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Acid Precipitation during 1988
at Kejinkujik, N.S.

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Report: MAES 1-89

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1. Introduction

A precipitation sampling station has been operated in Kejimikujik 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 sulphates 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 (the "air path to site"). This information gives an idea of the source of the pollutants that are associated with the precipitation events. The "air path to site" is determined from an analysis of weather patterns and by using a three-dimensional trajectory model (Olson et al, 1978). This model calculates the air parcel's previous positions during the past 48 hours using the wind and other meteorological data at various heights above ground (Desautels, 1985). The Acid Rain 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 (H^+) 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 annual 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 Kejimikujik. 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 1988

2.1 Preparation of the Data Set

The CAPMoN pH data set for 1988 was used as the basis for this report. In preparing the data set, it was found that 64 days out of 220 had insufficient precipitation amounts (usually less than 1 mm) for a proper pH measurement. These entries were eliminated from the data set. The precipitation total for these 64 days was 19.8 mm (less than 1.4% of the total annual precipitation of 1428.2 mm). Of the remaining 156 days, pH values were not measured for 7 samples due to leakage (January 25, February 12, March 9, July 14, 21, November 28, December 28). One additional sample (October 19) was a bulk sample and, thus, the pH was invalidated. For these 8 samples, the CAPMoN data set did not provide pH values; however, the on-site pH measurements were substituted for this analysis. Including these additional 8 values gave an increased annual hydrogen ion deposition compared to the CAPMoN deposition (0.4011 kg/ha versus 0.3685 kg/ha) and a lower value of pH (4.55 versus 4.59).

2.2 Annual Summary

The variations in precipitation pH at Kejimikujik, N.S. during 1988 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. slightly acidic level ($4.7 < \text{pH} \leq 5.6$)
2. damaging pH level ($4.0 < \text{pH} \leq 4.7$)
3. seriously acidic level ($\text{pH} \leq 4.0$)

An analysis of the distribution of pH in precipitation events (Figure 4) shows that only one of the precipitation events at Kejimikujik in 1988 was in the clean pH range (with a pH of 5.63) 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 3.41, which was 166 times more acidic than the least acidic event. Table 1 summarizes these events:

Table 1: Summary of Precipitation Events at Kejimikujik, N.S. During 1988

Level of pH	pH Range	Number of Occurrences	Percentage
Normal (clean)	pH > 5.6	1	0.6%
Slightly Acidic	4.7 < pH ≤ 5.6	58	37.2%
Damaging	4.0 < pH ≤ 4.7	77	49.4%
Seriously Acidic	pH ≤ 4.0	20	12.8%

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 depositions for the events 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. If there are events during the period for which the pH values were not measured or are invalid, the total hydrogen ion deposition is estimated by multiplying the precipitation-weighted average hydrogen ion concentration by the total precipitation for the period (which includes the precipitation amounts for which pH values were not available).

The annual average precipitation-weighted pH at Kejimikujik, N.S. in 1988 was 4.55 and the average hydrogen ion concentration was 0.0281 mg/l . This was calculated for 156 precipitation days which produced 1408.4 mm of precipitation and 39.6 mg/m^2 of hydrogen ion deposition during the year. The estimated annual hydrogen ion deposition was 40.1 mg/m^2 (.40 kg/ha) based on the

total annual precipitation of 1428.2 mm (220 days with precipitation).

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 Kejimikujik and had the highest average pH and highest deposition.

Table 2: Analysis of Precipitation Events by Precipitation Type for Kejimikujik, N.S. During 1988

Type	Precipitation Days	Precipitation Amount	Average pH	Deposition of Acid	Percentage Deposition
Rain	107	1068.4 mm	4.59	27.4 mg/m ²	69.4%
Snow	28	105.0 mm	4.45	3.7 mg/m ²	9.4%
Mixed	21	235.0 mm	4.45	8.4 mg/m ²	21.2%

The 64 days with small precipitation amounts were not included in this table, but were also predominately rain days (39 rain events giving 10.8 mm, 24 snow events giving 8.8 mm, 1 mixed event giving 0.2 mm).

2.3 Seasonal Summary

The seasonal characteristics of precipitation acidity were investigated by grouping the data 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. The winter period had the largest deposition and the summer period had the lowest pH with the lowest precipitation amount. The least acidic period was the fall.

Table 3: Analysis of Precipitation Events by Season for Kejimikujik, N.S. During 1988

Period	Precipitation Days	Precipitation Amount	Average pH	Deposition of Acid
January - April	58	471.8 mm	4.50	15.0 mg/m ²
May - August	48	378.0 mm	4.41	14.8 mg/m ²
September - December	50	558.6 mm	4.76	9.8 mg/m ²

The 64 days with small precipitation amounts were not included in this table. They were distributed amongst the

seasons fairly evenly (January - April: 21 days giving 7.0 mm; May - August: 19 days giving 4.4 mm; September - December: 24 days giving 8.4 mm).

2.4 Regional Contributions to Precipitation Acidity

The 156 precipitation events were then categorized by their pH value ($\text{pH} \leq 4.0$, $4.0 < \text{pH} \leq 4.7$, and $\text{pH} > 4.7$) and by the regions which the air mass had passed over before arriving at Kejimikujik (based on the "air path to site" information given in the Acid Rain Report). The regions are shown in Figure 5 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

There were 39 pH values in the data set for which "air path to site" information was not available. In these cases, the upwind regions were unknown.

In years previous to 1987, the meteorologist who prepared the Acid Rain Report identified the "Main Source Region" of pollutants for each precipitation event (Desautels, 1986; Pettipas and Beattie, 1987). However, this information was not available for the 1988 data. Instead, each region that was along the "air path to site" was categorized with the precipitation pH that occurred at Kejimikujik (ie. each pH could be associated with one or more upwind regions). This led to some ambiguity in correlating pH to source regions since the regions along the air path to Kejimikujik would not be equally "responsible" for the resulting precipitation pH (see sample Acid Rain Report in Appendix A). In particular, at least one of the regions surrounding Kejimikujik will be along the "air path to site" in every event due to their proximity.

Figure 6 summarizes the "air path to site" information for 1988. This clearly shows the effect of proximity, in that regions in closer proximity to Kejimikujik are identified as upwind regions more frequently. It also shows the controlling influence of the major storm tracks which bring precipitation

into the Maritimes. As shown in Figure 7 (from Bormann, 1982), one major storm track occurs along the U.S. East Coast, across New England and the Atlantic Ocean and into the Maritimes. Another track crosses the U.S. Great Lakes, Southern Ontario, Southern Quebec, New England and into the Maritimes.

The results of the analysis of regional contributions to acidity by pH range for the full year are plotted in Figure 8. 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). The percentage figure given after each source region is the frequency that that region occurs out of the total number of regions associated with that particular pH range. For example, for the pH range of 4.0 or less, there were 20 precipitation events during the year, but only 11 of them had "air path to site" information. The remaining 9 events with unknown upwind regions generally had small precipitation amounts. The number of regions associated with the 11 events totalled 25, of which 24%, for example, was the American East Coast (ECst) region. This region was along the "air path to site" for 6 of the 11 events (ie. 55%) and the New England (NEng) region was along the "air path to site" for 9 of the 11 events (ie. 82%). Four of the events had "air paths to site" that crossed both regions.

Figure 8 indicates that a correlation exists between the pH of precipitation at Kejimikujik and the levels of pollutant emissions from upwind regions. For example, precipitation events in the seriously acidic range ($\text{pH} \leq 4.0$) 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 and/or the U.S. East Coast in 100% of the seriously acidic events with known upwind regions.

Precipitation events with damaging acidity levels ($4.0 < \text{pH} \leq 4.7$) show a lessening influence from industrial regions. For instance, the "air paths to site" cross New England and/or the U.S. East Coast in 30 out of 58 events (52%) with known upwind regions in the damaging range of acidity as compared to 100% of the events in the seriously acidic range ($\text{pH} \leq 4.0$). Precipitation events with only slightly acidic pH values ($\text{pH} > 4.7$) predominantly have "air paths to site" over less industrialized parts of Canada or over the Atlantic Ocean. In particular, only 8 of the 48 events (17%) with known upwind regions in the non-damaging range of acidity passed over New England and/or the U.S. East Coast.

Figures 9, 10 and 11 show, for each of the four-month periods, how frequently the surrounding regions are identified with each pH range in different seasons. The patterns are similar to the annual ones shown in Figure 8. Note that the unusual pattern for $\text{pH} \leq 4.0$ for the September - December period is due to the small number of events represented (only one event with two upwind regions).

3. Comparison with Previous Years

In 1987 the average annual precipitation-weighted pH was 4.58 (Vet et al, 1989) compared to 4.55 in 1988 (based on this analysis) which indicates that, overall, the average acidity of precipitation had remained within about 6% of the 1987 acidity. The average pH was lowest in the May - August period during 1988. This indicates that the colder periods in 1988 experienced cleaner precipitation than the summer, the same as in 1987 (Allen and Beattie, 1988) and 1986 (Pettipas and Beattie, 1987).

Figure 12 shows the average annual pH of precipitation received at Kejimikujik from 1980 to 1988. (For Figures 12 and 13, 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; 1987 data from Vet et al, 1989). The least acidic year (highest average pH) was 1983 and most acidic year (lowest average pH) was 1985. The drop in acidity levels (increase in pH) from 1985 to 1987 levelled off for 1988. This general drop in acidity since 1985 may 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 is difficult to identify any trends over this short time period.

Deposition values (Figure 13), rather than pH, present a clearer picture of the cumulative effect on 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 Kejimikujik in 1988 was 40.1 mg/m^2 , an increase of 22.6% from the 1987 deposition of 32.7 mg/m^2 . This increase was partially due to a slight decrease in pH but mainly to a higher precipitation amount. The annual precipitation amount was 15% higher in 1988 than 1987 and there were 27 more days with precipitation (220 versus 193). Since the normal amount of precipitation at Kejimikujik National Park (based on 1951 - 1980) is 1436.2 mm (A.E.S., n.d.), the precipitation in 1988 was near normal (0.5% lower than normal), whereas the precipitation in 1987 was 13.8% lower than normal. Figure 13 illustrates that the

largest annual wet hydrogen ion deposition this decade was in 1985. The deposition in recent years has not reached the low levels observed in 1983 and 1984.

4. Summary

The average precipitation-weighted pH for 1988 at Kejimikujik National Park in southwestern Nova Scotia was 4.55, with the most acidic four-month average in May - August and the least acidic in September - December. The most acidic event of the year, with a pH of 3.41, was 166 times more acidic than the least acidic event (pH of 5.63). More than 12% of the events were seriously acidic (pH \leq 4.0).

The analysis indicates that a correlation exists between the pH of precipitation at Kejimikujik 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 of the United States and Canada. Conversely, precipitation events with only slightly acidic pH values (pH $>$ 4.7) predominantly have "air paths to site" over less industrialized parts of Canada or over the Atlantic Ocean.

In comparison with the previous year, Kejimikujik experienced 22.6% more acid deposition and 15% more precipitation, and had a slight decrease in average annual precipitation pH (representing an increase of 6.4% in hydrogen ion concentration). The increase in deposition is mainly a result of an increase in precipitation rather than an increase in acidity of precipitation from 1987 to 1988.

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Bob Vet and Bill Sukloff	Providing 1980-1983 annual pH and hydrogen ion deposition values and CAPMoN data for 1988 from the Atmospheric Environment Service's quality controlled data set
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Bernie Flynn	Assistance in preparation of Figures 1-3

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APPENDIX A
Sample Acid Rain Report

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 MM

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 46Z

Figure 1

pH of Precipitation at Kejimikujik, N.S.
January - April 1988

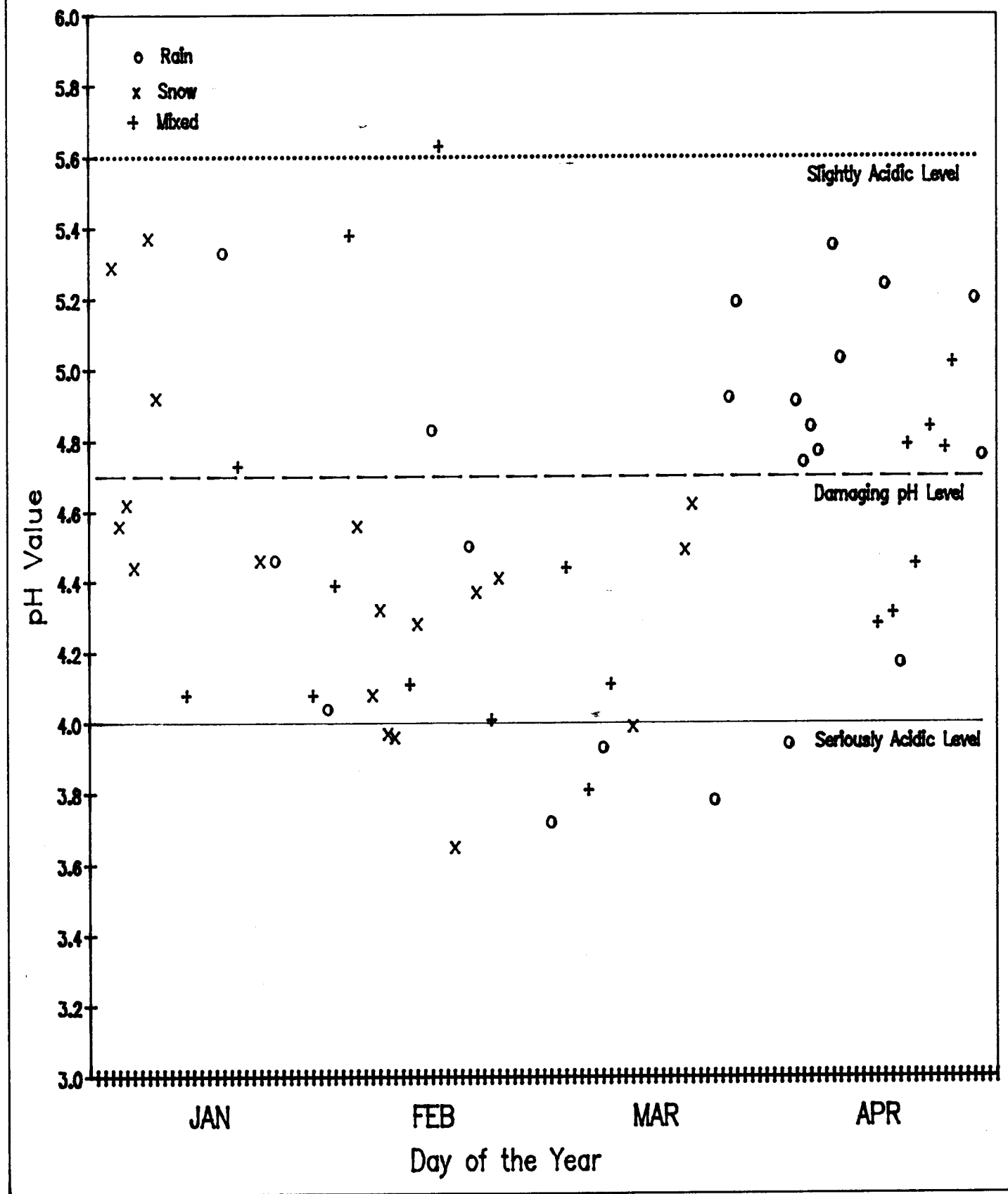


Figure 2

pH of Precipitation at Kejimikujik, N.S.
May - August 1988

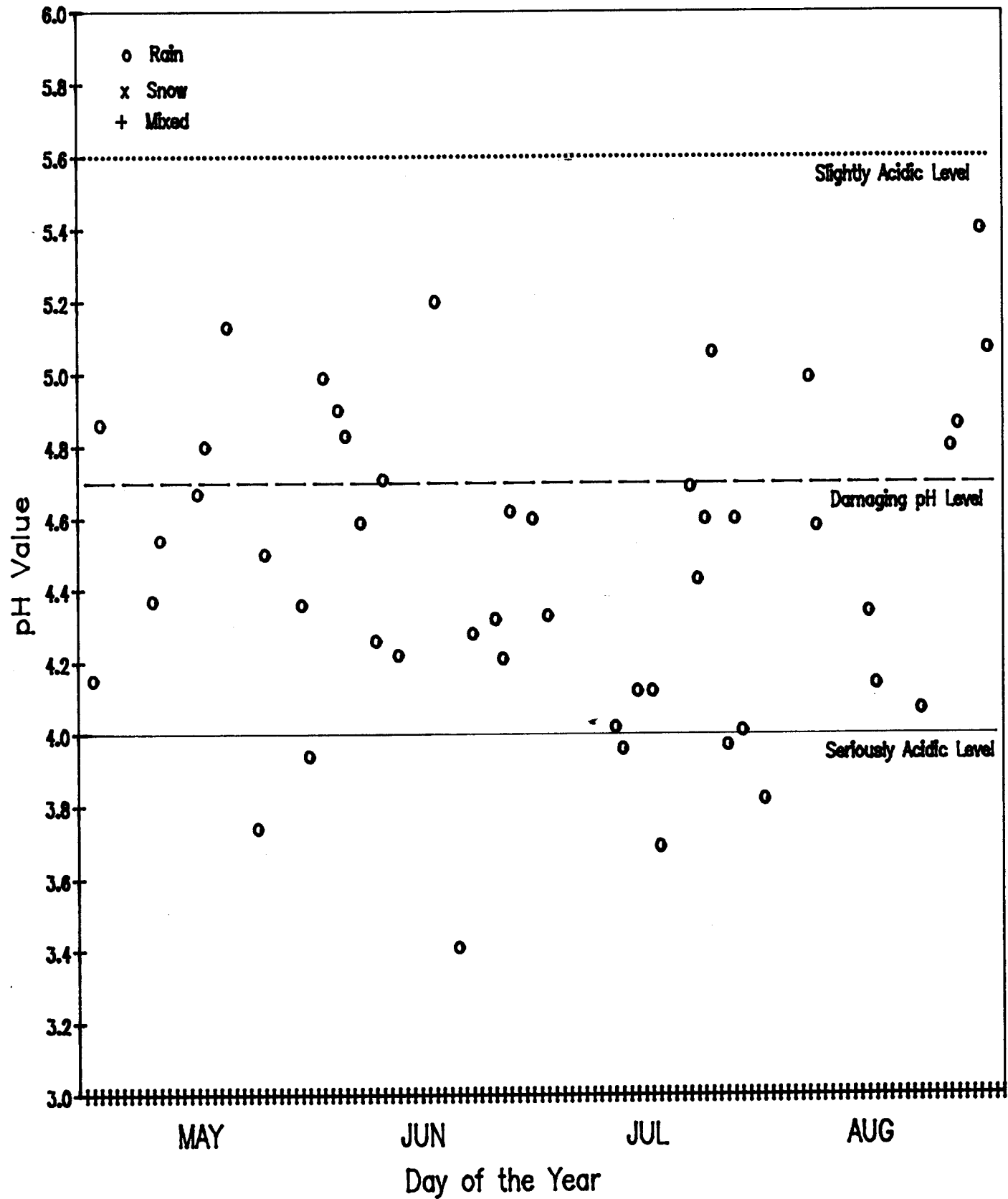


Figure 3

pH of Precipitation at Kejimikujik, N.S.
September - December 1988

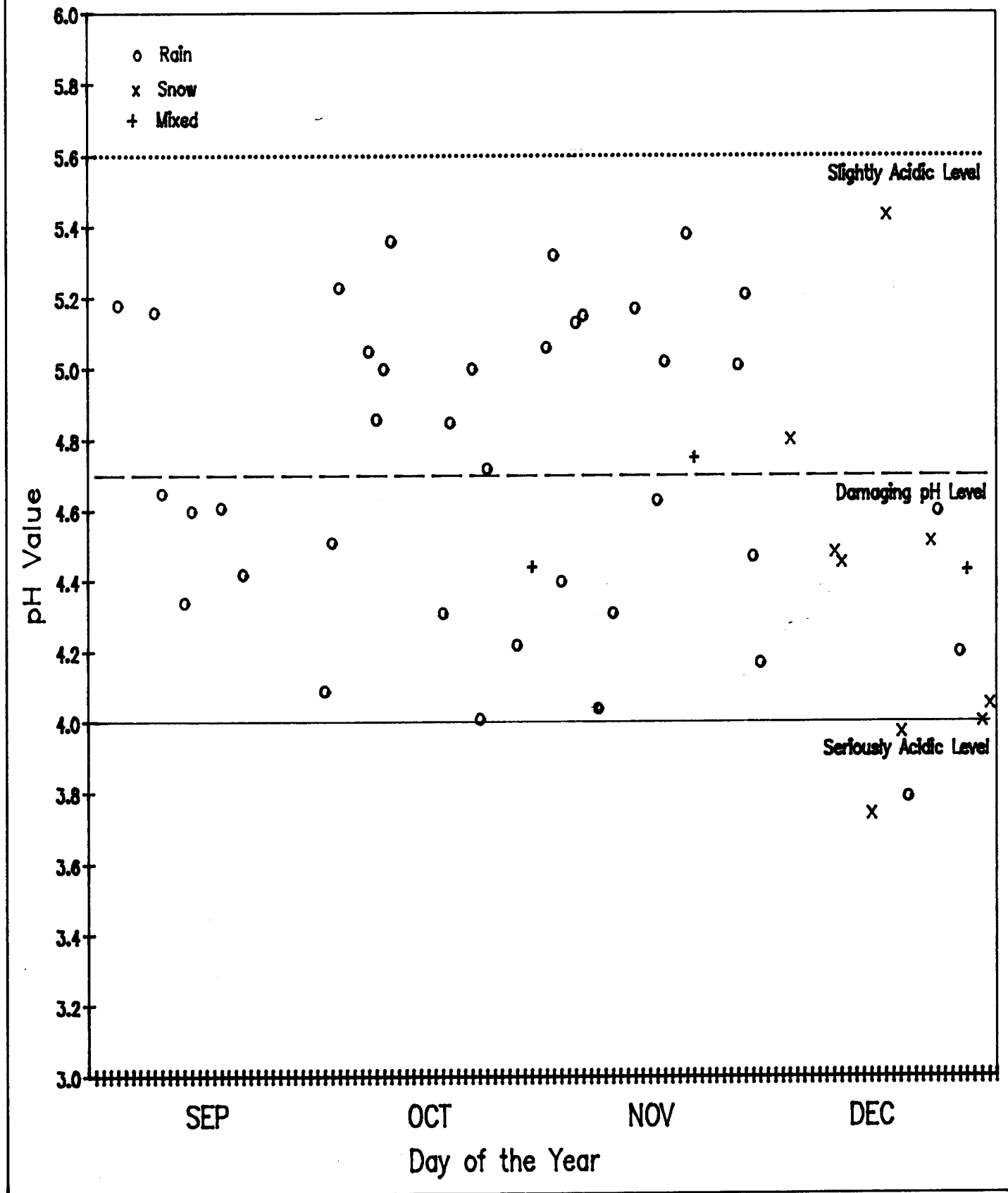


Figure 4

Distribution of pH in Precipitation Events Kejimkujik, N.S. 1988

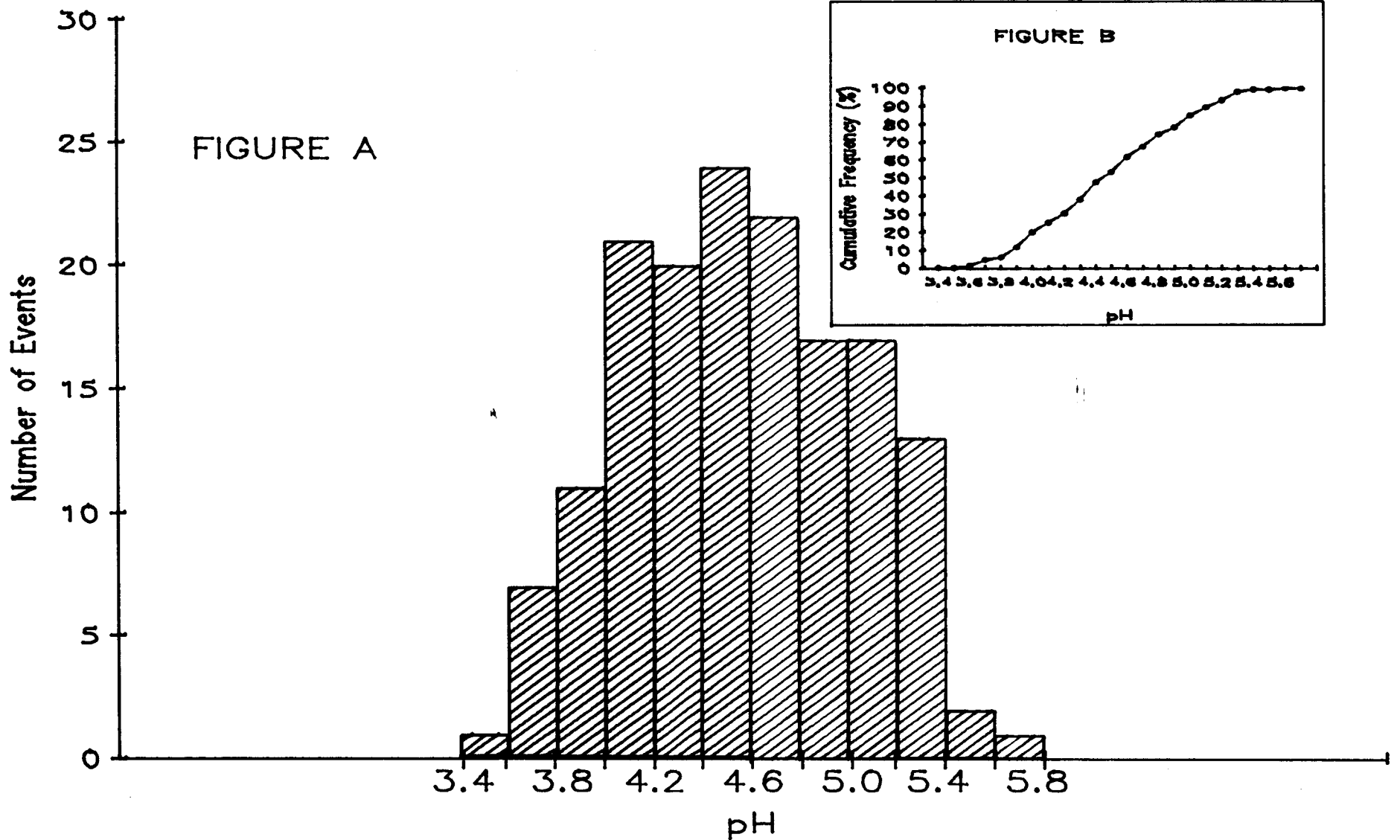


Figure 5

**Ten Regions Surrounding
Kejimikujik N.S.**

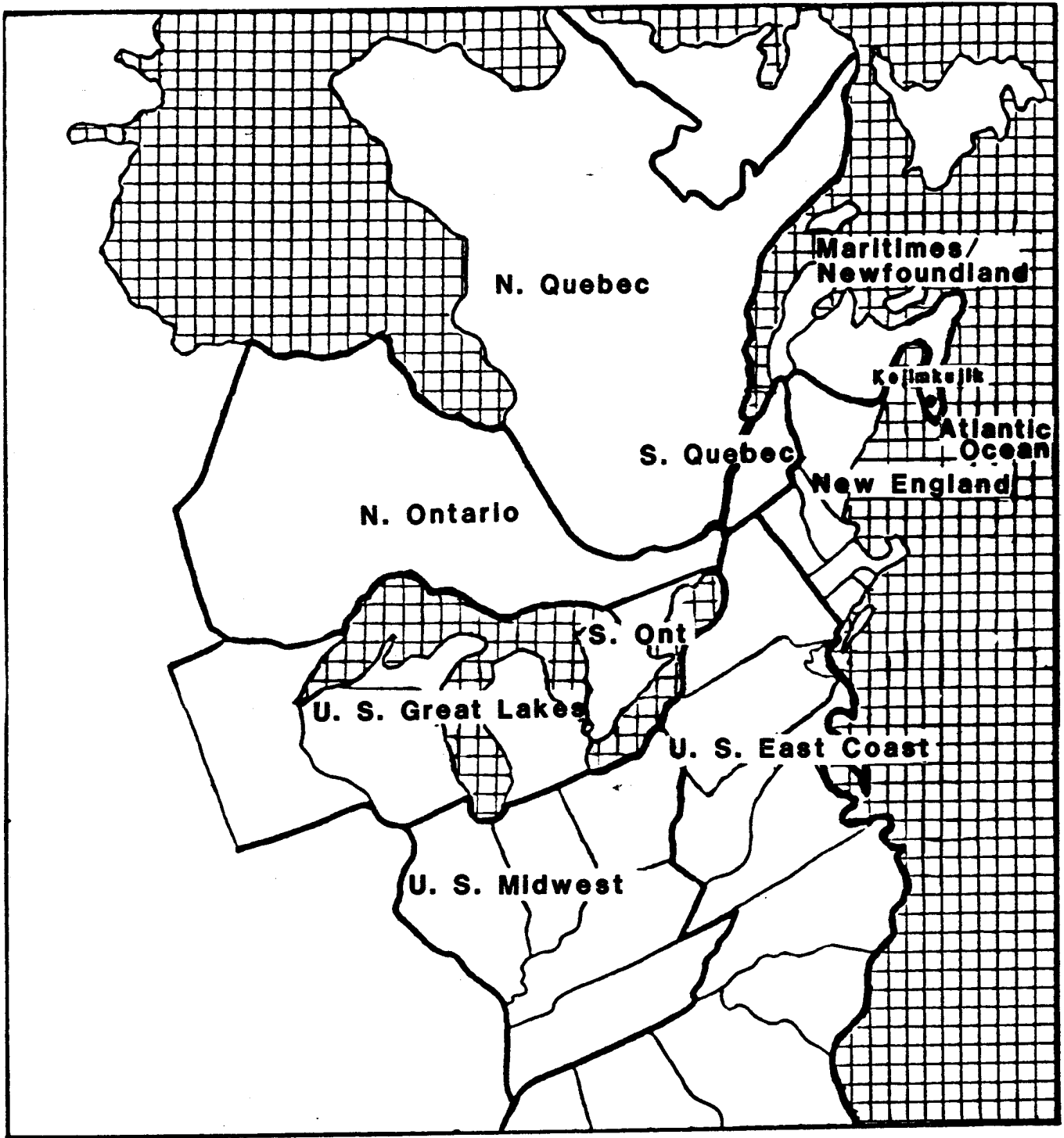


Figure 6

Number of Occurrences of Source Regions Contributing to Precipitation pH Kejimikujik, N.S. 1988

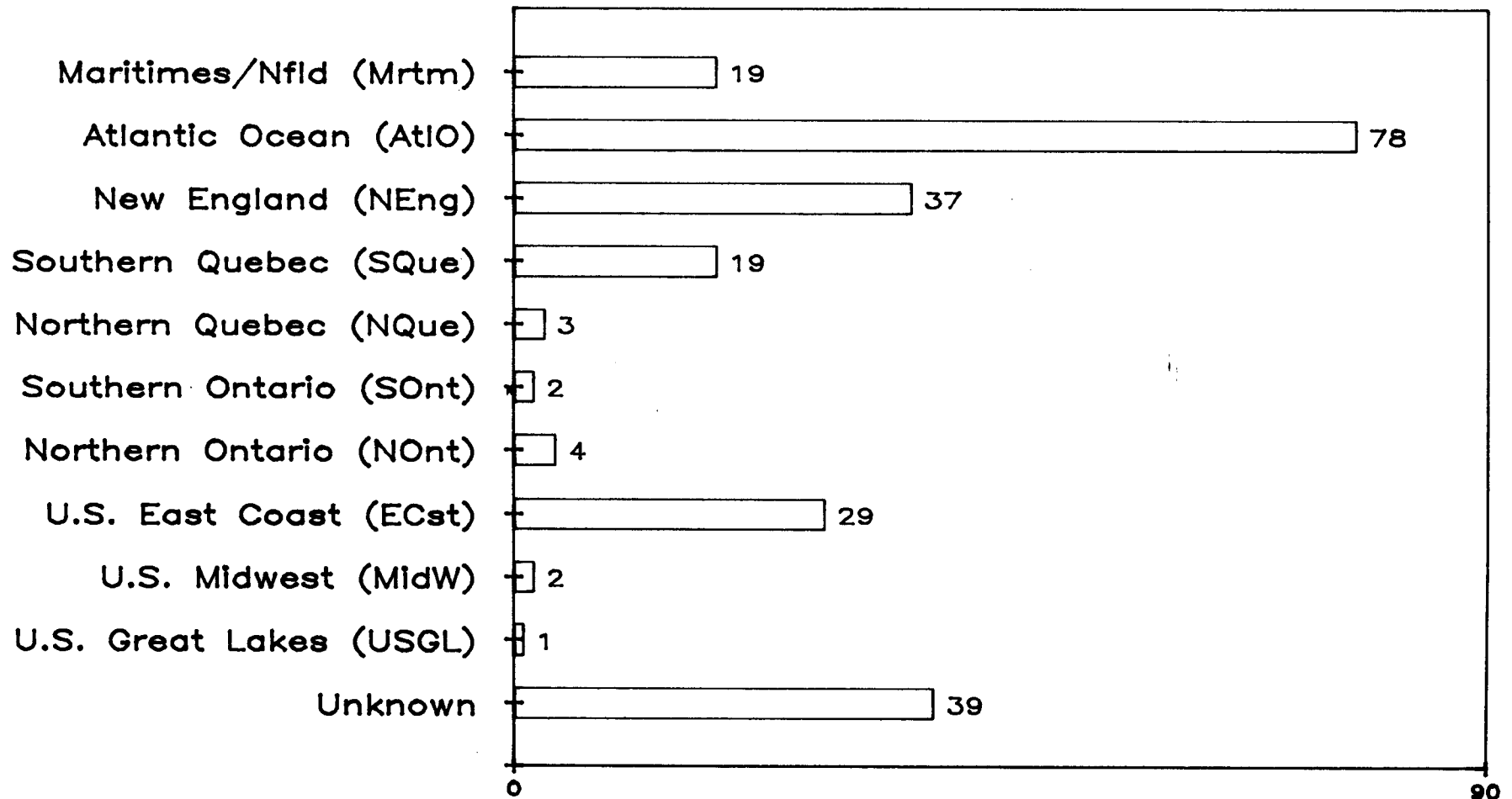
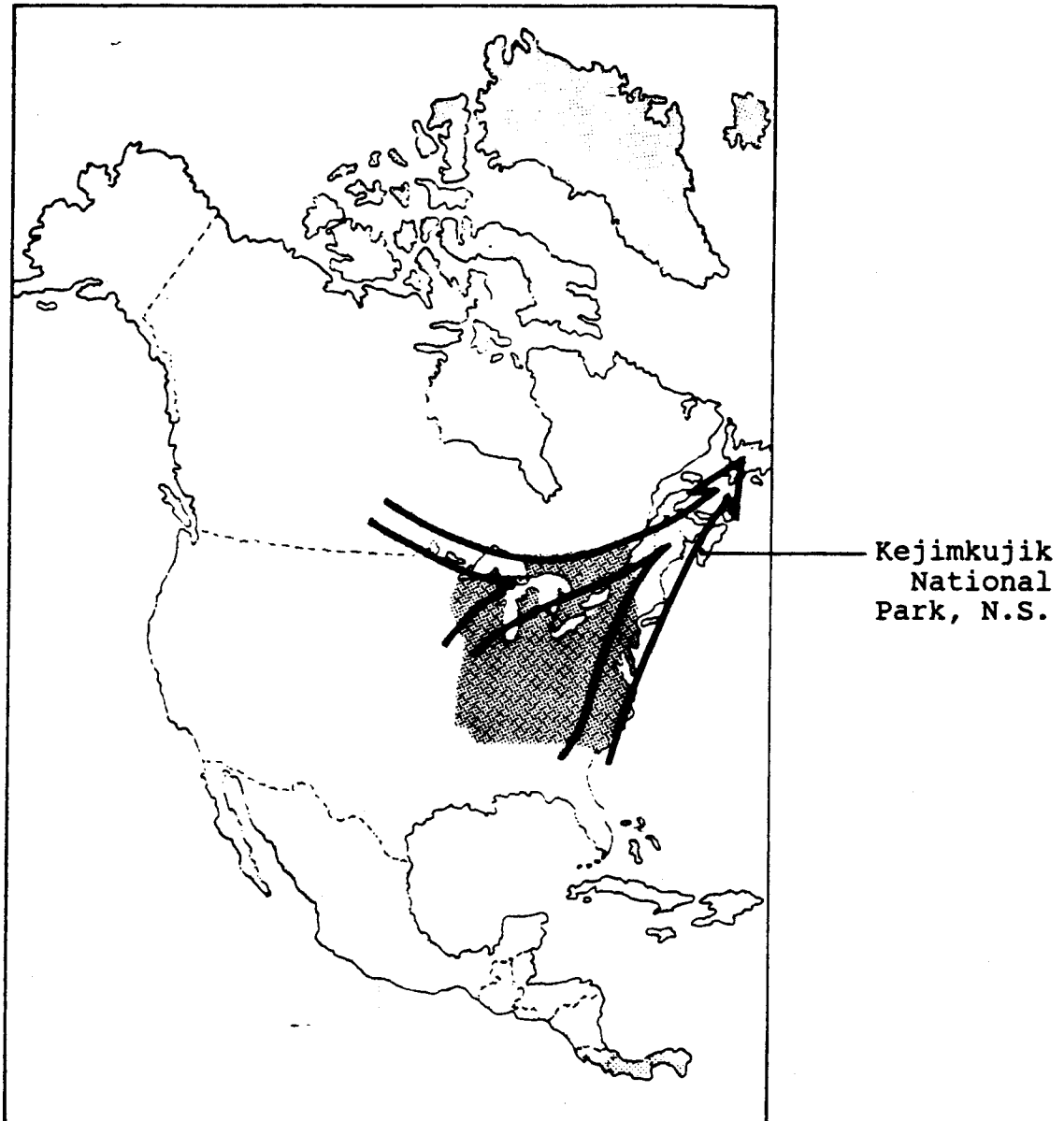


Figure 7

Location of Monitoring Site at Kejimikujik National Park,
Nova Scotia, in Relation to Pollution Sources and Storm Tracks



↗ Mean monthly tracks of frontal storms (1885-1980) in eastern North America. Sixty-five percent of all sulphur dioxide and 49 percent of all nitrogen oxides produced in North America are emitted in the dark area to the west of New England. (Bormann, 1982).

Figure 8

Frequency with which Source Regions
Contributed to Precipitation pH
by pH Range
Kejimikujik, N.S. 1988

Source Regions

NOnt: Northern Ontario

MidW: U.S. Midwest

SOnt: Southern Ontario

NQue: Northern Quebec

ECst: U.S. East Coast

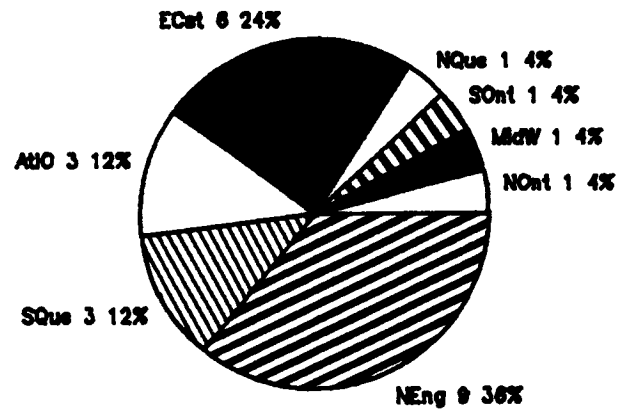
Mrtm: Maritimes/Nfld

AtIO: Atlantic Ocean

SQue: Southern Quebec

NEng: New England

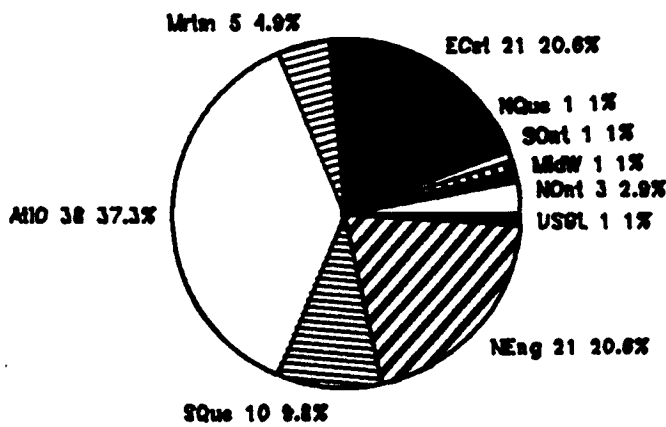
USGL: U.S. Great Lakes



pH <= 4.0

20 events

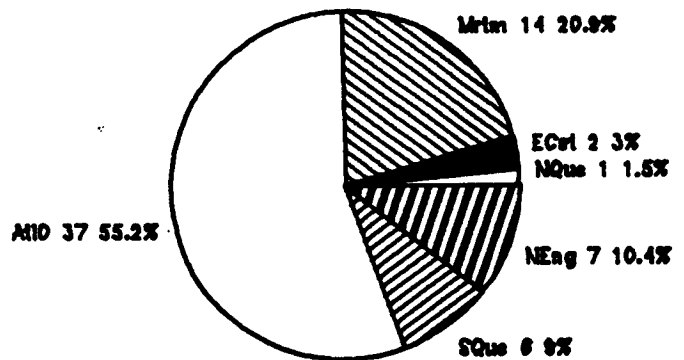
9 with unknown sources



4.0 < pH <= 4.7

77 events

19 with unknown sources



pH > 4.7

59 events

11 with unknown sources

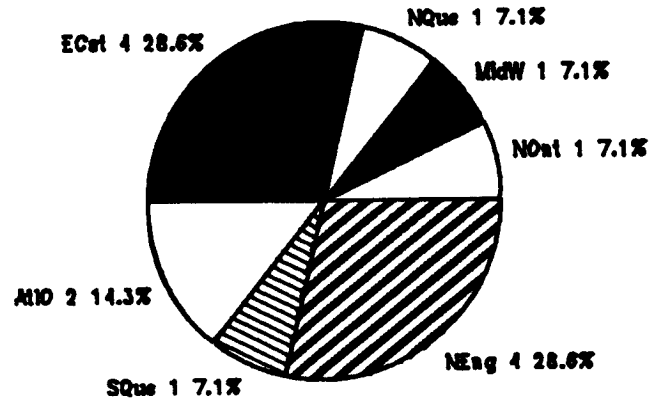
Figure 9

Frequency with which Source Regions
Contributed to Precipitation pH
by pH Range

Kejimkujik, N.S. Jan. - Apr. 1988

Source Regions

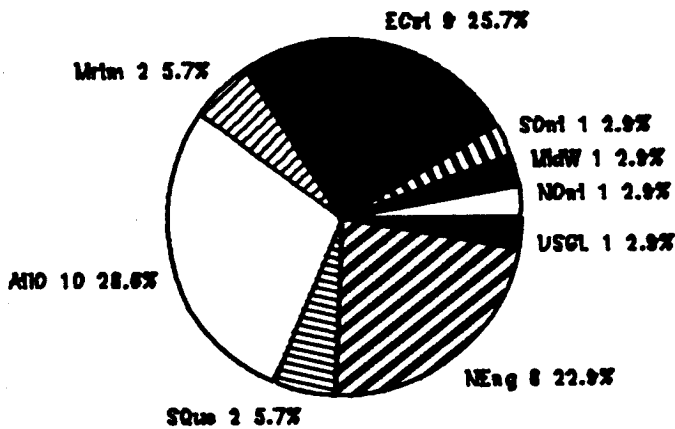
- NOnt: Northern Ontario
- MidW: U.S. Midwest
- SOnt: Southern Ontario
- NQue: Northern Quebec
- ECst: U.S. East Coast
- Mrtm: Maritimes/Nfld
- AtIO: Atlantic Ocean
- SQue: Southern Quebec
- NEng: New England
- USGL: U.S. Great Lakes



pH <= 4.0

9 events

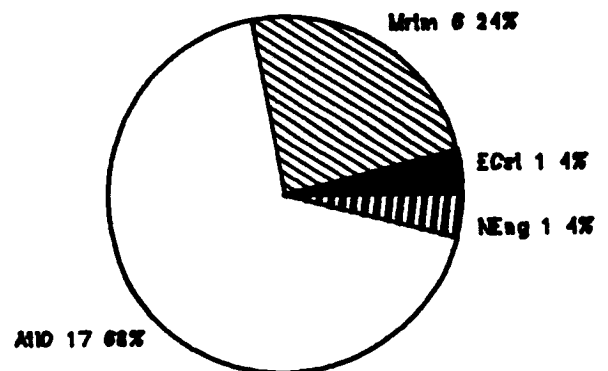
3 with unknown sources



4.0 < pH <= 4.7

26 events

8 with unknown sources



pH > 4.7

23 events

4 with unknown sources

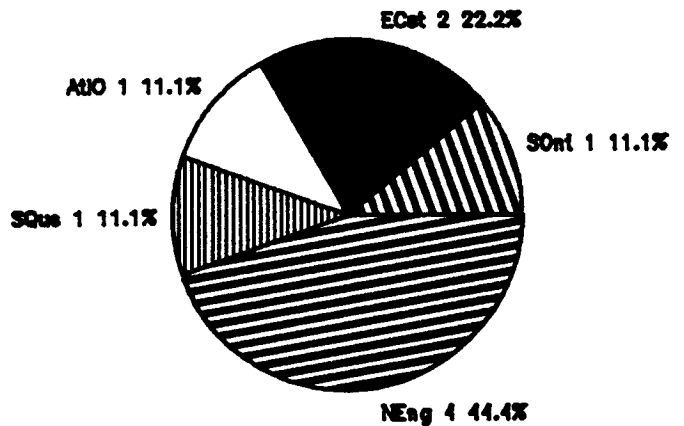
Figure 10

Frequency with which Source Regions
Contributed to Precipitation pH
by pH Range

Kejimkujik, N.S. May - Aug. 1988

Source Regions

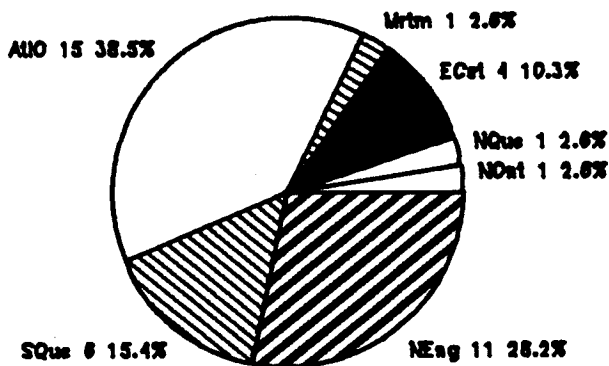
- NOnt: Northern Ontario
- MidW: U.S. Midwest
- SOnt: Southern Ontario
- NQue: Northern Quebec
- ECst: U.S. East Coast
- Mrtm: Maritimes/Nfld
- AtIO: Atlantic Ocean
- SQue: Southern Quebec
- NEng: New England
- USGL: U.S. Great Lakes



pH <= 4.0

7 events

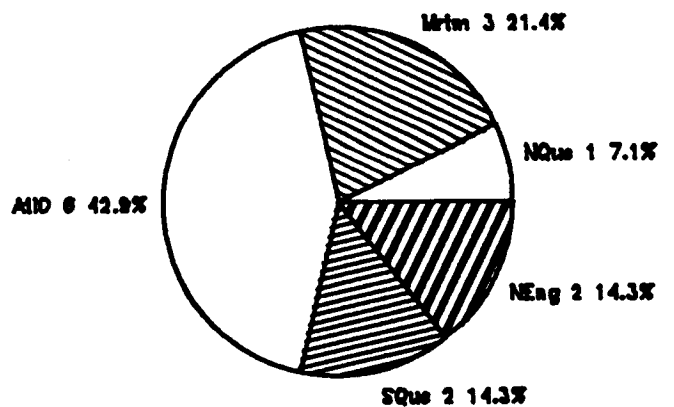
3 with unknown sources



4.0 < pH <= 4.7

27 events

4 with unknown sources



pH > 4.7

14 events

5 with unknown sources

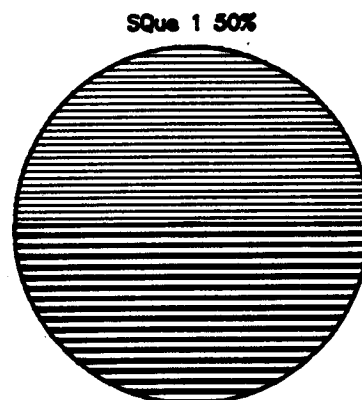
Figure 11

Frequency with which Source Regions
Contributed to Precipitation pH
by pH Range

Kejimkujik, N.S. Sept. - Dec. 1988

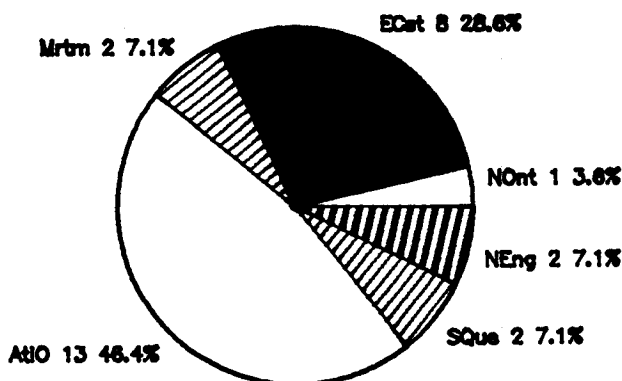
Source Regions

- NOnt: Northern Ontario
- MidW: U.S. Midwest
- SOnt: Southern Ontario
- NQue: Northern Quebec
- ECst: U.S. East Coast
- Mrtm: Maritimes/Nfld
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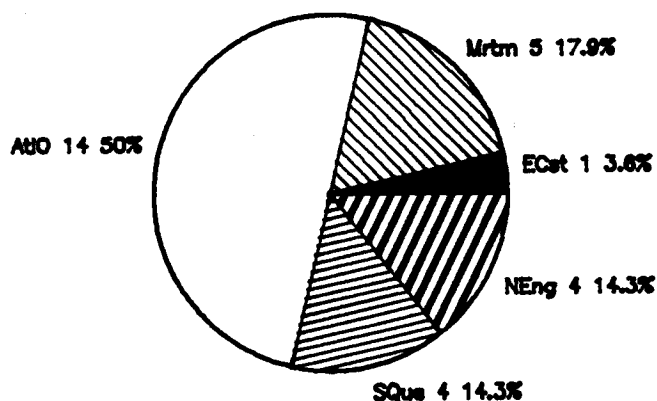
pH <= 4.0
4 events

3 with unknown sources



4.0 < pH <= 4.7
24 events

7 with unknown sources



pH > 4.7
22 events

2 with unknown sources

Figure 12

Average Annual pH of Precipitation
Kejimkujik, N.S.
1980-1988

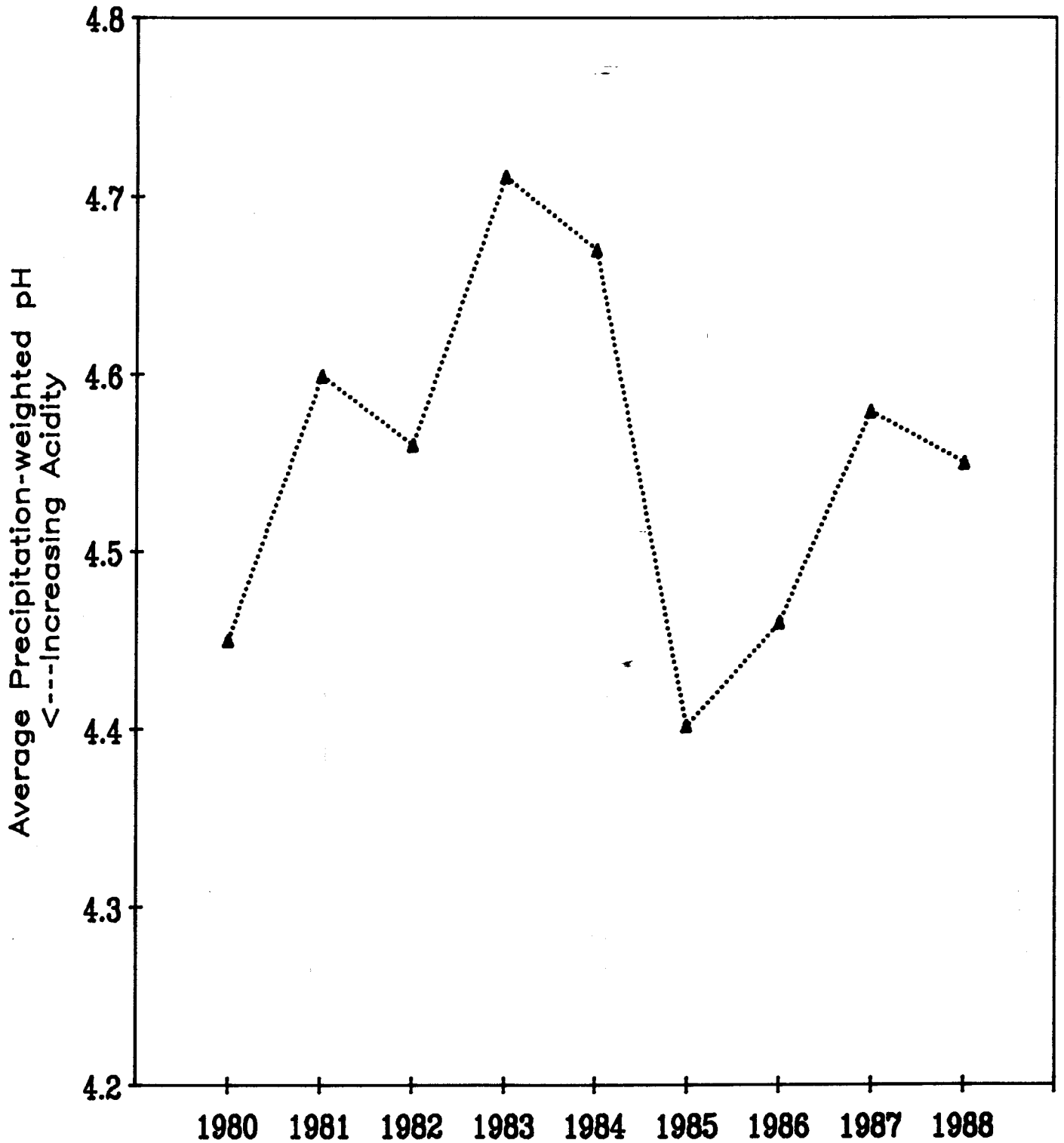
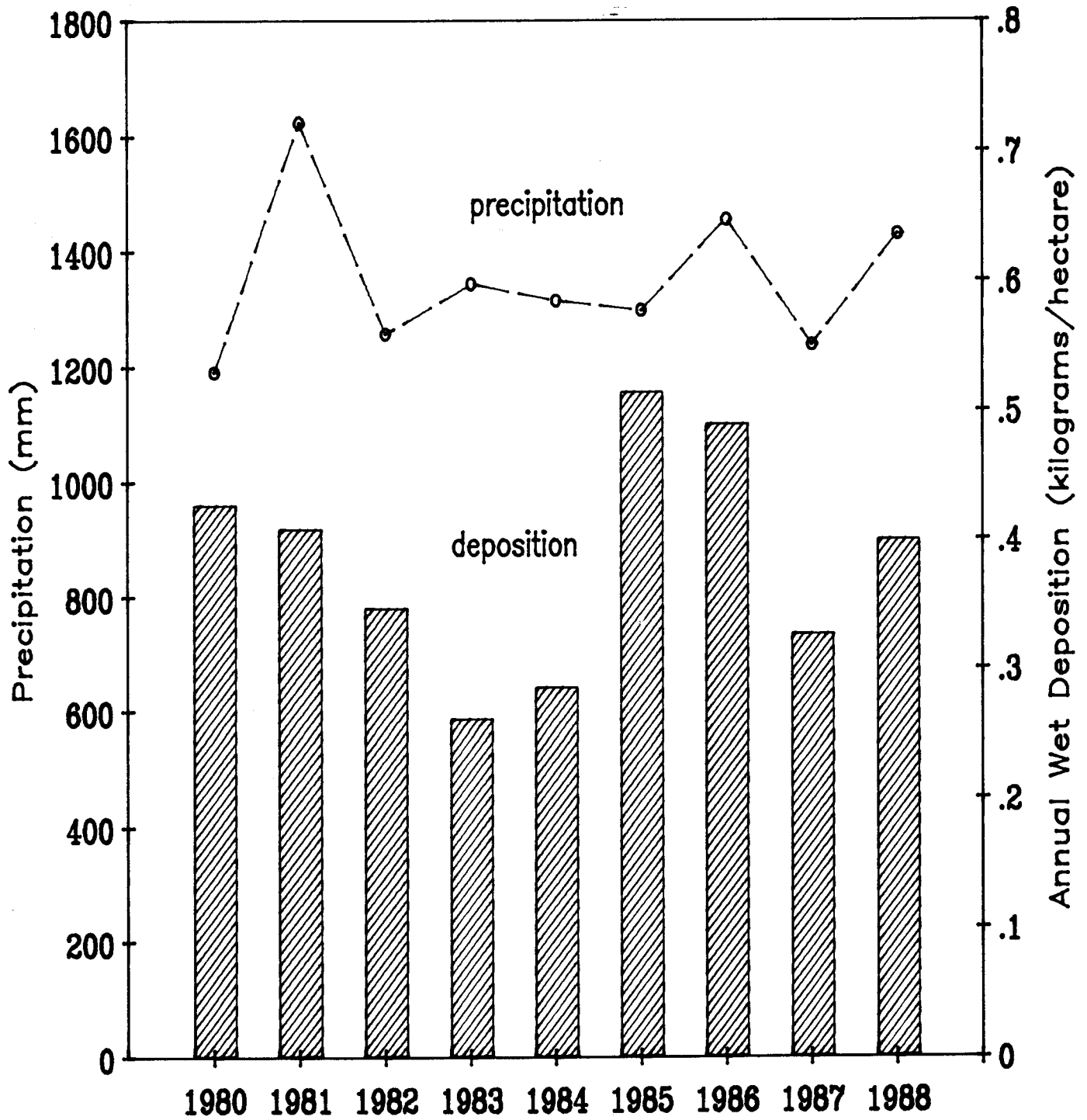


Figure 13

Annual Wet Hydrogen Ion Deposition
and Annual Precipitation
Kejimikujik, N.S.
1980-1988



Environment Canada - Environnement Canada

Acid precipitation during 1988 at Kejimikujik,
N.S.

HANLEY, D. E

QC 985.5.M4 M34 89-1
NSHW

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