength-dependent) dissociation constants and total concentrations of the three apparent functional group classes (Westall, 1982). Class 1 represents carboxylic acids, Class 2 represents weak carboxylic acid and amino functional groups, and Class 3 represents phenolic functional groups.

Results and Discussion

The pH values of soil extracts (Table 12) were generally higher than pH values of leaf litter extracts (Table 13). Except for the Pachic Cryumbrept soil extract, pH values were all lower than 5.6, the pH value expected for distilled water at equilibrium with atmospheric CO_2 (Stumm and Morgan, 1981). (These values are higher than those shown in Table 1, due to method of extraction.) The EC values and ionic strengths of soil extracts were lower than those of the leaf

Table 12. Soil extract data.

Soil Extract	pH	EC	Freeze-dry wt. (%)	Approximate Total Acidity
		($dS \cdot m^{-1}$)	($g \cdot L^{-1}$)	$mol(H^+) \cdot kg^{-1}$
Lithic Cryumbrept	4.91	0.0812	M†	M
Entic Cryumbrept	5.65	0.103	0.645	2.5
Typic Cryorthent	5.31	0.0328	0.307	M
Lithic Histic Cryaquept	4.65	0.127	0.839	3

† "M" denotes no data available.

Table 13. Leaf litter extract data.

Leaf Litter	pH	EC	Freeze-dry wt. (%)	Carboxyl Content	95% Confidence interval	Total Acidity
		($dS \cdot m^{-1}$)	($g \cdot L^{-1}$)	($mol(-) \cdot kg^{-1}$)		$mol(H^+) \cdot kg^{-1}$
Pinus	4.29	0.42	3.97	1.72	± 0.05	4.1
Castanopsis	4.11	0.558	6.49	1.02	± 0.13	4.1
Salix	5.06	1.03	8.68	0.38	± 0.10	2.9

litter extracts.

Calcium and Mg concentrations of leaf litter extracts appeared to be related to extract pH (Table 14). Higher Al concentrations were found in the Pinus extract than in the Castanopsis or Salix extracts. The carboxyl contents of the extracts were found to be on the order of 1 $mol(H^+) \cdot kg^{-1}$ for the leaf litter extracts (Table 13).

The carboxyl content of 1 $mol(H^+) \cdot kg^{-1}$ for these leaf litter extracts was an order of magnitude lower than the value reported for an average carboxyl content for organic matter in surface waters by Oliver et al. (1983). The titration data for the soil extracts may have been confounded by simultaneous titration of organic acids, carbonic alkalinity and other associated inorganic ions. Minimal pretreatment of samples also prevented loss and degradation of material (which would increase carboxyl content as well). The data of Oliver et al. (1983) were based on samples subjected to pretreatment with H^+-saturated resin to concentrate and purify them. Carboxyl contents were obtained by direct titration to an operationally-defined endpoint of pH 7.

The proton formation functions were determined after correction for a KCl blank. The result is a relation between the concentration of H^+ bound to dissolved organic matter and the pH of the solution (Fig. 11). Based on the distribution of functional group classes (1nH, 2nH, 3nH) the Pinus leaf litter has the highest Class 1 (carboxlylic acid) content of the three types (Table 15). The dissociation constant for the Pinus leaf litter extract is, however, smaller than that of Castanopsis, therefore the pH of the Pinus extract is higher (Table 13). Salix extract had the lowest class 1 and highest class 2 acid contents, thus had the highest pH.

These functional group classes were used to predict organic acid contents in throughfall based on DOC concentrations. The total deposition of organic acids in throughfall during four precipitation events is shown in Table 10. Castanopsis and Pinus throughfall are shown to contribute large quantities of class 1 (carboxlylic) acids. These large quantities of acids are responsible for the charge deficit demonstrated for inorganic anions in throughfall (Table 9).

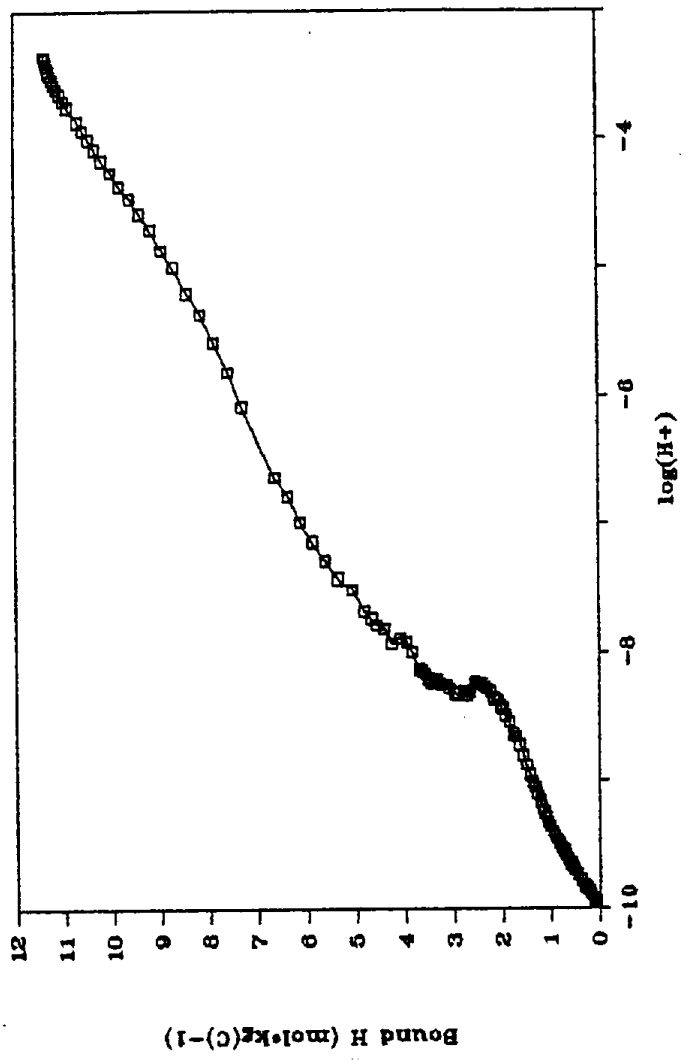

Fig. 11. Sample proton formation function for Castanopsis sempervirens leaf litter extract.

Table 14. Total elemental analysis of leaf litter extracts by ICP.

Element	Pinus	Castanopsis	Salix
	(mmol.kg^{-1})		
Ca	84.21	108.8	298.9
Mg	154.4	77.32	122.2
Na	20.17	249.8	9.627
K	405.8	227.4	660.0
Fe	0.171	0.304	0.115
Mn	19.85	22.24	9.562
Cu	0.108	0.082	0.059
Zn	0.787	0.348	1.168
Al	26.71	2.333	1.365
P	163.3	44.59	44.95
Si	1.085	2.315	2.670
B	0.412	3.674	7.340
Ba	0.052	0.059	0.046
Sr	0.088	0.131	0.406
Ti	0.016	0.010	0.002
Cd	0	0	0.001
Pb	0.070	0.046	0.006
Mo	0.010	0	0.003
Ni	0.099	0.030	0.037
Co	0.015	0	0.016
Cr	0.035	0.002	0.008
Sb	0.121	0.031	0.031

Table 15. Leaf litter extract acidic functional group classes [0.1 mol (KCl)·L^{-1}]

	$^{1}n_H$	$^{2}n_H$	$^{3}n_H$
Pinus	3.68 ± 0.11	0.113	0.287
Castanopsis	2.20 ± 0.28	0.821 ± 1.957	1.12 ± 0.61
Salix	0.862 ± 0.227	1.02 ± 1.09	0.968 ± 0.822

Table 16. Leaf litter extract conditional dissociation constants.

	0.1_{K_1}	0.1_{K_2}	0.1_{K_3}
Pinus	7.76×10^{-5}	9.33×10^{-8}	1.17×10^{-9}
Castanopsis	$1.60 \pm 3.70 \times 10^{-4}$	$1.59 \pm 2.53 \times 10^{-7}$	$3.59 \pm 9.88 \times 10^{-9}$
Salix	$1.39 \pm 0.86 \times 10^{-4}$	$2.64 \pm 2.25 \times 10^{-7}$	$8.52 \pm 9.19 \times 10^{-9}$