Environment Canada
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ACID PRECIPITATION DURING 1987
KEJIMKUJIK, N.S.

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Atlantic Region
Atmospheric Environment Service
Bedford, N.S.

Table of Contents

List of Figures

List of Tables

1. Introduction

A precipitation sampling station has been operated in Kejimkujik National Park in southwestern Nova Scotia since May 1979 by the Atmospheric Environment Service (AES) of Environment Canada. Precipitation samples are collected on a daily basis at the station and are sent to be analyzed in a quality controlled manner in a laboratory. The samples are analyzed for pH (acidity) and for the concentration of various chemical constituents, including sulfates and nitrates. The results are published in AES data reports; prior to June 1983, the APN (Air and Precipitation Monitoring Network) reports and, presently, the CAPMoN (Canadian Air and Precipitation Monitoring Network) reports.

Since December 1983, the acidity of the precipitation has also been measured on-site. Environment Canada issues 'The Acid Rain Report' each Tuesday, summarizing the information gathered on-site during the previous week (see Appendix A). This Report includes a list of areas over which the air mass has passed before arriving at the collection site. These data give an idea of the source of the pollutants that are associated with the precipitation events. The Reports show that precipitation pH varies considerably from event to event and that acidity levels are generally correlated with the levels of emissions from upwind source areas. Although the APN/CAPMoN pH data have more quality control features, they are not available as quickly as the on-site pH data and do not include the "air path to site" information.

The pH value of the precipitation is a measure of the hydrogen ion concentration (acidity) of the precipitation. The pH scale is a base 10 logarithmic scale from 0 (highly acidic) to 14 (highly alkaline), with a value of 7 being neutral. Since the scale is logarithmic, a pH of 4, for example, is ten times more acidic than a pH of 5. A pH value of 5.6 is the characteristic acidity of clean precipitation, that is, precipitation which has no pollutants. Precipitation which has a pH lower than 5.6 (more acidic) is called "acid precipitation". Most of eastern Canada receives precipitation with average pH values ranging from 4.2 to 4.5.

Environmental damage to lakes and streams is usually observed in acid sensitive areas that regularly receive precipitation with pH less than 4.7. Readings of 4.2 and below are considered strongly acidic and are common at Kejimkujik. Readings of less than 4.0 are considered to be serious events, although they do not constitute an immediate danger to human health or property. The effects of acid rain and snow are generally cumulative over time, although fish kills have been observed after low pH events and after the melting of acidic snow (MOI, 1983).

2. Analysis of Data for 1987

2.1 Preparation of the Data Set

The on-site pH data set with "air path to site" information for 1987 was used as the basis for this report. In preparing the data set, it was found that three days had insufficient sample volume for a proper pH measurement. These entries were eliminated from the data set.

The analysis of the pH data measured on-site yielded an unusually low annual average pH and an unusually high annual wet hydrogen ion deposition compared to previous years. Because the preliminary data set for 1987 was available, a comparison was made between the on-site data and the preliminary CAPMoN data. It was found that twenty-six deposition events had a difference in pH between the on-site and CAPMoN data of more than 0.4. In twenty-five instances, the preliminary CAPMoN value was used. In the one remaining instance, the CAPMoN value was rejected due to a poor ion balance (see Appendix B and Vet et al, 1988b).

2.2 Annual Summary

The variations in precipitation pH at Kejimkujik, N.S. during 1987 are shown in Figures 1-3. Each figure is a plot of the pH value of the precipitation against the day of the year for a four month period: January to April, May to August and September to December. Different types of precipitation (rain, snow or mixed) are indicated symbolically. Lines representing the following three significant pH levels are also indicated on each figure:

1. normal or clean precipitation (pH = 5.6)
2. damaging pH level (pH = 4.7)
3. seriously acidic level (pH = 4.0)

The Figures show that only one of the precipitation events at Kejimkujik in 1987 was in the clean pH range (with a pH of 5.74) and that most were within the slightly acidic or damaging ranges. A significant number were in the seriously acidic pH range. The most acidic event of the year had a pH of 3.38, which was 230 times more acidic than the least acidic event. Table 1 summarizes these events:

Table 1: Summary of Precipitation Events at Kejimkujik, N.S. During 1987

Level of pH	pH Range	Number of Occurrences	Percentage
Normal (clean)	$pH > 5.6$	1	0.8%
Slightly Acidic	$4.7 < pH \leq 5.6$	57	43.2%
Damaging	$4.0 < pH \leq 4.7$	50	37.9%
Seriously Acidic	$pH \leq 4.0$	24	18.2%

Very low pH values (high acidity) are generally associated with events that produce only a small amount of precipitation (Anlauf et al., 1975). The total acid deposition from these events may not be as large as for other, higher pH events with more precipitation. The deposition of acid (mg/m^2) for each event is calculated by converting the precipitation pH into a hydrogen ion concentration (mg/l) and multiplying by the amount of precipitation (mm). A water equivalent in millimeters is used for snow by assuming that 1 cm of snow is equivalent to 1 mm of water.

To calculate the average pH value over a number of events, a precipitation-weighted average hydrogen ion concentration is determined by summing the hydrogen ion deposition for each event and then dividing by the total precipitation from the events. The average hydrogen ion concentration is then converted into an average precipitation-weighted pH value.

The annual average precipitation-weighted pH at Kejimkujik, N.S. in 1987 was 4.48. This was calculated for 132 precipitation days which produced 1213.2 mm of precipitation during the year. The overall resultant hydrogen ion deposition was 40.1 mg/m^2 (.40 kg/ha).

Different precipitation types accounted for significantly different amounts of the total deposition of acid. Table 2 separates precipitation into three types : rain, snow and mixed (rain and snow in one day). Rain events predominated at Kejimkujik and had the lowest average pH and highest deposition.

Table 2: Analysis of Precipitation Events by Precipitation Type for Kejimkujik, N.S. During 1987

Type of Precipitation	Number of Days	pH Value	Deposition of Acid	Percentage Deposition
Rain	79	4.37	29.6 mg/m^2	73.8%
Snow	39	4.67	6.0 mg/m^2	15.0%
Mixed	14	4.74	4.5 mg/m^2	11.2%

2.3 Seasonal Summary

The data were grouped into four-month periods as shown in Figures 1 - 3: January to April, May to August and September to December. Table 3 shows the number of precipitation days in each four-month period, the total precipitation, the average precipitation weighted pH and the total deposition for the four month period.

Table 3: Analysis of Precipitation Events by Season for Kejimkujik, N.S. During 1987

Period	Precipitation Days	Precipitation Amount	Average pH	Deposition Amount
January - April	44	421.3 mm	4.60	10.4 mg/m^2
May - August	35	240.5 mm	4.13	17.8 mg/m^2
September - December	53	551.4 mm	4.67	11.9 mg/m^2

The summer period had the largest deposition and the lowest pH although the number of days and amount of precipitation were less than in the other two periods of the year.

2.4 Regional Contributions to Precipitation Acidity

The precipitation events were then categorized by their pH value ($pH \leq 4.0$, $4.0 < pH \leq 4.7$, and $pH > 4.7$) and by the regions which the air mass had passed over before arriving at

Kejimkujik. The regions are shown in Figure 4 and defined as:

MidW:	United States Midwest
ECst:	U.S. East Coast
USGL:	U.S. Great Lakes Region
NOnt:	North and Central Ontario
SOnt:	Southern Ontario
NQue:	Northern Quebec, Central Quebec and Northwestern Quebec
SQue:	Southern Quebec
NEng:	New England
AtlO:	Atlantic Ocean
Mrtm:	Maritimes, Gaspe, Newfoundland and Labrador

The U.S. Great Lakes area did not appear in the "air path to site" data for Kejimkujik N.S. in 1987 although it has been a source region in past years.

In previous years, the meteorologist who prepared the Acid Rain Report identified the "Main Source Region" of pollutants for each precipitation event (see Pettipas and Beattie, 1987). However, this information was not available for the 1987 data. Instead, each region that was along the "air path to site" was categorized with the precipitation pH that occurred at Kejimkujik. This led to some ambiguity in correlating pH to source regions since the regions along the air path to Kejimkujik would not be equally "responsible" for the resulting precipitation pH (see sample Acid Rain Report in Appendix A).

The results of the analysis are plotted in Figure 5. Each pie diagram represents a pH range and each slice represents a different region which is labelled just outside of the slice. The number, printed immediately after each region name, represents the number of precipitation events for which that region had been on the "air path to site" (with the precipitation pH in the range indicated).

This Figure indicates that a correlation exists between the pH of precipitation at Kejimkujik and the levels of pollutant emissions from upwind regions. For example, precipitation events in the seriously acidic range ($pH \leq 4.0$) generally have "air paths to site" that cross the more heavily industrialized regions in the United States and Canada. For instance, they cross New England in 17 out of 24 seriously acidic events. Furthermore, the U.S. Midwest only occurs on the "air path to site" in the seriously acidic event range. In contrast, the entire Maritimes region (including Newfoundland, Labrador and the Gaspe Peninsula) is only identified in four of the events.

Precipitation events with damaging acidity levels (4.0 < pH ≤ 4.7) show a lessening influence from industrial regions. For example, 19 of the 50 events in the damaging range of acidity passed over New England.

Precipitation events with pH values above the damaging level (pH 4.7) predominantly have "air paths to site" in Canada or over the Atlantic Ocean. Only 9 of the 58 events in the non-damaging range of acidity passed over New England.

Figures 6, 7 and 8 show, for each of the four-month periods, how frequently the contributing source regions are identified with each pH range in different seasons. The patterns are similar to the annual ones shown in Figure 5, with some variations. In the May - August period, 9 of the 10 seriously acidic events (pH ≤ 4.0) had paths over New England whereas the ratio was lower in the other periods. In the September-December period, 2 of the 5 seriously acidic events had paths over Southern Quebec, a significantly larger (by a factor of 2) ratio than during the rest of the year.

3. Comparison with Previous Years

In 1986 the average annual precipitation-weighted pH was 4.47 (Pettipas and Beattie, 1987) compared to 4.48 in 1987, which indicates that, overall, the average acidity of precipitation had remained within 3% of the 1986 acidity. The average pH was lowest and the deposition highest in the May - August period. This indicates that the colder periods in 1987 experienced cleaner precipitation than the summer, the same as in 1986 (Pettipas and Beattie, 1987), but opposite to what occurred in 1985 (Webber and Beattie, 1986).

Figure 9 shows the average annual pH of precipitation received at Kejimkujik from 1980 to 1987. (For Figures 9 and 10, data for previous years were obtained as follows: 1980-1983 data from R. Vet and W. Sukloff; 1984 data from Vet et al, 1986; 1985 data from Vet et al, 1988a; 1986 data from Vet et al, 1988b). The least acidic year was 1983 and most acidic year was 1985. The drop in acidity levels from 1985 to 1986 continued, to a lesser extent, for 1987. This drop in acidity <u>may</u> indicate that 1985 was an anomalously acidic year and that the decrease in acidity is a partial return to levels seen in the early 1980's. It should be noted, however, that the average acidity of the precipitation only decreased 3% from 1986 to 1987, so it is difficult to identify any trends.

Deposition values, rather than pH, present a clearer picture of the cumulative contamination to the area, since it is the total deposition of acid from precipitation that causes the long term damage to the environment (MOI, 1983). The annual acid deposition at Kejimkujik in 1987 was 40.1 mg/m^2, a decrease of 18% from the 1986 deposition of 49.0 mg/m^2. This drop was partially due to a slight increase in pH but mainly to a lower precipitation amount. The annual precipitation amount was 16% lower in 1987 than 1986 and there were 16 fewer days with precipitation. Since the normal amount of precipitation at Kejimkujik National Park (based on 1951 - 1980) is 1436.2 mm (A.E.S., n.d.), the precipitation in 1987 was 16% lower than the normal. Figure 10 illustrates that the annual wet hydrogen ion deposition has dropped since 1985 but has not reached the low levels observed in 1983 and 1984.

4. Summary

The average precipitation - weighted pH for 1987 at Kejimkujik National Park in southwestern Nova Scotia was 4.48, with the lowest four-month average in May - August and the highest in September - December. The most acidic event of the year, with a pH of 3.38, was two hundred and thirty times more acidic than the least acidic event (pH of 5.74). More than 18% of the events were seriously acidic (pH $\leq$ 4.0).

In comparison with the previous year, Kejimkujik experienced 18% less acid deposition and 16% less precipitation, and had a very slight increase in average annual precipitation pH. The decrease in deposition is mainly a result of a decrease in precipitation rather than a decrease in acidity of precipitation from 1986 to 1987. Although the deposition is the lowest since 1984, the amount of precipitation in 1987 is the lowest since 1980.

Acknowledgements

Bernie Flynn	- Preparation of Figures 1 - 3
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Fraser MacNeil	- Assistance with data handling
Cathy Pettipas	- Calculation of the 1986 results
Bob Vet and Bill Sukloff	- Providing 1980-1983 annual pH and hydrogen ion deposition values (and preliminary data for 1987) from the Atmospheric Environment Service's quality controlled data set
Michael Webber	- Calculation of the 1985 results and creation of the trajectory regions program

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Vet, R.J.; W. B. Sukloff; M.E. Still; J.B. Martin; W.F. Kobelka and A. Gaudenzi. 1988b. Canadian Air and Precipitation Monitoring Network (CAPMoN) Precipitation Chemistry Data Summary 1986. Report: AQRB-88-02. Atmospheric Environment Service, Downsview, Ont.

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APPENDIX A

WBCN3 CWUL 231800
ACID RAIN REPORT ISSUED BY ENVIRONMENT CANADA FOR THE PERIOD JUNE 14 TO 20 1987.

SITE	DAY	PH	AMOUNT	AIR PATH TO SITE
LONGWOODS NEAR LONDON ONT.	NO PRECIPITATION THIS WEEK			
DORSET MUSKOKA ONT.	18	3.8	2 R	MICHIGAN/SOUTHERN ONTARIO
CHALK RIVER OTTAWA VALLEY ONT.	16	3.9	1 R	NORTHERN AND CENTRAL ONTARIO
	18	3.6	1 R	MICHIGAN/CENTRAL ONTARIO
SUTTON QUE.	14	4.0	3 R	MICHIGAN/SOUTHERN AND EASTERN ONTARIO/NEW YORK
	16	4.6	10 R	NORTHERN ONTARIO/CENTRAL AND SOUTHERN QUEBEC
MONTMORENCY QUEBEC CITY QUE.	NO DATA AVAILABLE			
KEJIMKUJIK SOUTHWESTERN NOVA SCOTIA	14	4.7	17 R	NEW JERSEY/SOUTHERN NEW ENGLAND/ ATLANTIC OCEAN
	16	4.0	5 R	NORTHERN QUEBEC/MAINE/NEW BRUNSWICK
	17	3.9	1 R	EASTERN QUEBEC/NEW BRUNSWICK

R...RAIN MEASURED IN MM
M...MIXED RAIN AND SNOW MEASURED IN CM
S...SNOW MEASURED IN CM

DATA FOR DORSET SUPPLIED BY ONTARIO MINISTRY OF ENVIRONMENT.

ENVIRONMENTAL DAMAGE TO LAKES AND STREAMS IS USUALLY OBSERVED IN SENSITIVE AREAS REGULARLY RECEIVING PRECIPITATION WITH PH LESS THAN 4.7. PH READINGS LESS THAN 4.0 ARE SERIOUS.

TUESDAY JUNE 23 1987 1744Z

23 JUN 87 17 46 Z

APPENDIX B

Poor Ion Balance

The ion balance of a sample is considered poor when the sample ion balance failed to meet one of the following criteria:

(1) Ion Percent Difference $< \pm 50\%$ when the sum of anions plus the sum of cations ≤ 50 μeq/l.

(2) Ion Percent Difference $< \pm 25\%$ when the sum of anions plus the sum of cations > 50 μeq/l and < 100 μeq/l.

(3) Ion Percent Difference $< \pm 12.0\%$ when sum of anions plus the sum of cations ≥ 100 μeq/l.

where Ion Percent Difference is defined below.

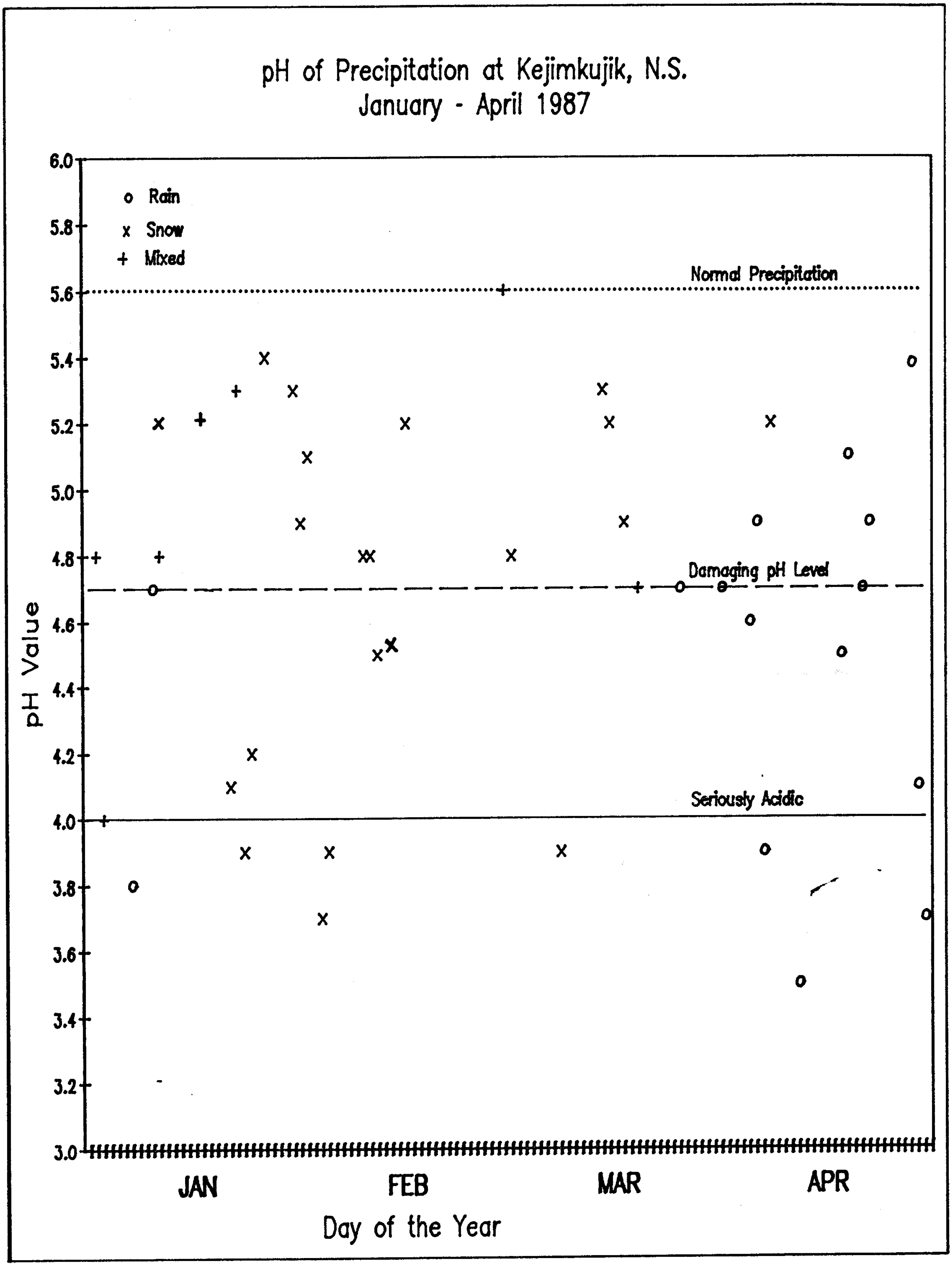
$$\text{Ion Percent Difference} = \frac{\Sigma\ \text{Anions} - \Sigma\ \text{Cations}}{\Sigma\ \text{Anions} + \Sigma\ \text{Cations}} \times 100$$

$$\text{Where } \Sigma\ \text{Anions} = [SO_4^{=}] + [NO_3^{-}\text{-}N] + [Cl^{-}] + 4.90/[H^{+}] \quad (\mu eq/l)$$

$$\text{and } \Sigma\ \text{Cations} = [H^{+}] + [NH_4^{+}\text{-}N] + [Na^{+}] + [Ca^{++}] + [Mg^{++}] + [K^{+}] \quad (\mu eq/l)$$

From: Vet et al (1988b)

Figure 1



pH of Precipitation at Kejimkujik, N.S.
January - April 1987
o Rain
x Snow
+ Mixed
Normal Precipitation
Damaging pH Level
Seriously Acidic
pH Value
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
JAN
FEB
MAR
APR
Day of the Year

Figure 2

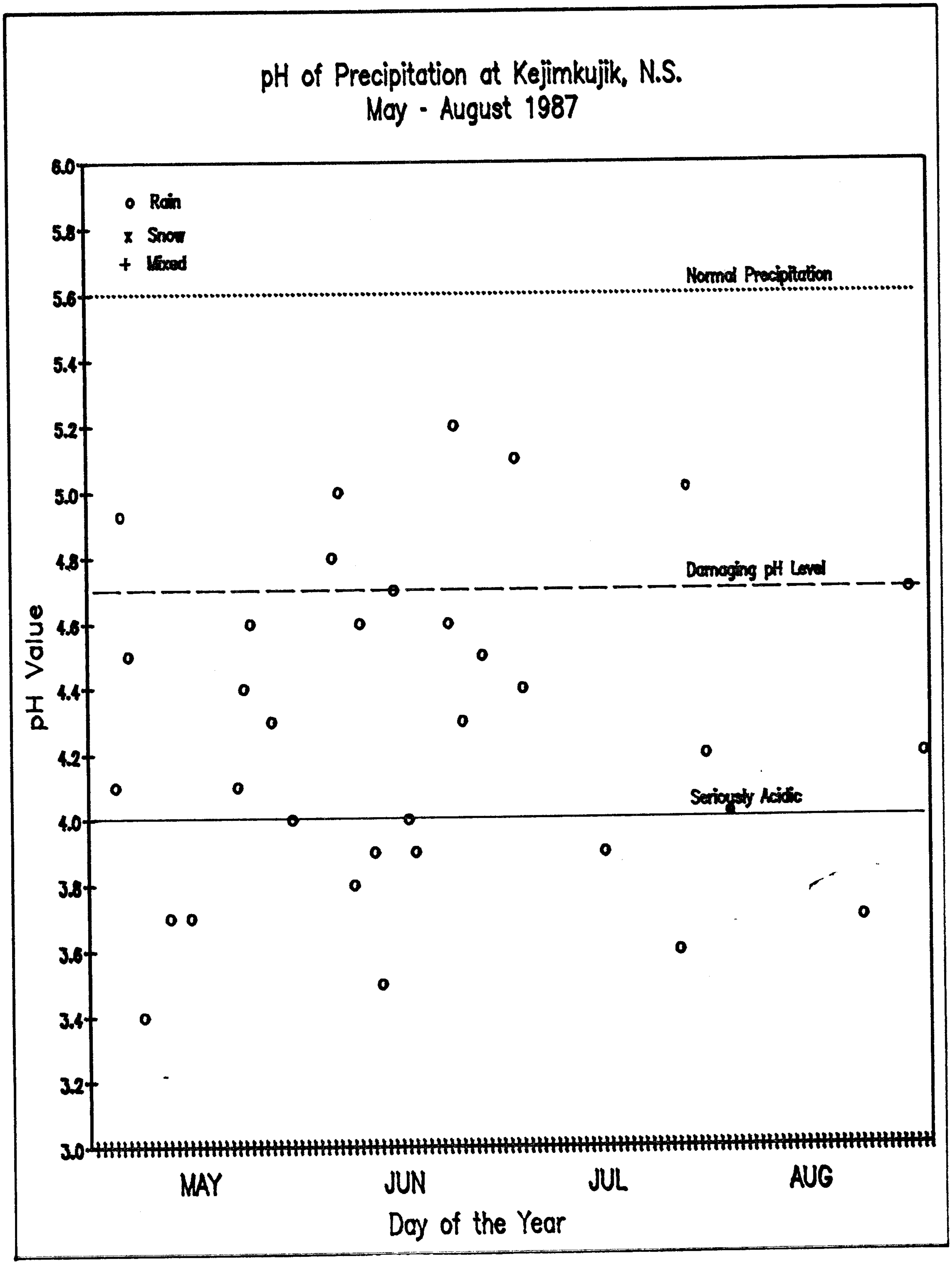
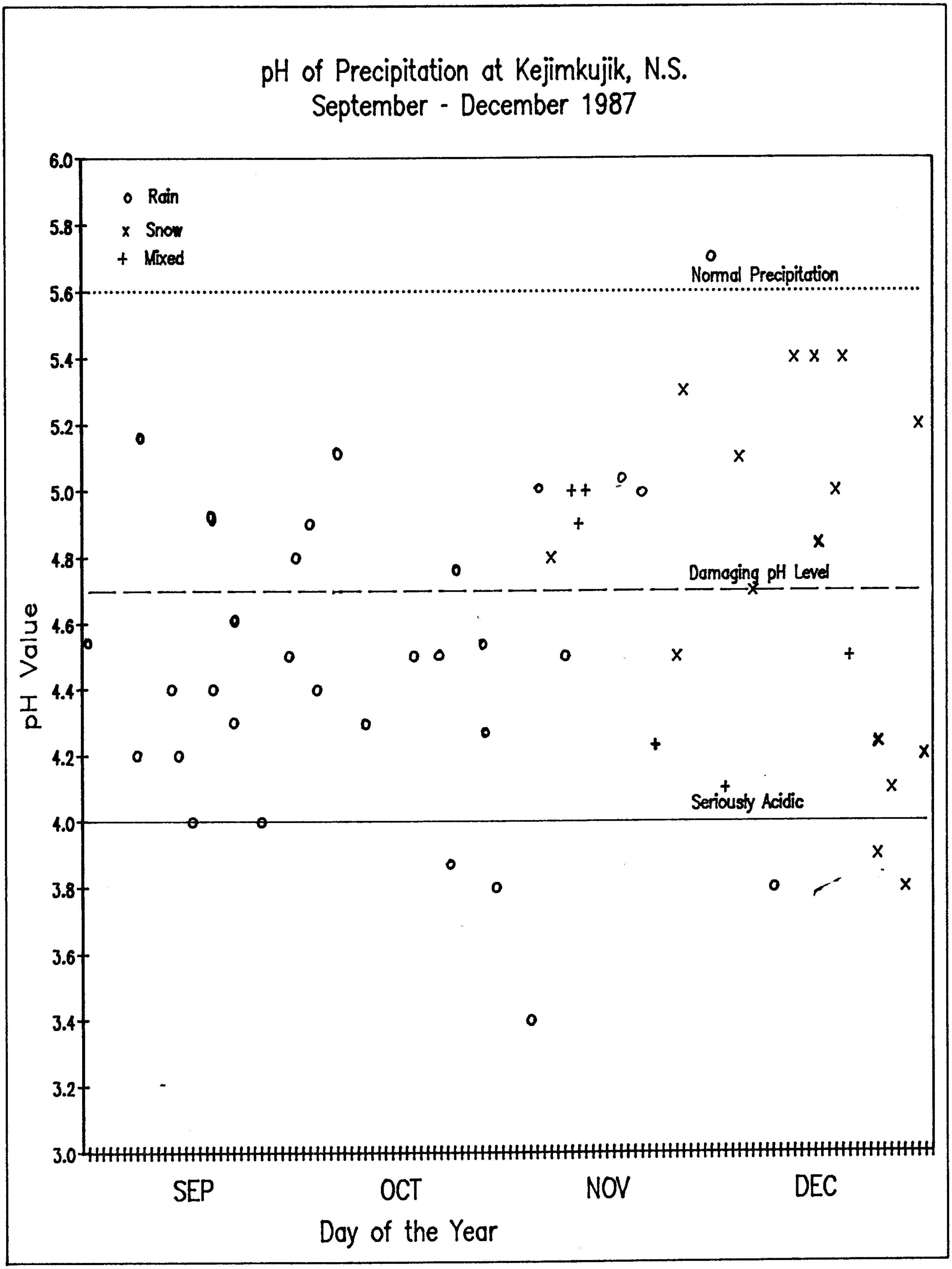

pH of Precipitation at Kejimkujik, N.S.
May - August 1987
o Rain
x Snow
+ Mixed
Normal Precipitation
Damaging pH Level
Seriously Acidic
pH Value
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
MAY
JUN
JUL
AUG
Day of the Year

Figure 3



pH of Precipitation at Kejimkujik, N.S.
September - December 1987
o Rain
x Snow
+ Mixed
Normal Precipitation
Damaging pH Level
Seriously Acidic
pH Value
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
SEP
OCT
NOV
DEC
Day of the Year

Figure 4

Ten Regions Surrounding Kejimkujik N.S.

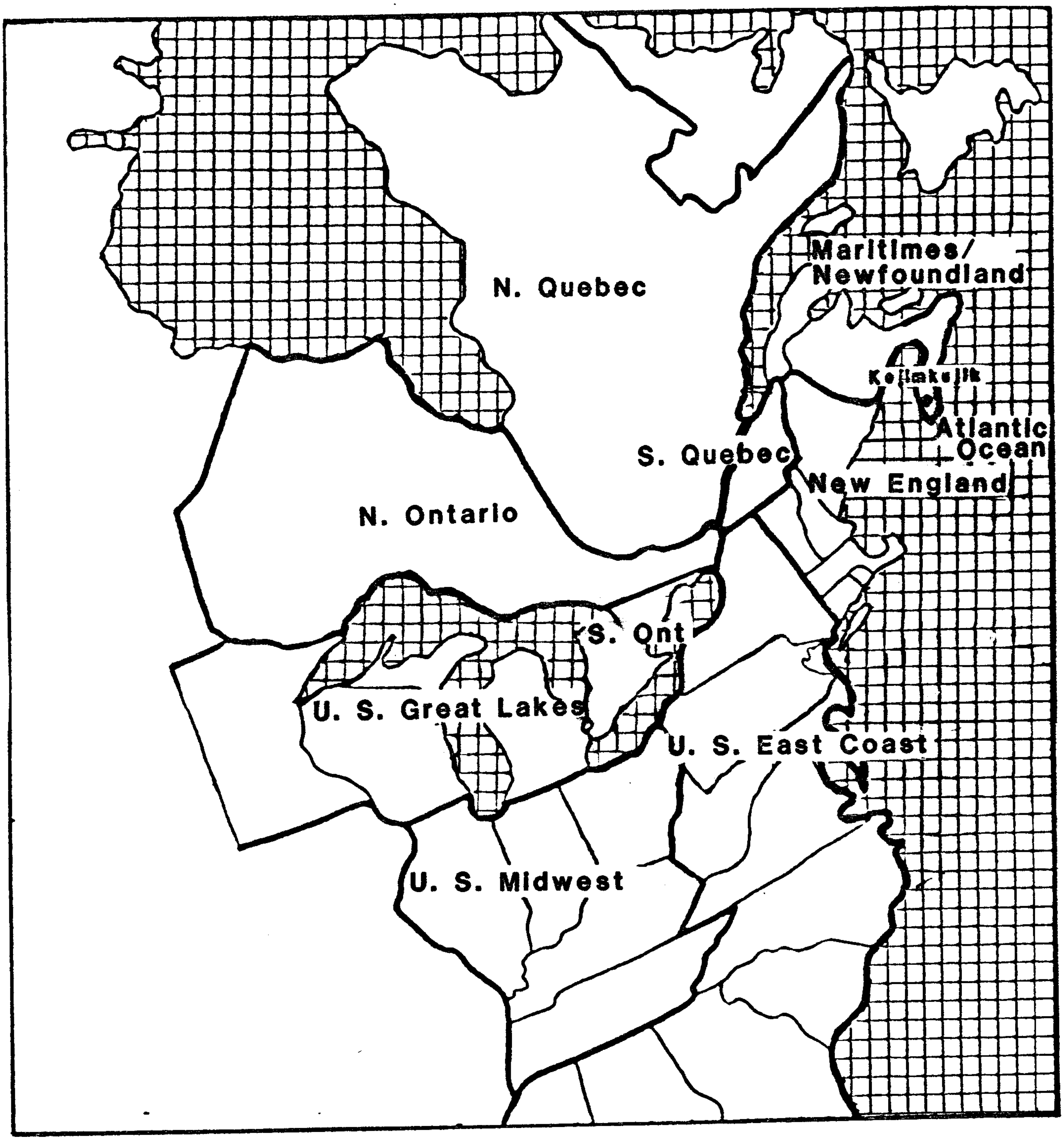
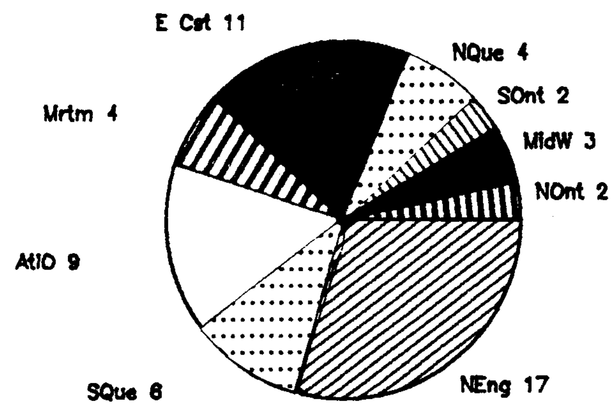


Figure 5

Frequency of Occurrence of Source Regions Contributing to Precipitation pH
Kejimkujik, N.S. 1987

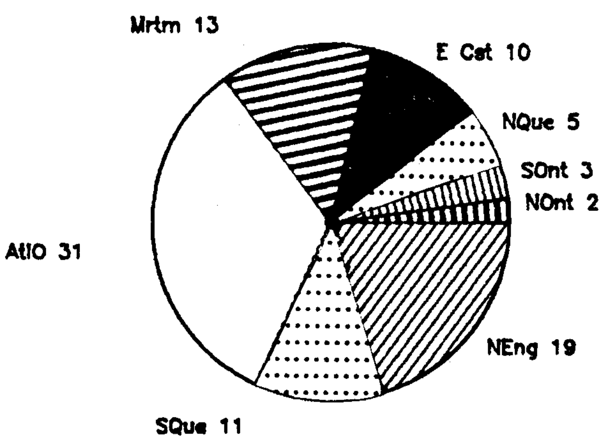
Source Regions

MidW: U.S. Midwest
E Cst: U.S. East Coast
NOnt: Northern Ontario
SOnt: Southern Ontario
NQue: Northern Quebec
SQue: Southern Quebec
NEng: New England
AtlO: Atlantic Ocean
Mrtm: Maritimes/Newfoundland



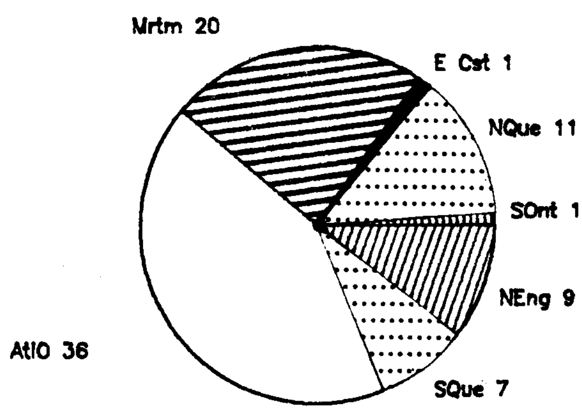
pH <= 4.0

24 Events



4.0 < pH <= 4.7

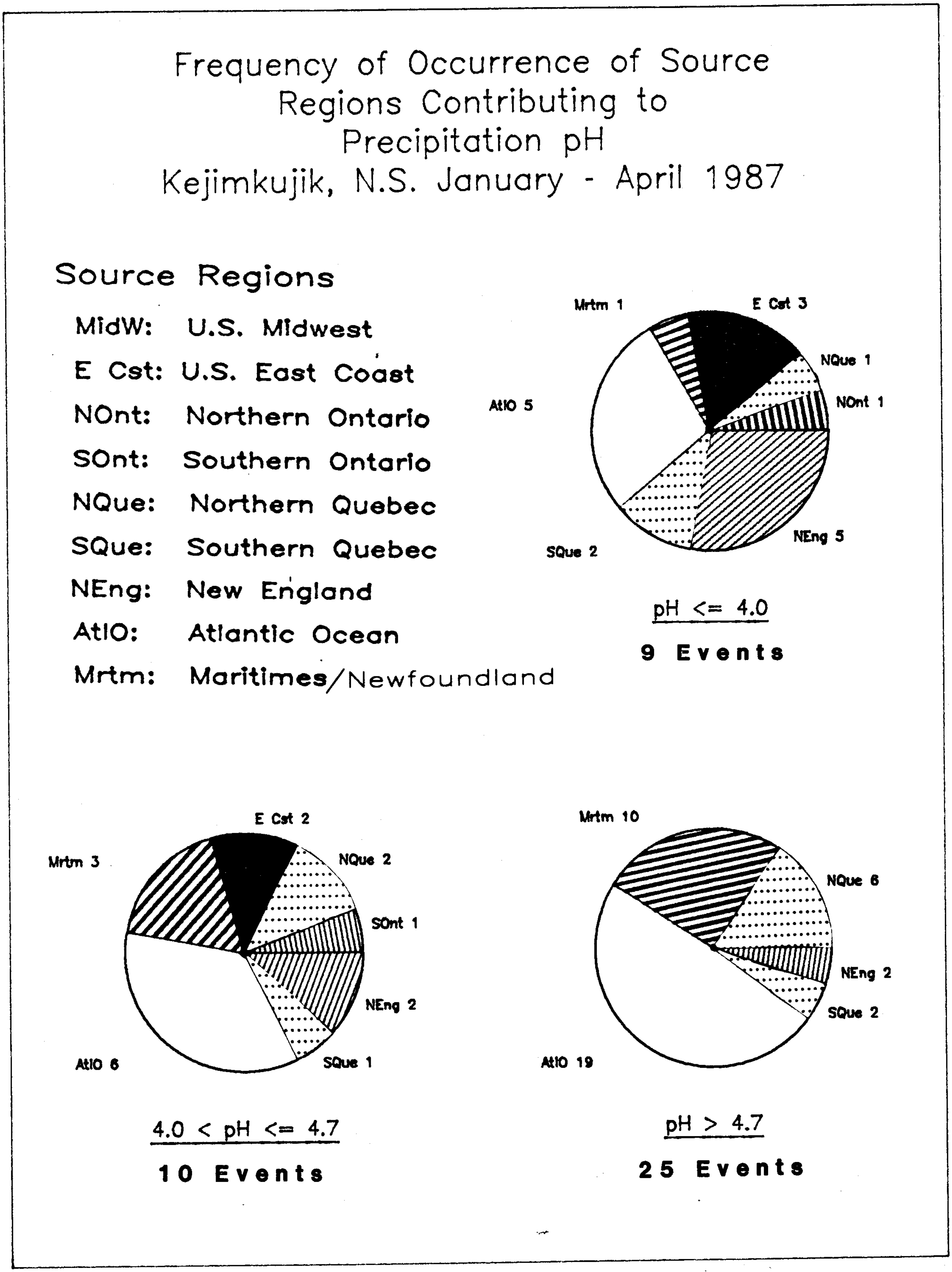
50 Events



pH > 4.7

58 Events

Figure 6



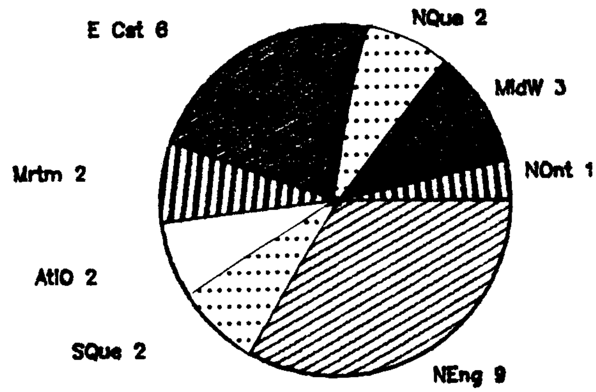
Frequency of Occurrence of Source
Regions Contributing to
Precipitation pH
Kejimkujik, N.S. January - April 1987
Source Regions
MidW: U.S. Midwest
E Cst: U.S. East Coast
NOnt: Northern Ontario
SOnt: Southern Ontario
NQue: Northern Quebec
SQue: Southern Quebec
NEng: New England
AtlO: Atlantic Ocean
Mrtm: Maritimes/Newfoundland
Mrtm 1
E Cst 3
NQue 1
NOnt 1
AtlO 5
NEng 5
SQue 2
pH <= 4.0
9 Events
E Cst 2
Mrtm 3
NQue 2
SOnt 1
NEng 2
SQue 1
AtlO 6
4.0 < pH <= 4.7
10 Events
Mrtm 10
NQue 6
NEng 2
SQue 2
AtlO 19
pH > 4.7
25 Events

Figure 7

Frequency of Occurrence of Source Regions Contributing to Precipitation pH
Kejimkujik, N.S. May - August 1987

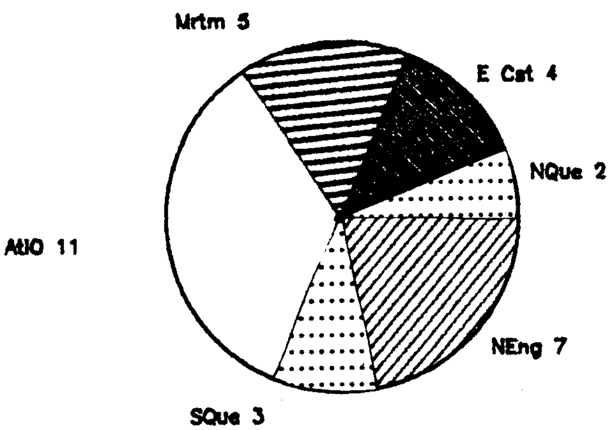
Source Regions

MidW: U.S. Midwest
E Cst: U.S. East Coast
NOnt: Northern Ontario
SOnt: Southern Ontario
NQue: Northern Quebec
SQue: Southern Quebec
NEng: New England
AtlO: Atlantic Ocean
Mrtm: Maritimes/Newfoundland



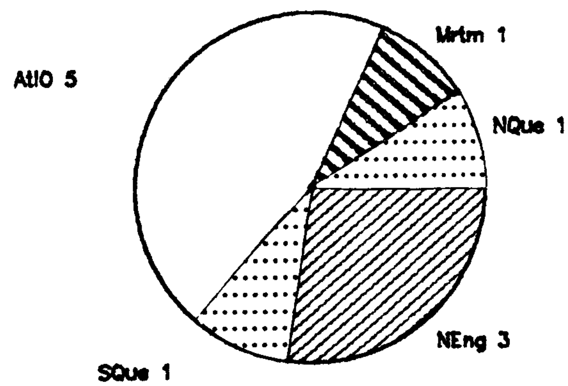
pH <= 4.0

10 Events



4.0 < pH <= 4.7

17 Events



pH > 4.7

8 Events

Figure 8

Frequency of Occurrence of Source Regions Contributing to Precipitation pH Kejimkujik, N.S. September - December 1987

Source Regions

MidW: U.S. Midwest

E Cst: U.S. East Coast

NOnt: Northern Ontario

SOnt: Southern Ontario

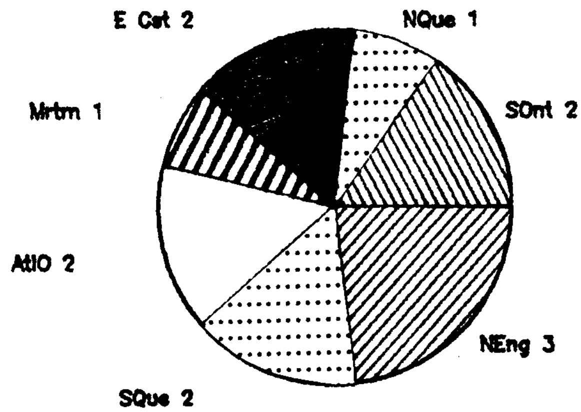
NQue: Northern Quebec

SQue: Southern Quebec

NEng: New England

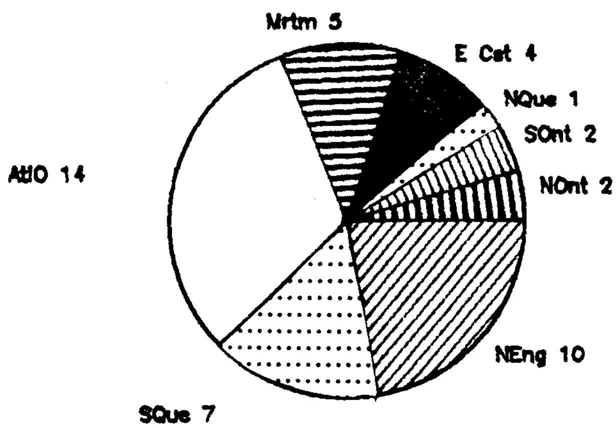
AtlO: Atlantic Ocean

Mrtm: Maritimes/Newfoundland



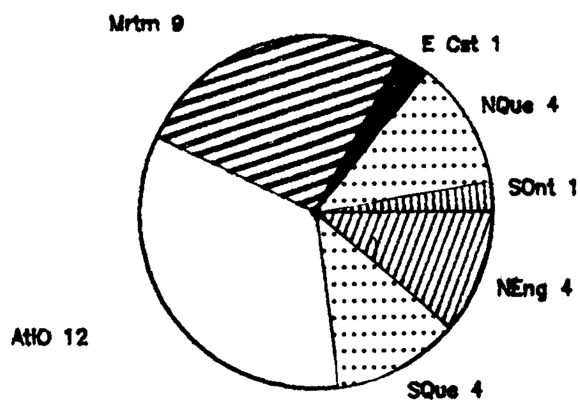
pH <= 4.0

5 Events



4.0 < pH <= 4.7

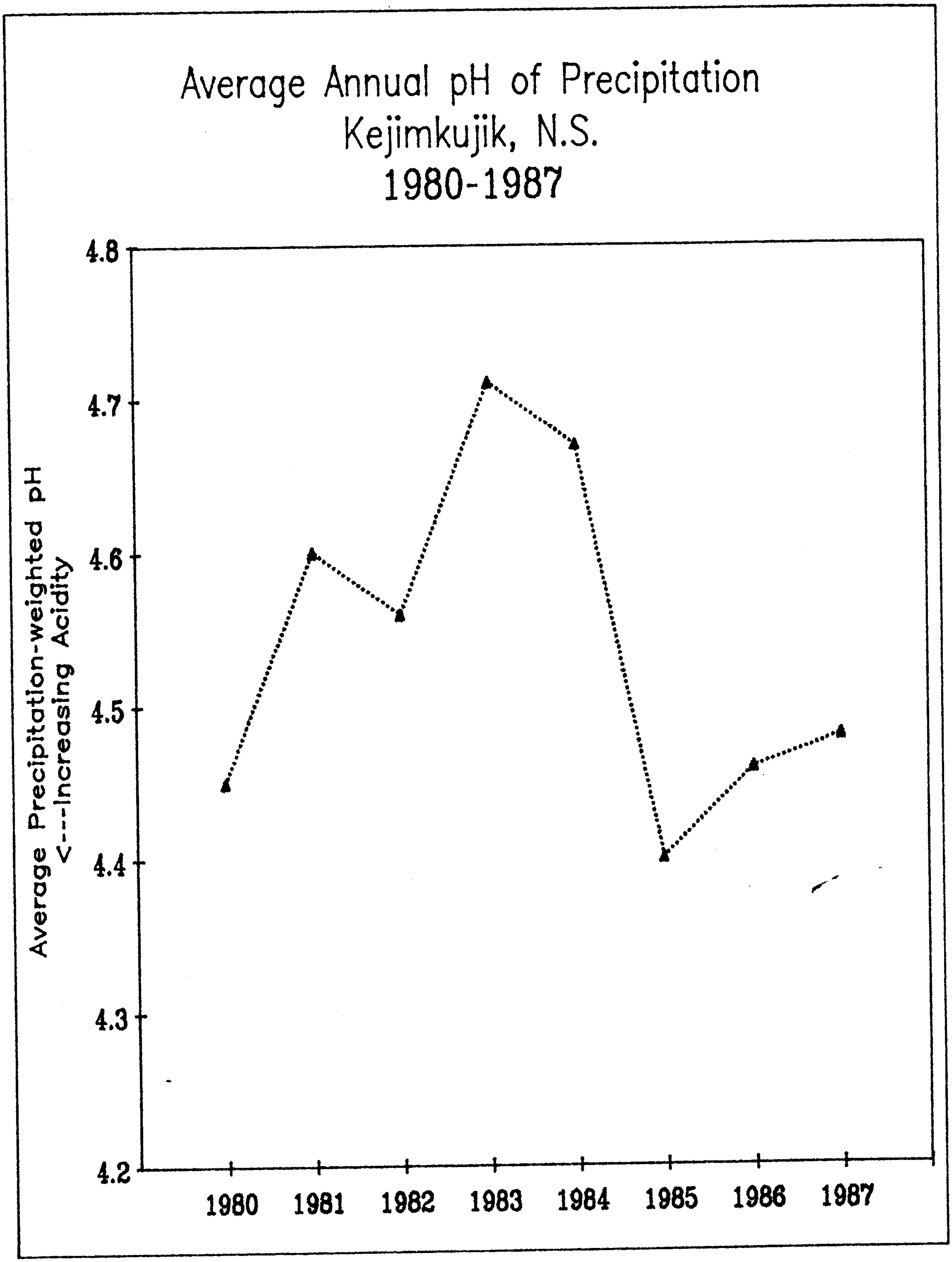
23 Events



pH > 4.7

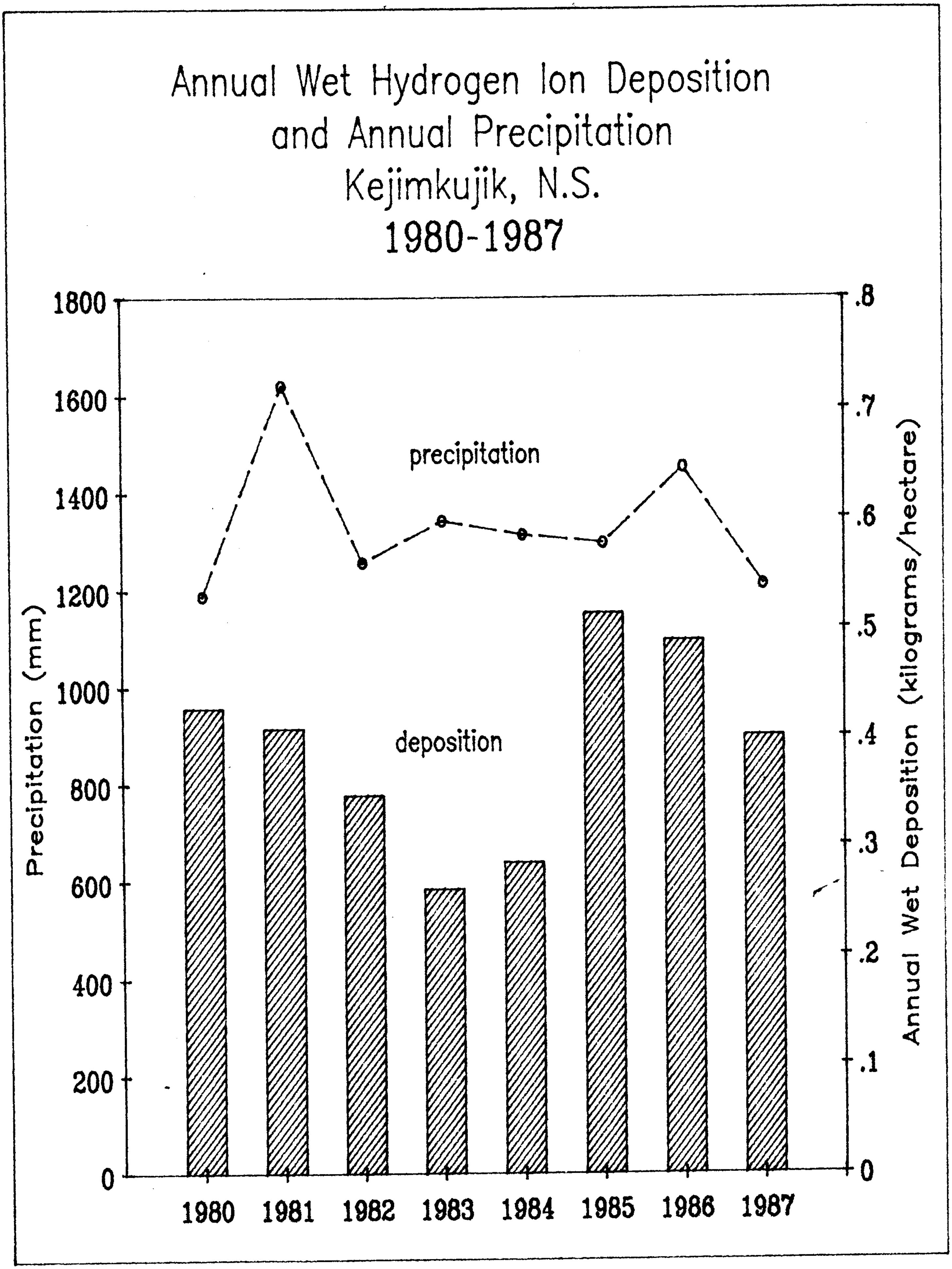
25 Events

Figure 9



Average Annual pH of Precipitation
Kejimkujik, N.S.
1980-1987
Average Precipitation-weighted pH
<---Increasing Acidity
4.8
4.7
4.6
4.5
4.4
4.3
4.2
1980
1981
1982
1983
1984
1985
1986
1987

Figure 10



Annual Wet Hydrogen Ion Deposition
and Annual Precipitation
Kejimkujik, N.S.
1980-1987
precipitation
deposition
Precipitation (mm)
Annual Wet Deposition (kilograms/hectare)
1800
1600
1400
1200
1000
800
600
400
200
0
.8
.7
.6
.5
.4
.3
.2
.1
0
1980
1981
1982
1983
1984
1985
1986
1987