D. NITROGEN AND SULFUR MINERALIZATION

Methods

Potentially mineralizable nitrogen (PMN) (Stanford and Smith, 1972) was determined by placing 50 g of air-dried soil (30 g for the Lithic Histic Cryaquept) mixed with 20% by weight of 2 mm plastic beads (to improve hydraulic conductivity) in 60 mL disposable plastic syringe jackets. Blanks were also included which consisted of 10 g of plastic beads. Prior to incubation and on a two-week schedule, the soils and blanks were leached with 100 mL of 0.01 M KCl, followed by 25 mL of a nutrient solution containing no N. Extracts were analyzed for NH_4^+-N and NO_3^--N.

To assess effects of ambient levels of acidic deposition on the N and S mineralization process, the above procedure was repeated for surface soils. Instead of nutrient solution, the soils were leached with 25 mL of treatment solution. The treatments were: CK (check, 0.01 M KCl); HCl (0.01 1M HCl) and $NS_{.5}$, NS_1, and $NS_{1.5}$ (0.01 M KCl with molar ratios of HNO_3:H_2SO_4 of 0.5, 1.0, 1.5, respectively). The pH of the solutions HCl, $NS_{.5}$, NS_1, and $NS_{1.5}$ were all 4.75 (mean annual pH of incoming precipitation) (Lawson and Wendt, 1982) while the pH of CK was 5.4 (the approximate pH of rain in a nonpolluted atmosphere) (Tabatabai, 1985). The 25 mL of acid solution added on a biweekly basis for 16 weeks corresponds to about one-third of the annual precipitation (Lawson and Wendt, 1982). The soils were incubated at 35°C for 16 weeks and the water content was maintained gravimetrically at about 60% water filled pore space. Leaching was facilitated by the use of suction. Leachates were analyzed for NH_4^+-N, NO_3^--N, SO_4^{2-}-S. To determine net N and S mineralization in treatments $NS_{.5}$, NS_1, and $NS_{1.5}$, the quantities of NO_3^--N and SO_4^{2-}-S added in treatment solutions were subtracted from the extracted NO_3^--N and SO_4^{2-}-S values, respectively.

Ammonium-N and NO_3^--N in all extracts were determined by automated colorimetric indophenol blue and cadmium reduction techniques, respectively (Keeney and Nelson, 1982). Sulfate-S in extracts was determined by liquid chromatography.

The first order rate constant for N mineralization (k) was calculated from: $\log(N_0 - N_t) = N_0 - k(t)/2.303$ where N_0 = PMN, N_t = quantity of N mineralized, and t = time (Stanford and Smith, 1972).

To determine in situ N mineralization, a buried bag technique (Eno, 1960) was implemented for two consecutive 30-day periods in July and August. Simultaneously, a sucrose inversion technique (Lee, 1969) was used to determine an integrated temperature for these 30-day periods. When the soil pits were excavated, soil samples were taken to measure soil moisture content, NH_4^+-N, NO_3^--N, and SO_4^{2-}-S. Part of this sample was then placed into three plastic bags, sealed and returned to the soil pit for incubation. After 30 days the bags were removed and the contents were analyzed for moisture content, NH_4^+-N, NO_3^--N and SO_4^{2-}-S. Nitrification was calculated as the percent of the mineralized N (NO_3^- and NH_4^+) in the NO_3^--N form.

Results and Discussion

In laboratory incubations, all soils demonstrated a rapid initial release of N followed by a slower linear release of the mineralized N (Fig. 12). Potentially mineralizable N was very high for both the Lithic Histic Cryaquept of the inlet meadow and the Entic Cryumbrept of the joint northeast of the lake (Table 17). Nitrification varied from about 0 to 60% in the controlled laboratory experiment (Table 18). Values for in situ N mineralization were low or negative in many cases and thus nitrification was impossible to calculate for those cases. Nitrification values ranged from 7 to 100 % (Table 18). In all soils, S mineralization was essentially linear with respect to time of incubation (Fig. 13) as has been reported in past studies (Tabatabai and Al-Khafaji, 1980; Maynard et al., 1983).

Nitrogen and S mineralization decreased as a result of the acid additions during the laboratory incubation (Table 19). Nitrification was not affected by the acid additions (Table 19) indicating the presence of an active population of heterotrophic nitrifiers (common in forest soils) which are less sensitive to pH changes than their auto-

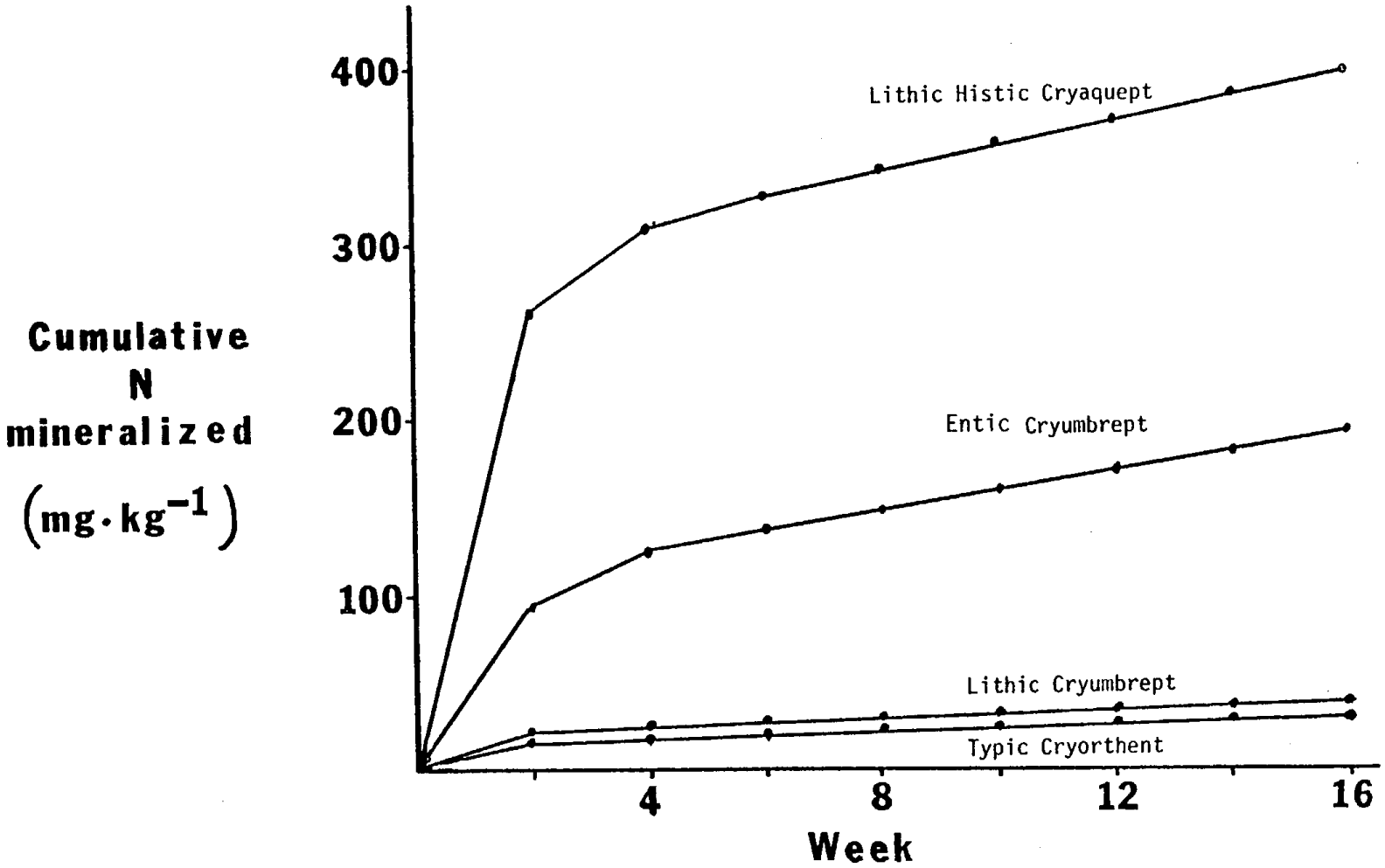

Fig. 12. Nitrogen mineralized during a 16 week laboratory incubation of soils from Emerald Lake Watershed.

Table 17. Potentially mineralizable N (PMN), S and k (1st order rate constant for N mineralization) determined from a 16-week incubation and quantities of N and S mineralized *in situ* in buried bags.

		N mineralized				S mineralized	
		Laboratory		In situ		Laboratory	In situ
Soil	Depth	k	PMN	July	August		July
	cm	wk^{-1}	- - - - - - - - - - - -			$mg \cdot kg^{-1}$	- - - - - - - -
Lithic	0-10	0.056	58	-0.64	0.33	3.71	-0.26
Cryumbrept	10-25	0.060	45	0.01	0.58	--	0.13
Typic	0-10	0.041	61	1.71	5.60	2.14	0.01
Cryorthent	10-45	--*	--	-0.55	-1.62	--	0.02
	45-68	--	--	0.13	-1.23	--	0.01
Lithic	0-15	0.055	478	-0.31	-6.77	29.17	-1.84
Histic	15-30	0.079	91	1.43	-1.48	--	-1.26
Cryaquept	30-45	0.120	52	-1.38	-1.88	--	-0.55
Entic	0-10	0.073	325	-1.08	-0.04	16.04	-0.13
Cryumbrept	10-28	0.066	135	1.66	-1.33	--	-0.01
	28-55	0.073	80	-0.46	1.67	--	0.01
	55-70	0.038	94	-0.20	-0.62	--	0.02

*Mineralization rates were too low for determination.

Table 18. Nitrogen mineralized during laboratory and field incubations, NO_3^- produced and nitrification rates for soils of Emerald Lake Watershed in 1985.

Soil	Depth	Laboratory			In situ (July 1985)			In situ (August 1985)		
		N min.	NO_3^-	Nitrification†	N min.	NO_3^-	Nitrification†	N min.	NO_3^-	Nitrification†
	cm	---mg•kg^{-1}---		%	---mg•kg^{-1}---		%	---mg•kg^{-1}---		%
Lithic	0-10	34.50	11.81	34	--*	--	--	0.33	0.33	100
Cryumbrept	10-25	27.91	17.08	61	--	--	--	0.58	--	--
Typic	0-10	29.50	12.27	42	1.71	1.23	72	5.60	4.13	74
Cryorthent	10-45	8.02	1.63	20	--	--	--	--	--	--
	45-68	2.07	0.66	32	--	--	--	--	--	--
Lithic	0-15	279.80	1.49	<1	--	--	--	--	--	--
Histic	15-30	65.40	0.96	1	1.43	0.56	39	--	--	--
Cryaquept	30-45	44.38	0.73	2	--	--	--	--	--	--
Entic	0-10	224.00	56.23	25	--	--	--	--	--	--
Cryumbrept	10-28	86.17	24.74	29	1.66	0.19	12	--	--	--
	28-55	55.24	5.63	10	--	--	--	1.67	0.12	7
	55-70	42.83	6.45	15	--	--	--	--	--	--

†Nitrification (%) = NO_3^- (mg•kg^{-1})÷N min(mg•kg^{-1})x100
*Values were negative or very low so net nitrification rates were impossible to determine.

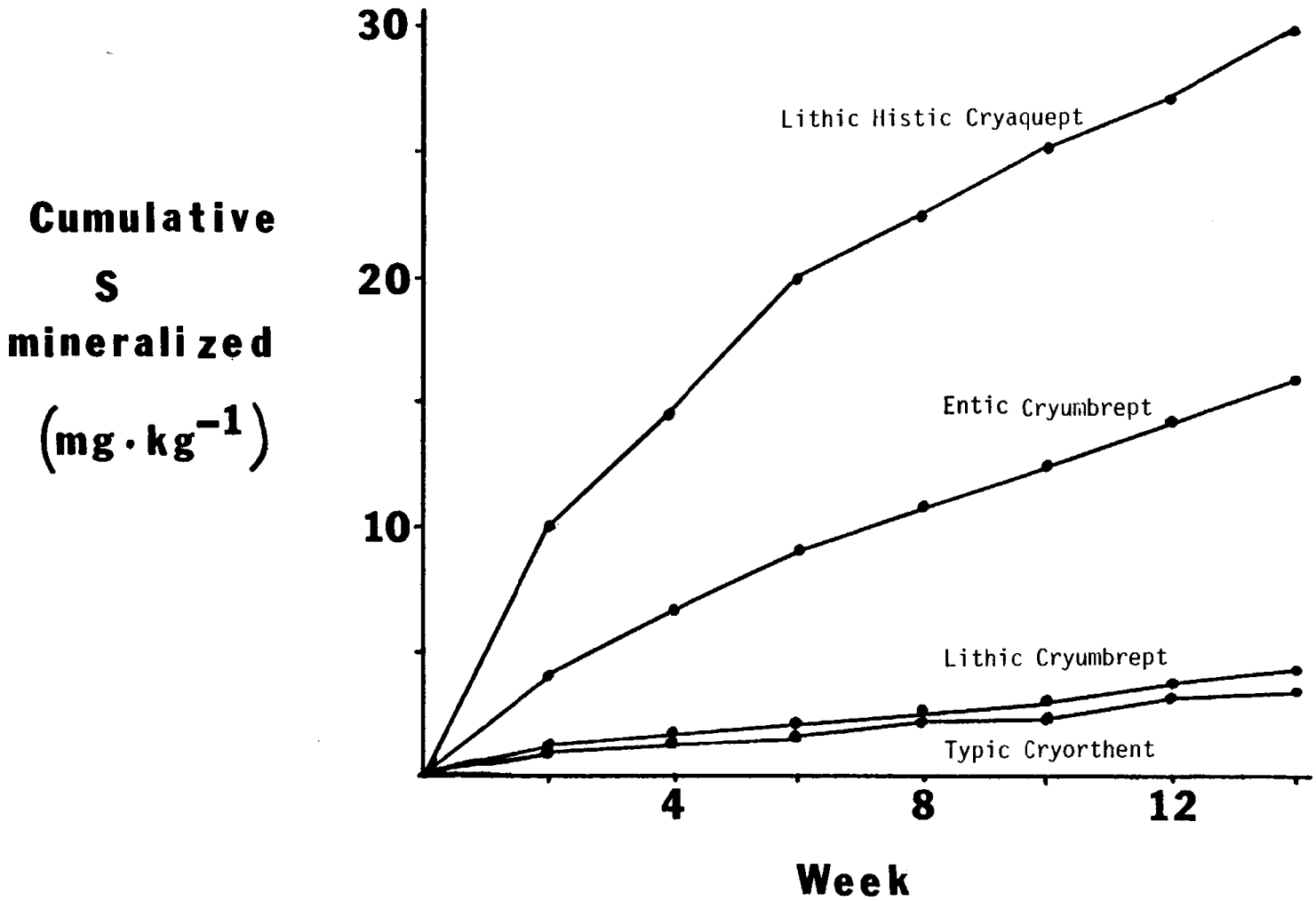

Fig. 13. Sulfate-S mineralized during a 16-week laboratory incubation of soils from Emerald Lake Watershed.

Table 19. Treatment means for potentially mineralizable N (PMN), k, nitrification, S mineralization and ratio of N/S mineralized after 16 weeks of incubation of Emerald Lake Watershed soils.

Treatment	PMN	k	Nitrification	Cumulative S Mineralized	Ratio of N to S Mineralized
	$mg \cdot kg^{-1}$	wk^{-1}	%	$mg \cdot kg^{-1}$	
CK	206	0.088	34	12.8	10.6
HCl	201	0.077	35	9.4	12.9
$NS_{.5}$	198	0.077	35	9.8	14.1
NS_{1}	191	0.093	30	10.0	13.7
$NS_{1.5}$	199	0.088	28	8.8	14.0
LSDα=.10	NS	NS	NS	1.20	NS
LSDα=.20	3.9	NS	NS	-	NS

trophic counterparts (Strayer et al., 1981). It is unlikely that the pH of the added acid solutions adversely affected the microbial population since the pH of the added solutions were all higher than the original soil pH (Table 1). The effect may have been caused by replacement of base cations on the soil or solubilization of organic components resulting in nutrient loss and limitations. The source of acid added had no effect on the mineralization of either N or S. There was no detectable interaction of organic C or total N with treatment.

Soil temperature data indicate that there was very little difference in soil temperature for the two consecutive 30-day in-situ incubations (Table 20). Also, as expected, soil temperatures decreased with increasing soil depth. Soil moisture contents were lower for the August sampling date than for the July date (Table 20), because of evapotranspiration.

A comparison of the laboratory and field techniques identified soil parameters important in the N and S mineralization processes (Table 21). Soil temperature and soil moisture were shown to be the major factors affecting S mineralization. In addition, N mineralization is dependent upon N and C substrate levels and k, the first order mineralization rate constant determined in the laboratory incubations (Table 21).

Because of the negative values obtained in the buried bag N mineralization study, PMN was poorly correlated with this technique (Table 17). These results indicate that processes other than N mineralization, such as the assimilation of N by soil microbes (immobilization), need more attention in future studies.

E. MEASUREMENT OF CONCENTRATIONS OF CARBON DIOXIDE IN SOIL-AIR AT ELW

Methods

Soil air sampling probes were made in spring, 1985 and installed at the four tension lysimeter sites in July. Duplicate probes were inserted in two horizons at each site. The probes, similar to those of Roulier et al. (1974), consist of a stainless steel inner tube sur-

Table 20. Integrated soil temperature determined by the sucrose inversion technique and soil moisture contents for buried bags in July and August, 1985, for 4 soils at the Emerald Lake Watershed.

Soil	Depth	Soil temperature July	Soil temperature August	Soil moisture July	Soil moisture August
	cm	- - -°C - - -		- - wt.% - -	
Lithic Cryumbrept	0-10	16.1	15.3	4.8	3.6
	10-25	15.3	14.5	2.1	1.8
Typic Cryorthent	0-10	14.4	14.7	17.2	10.6
	10-45	13.5	13.8	16.0	11.2
	45-68	12.1	12.9	13.0	11.6
Lithic Histic Cryaquept	0-15	12.1	11.9	90.0	90.1
	15-30	11.1	11.3	80.5	64.2
	30-45	9.8	10.4	46.4	44.5
Entic Cryumbrept	0-10	13.3	14.0	18.4	9.8
	10-28	12.2	13.7	20.6	13.9
	28-55	11.8	12.5	20.0	15.9
	55-70	11.7	11.8	20.7	15.6

Table 21. Regression coefficients, constants, multiple R and level of probability for N and S in-situ mineralization study in 1985.

	In situ mineralization			
	S	NH_4^+ and NO_3^-		
Parameters	July	July	August	July + August
Total soil N	--	0.0011	0.0022	-0.0022
Total soil C	--	--	-0.0005	-0.0001
PMN*	--	0.0213	-0.110	--
k**	--	--	-453	-143
Total N x k	--	-0.0127	0.156	0.0436
Soil temperature	-0.0987	--	1.16	0.182
Soil moisture	-0.0242	0.124	-0.0696	0.0779
Constant	1.65	-0.815	14.4	6.33
Multiple R (correlation coefficient)	0.9812	0.8403	0.9994	0.7427
Level of probability	0.0010	0.1295	0.0044	0.0653

*Potentially mineralizable N.

**First order rate constant for N mineralization.

--Term is not significant in stepwise regression.

Example: S mineralized <u>in situ</u>

= 1.65 - 0.0987 (soil temp) - 0.0242 (soil moisture)

rounded by an acrylic outer tube and tip (Fig. 14). Silicone septa are attached to the top of the tubes through which air samples are withdrawn with a syringe. The samples (approximately 5 cm^3) were collected in duplicate from each tube and stored in evacuated tubes (Vacutainer) for later determinations of CO_2 content by gas chromatography (Burford and Bremner, 1972).

Soil moisture contents were measured with porous cup tensiometers at the time of sampling of the soil air. Soil water samples were also obtained from tension lysimeters at the same site.

Results and Discussion

Soil air samples were collected biweekly; however, difficulties with clogging of the sampling probe with mud and water led to some sample losses and dilution with atmospheric CO_2. Results are shown in Table 22. The depth of maximum concentration changes during the season reflecting the balance between root and microbial respiration occurring in each horizon and diffusion of CO_2 up out of the soil. In the Typic Cryorthent in mid-July, higher concentrations of CO_2 at 50 cm indicate respiration exceeds diffusion rates while in mid-September, higher concentrations at 24 cm indicate the converse.

Solution pH can be calculated using thermodynamic data for the equilibrium speciation of aqueous CO_2 and carbonate, the pressure of CO_2 gas in equilibrium with the solution and the alkalinity (Stumm and Morgan, 1981). Such a calculation resulted in soil solution pH values quite different from those measured in the laboratory after solution CO_2 had equilibrated with the lab atmosphere. Due to the high percentage of CO_2 in the soil air, the calculated pH of the bench meadow soil solution in mid-summer was a full unit lower than the measured pH (Table 22). Wide fluctuations in soil pH due to respiration should be considered when evaluating the impact of acidic deposition.

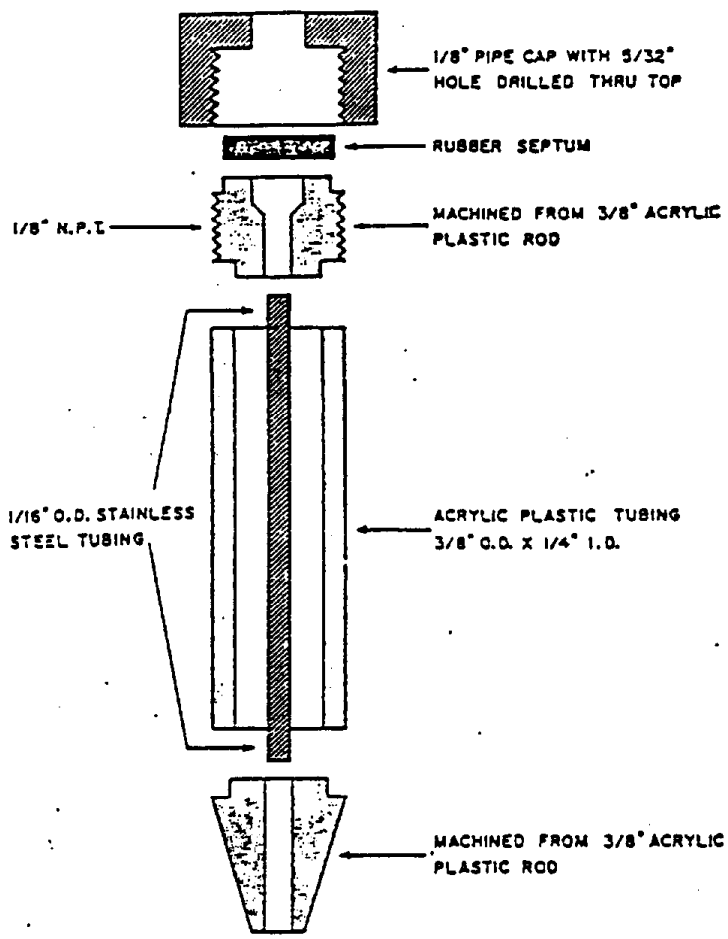

Fig. 14. Cutaway view and construction details of soil air sampling probe (Roulier et al., 1974).

Table 22. Partial pressure of CO_2 in soil air, alkalinity and pH for soil solutions collected in tension lysimeters in Emerald Lake Watershed.

Location	Depth	Soil Moisture Potential	Partial Pressure CO_2	ANC	pH	Calc. pH
	mm	bars	(%)	$\mu eq \cdot L^{-1}$		
Inlet Meadow						
July 12	200	-	--	40.6	5.46	--
	410	-	--	25.0	5.99	--
July 29	200	-0.106	0.175	53.2	5.85	6.28
	410	-0.109	0.098	45.9	6.12	6.46
Aug. 7	200	-0.174	--	-27.0	4.66	--
	410	-0.180	--	--	5.90	--
Aug. 25	200	-0.182	--	--	--	--
	410	-0.179	--	--	--	--
Sep. 18	200	-0.294	--	6.91	5.59	--
	410	-0.254	--	-7.81	5.13	--
Alta Cirque						
July 15	240	-0.155	0	0	4.83	--
	500	-0.165	--	--	--	--
July 25	240	-0.137	0.102	15.7	6.07	6.00
	500	-0.163	0.132	0	--	--
Aug. 8	240	-0.215	--	--	--	--
	500	-0.249	0.148	0	--	--
Sep. 18	240	-0.115	0.102	--	4.78	6.25
	500	-0.114	--	29.2	--	--
Bench Meadow						
July 25	150	-	0.187	54.9	6.22	6.26
	330	-	0.160	42.3	6.07	6.51
Aug. 2	150	-0.12	0.156	51.4	6.15	6.29
	330	-0.11	0.061	56.9	5.75	6.67
Aug. 10	150	-0.13	4.660	52.5	5.87	4.91
	330	-0.12	4.730	59.6	5.76	4.96
Aug. 22	150	-0.16	5.390	--	6.55	--
	330	-0.15	5.630	--	6.31	--
Sep. 18	150	-0.09	--	--	--	--
	330	-0.09	3.880	--	6.35	--

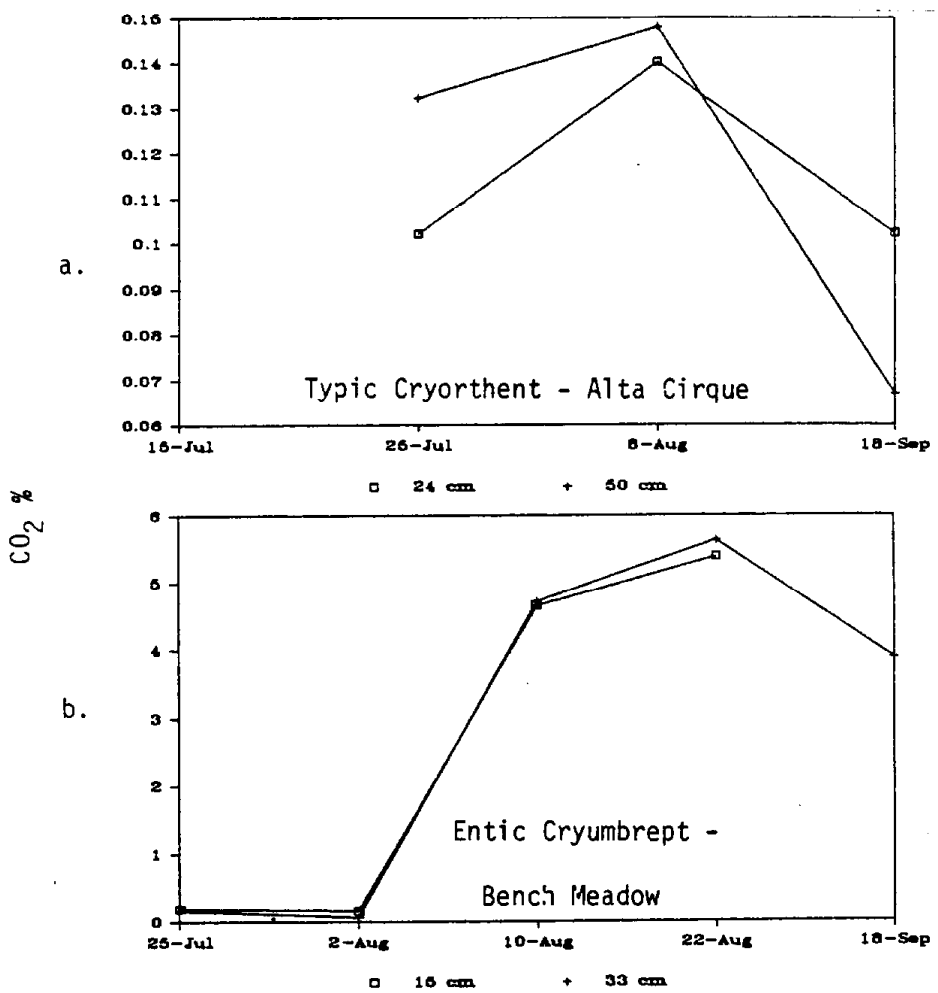

Fig. 15. Fluctuations in percent carbon dioxide in soil air at two depths in each of two soils at ELW in 1985.

PART III

INFLUENCE OF SOILS ON SURFACE WATER QUALITY

Recent research on the process of acidification of lakes under the influence of acidic deposition has resulted in the hypothesis that hydrologic flow paths through watersheds control the composition of surface waters (Chen, et al., 1984). A corollary to this hypothesis is that the residence time and depth of interaction of water with soil determines the extent to which acidic deposition may be neutralized. The effects of acidic deposition on soil solution and runoff have been modelled on this basis (Cosby, et al., 1985; Reuss and Johnson, 1985).

It is suggested that natural soil processes have an influence on the acidification of soil and drainage water that is comparable in magnitude to anthropogenic acidic deposition (van Breemen et al., 1984). Nitrate, SO_4^{2-}, CO_2 and organic acids arising from the decomposition of plant materials may determine the pH of the soil solution and solubility of minerals (Krug and Frink, 1983; Tabatabai, 1985; Magdoff and Bartlett, 1985). Soil processes which may influence surface water quality include the concentration of solutes through evapotranspiration, mineralization of soil N, adsorption of SO_4^{2-} on soil mineral surfaces and weathering of soil minerals producing dissolved Al and other cations.

One of the major soil forming processes, podzolization, involves two vertically separated processes in the soil column: mobilization and deposition (Jenne, 1980; Bloomfield 1953a, b, 1955). The mobilization process includes the dissolution and transport of Al, Si, and Fe from the surface horizons. Deposition of Al and Fe in the B horizon results in a spodic horizon rich in sesquioxides, while Si is transported out of the soil to surface waters (eg. Singer et al., 1978; Kennedy, 1971). It is possible that a perturbation of this natural process by acidic deposition may be contributing to increased concentrations of Al in lake waters (Nilsson and Bergkvist, 1983).

To assess the influence of soils on surface water quality at ELW direct measurements were made of soil solution and surface water composition at several sites.

A. IN SITU MEASUREMENT OF THE SOIL SOLUTION AT ELW

Methods

There are basically two types of sampling devices (lysimeters) for soil water. One type is a passive collector (zero tension) installed beneath an intact soil layer. Water is collected at the base of the lysimeter as it flows under the influence of gravity (Nilsson and Bergkvist, 1983). The second type of lysimeter (tension) is an active collector which exerts suction on the soil to withdraw water (Reikerk and Morris, 1983).

There are several difficulties in interpretation of results from soil water collectors. The zero-tension lysimeter collects only gravity flow occurring during or immediately following rain fall events and snow melt. The tension lysimeter collects water which is held in the soil by adsorptive and cohesive forces. The water sampled by the two types of lysimeters is, thus, physically different. The greater the suction exerted at the surface of the tension lysimeter plate, the greater the volume collected. Furthermore, tension lysimeters tend to have an indeterminate sampling zone which varies with the level of tension (potential) applied and time (van der Ploeg and Beese, 1977). Consequently, tension lysimeters provide larger sample volumes than zero-tension lysimeters at the expense of information on actual percolation rates.

Zero-tension lysimeters were constructed from two-liter polypropylene bottles and 100 mm polypropylene funnels. The funnels were filled with inert Teflon boiling chips and a PVC pipe inserted in the side of the bottle was used as a sampling port. Zero-tension lysimeters were buried in October, 1984 at two sites in ELW. One was located in the inlet meadow south of the lake (Lithic Histic Cryaquept) and the other at the bottom of the joint northeast of the lake (Entic Cryumbrept). These lysimeters were removed in September, 1985.

The tension lysimeter collectors consist of a 10 cm diameter base machined from solid, cylindrical PVC stock filled with a porous (35 um) polyethylene plate covered by a nylon reinforced filter membrane (0.2 um effective pore size Gelman Versapor) (Fig. 16). This membrane is rated for approximately -0.75 bars (or -11 psi) bubble pressure when moist, in excess of the -0.20 bars (-2.9 psi) vacuum used. The membrane is held over the polyethylene plate backing by a PVC ring machined to a tight fit around the PVC base. The tensiometer plate is connected to surface sample bottles via 3.18 mm (1/8 inch, outer diameter) teflon tubing. Polycarbonate collecting bottles (250 mL) are in the line between the lysimeter plates and the vacuum pump (Fig. 16). A manifold system connects four lysimeters to a single vacuum system and allows vacuum lines to be turned off individually. The vacuum system consists of a 12 V vacuum pump powered by a 90 amp-hour "deep cycle" battery which is continuously charged at a rate of about 0.5 amp·hr^{-1} by a 10 watt solar cell (Kyocera). The battery power is adequate to allow weekly sampling or other periodic use for 1 to 2 months without recharging. The vacuum is regulated at -0.20 bars (-2.9 psi) by a microswitch connected to an automobile vacuum advance unit (1956 Ford).

Tension lysimeters were installed in July, 1985 at each of four sites in representative soils. These sites are: (1) the wet inlet meadow south of the lake (Lithic Histic Cryaquept); (2) the pine stand at the top of the joint NE of the lake (Entic Cryumbrept); (3) on a bench east of the lake (Typic Cryumbrept); and (4) in the soil of the glacial moraine along the ridge east of the lake and below Alta Peak (Typic Cryorthent). Each of these soils have developed two or three distinct soil horizons which are sampled separately (in replicate) by lysimeter plates. Lysimeter sites are identified on the map in Fig. 17. These lysimeters were winterized and will remain in place for the winter of 1985-86.

Tensiometers were installed at each of the lysimeter sites to measure soil moisture tension in the range at which the lysimeters operate (0 to -0.8 bars). This provides a record of the physical state of the water when extracted and indicates when soil moisture is too low for the tension lysimeters to be effective. Soil air sampling tubes

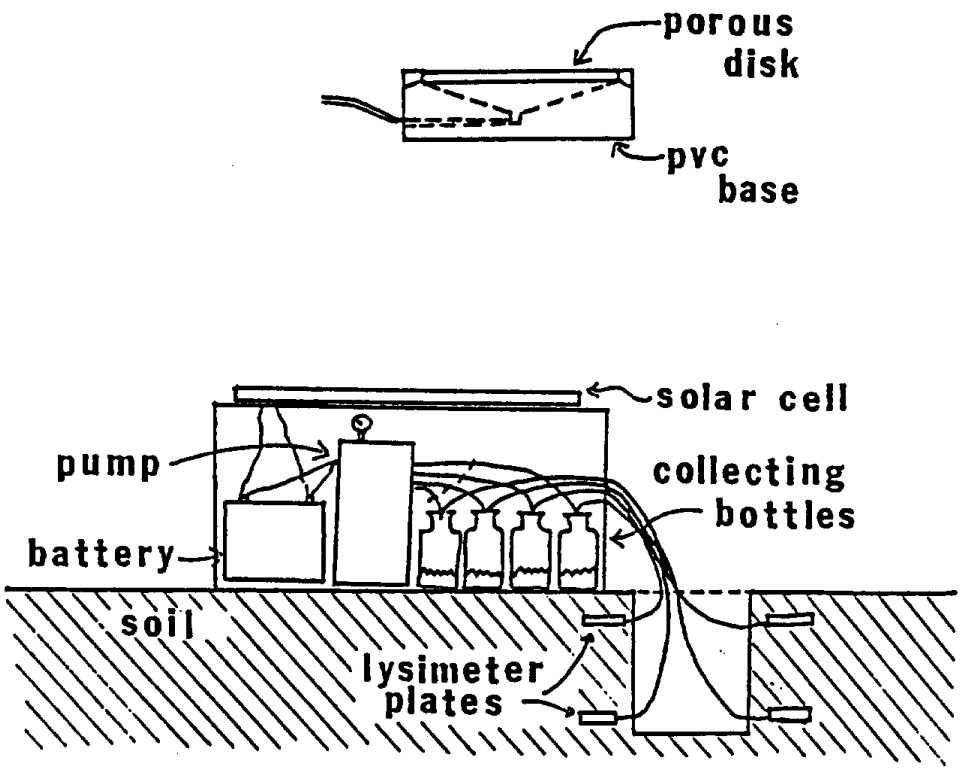

Fig. 16. Design of tension lysimeter collectors and vacuum pump apparatus.

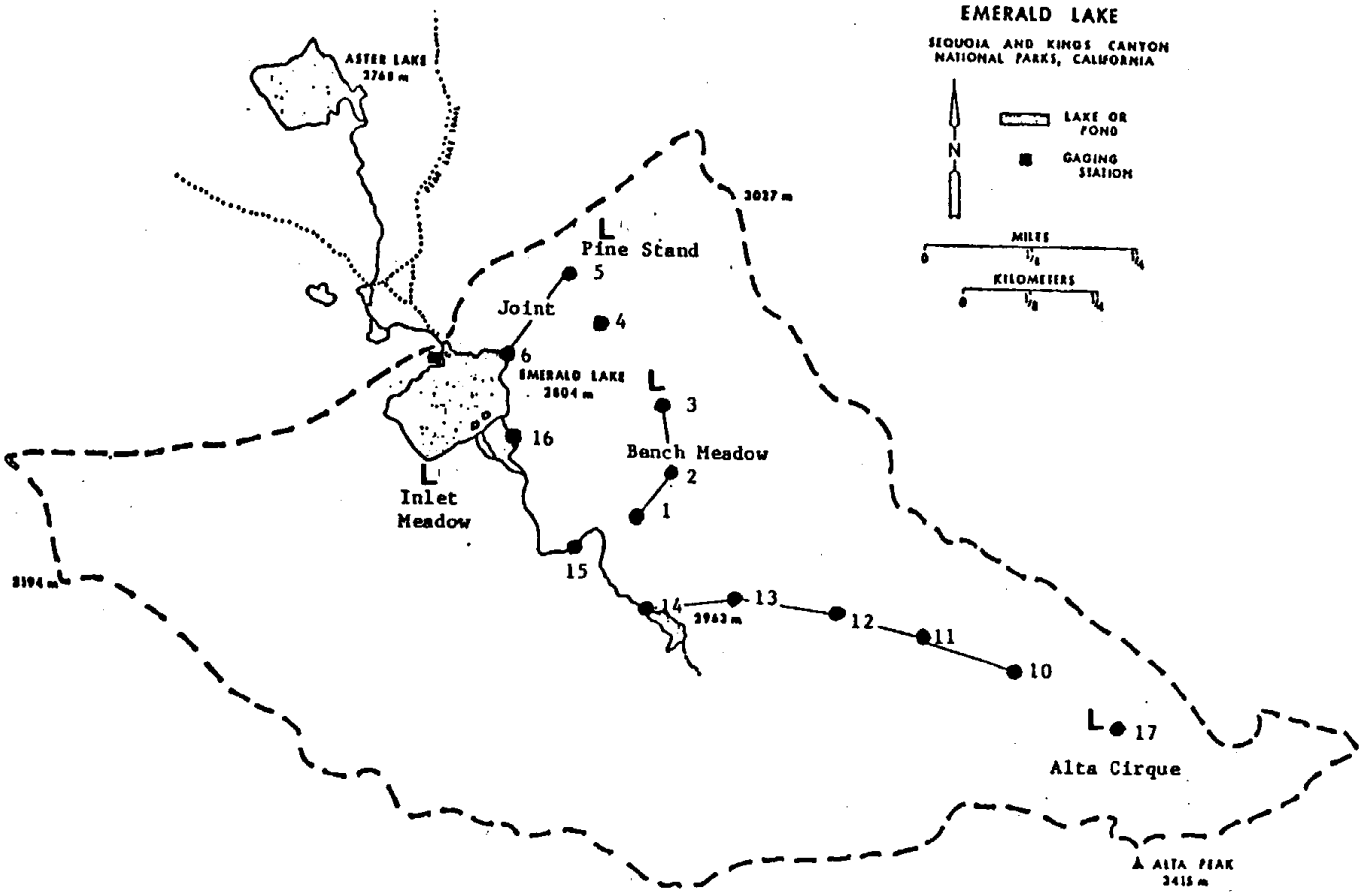

Fig. 17. Location of stream sites (solid circles) and lysimeter sites (L) sampled during 1985.

were also installed at the same sites to provide information for interpretation of solution analyses.

The tension lysimeters were activated manually only when there was sufficient moisture in the soil (greater than -0.20 bars tension). Usually 2 to 3 hours of operation was sufficient to obtain samples.

Anion analyses were performed by ion chromatography (Cl^-, SO_4^{2-}-S) and automated colorimetric analysis (NO_3^--N and F^-). Cation analyses were performed by AA spectrometry (Ca^{2+}, Mg^{2+}, Al^{3+}), emission spectrometry (Na^+, K^+) and automated colorimetric analyses (NH_4^+-N). Titrations for ANC were performed with dilute HCl under controlled conditions. Dissolved organic C was determined by an automated persulfate oxidation method.

Results and Discussion

Soil moisture potential in the inlet meadow decreased throughout the summer (Fig. 18a) as a result of evapotranspiration losses and was uniform with depth. Concentrations of Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+, NO_3^--N, and SiO4 in the inlet meadow all tended to increase during the season perhaps due to concentration by evaporative water loss (Table 23). Also, DOC in solution increased throughout the season until September when the concentration plummeted (Fig. 19a).

Soil moisture potential in Alta Cirque and the bench meadow reached a minimum in August and by September had reached a high point due to rains in mid-September (Figs. 18b and 18c). In Alta Cirque most elemental concentrations increased with time with the exception of Ca^{2+} and NO_3^--N (Table 23). Concentrations of Ca^{2+}, Mg^{2+} and Na^+ were higher in the lower soil depth than the upper.

In the bench meadow, concentrations of most elements tended to decrease with time except for Na^+, NO_3^--N and SO_4^{2-}-S. Aluminum, Ca^{2+} and Mg^{2+} concentrations were all higher in the lower soil depths whereas all other elemental concentrations decreased with depth. At the 33 cm soil depth, DOC was nearly uniform throughout the season (Fig. 19b). However, at the 15 cm depth, DOC was higher in late July and late August than in early August.

The role of dissolved organics in controlling Al solubility in the bench meadow soil is evident when the concentrations of Al at 15 and

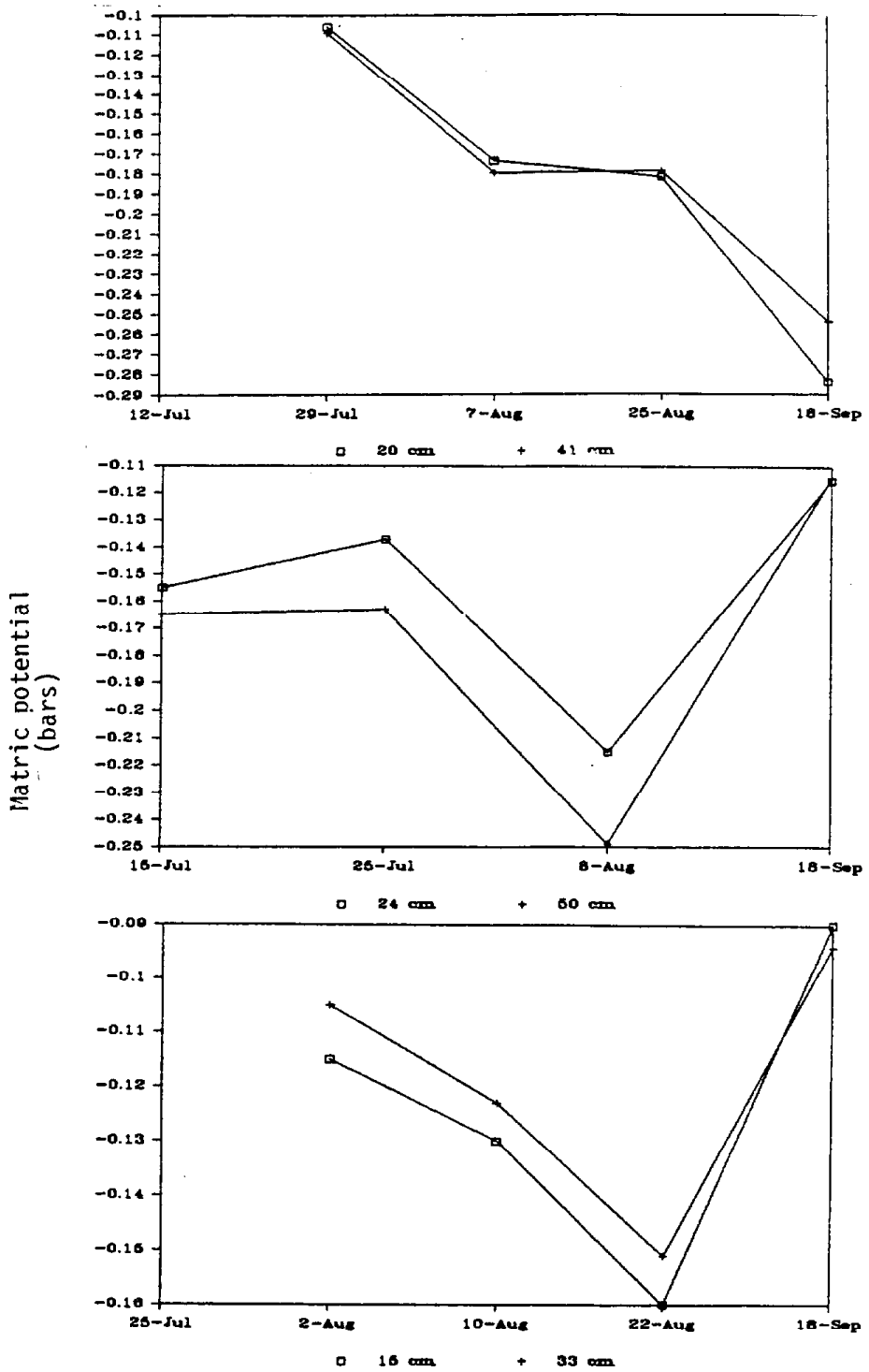

Fig. 18. Soil moisture potentials (in bars) measured at two depths during the 1985 season (a) the Emerald Lake inlet meadow lysimeter site (Histic Cryaquept), (b) Alta Cirque lysimeter site (Typic Cryorthent); and (c) bench meadow lysimeter site (Entic Cryumbrept).

Table 23. Elemental analysis of soil solution samples from tension lysimeters in 1985.

Location	Depth	Soil Moisture Potential	Al	Fe	Ca	Mg	Na	K	H^+	N NH_4^+	N NO_3^-	SO_4^{2-}	$H_2PO_4^-$	HCO_3^-	SiO_4
	mm	bars	- - -

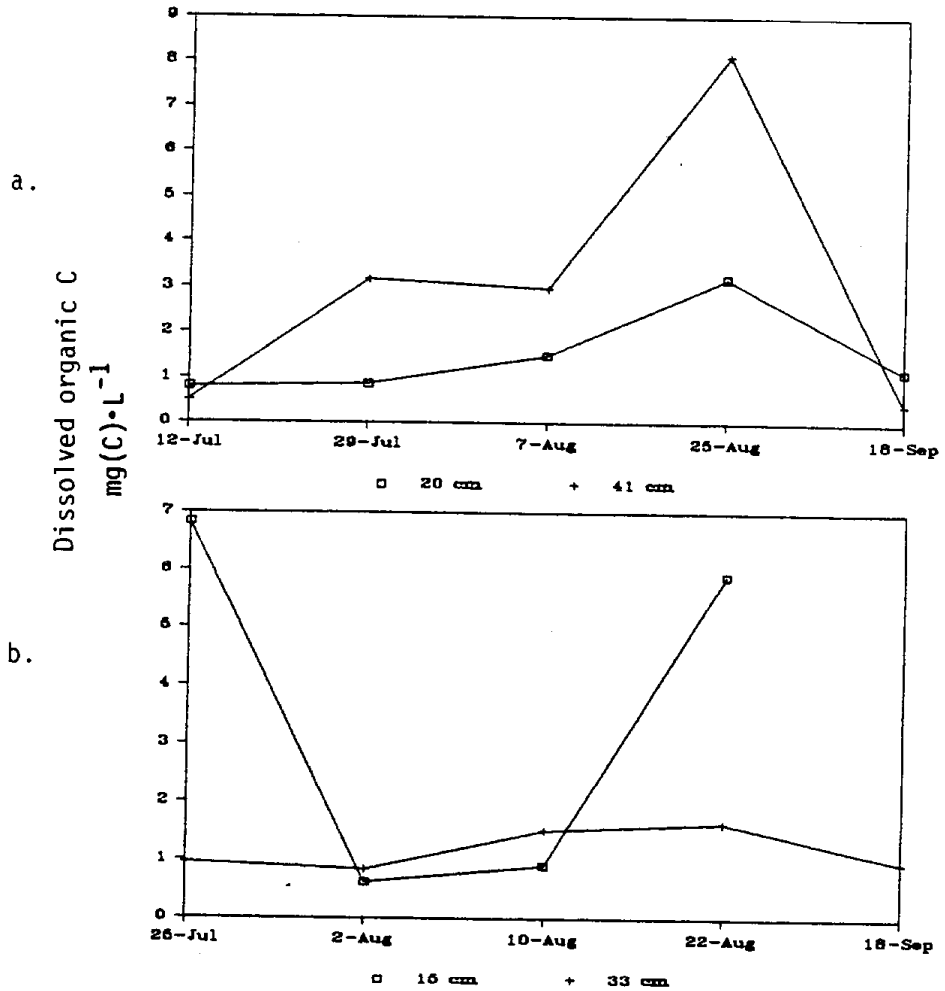

Fig. 19. Dissolved organic carbon concentrations in solution collected with tension lysimeters at two depths (a) the Emerald Lake inlet meadow (Histic Cryaquept); and (b) bench meadow site (Entic Cryumbrept).

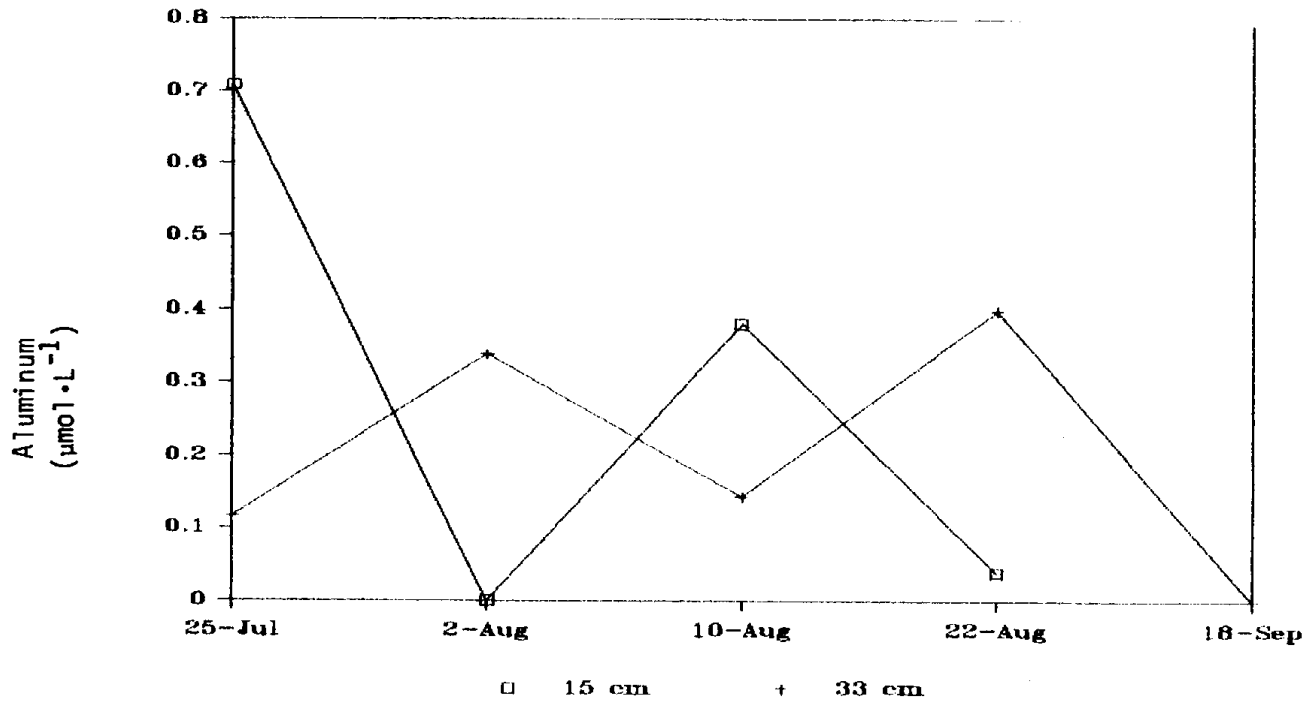

Fig. 20. Concentrations of Al in tension lysimeter samples from the bench meadow during the 1985 season.

33 cm are compared with DOC (Fig. 20). Equilibrium speciation calculations for soluble Al were performed using the computer model GEOCHEM (Sposito and Mattigod, 1979). Like the stream transect data, soluble Al was found to be in reasonable agreement with the predictions of gibbsite solubility. The mean concentration of Al in the bench meadow lysimeter solutions (0.23 $mmol \cdot m^{-3}$) was 47.5% in OH-complexes and the balance in excess of gibbsite solubility. The inlet meadow Al concentration (2.23 $mmol \cdot m^{-3}$) was 34.1% in OH-complexes and the balance in excess of gibbsite solubility. The excess is probably due to temperature variation and organic matter complexation of Al.

Nitrogen mineralization and NO_3^--N uptake are also demonstrated in the bench meadow samples. Nitrate uptake occurs during the months of July and early August when moisture potentials are optimum (Fig. 21a). Ammonium concentrations were highest in the surface horizon in early August and greatest in the deeper horizon in late August (Fig. 21b). This may follow a soil moisture regime.

The zero-tension lysimeters did not provide us with adequate data. The one placed in the fault did not collect any water due to dry soil conditions, whereas the one in the inlet meadow was completely submerged, thus making it inaccessible.

B. STREAM SAMPLING

Methods

A stream transect was chosen in April, 1985 and sampled regularly during the summer through September. The transect started in the cirque beneath Alta Peak and followed a continuous channel down to Emerald Lake. A second transect traversed a meadow on a bench east of the lake. Samples were also collected just below the *Pinus monticola* stand and at an inlet to the lake in the joint north of the lake. Transects are shown in Fig. 17.

Four aliquots were filtered with a Nucleopore polycarbonate membrane with a pore size of 0.4 um. These were stored in 50 mL polypropylene tubes for analysis of anions, cations and dissolved organic

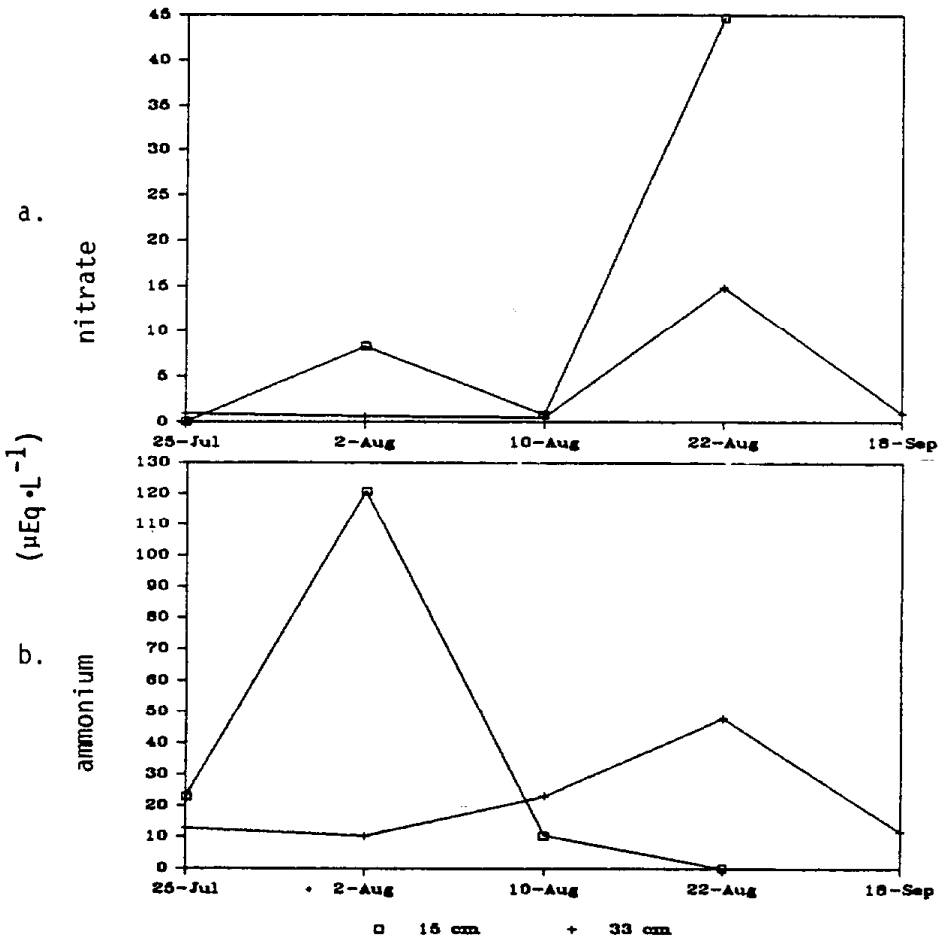

Fig. 21. Patterns of nitrogen-mineralization and uptake in the bench meadow soil (Entic Cryumbrept), 1985.

carbon. A fifth aliquot was filtered with Whatman GF/F glass fiber filters with an effective retention size of about 0.7 um. These aliquots were stored in 125 mL polyethylene bottles and used for ANC titrations and DOC determinations. All samples were refrigerated just above freezing until analyses were performed.

Results and Discussion

When the stream transects were first sampled extensively in May and June, 1985, water flow was continuous from below Alta Cirque (site 10) to the pond (site 14) and from the pond to the last sampling point just above the meadows (site 16) where several streams converge on the lake. Water was also flowing in the joint NE of the lake and on the bench east of the lake. Peak snowmelt runoff occurred during our sample collection in May (D. Marks, 1985, personal communication). As the snow melted, the channel flow in the joint ceased first, then in the main transect between the cirque and the pond.

The concentrations of dissolved substances in samples from each transect demonstrate that soil-stream interactions are occurring. The results of these interactions follow:

1. Ionic Strength: The effect of reduced stream flow and increased evaporation was to increase concentrations of dissolved substances. This is reflected in a general increase in ionic strength of the samples at all sites as the summer progressed. The soil interactions in the bench meadow and above the pond inlet caused dramatic increases in ionic strength (Figs. 22 and 23). Mixing with snowmelt from other sources apparently caused decreases in ionic strength downstream from the cirque.

Concentrations between the pond and the inlet meadow were similar on any given sample date indicating minimal soil-stream interactions. Since stream discharge was observed to be consistently higher along this reach small differences in concentration would result in large changes in loading (flux).

2. Nitrogen: The concentrations of NO_3^--N and NH_4^+-N in streamflow appear to be controlled by three processes: 1) plant and

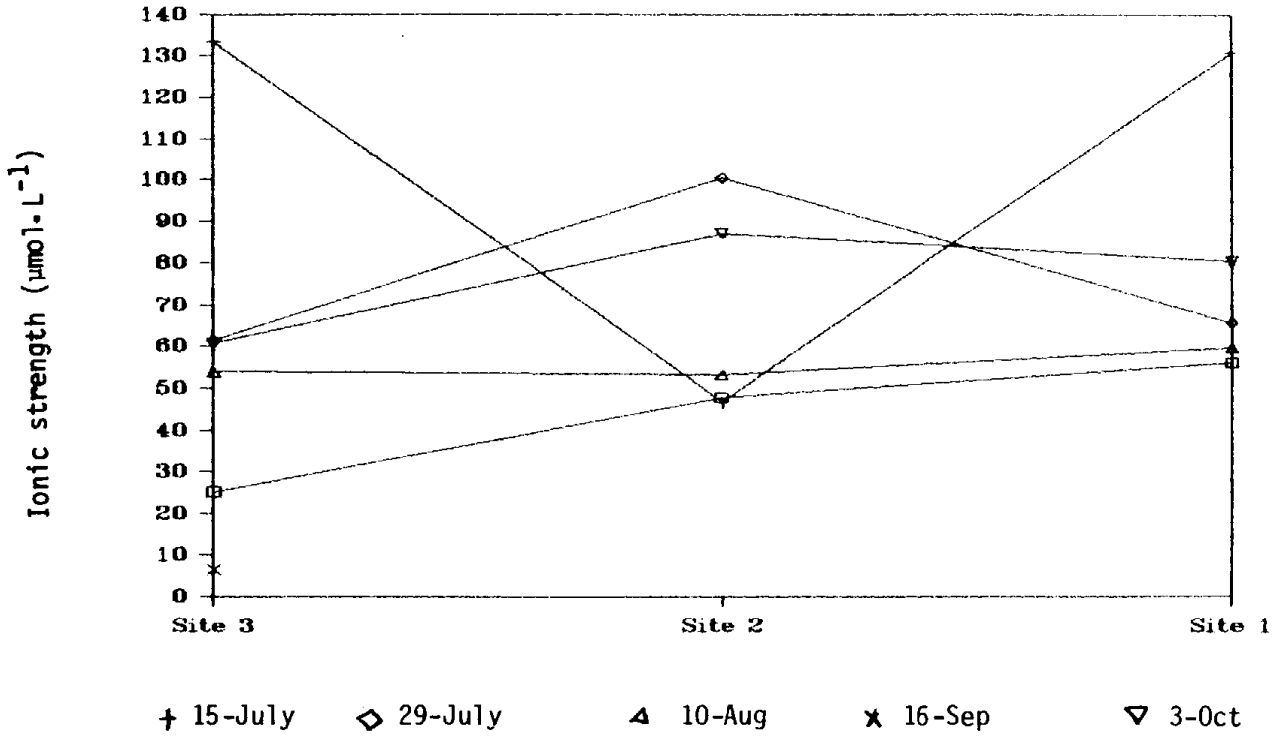

Fig. 22. Concentrations of dissolved salts for the bench meadow transect.

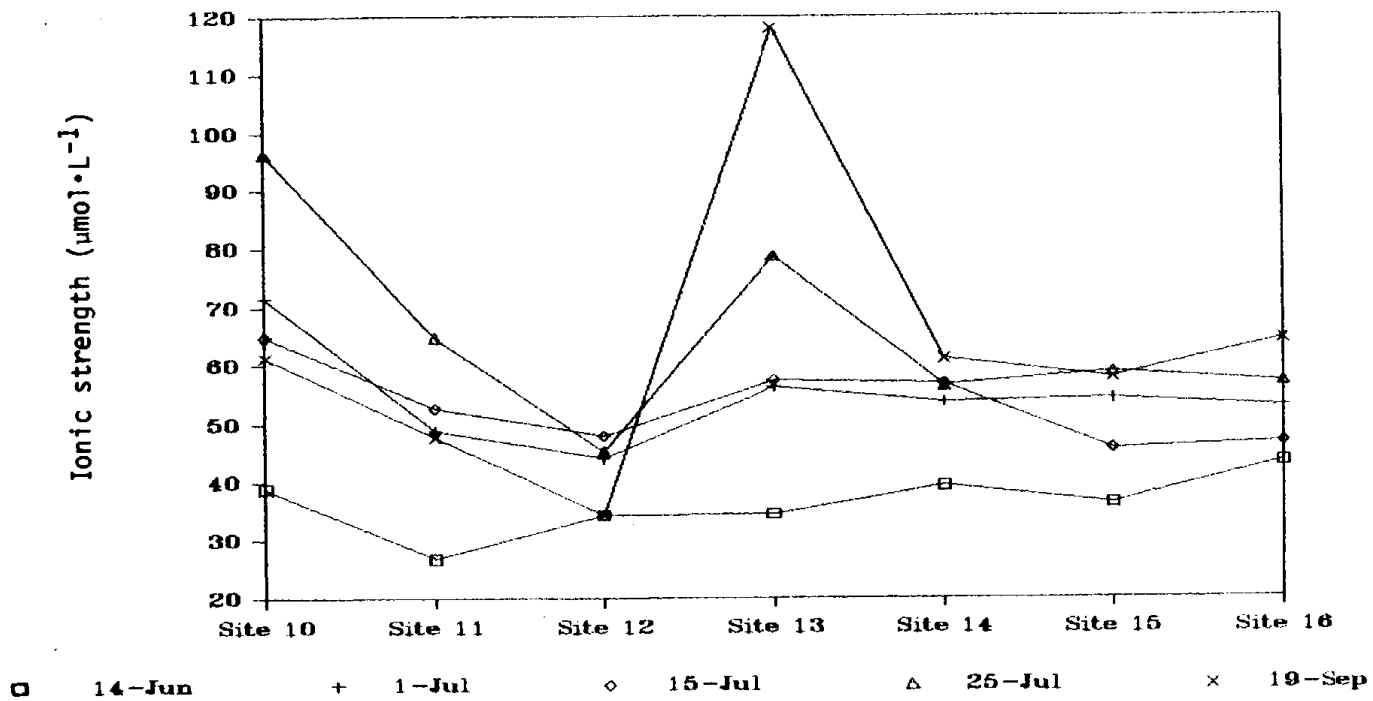

Fig. 23. Concentrations of dissolved salts for the main stream transect.

microbial uptake, 2) mineralization of organic N, and 3) snowmelt. The mean concentration of NO_3^--N for 1985 was highest in Alta Cirque and in the reach below the pond, a result of the length of time during which snowmelt influenced these sections (Fig. 24). In the middle reach, N-mineralization and NO_3^- uptake by the biota could explain the increase in ammonium concentrations and decrease in NO_3^--N concentration. The seasonality of these processes is shown in the mid-summer peaks in NH_4^+-N and spring and fall peaks in NO_3^--N at the sample sites below Alta Cirque (Fig. 25a) at the waterfall above the Emerald Lake inlet meadow (Fig. 25b) and at the bottom of the bench meadow (Fig. 25c). Rainfall in July preceded the peaks in NH_4^+-N concentrations below Alta Cirque and the bench meadow. Ammonium concentrations declined in August and September as the growing season came to an end. When the fall rain and snow began in September, NO_3^--N concentrations increased in the streamflow instead of NH_4^+-N.

Ammonium concentrations in the bench meadow decreased downstream for all but the samples collected during snowmelt (Fig. 26). Possibly, microbial activity or chemical adsorption by clay minerals and organic matter removed NH_4^+ from the streamflow.

Nitrate and NH_4^+-N always constituted a significant portion of the charge balance for ELW. Fluctuation in concentrations of these ions during the season caused high standard error reported in Table 24. Like Bickford Watershed, Massachusetts (Hemond and Eschleman, 1984), ELW appears to retain NO_3^- and NH_4^+. Nitrate retention at Bickford accounted for a significant portion of the acid neutralizing process.

3. Sulfate: Although the SO_4^{2-} adsorption capacity of ELW soils is low, some adsorption is apparently occurring. While total concentrations of dissolved salts appear to increase in the reach between the Saddle and the pond (Fig. 26) SO_4^{2-} concentrations tended to decrease or remain constant (Fig. 27a). This trend is also shown in the decrease in SO_4^{2-} concentrations down the bench meadow transect for all but spring melt conditions (Fig. 27b).

4. Mineral Weathering: On the average, stream concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ appeared to reflect the weathering patterns of

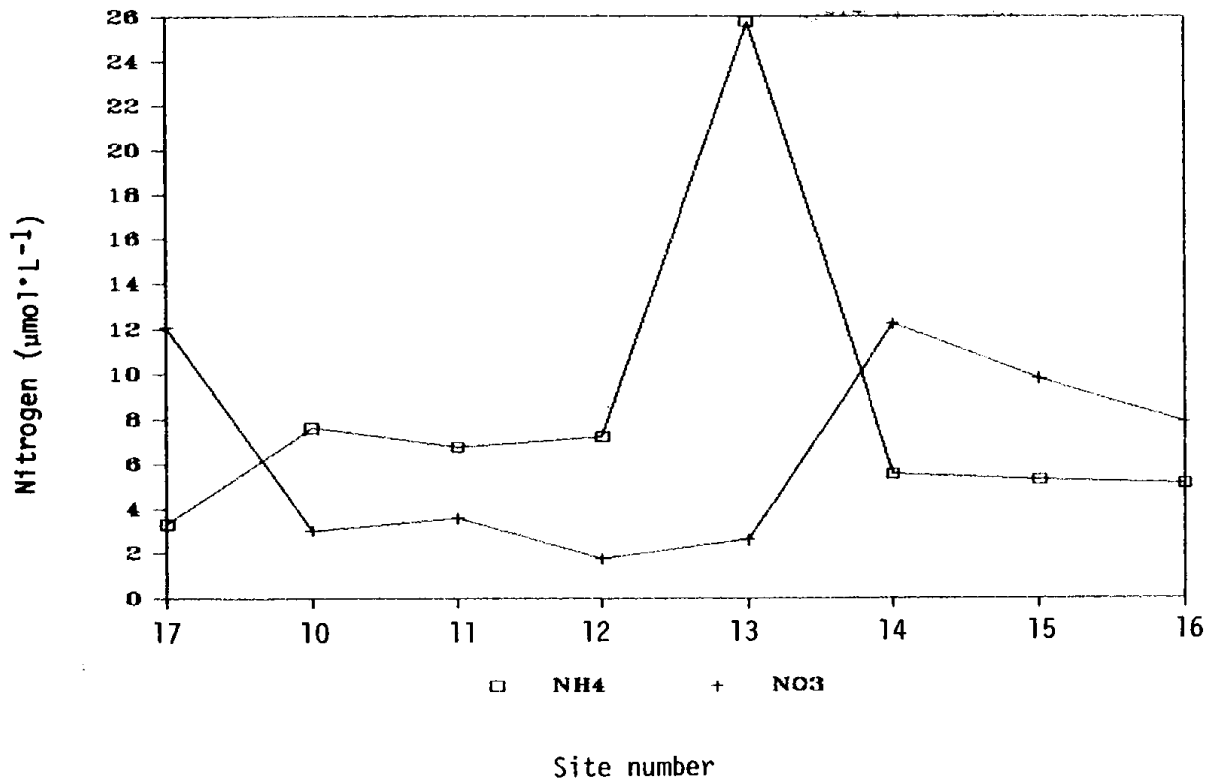

Fig. 24. Mean concentrations of nitrate and ammonia in the ELW main stream transect during the 1985 sample season.

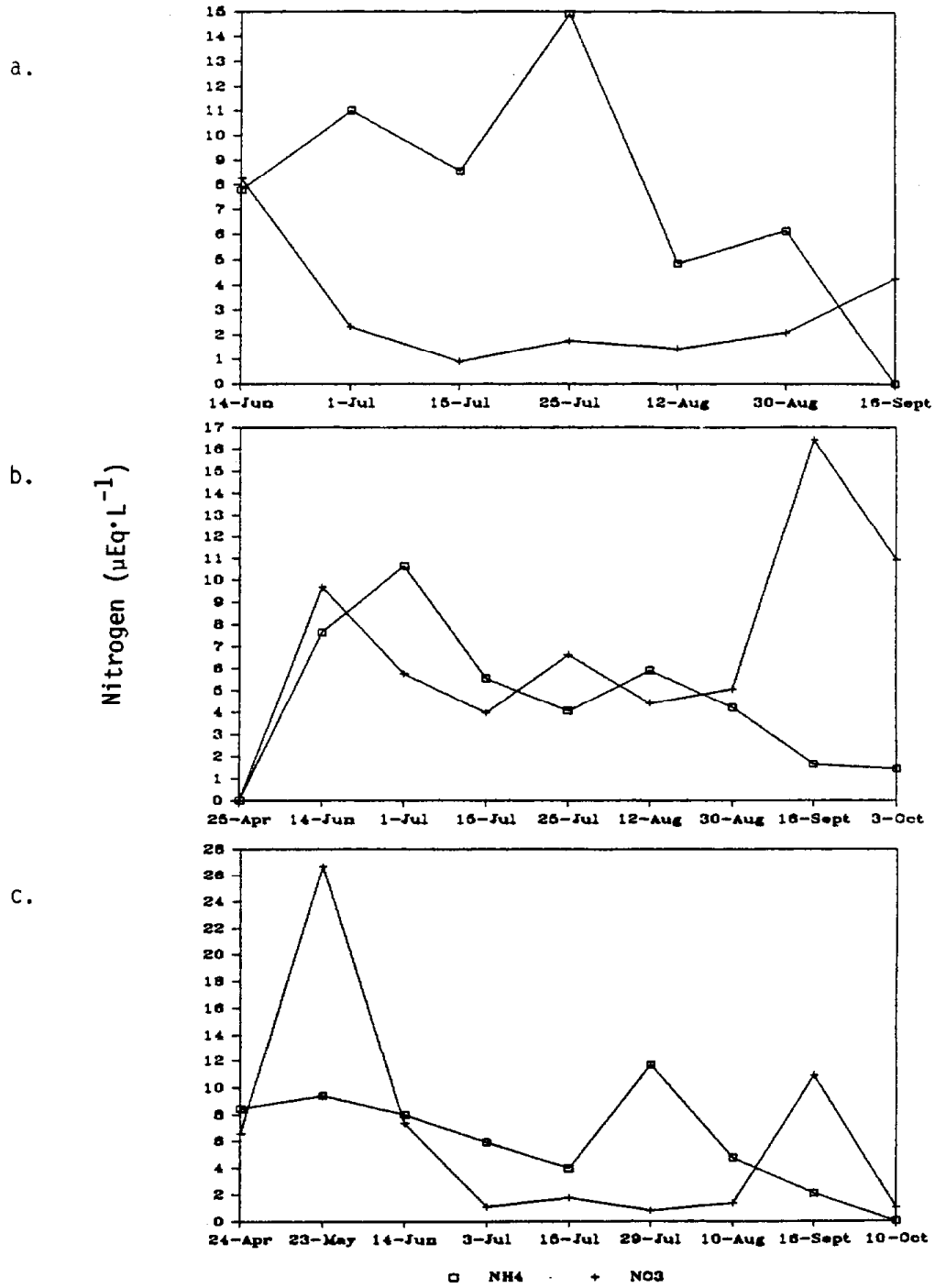

Fig. 25. Concentrations of nitrate and ammonium in streamflow in ELW during the 1985 season.

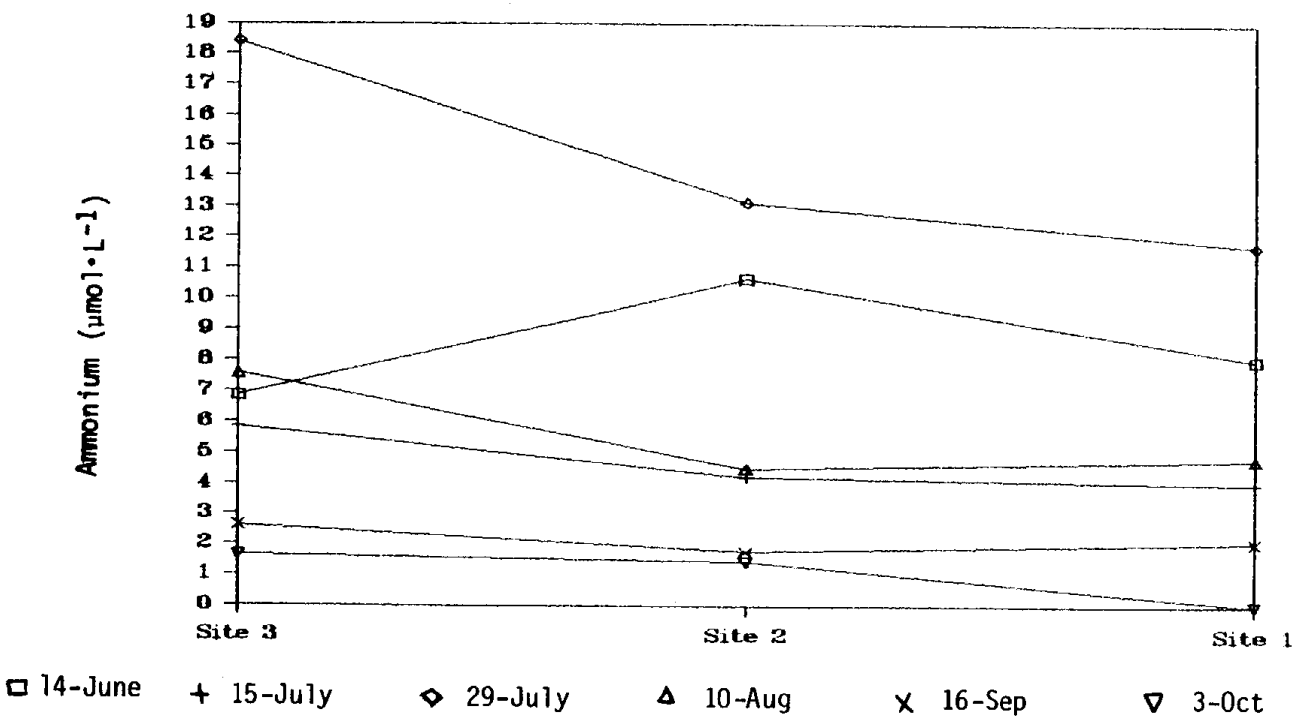

Fig. 26. Concentrations of ammonium in the bench meadow transect.

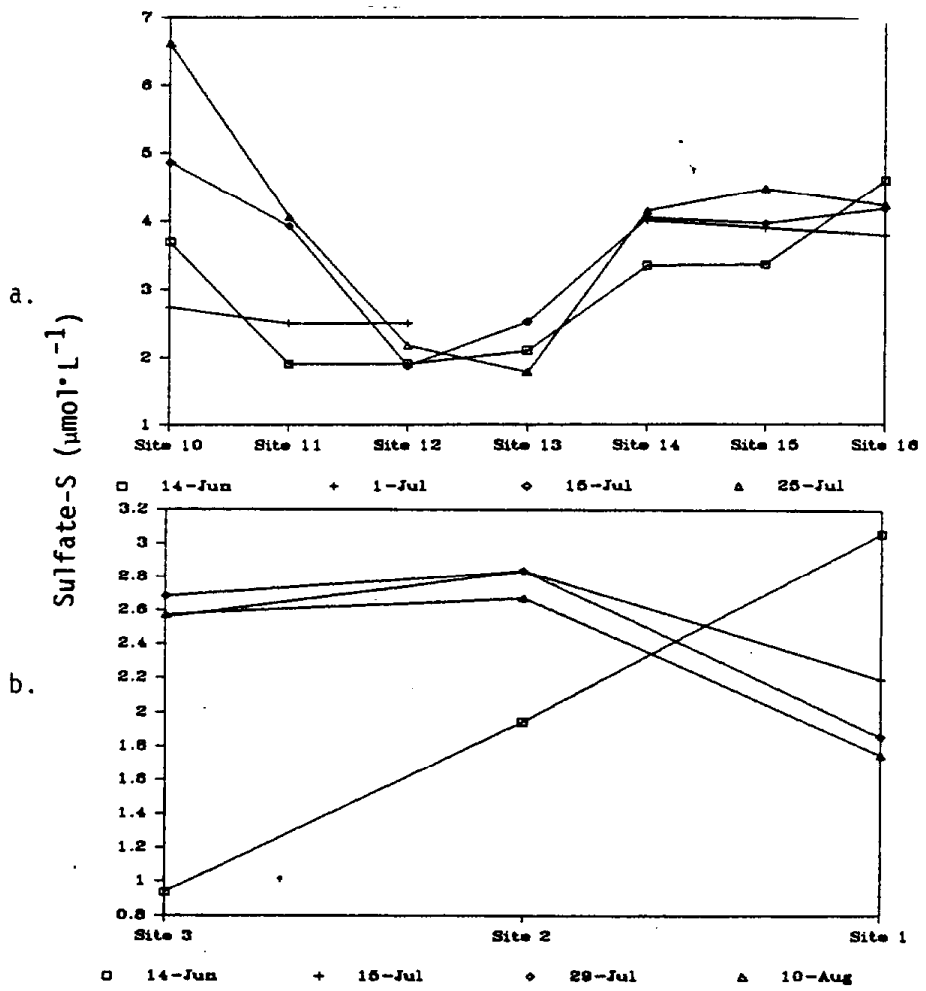

Fig. 27. Concentrations of sulfate in the (a) ELW main stream transect, and (b) bench meadow transect during the 1985 season.

primary and secondary minerals known to be present at ELW. The average concentrations of Na^+ and Ca^{2+} are highest, several times greater than those of K^+ and Mg^{2+} (Table 24). The mean concentrations of Na^+ and Ca^{2+} appear to increase between Alta Cirque and below the cirque, and the concentrations of all four elements increase between the saddle and the pond inlet (Figs. 28a and 28b). The mean ANC or alkalinity (as HCO_3^-) parallels the concentrations of Na^+ and Ca^{2+} (Fig. 29) indicating mineral weathering is a primary source of acid neutralizing substances in these waters. A summation of equivalent concentrations of Na^+, Ca^{2+}, K^+ and Mg^{2+} and comparison with alkalinity shows that HCO_3^- must be the primary anion present.

These data closely parallel the data of Feth et al. (1964) for streams in the Sierra Nevada. Garrells and MacKenzie (1967) used a thermodynamic approach to explain the relative concentrations of Na^+, Ca^{2+}, K^+ and Mg^{2+}. The predominance of Na^+ and Ca^{2+} in stream water is explained by the abundance and high weathering rates of plagioclase in the granite found in the watershed. One analysis conducted in the vicinity of ELW showed the rock to contain approximately 34% plagioclase consisting of 28 to 40% anorthite (Ca-feldspar) and the rest albite (Na-feldspar), 21% orthoclase (K-feldspar), 29% quartz, 7% biotite and 9% hornblende (amphibole) (Ross, 1958). The relative concentrations of Na^+ and Ca^{2+} in stream water apparently reflect the albite to anorthite ratio in the feldspar minerals. The ratio of Na^+ to K^+, on the other hand, is large (around 5:1 or greater) because of the comparatively low weathering rate of K-feldspar (in spite of its relatively high concentration in the rock) and the relatively small amounts of biotite and amphibole, minerals which also contain K^+. Likewise, Mg^{2+} concentrations should be relatively low.

Examination of the Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations at two sample sites along the stream transect during the 1985 season shows that concentrations were lower during snowmelt (presumably due to dilution) and increased during the growing season as evapotranspiration and residence time of the soil water increased. During August, the concentrations of Ca^{2+} and Na^+ appeared to decline drastically relative to Mg^{2+} and K^+ (Fig. 30 and 31). This contradicts the expectations of Garrells and MacKenzie (1967) for weathering of gra-

Table 24. Stream transect data: means and standard errors for Emerald Lake Watershed in 1985.

Conc'n	Alta Cirque (17)	Below Cirque (10)	Saddle (11)	Below Saddle (12)	Pond Inlet (13)	Pond Outlet (14)	Above Bench (15)	Above Inlet Meadow (16)
	Description and Site Number							
	$mmol \cdot m^{-3}$							
Al	0.18±0.15	0.15±0.17	0.26±0.24	0.35±0.52	0.21±0.12	0.19±0.09	0.30±0.45	0.23±0.07
Ca	4.55±0.22	9.79±0.40	6.70±0.42	5.95±0.01	9.36±0.15	7.69±0.21	7.78±0.18	7.61±0.37
Mg	2.84±0.06	2.09± 0	1.43± 0	1.37± 0	1.85± 0	1.82± 0	1.75± 0	1.53± 0
Na	11.5±0.04	17.5±0.58	12.0±0.20	12.9±0.07	16.8±0.58	10.4±0.19	9.39±0.16	7.93±0.17
K	3.35±0.06	3.02±0.21	2.75±0.01	3.30±0.04	3.53±0.07	2.86±0.03	2.60± 0	1.73±0.01
H	1.03±0.07	0.61±0.01	0.97±0.20	1.08±0.11	0.74±0.05	0.97±0.13	0.92±0.05	1.10±0.19
NH_4	3.33±94.4	7.61±118	6.75±101	7.20±69.3	25.7±13900	5.55±69.3	5.30±117	5.14±46.2
F	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
Cl	3.01±22.0	3.54±13.3	2.42±8.68	2.20±4.12	3.19±49.6	7.27±1773	2.74±8.43	2.07±14.9
NO_3	12.1±309	3.01±34.4	3.61±13.6	1.75±0.58	2.64±27.4	12.2±322	9.81±121	7.86±89.6
SO_4	3.48±1.78	4.62±0.17	3.39±0.24	2.12±1.38	2.14±2.55	3.97±1.34	4.10±4.48	4.28±1.62
H_2PO_4	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
HCO_3	20.3±22.2	37.6±114	24.7±0.42	19.0±51.2	34.6±62.1	18.1±22.0	12.4±7.07	20.8±51.7
Ionic Strength	47.0±34.6	64.4±148	47.4±62.7	41.2±18.3	68.1±327	49.3±40.7	48.9±35.1	42.6±133

Table 24. (cont.)

Conc'n	Meadow Spring (4)	Top of Meadow (3)	Middle of Meadow (2)	Meadow Outlet (1)	Top of Joint (5)	Bottom of Joint (6)
	Description and Site Number					
	$mmol \cdot m^{-3}$					
Al	0.13±0.13	0.08±0.02	0.40±0.59	0.20±0.58	0.43±0.59	0.59±0.43
Ca	12.1±0.34	6.55±0.22	10.8±0.79	15.3±1.04	19.7±6.80	17.9±1.42
Mg	2.59± 0	2.03± 0	3.96±0.10	2.86±0.01	2.55±0.11	2.03±0.04
Na	17.4±0.27	18.6±0.59	18.1±0.69	16.0±0.41	34.8±7.66	24.5±1.30
K	4.20±0.04	3.81±0.09	3.05±0.01	3.58±0.03	5.46±0.26	2.84±0.01
H	0.38±0.01	0.72±0.05	0.70±0.04	0.71±0.05	0.99±1.48	0.39±0.05
NH_4	6.53±225	8.62±237	5.66±92.1	6.04±64.8	12.2±1100	5.21±153
F	0 ± 0	0 ± 0	0 ± 0	0.03±0.06	0 ± 0	0 ± 0
Cl	3.09± 0	4.57±334	2.50±11.5	3.71±24.8	4.40±82.0	3.16±6.92
NO_3	9.59±152	3.47±53.4	2.80±34.0	6.40±331	3.60±173	2.56±5.54
SO_4	4.23±0.13	2.40±10.8	2.62±11.1	3.22±21.8	3.39±13.7	2.55±7.70
H_2PO_4	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0 ± 0
HCO_3	13.5±14.6	62.0±1234	46.7±133	48.8±214	73.5±1530	62.5±434
Ionic Strength	67.5±36.3	71.2±543	71.3±197	79.0±250	96.6±3950	69.0±1250

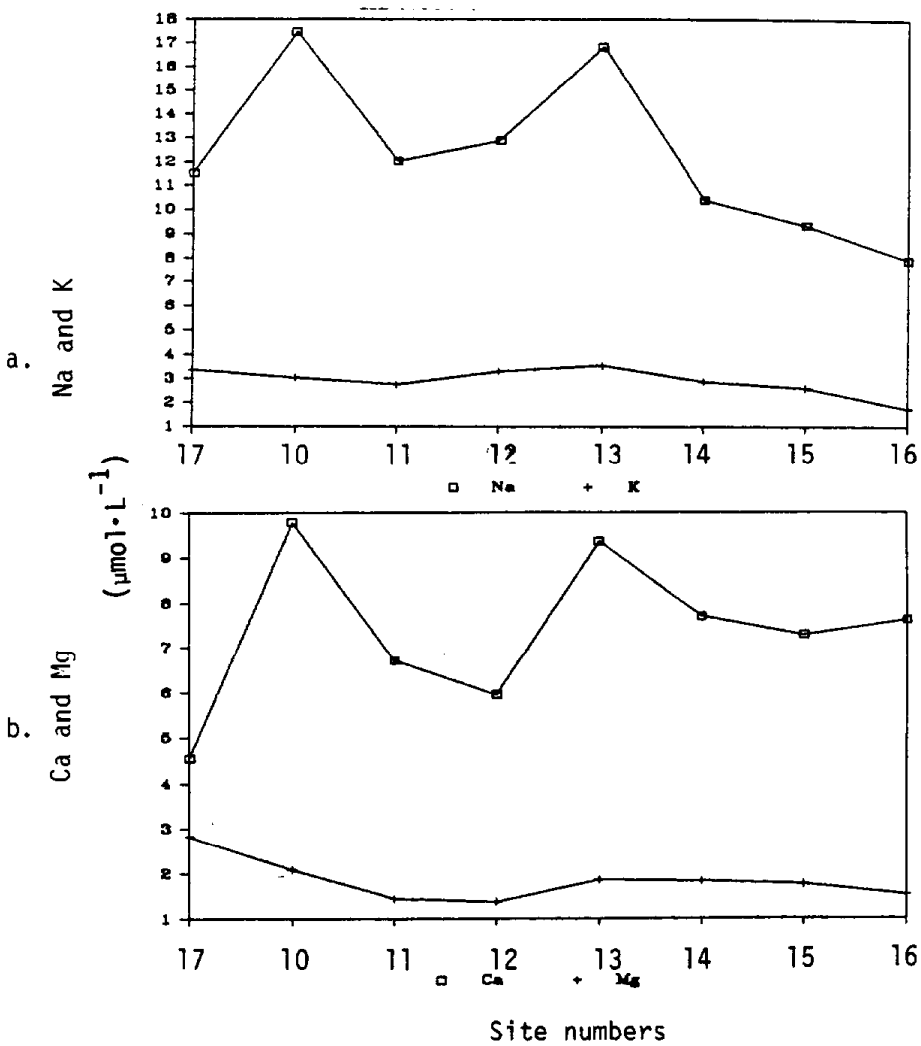

Fig. 28. Mean concentration of (a) Na and K, and (b) Ca and Mg in the main ELW stream transect in the 1985 season.

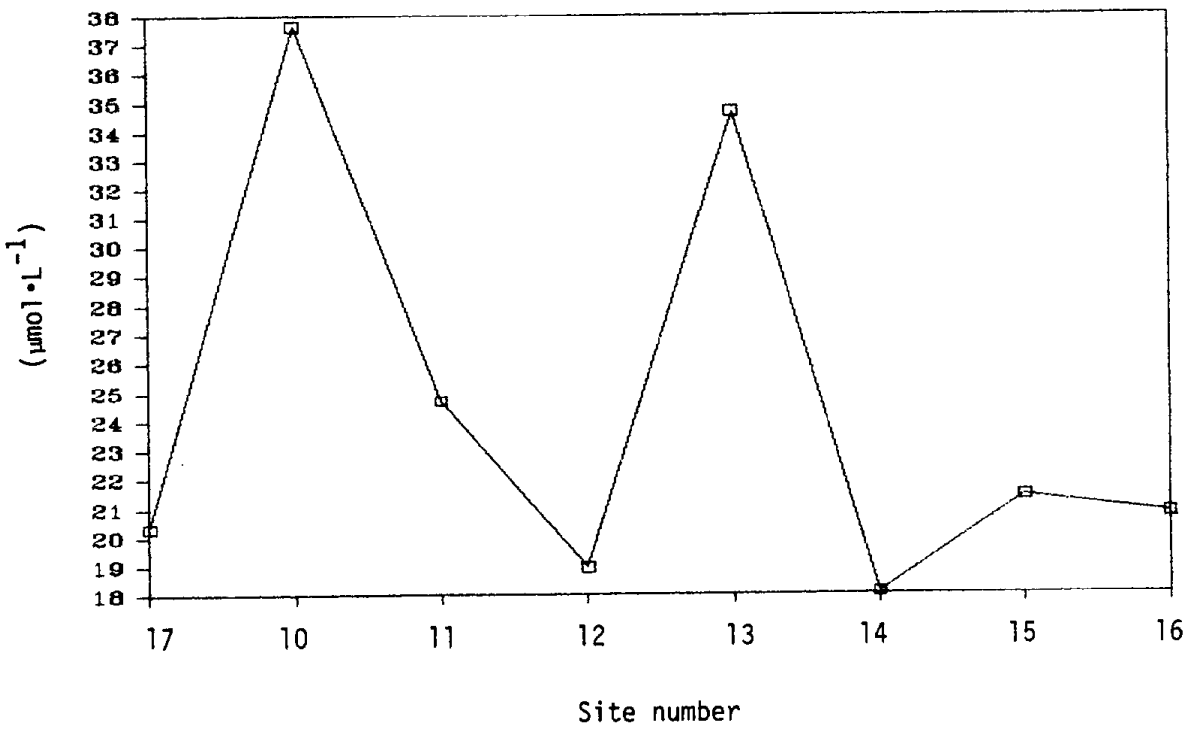

Fig. 29. Mean ANC or alkalinity (as HCO_3^-) of the main ELW stream transect in the 1985 season.

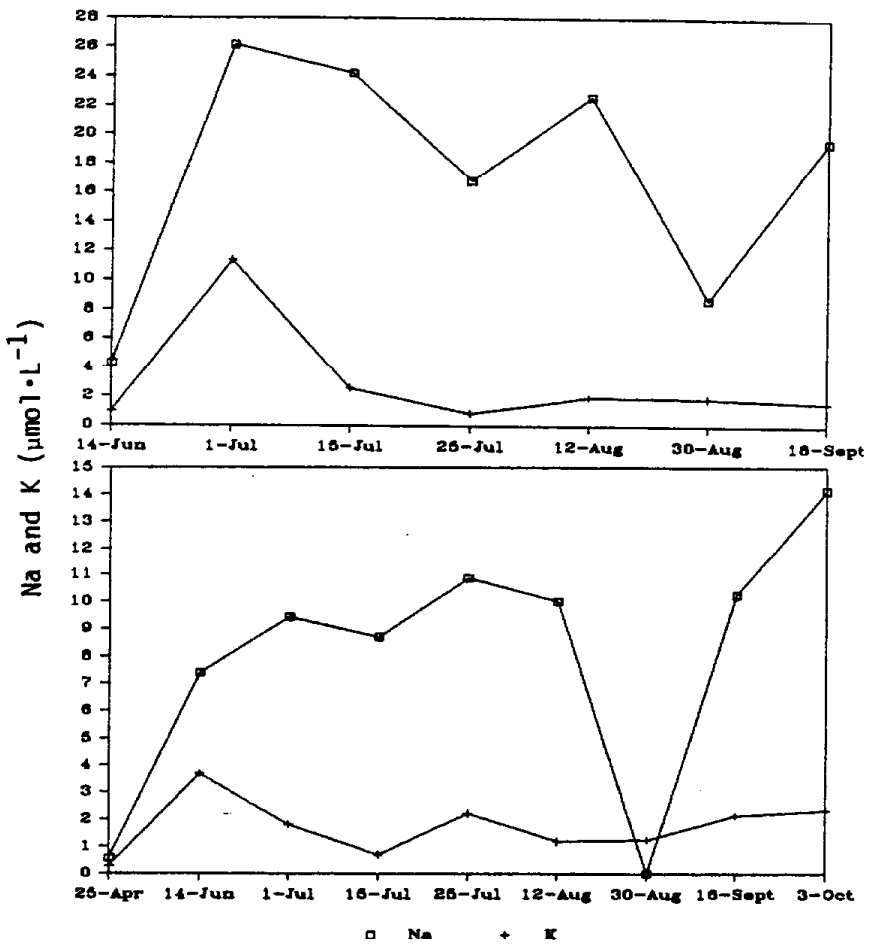

Fig. 30. Concentrations of Na and K in stream samples during the 1985 season (a) below Alta Cirque (site 10) and (b) above the Emerald Lake inlet meadow (site 16).

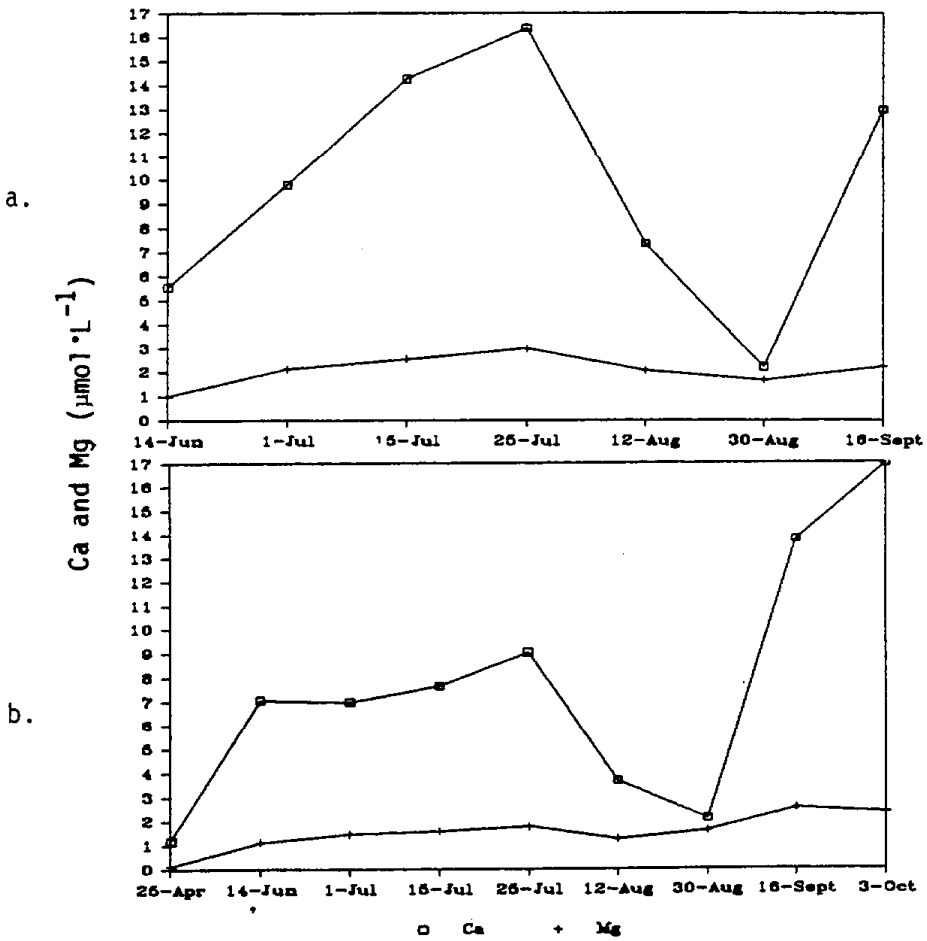

Fig. 31. Concentrations of Ca and Mg in stream samples during the 1985 season (a) below Alta Cirque (site 10); and (b) above Emerald Lake inlet meadow (site 16).

nitic rocks. This was a period of very low streamflow and may have in part resulted from longer residence time and higher evaporative concentration of K^+ and Mg^{2+} in solution. This may also be an effect of weathering from a source other than feldspars. One possible explanation is that volcanic glass from an eruption of one of the Mono-Inyo craters approximately 730 years ago is actually the most rapidly weathering material in ELW and is the major source of Mg^{2+} and K^+ in soil and surface waters (Whittig, 1985, personal communication).

5. Aluminum Mobility: The mean total concentrations of Al in the main stream transect appear to parallel the measured mean H^+ concentrations (Fig. 32). There is a trend for Al concentrations to increase in the reach below Alta Cirque and above the pond and in the reach between the pond and the falls above the Emerald Lake inlet meadow. There appears to be an inverse relationship between DOC and measured Al and H^+ concentrations (Fig. 33). This may arise from the complexation of H^+ by organic matter, confounding the measurement of H^+ by glass electrode. The complexation of organic matter with Al has been suggested as a mechanism for removal of DOC from stream water (McDowell, 1985). Aluminum concentrations in stream water appear to be highest in the early summer in spite of higher H^+ acidity during the spring melt (Fig. 34a-c). A second peak was evident in the main stream transect late in the summer. Aluminum concentrations were highest in April at the bench meadow outlet, but dropped to nearly zero during the summer (Fig. 34c).

Mean concentrations of Al in stream transects of Falls Brook, Hubbard Brook Experimental Forest ranged from 5.6 to 26 $mmol \cdot m^{-3}$ over a three year period. Mean pH ranged from 5.7 to 4.7 (Johnson et al., 1981). Mean Al concentrations at ELW stream transects were less that 1 $mmol \cdot m^{-3}$. In both examples Al concentration are probably related to the solubility of an $Al(OH)_3$ compound similar to gibbsite. The difference in total concentration is related to pH differences. Gibbsite is more soluble at the lower pH found at Falls Brook compared with ELW.

The effects of Al on biological activity in Norris Brook at the Hubbard Brook site have been measured in terms of increased migra-

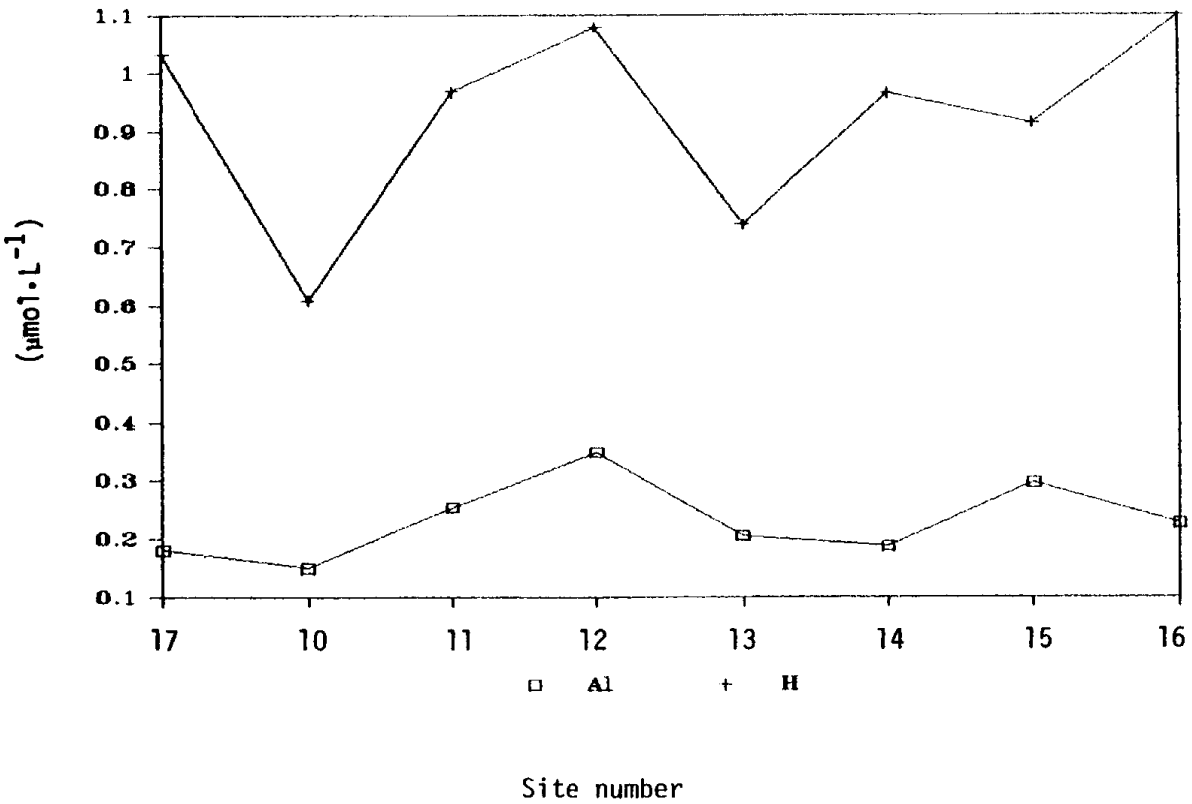

Fig. 32. Mean concentrations of Al in ELW main stream transect for the 1985 season.

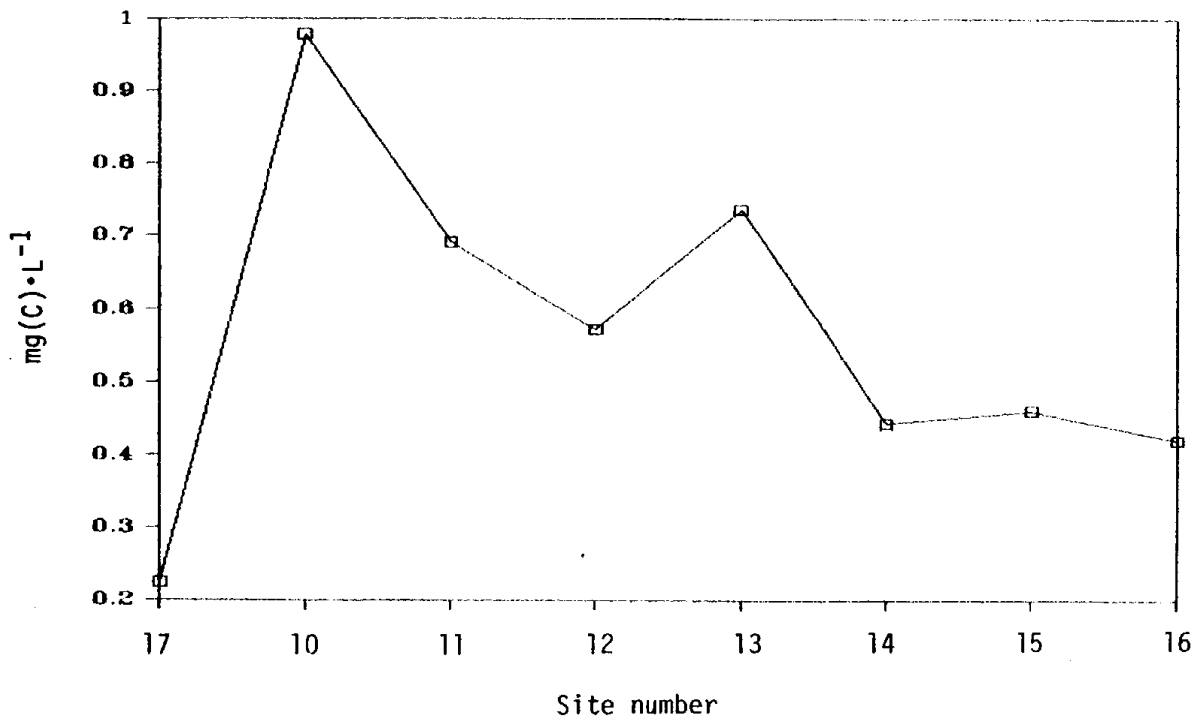

Fig. 33. Mean concentrations of dissolved organic carbon in ELW main stream transect during the 1985 season.

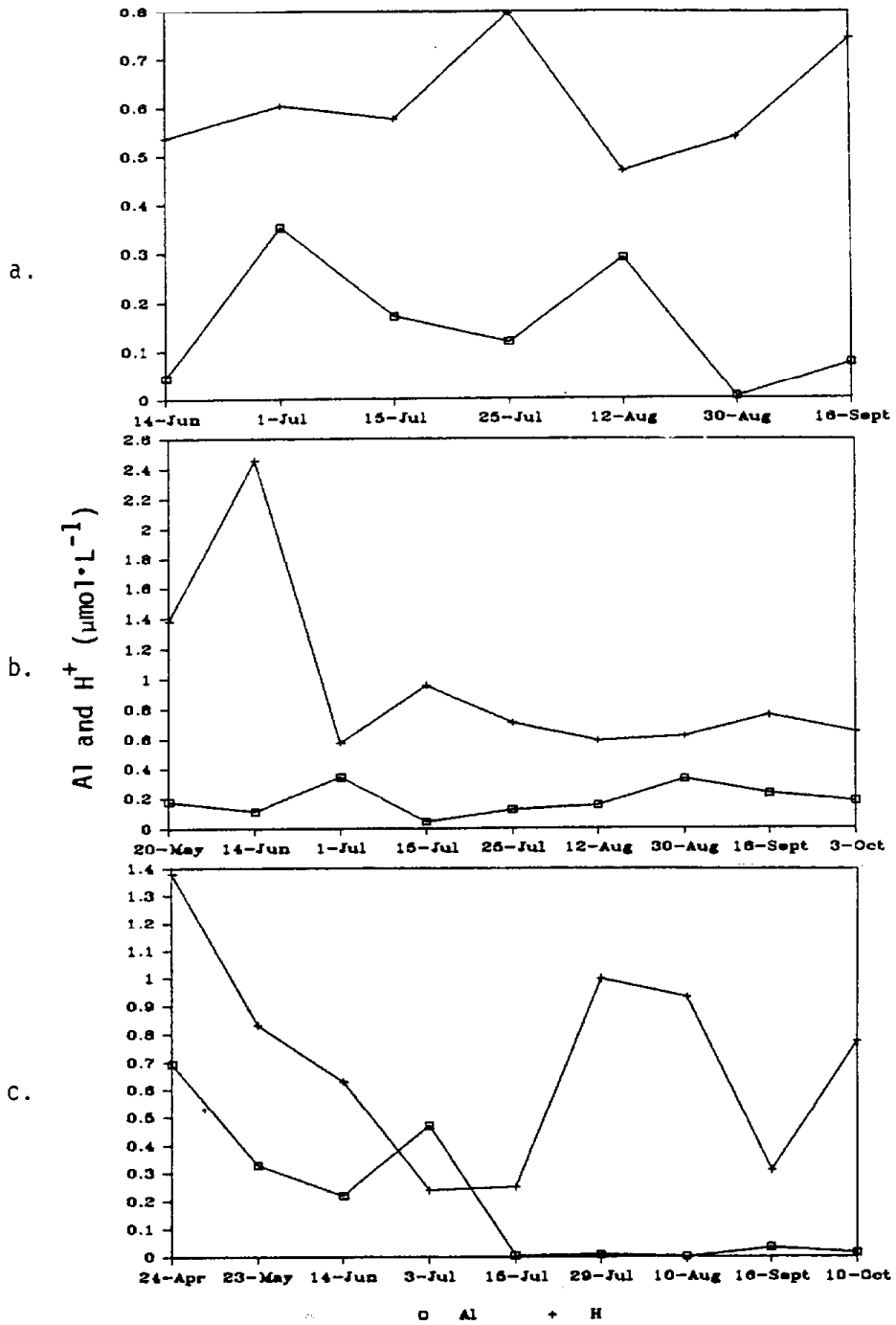

Fig. 34. Concentrations of Al and H^+ at sample sites (a) below Alta Cirque (site 10), (b) below the pond (site 14); and (c) at the bench meadow outlet (site 1) during the 1985 season.

tion of aquatic insects (drift). Migration increased as Al additions increased from 26 $mmol \cdot m^{-3}$ (pH 5.5) to 177 $mmol \cdot m^{-3}$ (pH 4.8). The ambient concentration of Al was approximately 0.4 $mmol \cdot m^{-3}$ (pH 6.4) (Hall et al., 1985). The concentration of Al measured in ELW during the 1985 season never reached these levels.

The Al concentration found in ELW stream waters are probably related to the solubility of a well-ordered $Al(OH)_3$ compound similar to gibbsite. Unlike Hubbard Brook watershed, ELW surface waters did not exhibit wide variations in pH, thus pH dependent solubility relationships cannot be constructed for ELW data. Based on the data of Johnson et al. (1981) and Nordstrom and Ball (1986) it is reasonable to assume that in the pH range 5 to 8 a microcrystalline gibbsite is controlling Al solubility. This assumption was tested by using the computer program GEOCHEM (Sposito and Mattigod, 1980) to calculate thermodynamic equilibrium speciation of total Al concentrations found at ELW. An ionic strength corrected Ks for gibbsite of approximately $2 \cdot 10^{-9}$ (at 25°C) was used.

Calculations showed that for the mean stream water compositions shown in Table 24, the concentrations of Al were slightly supersaturated with respect to gibbsite (Table 25). This calculated difference is minimal. Colder temperatures and organic matter complexation are probably more than sufficient to account for the slightly elevated solubility relative to the calculations at 25°C (D. K. Nordstrom, 1986, personal communication).

Recent data for Watershed 3 at the Hubbard Brook site indicate that the Al concentrations of stream water may not always be related to gibbsite solubility (Hooper and Shoemaker, 1985). These data were collected for a pH range of 4.4 to 5.3 under spring melt conditions. Deviations from solubility equilibrium are likely to be related to the complexation of Al by organic matter in soils (Bloom et al., 1979) and the dilution of Al-saturated waters by runoff (Nordstrom and Ball, 1986). More snowmelt data needs to be collected at ELW to determine if this effect is evident in stream runoff.

Table 25. Speciation of soluble Al in ELW stream waters.

Site #	Soluble Al-OH Complexes	Excess Soluble Al Relative to Gibbsite
	- - - - - - (%)	- - - - - - - -
17	58.7	40.9
10	76.4	23.5
11	41.4	58.4
12	31.1	68.7
13	53.0	46.9
14	57.0	42.7
15	35.9	64.0
16	48.4	51.3
4	100.0	0.0
3	99.8	0.0
2	27.5	72.5
1	56.1	43.8
5	25.0	74.9
6	25.4	74.6

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GLOSSARY

Abbreviations

ANC	acid neutralizing capacity
aq	aqueous, dissolved in water
C	carbon
CEC	cation exchange capacity
CO_2	carbon dioxide (gas)
DOC	dissolved organic carbon
EC	electrolytic conductivity
ELW	Emerald Lake Watershed, Sequoia National Park, CA
g	gaseous, mixed with air
H^+	hydrogen ion, proton
HCO_3^-	bicarbonate
N	nitrogen
NH_4^+	ammonium (solution cation)
NO_3^-	nitrate (solution anion)
N_2O	nitrous oxide
O_2	oxygen (gas)
P	phosphorus
pH	-log (concentration of hydrogen ions)
PO_4^{3-}	phosphate (solution anion)
S	sulfur
SO_4^{2-}	sulfate (solution ion)

Commonly Used Terms

adsorption	attraction of an ion to a charged surface of a soil mineral; adsorbed ions are no longer strictly in solution, but can easily return to solution by exchanging for an ion of similar charge.
Alta cirque	basin in ELW below Alta Peak
aqueous	dissolved in water
bench meadow	area of the watershed southeast of Emerald Lake which is relatively level
buffer	a component which provides resistance to change
bulk density	the weight of soil divided by the volume of soil
Castanopsis sempervirens	a broad-leafed, evergreen shrub commonly called a chinquapin
cation exchange	solution cations such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al^{3+}, and H^{+} are attracted to negatively charged soil clay mineral surfaced and organic matter soils; these exchangeable cations are not strictly in solution, but can easily be returned to solution by trading or exchanging for another cation
complex	an association of more than one free ion and/or compounds

Cryaquept	a soil formed in a cold climate that is saturated with water much of the time
Cryorthent	a soil formed in a cold climate with poorly developed horizonation
Cryumbrept	a soil formed in a cold climate with a thick, dark surface horizon but low nutrient content
decomposition	the microbial breakdown of organic matter in the soil to simpler compounds
denitrification	the biochemical reduction of NO_3 to gaseous forms which are unavailable to plants and may be lost to the atmosphere
diffusion	movement of a chemical species as a response to a concentration gradient
electrolytic conductivity	a measure of how easily a solution conducts electricity; this is directly related to the total salt concentration
free ion	a dissociated ion either positively or negatively charged
immobilization	the incorporation of inorganic substances (NH_4^+, NO_3^-, SO_4^{2-}, PO_4^{3-}, etc.) into microbial biomass and other organic compounds which are unavailable to plants
<u>in situ</u>	experiment in the field rather than in the laboratory; in place

inlet meadow	area of the watershed near the lake inlet
ionic strength	a measure of the total salt concentration of a solution; one-half the sum of the products of all solution ions and the square of their respective charges
joint	area northeast of Emerald Lake where two geologic masses meet forming an area of relatively deep soils
kinetics	a description of how fast a chemical or biological process occurs
leaching	the loss of constituents in soil solution by movement of water through the soil
litter	plant debris including leaves, stems, twigs, branched, etc. which have fallen to the ground
mass transport	movement of a substance from one point to another without any chemical transformations
matric potential	portion of water potential that can be attributed to the attraction of the soil or plant matrix for water
mineral	a homogeneous solid, usually crystalline
mineralization	the microbially mediated release of inorganic substances from organic matter (the reverse of immobilization)
organic carbon	all carbon that is bound up in organic matter (excludes CO_2 and HCO_3^-)

GLOSSARY (continued)

pH	a measure of the acidity of a solution in terms of free H^+
Pinus Monticola	a needle-bearing evergreen tree; western white pine
pi-mo stand	*Pinus Monticola* map designation
pore space	the volume of voids in soil occupied by air and water
porosity	the volume of soil pores expressed as a percentage of soil volume
reserve sulfur	organic S plus reduced inorganic S
respiration	the consumption of organic matter and oxygen releasing carbon dioxide, water and energy for biological activity
Salix oreochilla	a deciduous shrub; willow
saturated hydraulic conductivity	rate of water flow through a saturated soil column
soil solution	soil water plus all dissolved constituents
substrate	food for microbial or plant growth
throughfall	precipitation which reaches the soil surface by dripping off plant surfaces
total Kjeldahl nitrogen	organic N plus inorganic NH_4^+

unsaturated hydraulic conductivity	rate of water flow through a non-saturated soil column
weathering	the chemical and physical breakdown of minerals to form more stable minerals or soluble substances