LONG-TERM RESEARCH INTO THE EFFECTS OF ACIDIC DEPOSITION IN ROCKY MOUNTAIN NATIONAL PARK

SUMMARY REPORT 1980-1984

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NATIONAL PARK SERVICE
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TECHNICAL REPORT NO. 84-ROMO-2

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November, 1984

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ABSTRACT

The biogeochemical processes of several watershed ecosystems in Rocky Mountain National Park have been studied since 1981 to determine if they are being affected by atmospheric acidic deposition. This report tells how this long-term study is being conducted and presents some of the results we have obtained from three years of work (1981-1983). Our findings to date can be summarized as follows:

The high elevation front range ecosystems of Rocky Mountain National Park are extremely vulnerable to acidification from atmospheric deposition. Atmospheric deposition at this time is not acidic, and neither have we found historical trends toward acidification over the past 150 years. The terrestrial and aquatic ecosystems of the Loch Vale watershed are close to pristine with respect to effects of atmospheric deposition, although increases in lead over time indicate some industrial influence.

Should precipitation in the park become more acidic, however, potential for damage could occur for two reasons. First, the bedrock, soils, and surface waters of the park have almost no buffering capacity, so acidic deposition will result in acidic surface waters. Second, should the park's lakes and streams acidify, soil inputs may aggravate the situation by contributing additional acidity and soluble aluminum.

Currently, enough interaction occurs within the bedrock, soils, and groundwaters to maintain the pH of the waters in the lakes and

streams. However, exceptions occur in the spring, when the sheer volume of water from snowmelt runoff prevents exchange from taking place. The lower elevation waters of Loch Vale are more concentrated and more acidic due to input from surrounding acidic soils.

ACKNOWLEDGMENTS

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CHAPTER 1

INTRODUCTION

1.1 Overview

The ecosystems within Rocky Mountain National Park are extremely sensitive to acidic deposition because of their granitic and metamorphosed parent material, thin soil veneers, and pristine, poorly buffered waters. Projected increase in sulfur dioxide (SO_2) and nitric oxides (NO_x) emissions (Colorado Department of Health 1983) for the western United States make it possible that these fragile alpine and subalpine landscapes could become acidified. Because of this concern, a program was initiated in 1981 to study the ability of these systems to buffer increasing acidic deposition. The study also seeks to determine if the park's alpine and subalpine ecosystem are being affected by acidic deposition, and to understand how increasing acidic deposition will alter the different components of the ecosystem.

What follows is a discussion of our approach to the research and report of progress through 1983. We then discuss the findings we have obtained to date and conclude with a discussion of further work to be done. Because the effects of acidic deposition upon ecosystems may be subtle, and because they may occur over a period of years, our project is by necessity a multi-year study. It is possible that our long-term investigations may detect a trend before detrimental effects occur within Rocky Mountain National Park. Such a detection could be valuable on a regional scale and may serve to help prevent widespread acidification of the natural resources.

This project was implemented as a part of the National Park Service's involvement with the National Acid Precipitation Assessment Program (NAPAP). The National Park Service's (NPS) goal under the NAPAP program is to establish research sites that emphasize whole system studies in nationally representative ecological regions. In addition to Rocky Mountain National Park, other active NPS sites include Olympic National Park, Sequoia National Park, and Isle Royale National Park.

1.2 Study Area

Rocky Mountain National Park is located along the Continental Divide in north-central Colorado. The park's elevations range from 2330 m (7640') to 4350 m (14256'). Over one-third of the park area is above 5350 m (11000'). The mountains were formed by a series of granitic intrusions into Precambrian metamorphic schists and gneiss. Pleistocene glaciation has created a classic glaciated landscape of cirques, rock glaciers, and u-shaped and hanging valleys. Over 200 glacially-formed lakes are found within the park.

The parks's climate is typical of the mountainous western United States. Mean annual precipitation at Estes Park is 410 mm (16.4 in), with precipitation increasing with elevation. Over 50% of the annual precipitation occurs as snow. The heaviest snow events occur during March and April. Summer rains are often severe. Mean annual temperature at Estes Park is 6°C (42.8°F). Strong winds, sometimes in excess of 160 km/h (99 mph), are common at the higher elevations (Stevens 1980). The park's vegetation is typical of the Rocky Mountain biome, with alpine tundra above 3000 m (9800 ft) grading into subalpine spruce and fir below this elevation. The lower elevations (below 2743 m, or

9000 ft) contain lodgepole and ponderosa pine forests as well as aspen stands. Sedge meadows and bogs may be found at all elevations in areas of low relief. Figure 1 depicts the park area and the locations of the study sites, which are described below.

1.3 Approach to the Research

The primary objective of this research was to understand the biogeochemical processes that will respond to increasing acidic deposition in Rocky Mountain National Park. Four major hypotheses were formulated to structure the research so as to meet the objective (Table 1).

Our first hypothesis is stated as follows:

1. Current levels of acidity in precipitation falling in Rocky Mountain National Park are greater than historical levels.

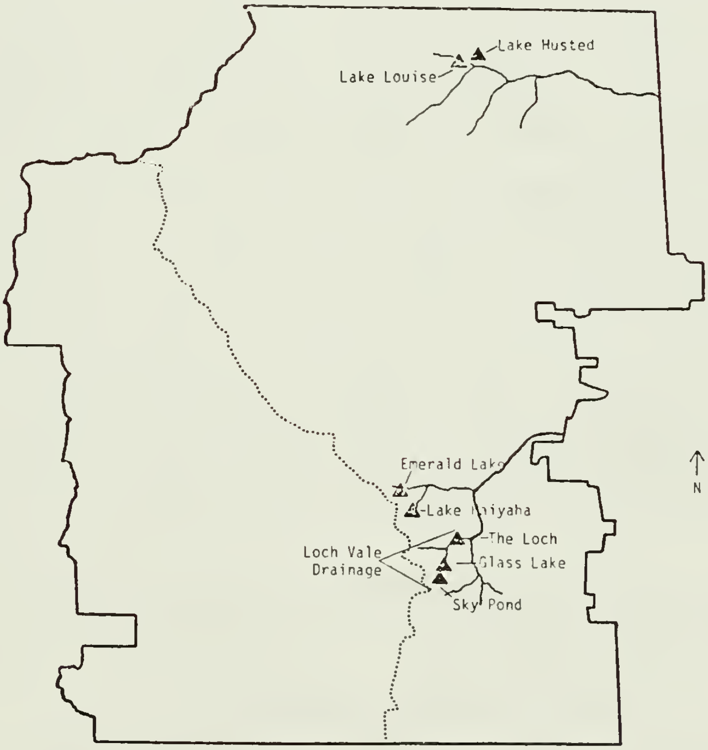

Fig. 1. Map of Rocky Mountain National Park, showing locations of study sites. Dotted line indicates the Continental Divide.

Table 1. Hypotheses being tested at Loch Vale.

---

1. Current levels of acidity in precipitation falling in Rocky Mountain National Park are greater than historical levels.

2. The buffering capacity of surface waters in subalpine zones is due to weathering of inorganic soil materials and exchange reactions from soil clays and organic matter.

3. The composition of surface waters is affected by hydrologic patterns which are seasonally controlled. Summer hydrologic inputs are subject to maximum ecosystem influence, namely precipitation and weathering and biologic activity. Winter inputs such as snowmelt effectively bypass the soil exchange system. These inputs will be reflected in surface water composition.

4. The chemistry of lake and stream waters is some definable and predictable combination of precipitation chemistry, weathering reactions of soil and parent materials, and chemical products of biological activity.

Since historical data before 1981 was not available for the park area, to test this hypothesis we took a paleoecological approach using biological and physical indicators to compare present day conditions with those of the past. This approach consisted of sediment cores collected from four study lakes in the park: Emerald, Haiyaha, Louise, and Husted. These lakes are characteristic of many other lakes east of the Continental Divide; thus, the history derived from their sediments can be extrapolated to the eastern part of Rocky Mountain National Park. This type of analysis has been used in acid precipitation studies throughout the United States and Europe (Davis et al. 1983; Tolonen and Jaakola 1983). A discussion of the theory, methods and results to date are found in Chapter 2.

The second, third and fourth hypotheses are:

2. The buffering capacity of surface waters in subalpine zones is due to weathering of inorganic soil materials and exchange reactions from soil clays and organic matter.

3. The composition of surface waters is affected by hydrologic patterns that are seasonally controlled. Summer hydrologic inputs are subject to maximum ecosystem influence, namely precipitation and weathering and biologic activity. Winter inputs such as snowmelt effectively bypass the soil exchange system. These inputs will be reflected in surface water composition.

4. The chemistry of lake and stream waters is some definable and predictable combination of precipitation chemistry, weathering reactions of soil and parent materials, and chemical products of biological activity.

A biogeochemical study of one watershed in Rocky Mountain National Park was set up to test these hypotheses. When a lake or stream acidifies, it is due not only to acidic substances that fall directly on the water, but also to the biogeochemical reactions that occur throughout the watershed drainage. It is these reactions that were subject to examination with the approach to the second, third, and fourth hypotheses. The approach, methods, and results to date are discussed in Chapters 4, 5, and 6, respectively.

Figure 2 shows a conceptual diagram of the ecosystem components responsible for influencing the passage of deposition constituents through a watershed. Our studies attempt to understand the role of each component. The Loch Vale drainage (Figs. 1 and 3) was chosen for in-depth study for the following reasons:

1. Of 40 lakes within Rocky Mountain National Park that were surveyed for water chemistry in 1981 (Gibson et al. 1981), lakes of the Loch Vale drainage had the lowest summertime alkalinities.

2. Loch Vale drainage is a relatively small (860 ha), simple (first order) drainage from which inputs and outputs can be gauged.

3. Three lakes in the main drainage are linked by a connecting stream. Two lakes above treeline and one below give the opportunity to make comparisons along an elevational gradient.

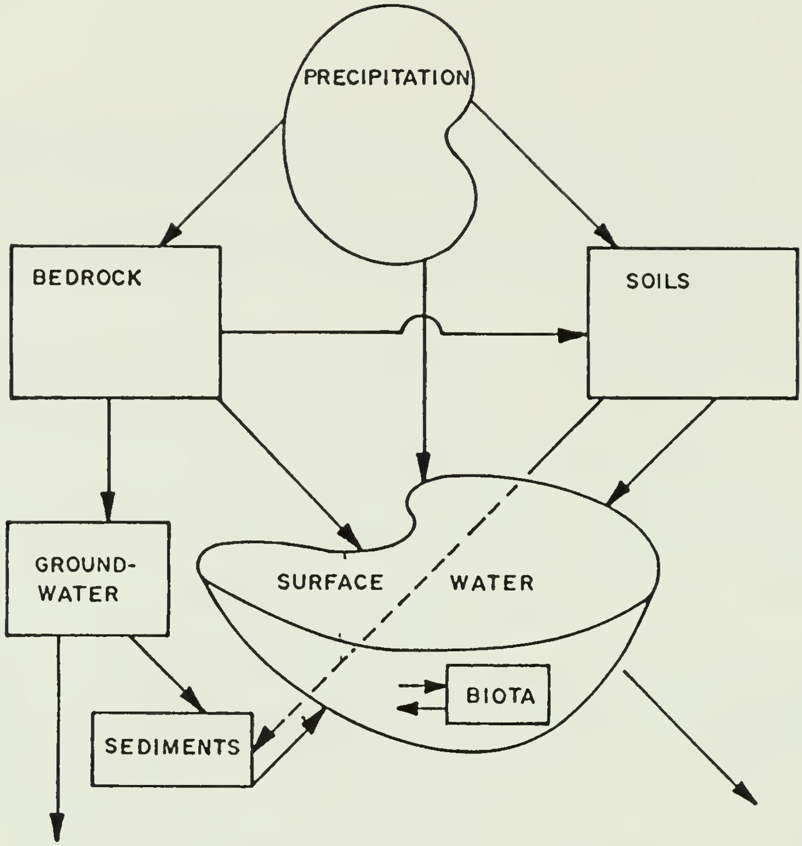

Fig. 2. Conceptual model of biogeochemical flow through Loch Vale drainage.

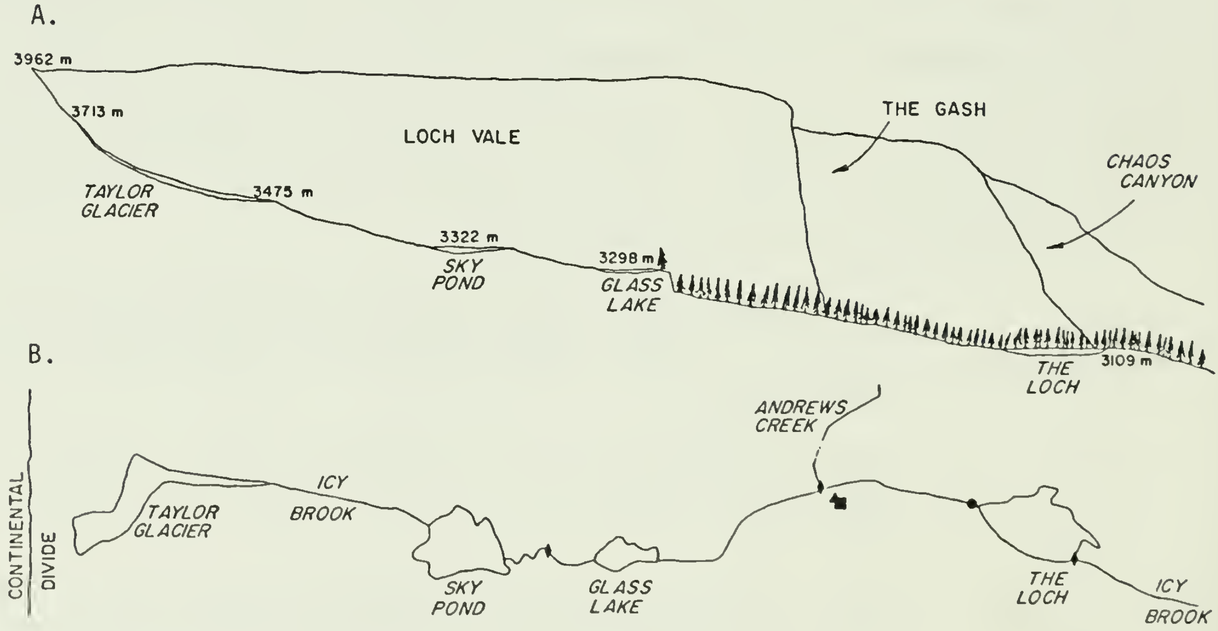

Fig. 3. (A) Cross-sectional and (B) plan view of Loch Vale drainage. Diamonds and circle are sites of planned flumes; square and triangle show weather station and NADP monitor, respectively.

4. The drainage has a northeast-facing aspect, which lessens the direct upslope influence from metropolitan Denver.

5. The wide representation of alpine and subalpine soil types in the Loch Vale drainage allowed us to conduct an intensive study of the chemistry and influences of the soil components.

6. All parts of the drainage are accessible during all times of the year.

The physical characteristics of the lakes in Loch Vale are summarized in Table 2.

Table 2. Physical characteristics of The Loch, Glass Lake, and Sky Pond.

	Elevation (m)	Drainage Area (ha)	Surface Area (ha)	Maximum Depth (m)	Volume (m^3)	Avg. Flushing Rate (m^3/y)
The Loch	3109	860	5.0	4.7	61,099	19
Glass Lake	3298	266	1.0	4.7	25,689	26
Sky Pond	3322	204	3.0	7.3	121,684	3

CHAPTER 2

PALEOECOLOGICAL WORK

2.1 Study Sites

The four study lakes sampled for paleoecological work are located east of the Continental Divide above 3000 m within Rocky Mountain National Park. All of these lakes are at the head of their respective drainages and constitute geologically similar pairs. The first pair, Lakes Louise (3365 m) and Husted (3380 m), are located in a cirque valley of primarily Sherman quartz monzonite. They are less than 1.0 km from each other at the head of the north Fork of the Big Thompson River. Husted is above treeline and has wet sedge meadow at its inlet; Louise is partially bordered by krummholz. The lakes have separate drainages, 107 ha for Husted and 111 ha for Louise. Above Lake Louise is a permanent snowfield. The other two lakes, Lake Haiyaha and Emerald Lake, are 2.5 km apart within the Glacier Gorge area of the park. The parent materials are metasediments of biotite gneiss and schist intruded by Silver Plume granite (Johnson and Herzog 1982; Cole 1977). Both lakes are at 3110 m and are partially surrounded by subalpine coniferous forests. The lakes have separate drainage areas of 404 ha and 205 ha, respectively (Table 3) (Baron 1983).

2.2 Methods

Sediment cores were taken from the deeper part of each lake in July 1982. A 6.5 cm diameter stationary piston corer (Davis and Doyle 1969) was used to obtain cores with undisturbed and uncompressed

Table 1 Some physical characteristics of four lake watersheds in Rocky Mountain National Park.

	Elevation (m)	Drainage area (ha)	Ratio of drainage area to lake area	Maximum lake depth (m)
Louise	3365	111	40:1	6.0
Husted	3380	107	10:1	8.3
Emerald	3110	205	40:1	17.0
Haiyaha	3110	404	30:1	10.0

stratigraphy and undisturbed sediment/water interface. Sediments were extruded upward from the core tube and sectioned in the field in 0.5 cm increments from 0 to 20 cm and in 1.0 cm increments from 20 to 40 cm. Isotope dating techniques using ^{210}Pb were used to determine sediment depth/time relationships (Eakins and Morrison 1978; Appleby and Oldfield 1978). The major elements--aluminum (Al), titanium (Ti), iron (Fe), manganese (Mn), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), zinc (Zn), and copper (Cu)--were analyzed by flame atomic absorption spectrophotometry (Perkin-Elmer 703). Lead (Pb) was analyzed with a graphite furnance (HGA 2200). The chemistry of the sediment cores is presented as concentration units.

Extraction of diatom material from a known volume of sediment material involved digestion in chromic acid, separation of large particulates, and replacement of residual acid by distilled water. Microscope slide preparation used the settling chamber method of Battarbee (1979); diatom tests were then permanently mounted in Hyrax mounting media. Enumeration and taxonomic identification was done by microscope under oil at 1000x total magnification. A minimum of 600 diatom valves were counted per sediment level, and all taxa possible were assigned to a pH-preference group based on Husted (1939).

Calculation of inferred pH values from diatom counts from each level was done by Index B (Renberg and Hellberg 1982), where

$$\text{Index B} = \frac{\%\ \text{IND} + (5 \times \%\ \text{AC}) + (40 \times \%\ \text{ACB})}{\%\ \text{IND} + (3.5 \times \%\ \text{ALK}) + (108 \times \%\ \text{ALB})} \quad \text{and}$$

$$\text{pH} = 6.4 - (.85 \log \text{Index B}).$$

Species were assigned to one of five pH preference categories, acidophilic (AC), acidobiontic (ACB), indifferent (IND), alkalibiontic (ALB), or alkaliphilic (ALK), according to their preferred pH ranges as found in the literature.

2.3 Results

Stratigraphic profiles of heavy metals and other selected parameters for the four lakes are shown in Figures 4-7. The increase in Pb concentration beginning at a core depth of 12.0 cm corresponds with a date of about 1870; however, it is not accompanied by concurrent increasing concentrations of Zn or Cu. Deposition rates (µg/cm/yr) instead of sedimentation rate (cm/yr) can signal concentration increases of elements independent of enrichment factors that add bulk material such as water and organic content. The deposition rate of Pb mirrors the chemical profile of Pb shown in Figures 4-7, again not accompanied by concurrent increases for Zn and Cu. The increased deposition rate of Pb was observed simultaneously for all four lakes (Fig. 8) at comparable magnitude, suggesting an atmospheric origin (Norton 1983). It is unlikely the Pb comes from the combustion of fossil fuels because there is no associated Cu or Zn signal as in

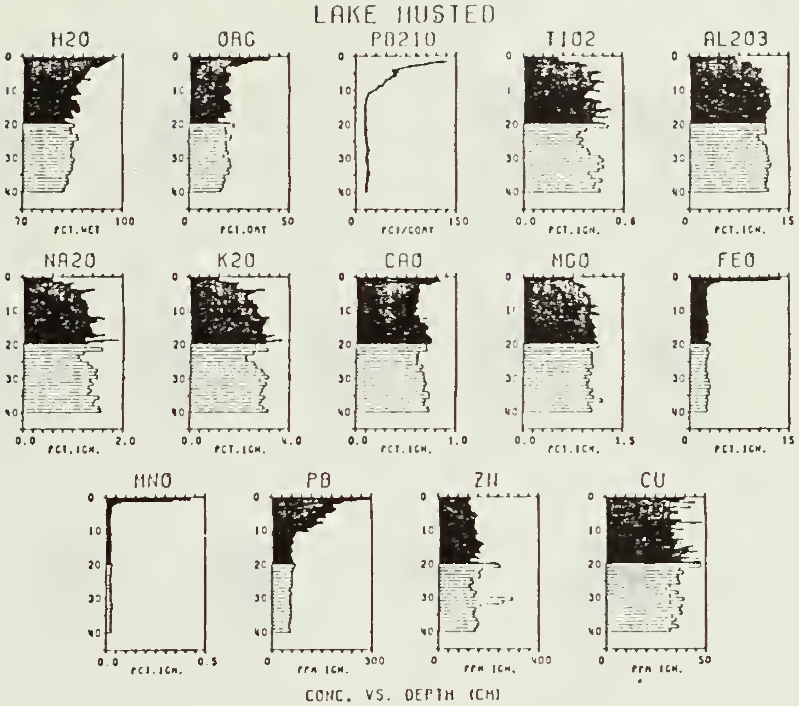

Fig. 4. Stratigraphic profiles of metals and other parameters from Lake Husted.

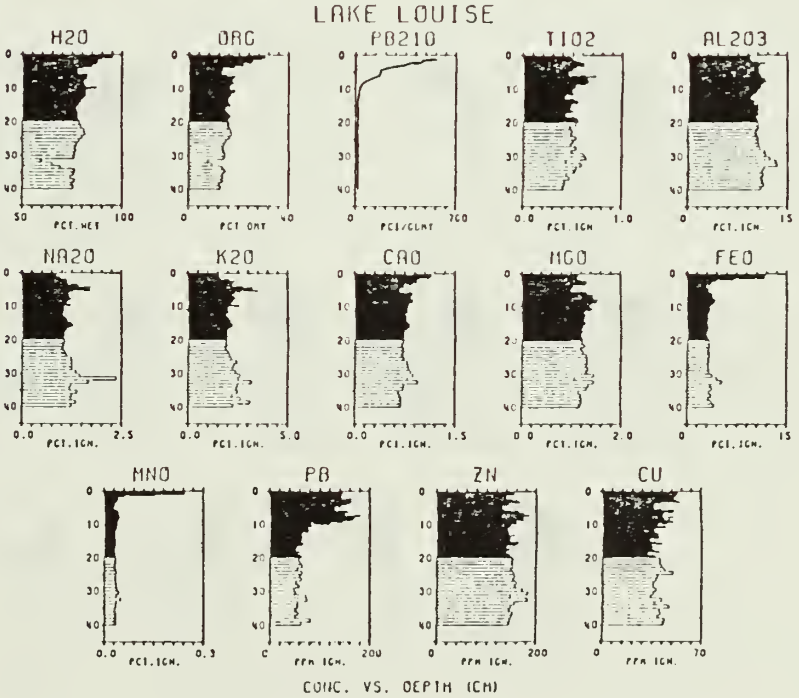

Fig. 5. Stratigraphic profiles of metals and other parameters from Lake Louise.

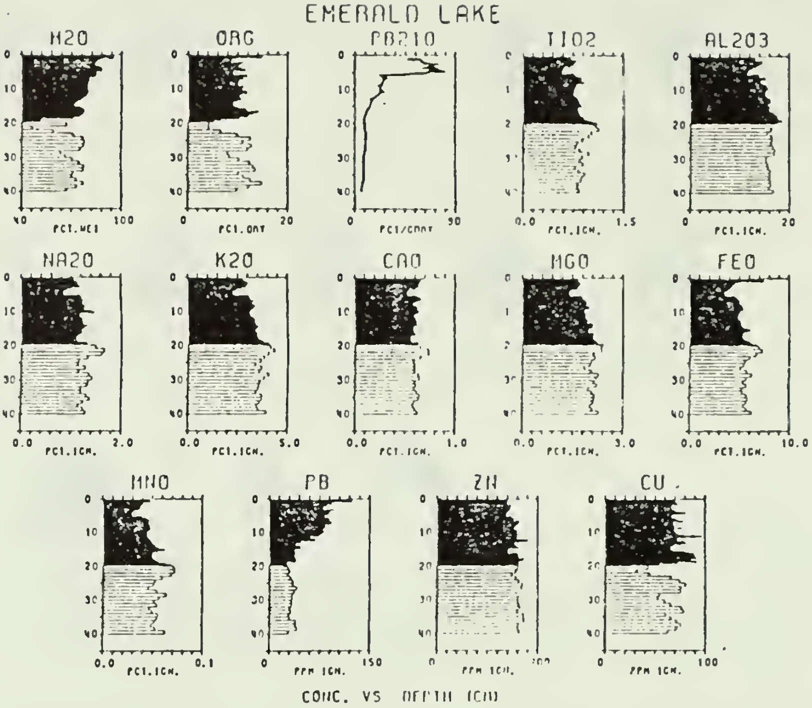

Fig. 6. Stratigraphic profiles of metals and other parameters from Emerald Lake.

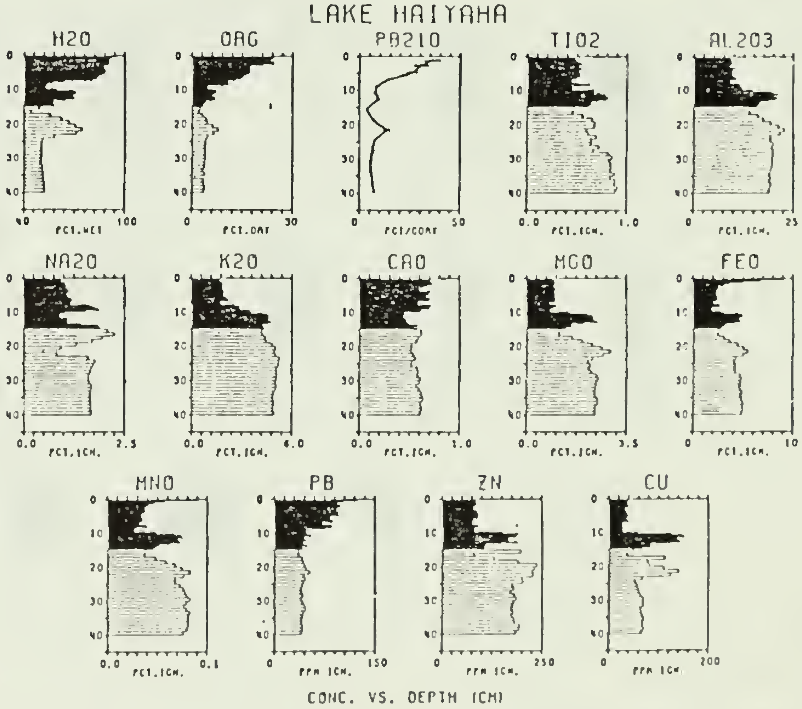

Fig. 7. Stratigraphic profiles of metals and other parameters from Lake Haiyaha.

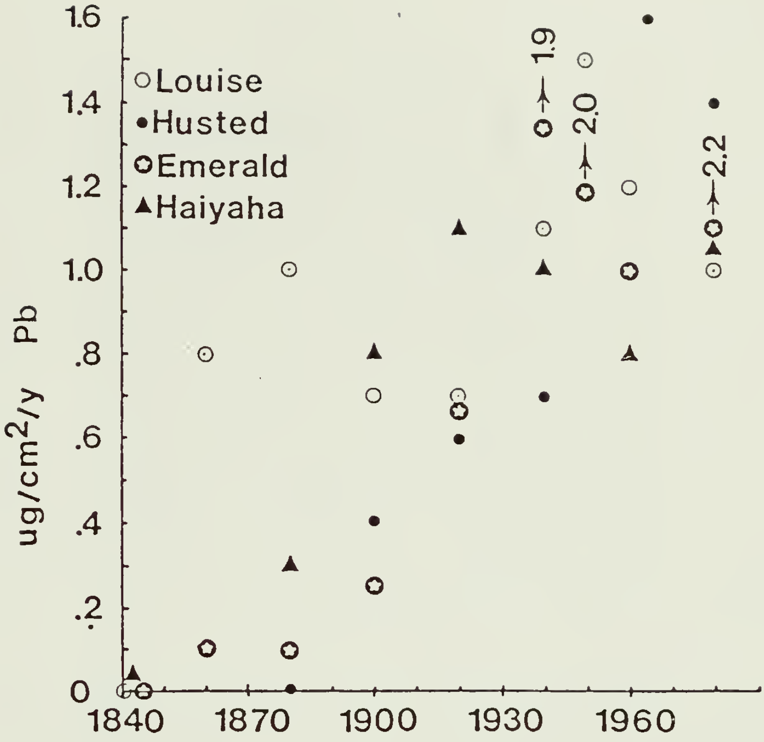

Fig. 8. Deposition rate of lead ($\mu g/cm^2/y$) in Lakes Emerald, Haiyaha, Louise, and Husted.

eastern North American and European sediments. Increased mining activity in Colorado during this time period, coupled with a global industrial signal similar to the results found by Murozumi et al. (1969) in Greenland ice cores, may be responsible.

All four lakes are being analyzed for diatom assemblages; work is still in progress for Lakes Louise, Emerald, and Haiyaha. Fifteen sediment section levels in Lake Husted were chosen to be analyzed for diatom remains. One hundred ten taxa were identified from the sediment material with a mean of 40 taxa identified per level. None of the species identified belong to the acidobiontic or alkalibiontic pH-preference groups. Diatom stratigraphy from all levels analyzed show little change in the relative proportion of acidophilic taxa per level

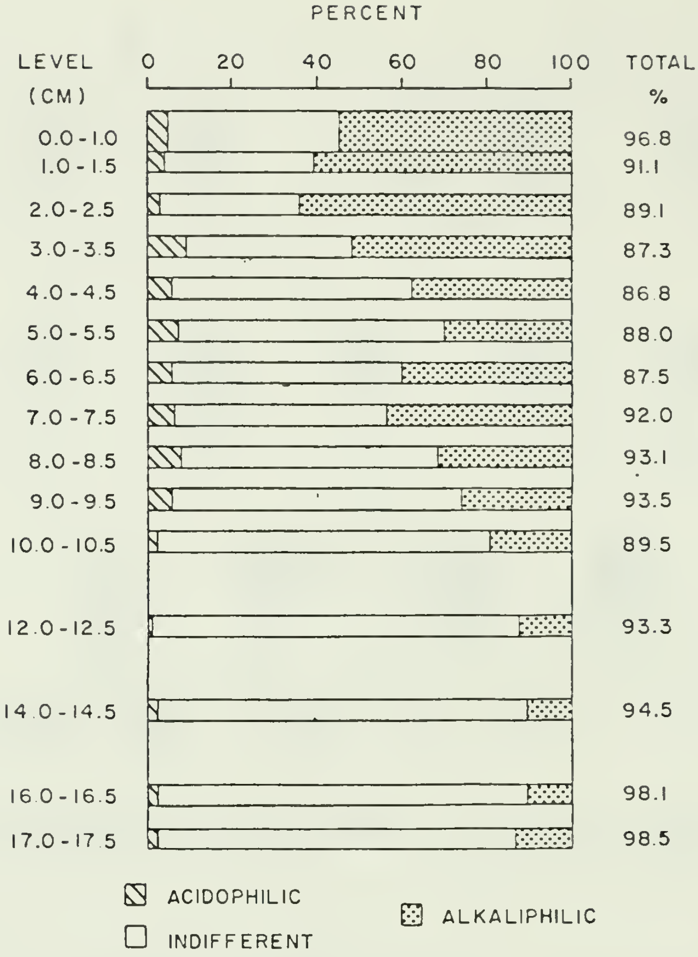

Fig. 9. Diatom stratigraphy for Lake Husted using pH preference categories.

from 1802 to the present (Fig. 9). A decreasing trend in the relative proportion of the indifferent taxa begins at the 10.0-10.5 cm sediment level (1896); this corresponds to an increasing trend in alkaliphilic taxa. These trends continue to the surface sediment.

Lake Husted inferred pH stratigraphy, as calculated by Index B for each level, indicates a steady condition of pH 6.5 from the 17.0-17.5 cm level to the 10.0-10.5 cm level corresponding to ^{210}Pb dates of 1802 to 1896 (Fig. 10). From the 10.0-10.5 cm level to the surface, the inferred pH values start to fluctuate and increase from pH 6.5 at a level of 9.0-9.5 cm (1910) to pH 7.0 at the 2.0-2.5 level (1974). The

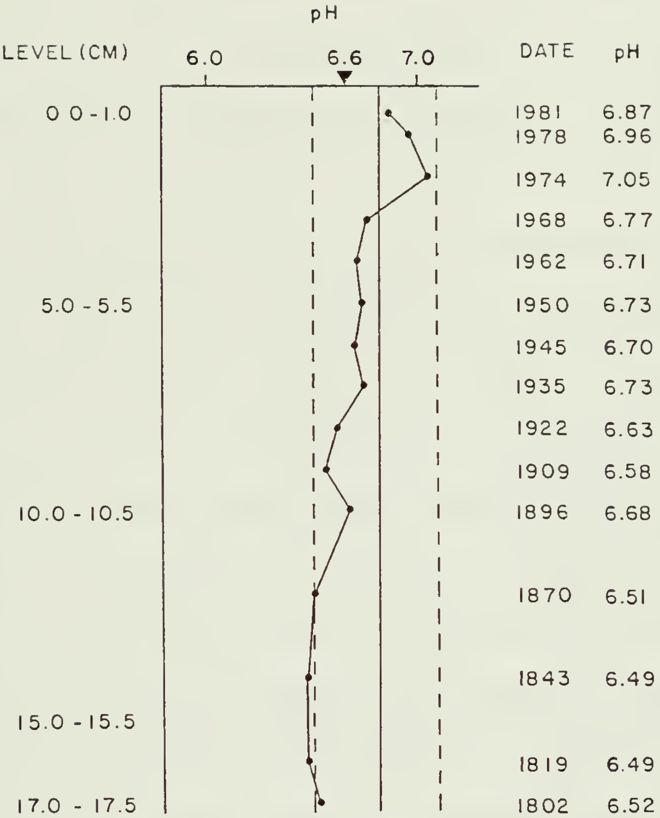

Fig. 10. Inferred pH stratigraphy from Lake Husted using Index B.

mean hydrogen ion concentration of the inferred pH values for all levels analyzed corresponds to pH 6.66. A t-test for paired observations indicates there is a significant difference (p>.05) between the 95% limits of present-day field-measured mean pH and the inferred mean pH (t=2.59, p.05=2.14, df=14). Field-collected pH values for Lake Husted surface waters from 1982 and 1983 (n=5) show a mean hydrogen ion concentration equal to pH 6.81 with 95% confidence limits equal to a range of pH 6.48 to pH 7.14.

The diatom stratigraphy clearly demonstrates that acidic atmospheric deposition has not affected Lake Husted. The increase in alkaliphilic taxa from a sediment level corresponding to a ^{210}Pb date of about 1900 to the surface indicates a change that generally favors nonacidic forms. The diatom stratigraphy for Lake Husted is therefore not a characteristic example of an acidified lake. Conditions that indicate acidification are increasing acidophilic proportions and decreasing alkaliphilic proportions (Renberg and Hellberg 1982; Tolonen and Jaakola 1983; Davis and Berge 1980) including observations of acidiobiontic taxa. The inferred pH profile shows that the mean pH of Lake Husted has not changed significantly since 1819 to the present. A fluctuation and increase of the inferred pH values begins at the same level as the alkaliphilic taxa start to increase (around 1900); this suggests that the nature of the apparent change may be alkaline. The inferred pH profile in Lake Husted is not characteristic of acidified lakes due to high overall pH values throughout the profile and the lack of an overall decrease within the last 80 years.

2.4 Conclusions

Based on diatom analysis, calculated inferred pH stratigraphy, and study area geochemistry, the present day pH values are no different from the historical values. This suggests that the ecosystem has not been and is not acidified from atmospheric deposition. The fluctuation of pH, the increase in alkaliphilic taxa commencing around 1896, and the rise in the deposition rate of Pb indicate that other physical or chemical factors have influenced Lake Husted.

CHAPTER 3

PRECIPITATION CHEMISTRY

3.1 Local Values

Precipitation chemistry data have been collected at an elevation of 3050 m since 1981 to characterize inputs to Loch Vale. These collections became a part of the National Atmospheric Deposition Program (NADP) in September 1983. An NADP collector is also located at Rocky Mountain National Park headquarters (2500 m) and the data presented here come from this headquarters station. A comparison between elevations is planned. Precipitation volume is measured throughout the study drainage of Loch Vale, and a weather station collecting information on humidity, barometric pressure, wind speed and direction, and solar radiation is located midway between The Loch and Glass Lake. Another weather station is planned for an island in The Loch, and will be used to calculate a hydrologic budget for the lake.

Monthly weighted averages of major anions and cations are shown in Table 4 and precipitation volume is shown in Figure 11. The great

Table 4. Volume-weighted annual average precipitation values for Rocky Mountain National Park headquarters NADP site (values in μeq/1).

Year	Total Precip (cm)	Ca^{++}	Mg^{++}	K^{+}	Na^{+}	NH_4+	NO_3-	Cl^{-}	$SO_4=$	pH
1980	13.77[1/]	13.90	2.87	1.14	2.43	20.47	22.10	5.04	25.29	4.99
1981	31.70	19.41	6.76	1.18	5.09	18.73	23.33	4.38	32.69	5.01
1982	28.30	10.47	2.96	1.23	2.44	7.76	14.97	2.54	18.95	4.97

[1/] 1980 reflects only 6 months of data, as the site began operation in June 1980.

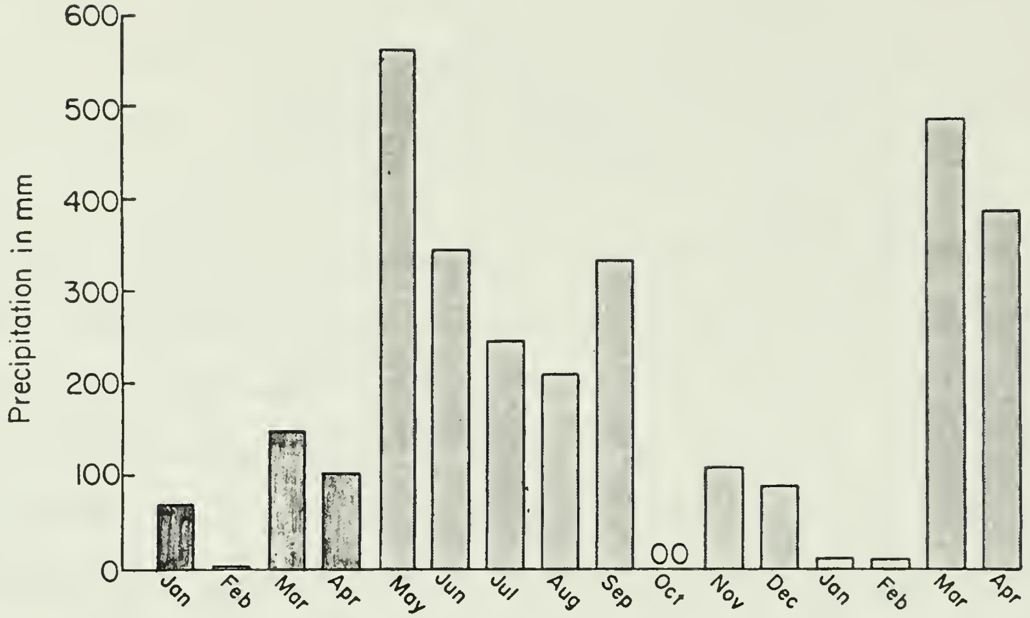

Fig. 11. Precipitation volume, 1/82-4/83, Rocky Mountain National Park headquarters. Data was not available for October 1982.

variability between months for a given parameter may be due to precipitation from different air masses, although this has yet to be tested. Values for pH range between 4.36 and 6.41 during this period and do not seem to reflect seasonal differences.

3.2 Regional Comparison

To place deposition chemistry in perspective with other locations, a comparison has been made of the Rocky Mountain headquarters NADP site with other NADP sites within the state of Colorado. Two additional sites outside Colorado are also included in the comparison. Parsons, West Virginia represents an area currently receiving acidic deposition, and deposition at Olympic National Park is comparable to background values found in the southern hemisphere. In Colorado, Rocky Mountain National Park, Pawnee, and Manitou are located east of the Continental

Divide ("east slope" locations) and Alamosa and Sand Springs are west of the Divide ("west slope" locations). Data is presented not only for hydrogen ion, sulfate, and nitrate concentrations but also for calcium, magnesium, and ammonium ions, which represent alkaline materials responsible for reducing potential acidity. Table 5 represents concentration values (μeq/l) for 1981 and Table 6 shows the deposition values for 1981, where input is given as loading rates in kg/ha.

Table 5. Average annual concentration of wet precipitation, 1981.

Site	pH	$SO_4^=$	NO_3^-	NH_4^+	Ca^{+2} & Mg^{+2}
	μeq/l (precipitation-weighted)				
Alamosa, CO	5.2	38.0	17.0	23.0	28.0
Sand Springs, CO	5.0	33.0	16.0	10.0	31.0
Rocky Mountain National Park	5.0	33.0	23.0	19.0	26.0
Manitou, CO	4.8	34.0	24.0	13.0	24.0
Pawnee, CO	5.1	45.0	28.0	39.0	29.0
Olympic National Park, WA	5.4	8.0	1.5	1.0	10.0
Parsons, WV	4.2	74.0	30.0	16.0	18.0

Table 6. Annual deposition of wet precipitation, 1981.

Site	H^+	$SO_4^=$	NO_3^-	Precipitation (cm)
	kg/ha			
Alamosa, CO	0.01	5.4	2.7	22.0
Sand Springs, CO	0.04	7.3	4.4	40.0
Rocky Mountain National Park, CO	0.03	4.9	4.5	32.0
Manitou, CO	0.07	6.7	6.2	40.0
Pawnee, CO	0.03	7.2	5.7	30.0
Olympic National Park, WA	0.10	18.0	4.4	366.0
Parsons, WV	0.90	46.0	24.0	130.0

The following conclusions can be drawn from these two tables:

1. Precipitation pH in the state of Colorado ranges from approximately 4.8 to 5.6. Rocky Mountain National Park's four-year average is 5.0.
2. Calcium and ammonium concentrations represent significant levels of alkalizing materials which are responsible for lower acidities than would be expected from the concentrations of sulfate and nitrate (if these are considered to originate as sulfuric and nitric acid).
3. Concentrations of sulfate in Colorado are four to five times those found in Olympic National Park and approximately one-half to one-third those found in West Virginia.
4. While there are small variations, sulfate concentrations are reasonably consistent across Colorado, indicating limited influence of local sources.
5. Concentrations of nitrate in Colorado are 10 to 20 times greater than those in Olympic National Park, with levels in Rocky Mountain National Park, Manitou, and Pawnee approximately equal to those in Parsons, West Virginia.
6. Nitrate concentrations are approximately 50% of sulfate levels on the west slope but 70% of those on the east slope. This is most likely due to east slope urban sources.
7. Because of lower concentrations and low precipitation at Colorado sites (20 to 40 cm/yr), sulfate deposition values are less than 20% and nitrate deposition values less than 25% of those in Parsons, West Virginia.

3.3 Conclusions

One of the major factors that determines potential for acidification in aquatic and terrestrial systems is the rate of deposition. A recent survey conducted in Scandinavia and the United States by Wright (1983) suggests that acidification of lakes and streams in sensitive areas occurs when the pH of precipitation drops below 4.7. This is comparable to a sulfate deposition between 20-30 kg/ha. The pH of precipitation in Rocky Mountain National Park on the average is not below 5.0. However, it should be kept in mind that the threshold value of 4.7 was determined in areas of the world that receive considerably more precipitation than the Rocky Mountain region of Colorado. The deposition of nitrates and sulfates in the park is less than 20% of that found in the eastern United States. Deposition can therefore be considered to be currently below what would be considered significant in terms of lake or stream acidification. Nitrate levels in Rocky Mountain are higher than expected, however; this may be a cause for concern in view of its potential effects upon vegetation.

CHAPTER 4

SOILS

4.1 Distribution

Six major land forms and soil regimes have been identified within the watershed (Baron and Walthall 1983). The areal and proportionate extent of these units and surface areas are given in Table 7. The forest soils cover five percent of the watershed and have developed under spruce and fir forest types. Two major soil types are recognized: a Cryoboralf from the forest floor, and a Cryumbrept where talus and glacial till deposits occur. Drainage from these soils is expected to have an influence on the lowest of the study lakes, The Loch. While alluvial soils constitute only one-half percent of the drainage, they are found adjacent to the stream channel and are expected to influence the surface waters into which they drain. Two soil types were found here. Cryohemists occur where a minimal slope

Table 7. Approximate areal and proportionate extent of landforms in Loch Vale.

Soil Regime	Hectares	Percent
Forest soils	45	5.0
Alluvial soils	4	0.5
Rock outcrop--organic soils	15	1.5
Rock outcrop	465	54.0
Rock slides	230	27.0
Alpine ridge	91	11.0
Surface water	10	1.0
Total	860	100.0

creates conditions for bog development, and Cryofluvents occur in forested, low-relief areas more characteristic of a depositional environment.

4.2 Properties

Chemical data characterizing the soil environment are given in Table 8 for typical pedons of the major soil types occurring in the forest and alluvial regimes. Extremely acid soil pH values (determined from 1:1 saturated paste extracts) were found to occur in all of the pedons and ranged from a maximum of 4.8 to a minimum of 3.7. Such extreme acidity would indicate that some source other than carbonic acid (H_2CO_3) dominates the soil system. Organic acids originating in surface litter and preserved by the cool temperatures of this alpine environment are most likely responsible for this extreme acidity (Ugolini et al. 1977). Two distinct patterns exist within the soil profiles of the forest and alluvial soil regimes. In both of the forest soils, the Cryoboralf and Cryumbrept, pH values are highest in the organic layers and decrease with depth. In the alluvial soils, the Cryohemist and the Cryofluvent, the opposite trend occurs with a slight increase in pH with depth.

Cation exchange capacities (determined with neutral soil solutions) are relatively high and originate from two primary sources: (1) the organic component of these soils, and (2) the clay fraction which was found to be dominated by smectite. The exchange complex in organic matter is highly pH-dependent and for the humic fraction is expected to have an exchange capacity of approximately 90 meq/100 g at a pH of 4.0 (Brady 1974). It is important to point out that this value is for the humic fraction and not for the entire organic mass as reflected in cation exchange capacity (CEC) values found in the organic surface layers. These organic layers have an average value of approximately 50 meq/100 g. The organic surface of the Cryoboralf

Table 8. Chemical properties of soils.

HORIZON	DEPTH	pH	Exchangeable Bases				E.A.	C.E.C.	B.S.	O.M.
			Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}				
	(cm)		(meq/100g)						(Percent)	
						Cryoboralf				
Oe	9- 0	4.8	53.1	4.3	2.3	0.2	35.7	95.5	62.6	--[1]
E	0-19	3.8	6.7	0.6	0.3	0.1	12.3	20.0	38.7	2.7
Bt	19-32	3.7	5.2	0.4	0.3	0.1	22.8	28.9	21.0	3.1
BC	32-56	3.7	1.7	0.2	0.3	0.1	14.3	16.5	13.7	1.6
R	56+									
						Cryumbrept				
Oi	1- 0	4.8	20.1	2.7	1.3	0.1	26.7	50.9	47.6	--
A	0-15	4.3	7.2	0.9	0.4	0.1	28.4	36.9	23.2	11.9
2Bw1	15-46	4.2	1.9	0.2	0.1	0.1	13.7	16.0	14.3	2.1
2Bw2	46-74	4.1	1.1	0.1	0.1	0.1	12.9	14.3	9.9	1.3
2R	74+									
						Cryohemist				
Oi	0- 4	3.8	8.0	1.2	1.2	0.6	38.5	49.4	22.1	--
Oe1	4-15	4.0	2.9	0.2	0.3	0.3	38.1	41.8	8.8	--
Oe2	15-25	4.1	4.3	0.2	0.2	0.2	34.9	39.8	12.3	--
Oa	25-33	4.3	5.6	0.2	0.1	0.2	35.1	41.3	14.9	--
Cg	33-43	4.4	5.7	0.4	0.1	0.2	19.0	25.4	25.2	7.0
R	43+									
						Cryofluvent				
Oi	9- 0	3.8	10.0	2.5	1.9	0.4	34.1	48.9	30.2	--
A	0-10	3.8	2.4	0.2	0.2	0.2	34.9	37.9	7.9	11.5
Ca1	10-24	4.0	2.5	0.2	0.1	0.2	26.4	29.4	10.1	6.8
Cg2	24-30	4.0	4.0	0.5	0.1	0.3	25.1	30.0	16.4	12.7
Cg3	30-37	4.2	5.0	1.0	0.1	0.3	28.9	35.4	18.3	26.9
Ob	37-47	4.4	7.5	1.3	0.1	0.4	33.1	42.4	21.9	--
R	47+									

[1] --: Organic matter percentages were not determined for organic horizons.

(pH 4.8) was noted to be more highly decomposed than the other surface layers and was found to have a value of 95.5 meq/100 g.

The clay mineral group of smectites has a characteristic CEC value of 100 meq/100 g that is largely independent of pH. X-ray analysis and CEC determinations of the coarse and fine clay fractions indicate a dominance of this material. Smectite is believed to be a weathering product of biotite and chlorite which commonly occur in the parent rock of this environment. Smectites are not generally considered to be stable weathering products in acidic environments. However, their occurrence in such environments has been noted when accompanied by high silica levels (Borchardt 1979). The highest clay percentages were found in the alluvial soils and ranged from 19.7 to 24.6 percent. Clay distribution in the Cryoboralfs was highest in the argillic horizon at 15.7 percent, with 9.1 and 5.6 percent occurring in the E and BC horizons, respectively. The Cryumbrept had a maximum of 13.4 percent clay in the A horizon and dropped to 4.2 and 4.4 percent in the 2Bw1 and 2Bw2 horizons, respectively.

Base saturation percentages (Thomas 1982) were extremely low for the soil environment as a whole, with maximums occurring in the organic surface layers ranging from 22.1 to 62.6 percent (Figure 12). Extremely low values ranging from 7.9 to 38.7 percent were found in underlying horizons. The sum of the exchangeable bases (Ca^{++}, Mg^{++}, K^{+}, Na^{+}) plus the exchangeable acidity equals the exchange capacity of the soil. Calcium was found to be the dominant basic cation, followed by lesser amounts of Mg^{++}, Na^{++}, and K^{+}. Concentration of these cations in surface layers is apparently a result of nutrient cycling. This process seems quite effective in recovering K^{+} from the soil solution

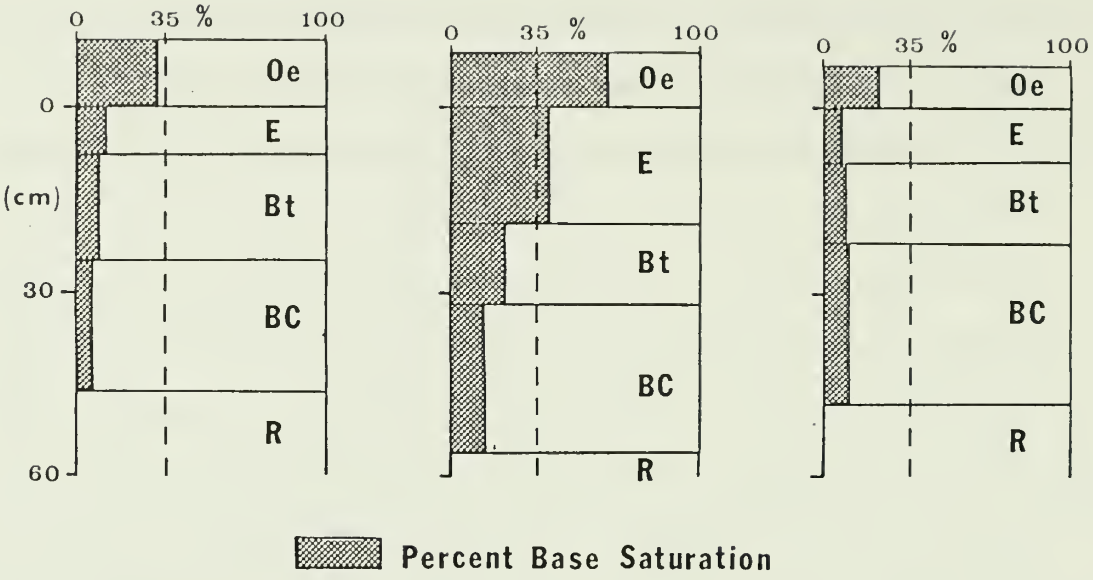

Fig. 12. Percent base saturation of three Cryoboralfs.

as evidenced by its significantly higher concentrations in the organic surface layers compared to Na^{++}. In underlying horizons these two cations occur at similarly low levels. Total aluminum values determined on saturated-paste extracts ranged from 6.5 mg/l to 1.4 mg/l (Bloom et al. 1978).

4.3 Conclusions

The buffering capability provided by these soils to the surface water environment is minimal compared to less acidic, less organic soils. Aluminum and hydrogen dominate the soil exchange chemistry and are flushed into surface waters at the same time as the exchangeable bases and carbonic acid that provide buffering. The Loch, the only lake surrounded by a soil environment, shows significantly lower pH values throughout the hydrologic year (Fig. 13), which may be explained by the input of soil water. The aluminum contained in the soil waters cannot remain in solution at the higher pH of the surface waters and

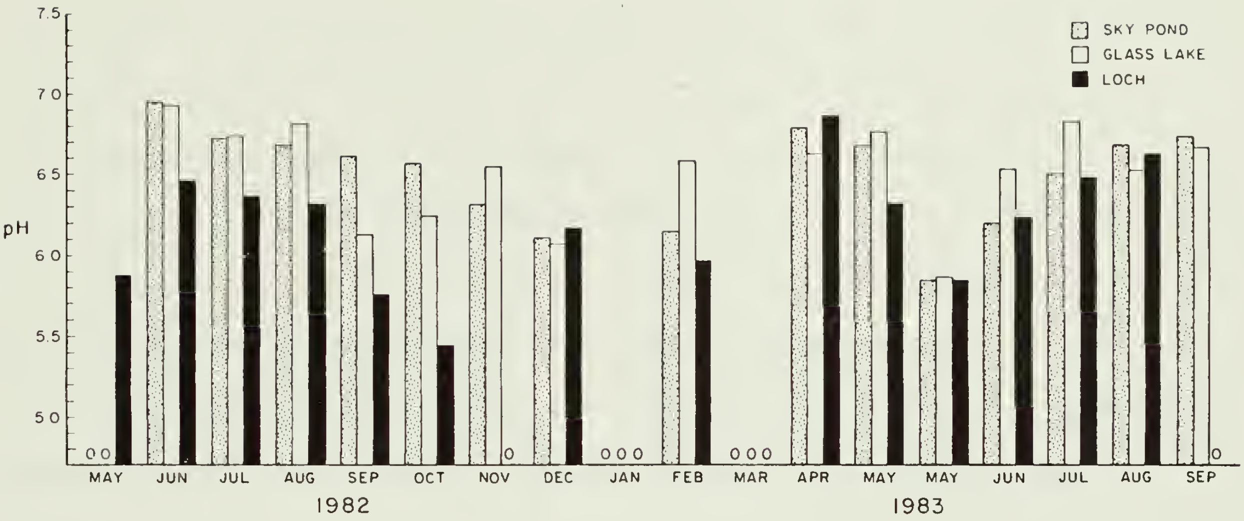

Fig. 13. pH values from epilimnion of The Loch, Glass Lake and Sky Pond over time. Missing values are denoted by 0.

either settles into the sediments or is flushed downstream as it precipitates.

CHAPTER 5

SURFACE WATERS

5.1 Methods

The three lakes of the study drainage, Sky Pond, Glass Lake, and The Loch, are oligotrophic, dilute cirque lakes connected by Icy Brook, a perennial stream. Lake samples have been taken monthly since 1982 from three depths within each lake. Based upon the rate of change observed during different seasons of the year, sampling during the winter months was decreased to once every other month in 1983, and increased to weekly during the months of May-July, to correspond with melting of the accumulated snowpack. Gaging stations are located at the inlet and outlet of The Loch, and daily samples are collected April-July to record snowmelt chemistry. Inlets and outlets from each lake are sampled monthly except when winter conditions make this impossible. Volume is measured continuously at stage height with a remote data recorder (Omnidata); a strip chart recorder serves as a back-up. Field analyses are made for the following parameters: temperature, depth of sample, flow if in streams (Pygmy meter), secchi depth, pH (Corning meter #4 and probe), and conductivity (Fisher specific conductance unit). Conductivity and pH measurements for winter collections are conducted in the laboratory. Subsamples are collected in acid-washed bottles after filtration according to National Acid Precipitation Assessment Program sampling and analysis protocol and sent to the U.S. Geological Survey Denver Laboratory for analysis. The following exceptions to the protocol are made: samples to be analyzed for metals are acidified with 1N HNO_3 rather than HCl, and samples analyzed for NH_4 and PO_4 are fixed with tablets of $HgCl_2$ supplied by the Denver Laboratory. Analyses are made for the following cations and anions: Ca, Mg, Na, K, NH_4, Fe, Mn, Al, NO_3, PO_4, SO_4, Cl, Br, and F. Color and SiO_2 are also measured. Total organic carbon (TOC) and dissolved organic carbon (DOC) were added in 1984.

Alkalinity (including HCO_3 and weak organic acids) is measured at the Natural Resource Ecology Laboratory using a ten-point Gran titration from pH 4.0-3.3 and back-calculating the precise inflection point (Gran 1952; Galloway 1979). Samples collected for alkalinity titrations are preserved with 1 ml reagent-grade chloroform (Keene et al. 1983).

Quality assurance for all samples is maintained by running ten percent of the total samples either as replicates or de-ionized water blanks. Storm event sampling will also begin with the 1985 sample season to determine the importance of these short-term occurrences on the water chemistry of lakes and streams. Approximately six grab samples will be taken on the rising limb of the storm hydrograph and as many will be taken on the falling limb. Samples will be filtered and treated as discussed in Section 5.1.

5.2 Water Chemistry

Results from the lake chemistry study are by no means complete but can be summarized both spatially and temporally to assist with testing the third hypothesis. Major anions and cations for the three lakes are summarized in Figure 14. All three lakes are classified as ultra-oligotrophic, with specific conductance values ranging from 4 to 24

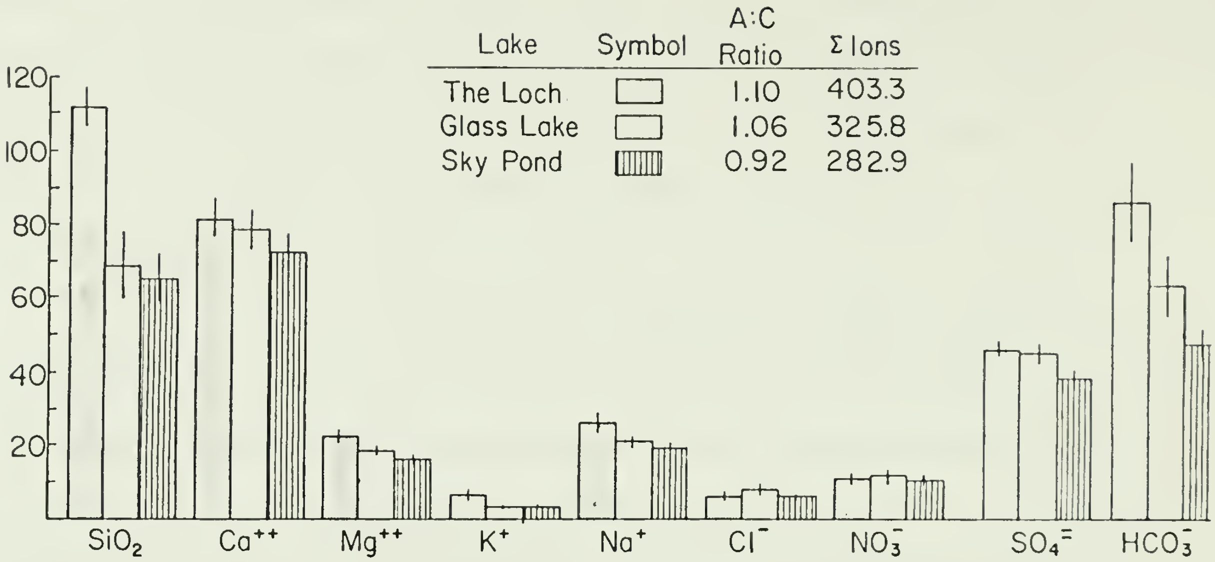

Fig. 14. Average μeq/l (s.e.) of lake surface waters, 5/82-5/83.

μmhos/cm. There is a slight inverse gradient of concentration of most major ions with elevation, with total concentrations of 282.9 μeq/l at Sky Pond, 325.8 μeq/l at Glass Lake, and 403.3 μeq/l at The Loch (values are yearly averages for the period 5/82-5/83). Physically, Sky Pond is surrounded primarily by talus. Icy Brook flows through the rock material to the lake, and much of the input must also occur as ground and surface flow. Glass Lake is also above treeline and is surrounded by talus and somewhat more vegetation in the form of krummholz and tundra. The inlet and outlet are pronounced, with flows ranging from up to 18 cfs at the inlet to 25 cfs at the outlet. The Loch is almost entirely surrounded by subalpine forests and sedge meadows. Icy Brook flows through an extensive area of meadow underlain by Cryohemist and Cryofluvent soils before it enters the lake. Flows at the inlet and outlet of the Loch are measured with Parshall flumes, and range to 43 cfs at the inlet and to 50 cfs at the outlet.

The increasing ionic concentration from Sky Pond to The Loch can be explained in part by the increasing amount of drainage area. The surrounding soils also contribute to the greater ionic concentration in The Loch. As was discussed in the soils section, it is felt that the very acidic soil solution contributes to significantly lower pH values ($p<.01$) recorded for The Loch.

Although samples from three depths are taken from each lake, none of the lakes has yet been seen to stratify strongly. Temperatures range from 0°C to 4°C in the winter and from 7°C to 12°C in the late summer months. Strong winds are a feature of the Colorado Front Range, and it is felt that these winds, which may occur at any time of the year, are responsible for mixing lake waters. The flushing rate in these lakes is also high; the volume of water flowing out of the drainage in 1983 was 19 times greater than the volume of The Loch. The high volume of water may also be responsible for preventing stratification.

5.3 Aquatic Biota

Stream benthos and periphyton collections are made regularly, although systematic work is not yet complete. Phytoplankton are also collected from the lakes whenever water samples are taken. Work on the cycling of organic carbon and primary productivity began in 1984.

5.4 Hydrologic Quantification

Water is the most important means of biogeochemical movement in the Loch Vale drainage. Transport of materials from one compartment to another is a mostly water-mediated process. To understand the changes that will occur due to weathering enhanced by increased atmospheric deposition, it is felt that an attempt at hydrologic quantification must be made. We feel it is important to the overall objectives of the study to know the fate of the water that enters the drainage. Such knowledge will help in model development by indicating residence times within the various compartments where chemical alteration can occur. The approach to the hydrology of Loch Vale follows the approach addressed by Winter (1981). Hydrologic quantification will focus upon the Loch, the lowest of the study lakes, and will begin with the measurement of precipitation, stream flow, and lake volume. Currently, three Belfort weighing bucket rain gages record precipitation. Seven plastic gages are placed around all lakes in the summer as backup. A weather station (Campbell Scientific 21x micrologger with probes for air and water temperature, wind speed, and relative humidity) will be installed in the middle of The Loch. Backup measurements will be made with hand-held instruments, and correlations will be made with the main weather station located 2/3 km away. One Parshall flume is in place at The Loch outlet. Remote data recorders (Omnidata) serve as primary instrumentation, and Stevens stage height recorders serve as backup. Seismographic work will help in determining whether a sizeable fraction of water moving through the drainage occurs as subsurface flow.

5.5 Conclusions

The volume of flow appears to be the single most important feature controlling the water chemistry of these lakes. All waters sampled exhibit a seasonal temporal variation which can be related to the movement of waters (Figs. 15 to 18). Figure 19 shows a strong inverse relationship (r=.66) between conductance and spring stage height.

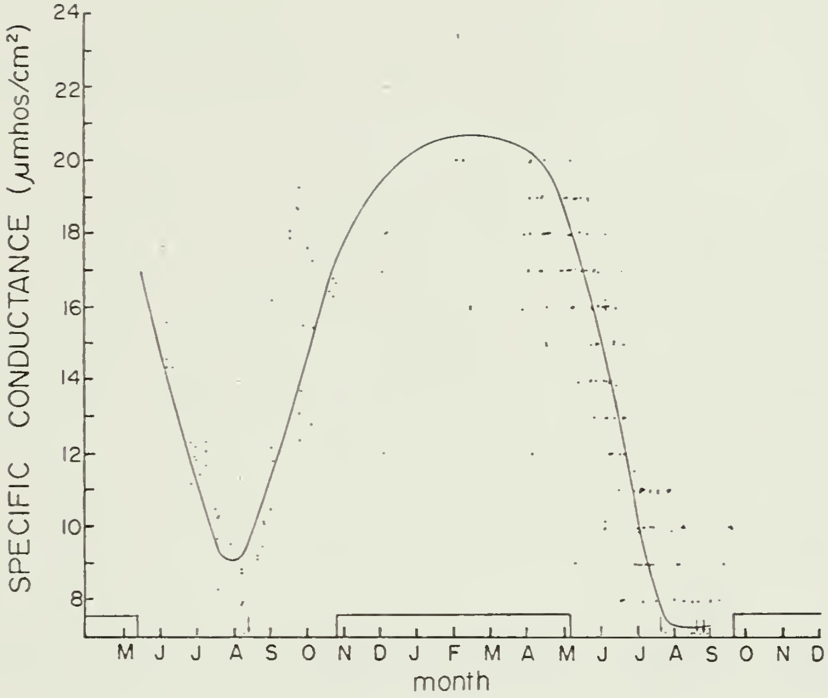

Fig. 15. Specific conductance values from all sample locations in Loch Vale, 5/82-12/83.

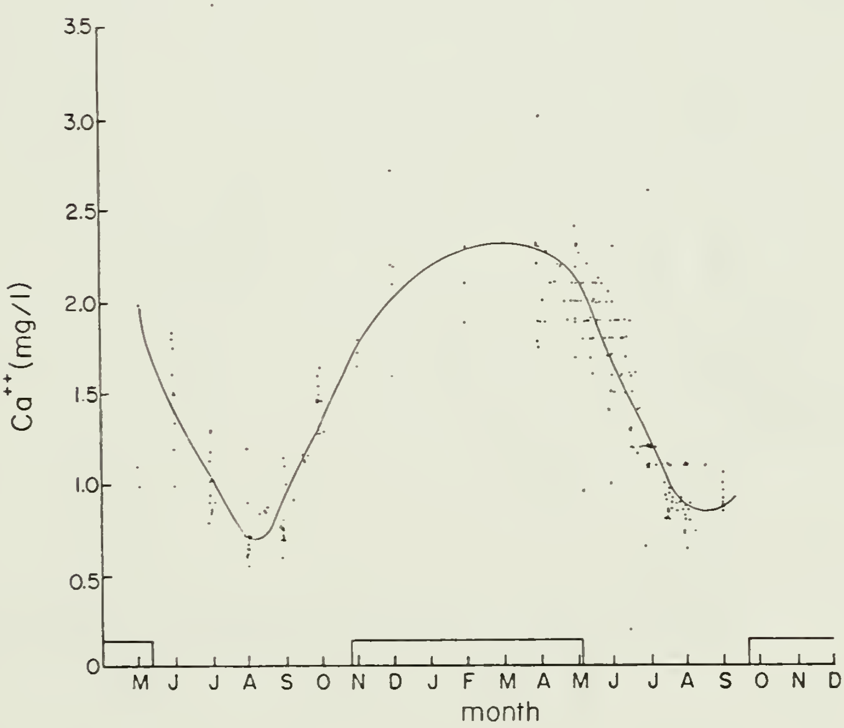

Fig. 16. Calcium concentrations from all sample locations in Loch Vale, 5/82-12/83.

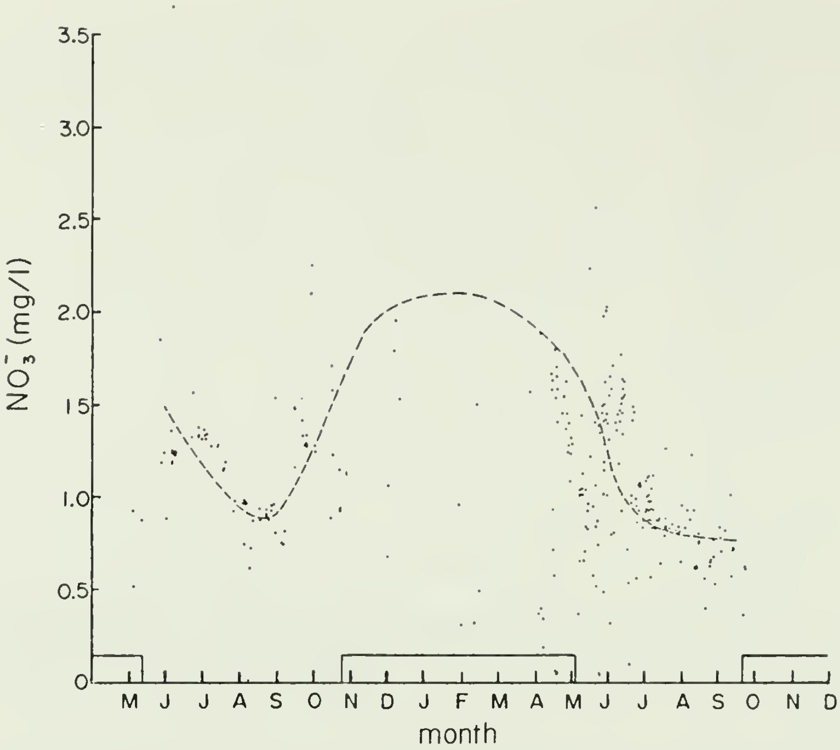

Fig. 17. Nitrate concentrations from all sample locations in Loch Vale, 5/82-12/83.

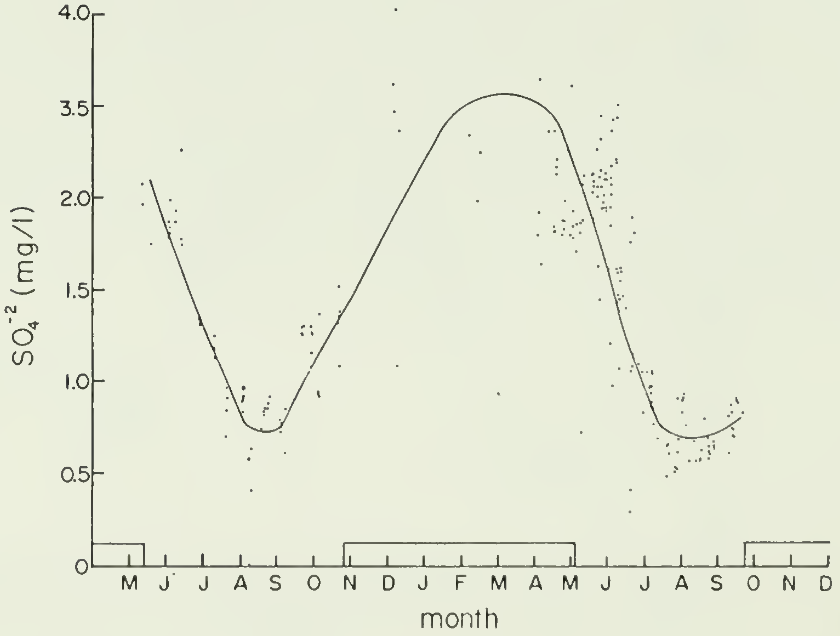

Fig. 18. Sulfate concentrations from all sample locations in Loch Vale, 5/82-12/83.

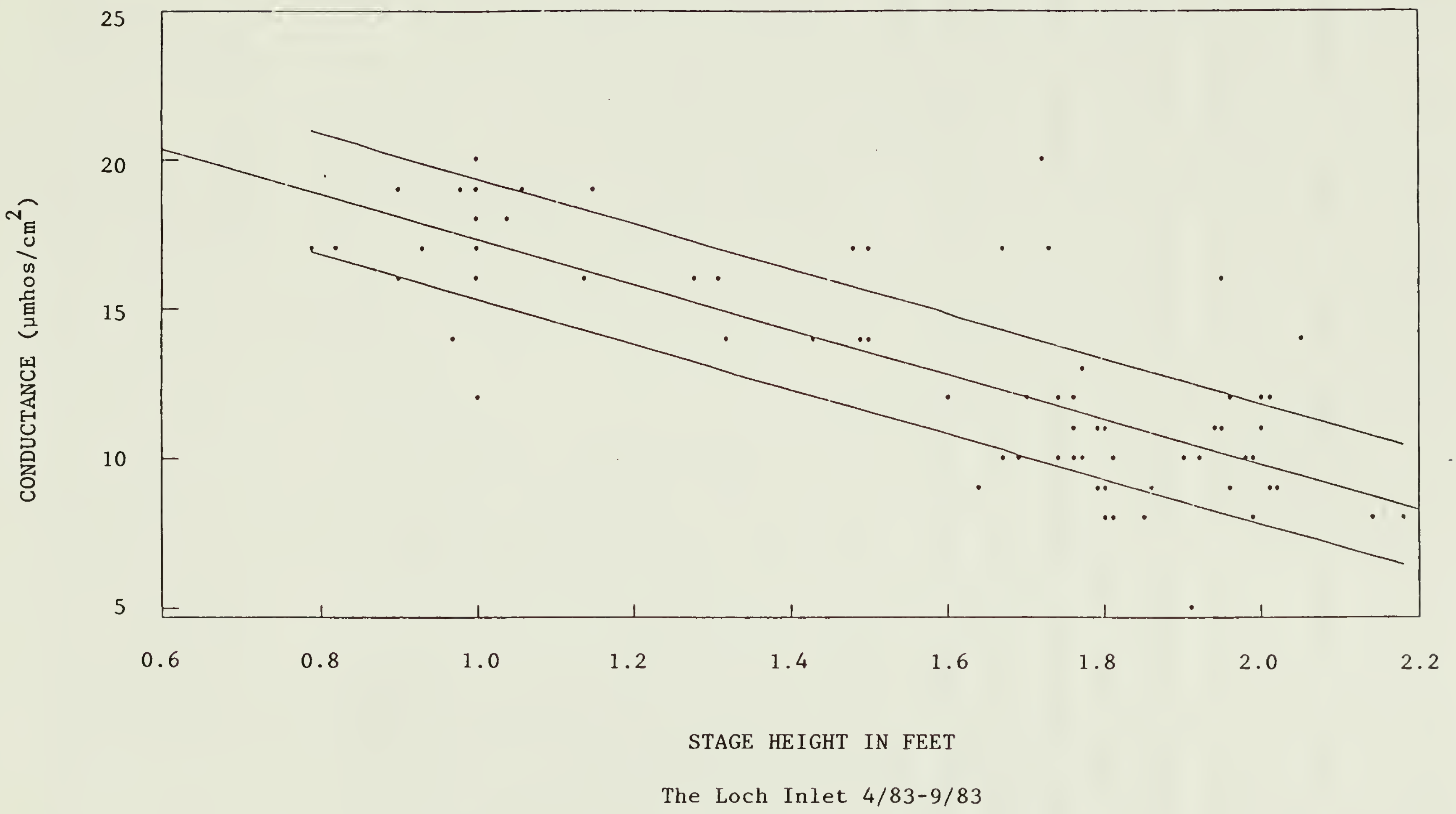

Fig. 19. Regression of spring 1983 stage height vs. conductance, The Loch Inlet. 95% confidence intervals are shown.

Conductance, Ca, SO_4, and to a lesser degree NO_3 exhibit a seasonal undulation in concentration. This undulation is explained as follows: the lack of flushing due to winter freezing allows an accumulation of cations and anions, resulting in increased conductance. The advent of snowmelt (between April and July) causes dilution of these solutions, and the ionic concentration decreases dramatically. The summer months of August and September show water chemistry at its most dilute, perhaps due to reduced precipitation and to maximal terrestrial biological activity, which immobilizes nutrients and ions available for flushing. These waters typically freeze over during October and November, again with a corresponding rise in ionic concentration.

CHAPTER 6

SYNTHESIS

6.1 Introduction

Our initial paleoecological work in Rocky Mountain National Park provides a baseline of past conditions that can be compared to what we find for the present and future. Information from sediment cores has been used to infer historical levels of pollutants, and the findings give us strong reason to state that there are as yet no trends toward acidification.

From this starting point we were able to go into the Loch Vale drainage and characterize the various components of the ecosystem that contribute to the surface water makeup. Up until now, the work has been primarily descriptive in nature. Precipitation, soils, surface waters and their biota, and geologic material have been characterized to some extent. In order to meet the objective of understanding biogeochemical processes in Loch Vale and in subalpine areas elsewhere, one must go beyond empirical description. We are now in a position to do so, and the plans for synthesis work include addressing the intercompartmental flow of materials with the use of models, and testing such models with actual data.

6.2 Model Development

Concurrent with synthesis work will be the application or development of interface models. The conceptual model shown in Figure 3 represents the perceived important interfaces. A number of existing biogeochemical models address these interfaces from a point of chemical equilibrium: ILWAS (EPRI 1983), and models by Schnoor (1984) and Cosby et al. (1984). We currently plan to adapt these existing models until we obtain outputs that resemble the actual Loch Vale system. Completion of the hydrologic quantification and representation of the Loch Vale drainage will take several years. By knowing the rates of movement of solutions through Loch Vale and understanding the biogeochemistry which controls the compartments under study, we will finally be in a position to explain the current processes and perhaps even to predict changes due to increased acidic deposition, should it occur.

6.3 Research Results

The high elevation Front Range ecosystems of Rocky Mountain National Park are extremely vulnerable to acidification from atmospheric depositon. Atmospheric deposition at this time is not acidic, and neither have we found historical trends toward acidification over the past 150 years. The terrestrial and aquatic ecosystems of Loch Vale are close to pristine, although increases in lead over time indicate some industrial influence.

Should precipitation become more acidic, however, potential damage could occur for two reasons: (1) almost no buffering capacity is found in the bedrock, soils, or surface waters themselves, so acidic deposition will result in acidic surface waters, and (2) if the park's lakes and streams acidify, soil inputs may aggravate the situation by contributing additional acidity and soluble aluminum.

Currently, enough interaction occurs within the bedrock, soils, and ground waters to maintain the pH of the waters in the lakes and streams. However, exceptions occur in the spring, when the sheer volume of water (caused by snowmelt runoff) prevents exchange from taking place. The lower elevation waters of Loch Vale are more concentrated and more acidic due to greater acidic inputs from the soils of the watershed.

6.4 Further Work

The work described above should fulfill the original stated objectives. Some additional questions and ideas for further study that are equally pertinent to the examination of the effects of acidic deposition are the following:

1. Examination of the nutrient status of the different plant communities. Eastern U.S. forests are declining in vigor, and the hypothesis has been raised that excessive loading of NO_3 may be partially responsible. One would suspect alpine/subalpine systems to be nitrogen-limited, so increased amounts of atmospheric N (such as is currently occurring) might be expected to cause a minor growth surge initially. The question of how this would occur and what might happen afterwards (e.g., would nitrogen ever become excessive?), as well as questions of primary productivity and biomass production, deserve work.

2. Transport and deposition mechanisms. Our work has focused specifically on what happens to precipitation after it falls to the ground. A study of the kinds of deposition and its sources is needed. Knowledge of atmospheric movements would enable us to predict actual increases in polluted deposition. Knowledge of the proportion of gases and aerosols to wet deposition bringing ions to the drainage would give a much better idea of overall deposition.

3. Physical limnology. It has been postulated that some Loch Vale lakes may behave like "stream pools" rather than discreet bodies of water. This might result in profound differences in response to acidification. To our knowledge, a physical limnology study of alpine/subalpine lakes has not been done.

4. Aquatic population dynamics. The need to understand aquatic population dynamics has been discussed for several years, but such study is beyond the scope of the current work. Even so,

our preliminary investigations of benthic arthropods have raised some interesting questions on how these populations live in a stressed environment. How stressed are these populations naturally? What might happen if one increases the amplitude of chemical variability with the occurrence of acidic deposition? These questions and others need to be addressed not only for arthropods but also for algae, zooplankton, and fish populations.

5. Ground-water hydrology. Some knowledge of ground-water movement will be gained in the hydrologic portion of this work, but not enough. It will be not only interesting but necessary to observe the changes in ground-water chemistry from water flowing through unconsolidated parent material to the soil mantle.

6. Sediment-water interface. An understanding of the sediment-water interface must be obtained. At present we can only speculate on the migrations of materials, both soluble and particulate, to the sediments from other system compartments, and we have little idea what biogeochemical processes then occur. The question of the sources and sinks for aluminum is particularly pressing, especially since the current spring pH depression brings waters near values where aluminum becomes soluble.

7. Terrestrial microorganisms. Microorganisms and arthropods may be affected by changes in the chemical equilibrium of soil due to altered atmospheric inputs. These organisms play an important but undefined part in the decomposition of litter and in nitrogen fixation. A study of their rôle in the terrestrial environment of alpine and subalpine areas would be valuable.

8. The role of terrestrial vegetation in influencing aquatic chemistry. How influential are the different vegetation types upon the flux of major anions and cations? How could that be expected to change with different seral stages?

We hope that the data-gathering effort we have begun here will attract other researchers who not only will help answer the above questions but who also will generate questions of their own. Over the coming years, then, the data base will grow far beyond what could be provided by a biogeochemical study into the effects of acid deposition.

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