

THE SPATIAL AND TEMPORAL VARIATION OF
ACIDIC PRECIPITATION IN NEWFOUNDLAND:
FROM SOURCE TO RECEPTOR

CENTRE FOR NEWFOUNDLAND STUDIES

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THE SPATIAL AND TEMPORAL VARIATION OF ACIDIC PRECIPITATION
IN NEWFOUNDLAND: FROM SOURCE TO RECEPTOR

by

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5
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ABSTRACT

In 1981 between the months of July and December precipitation event samples were collected at the sites of St. John's, Cape Broyle, Bishop's Falls, Grand Lake, Norris Point, Salmon Dam and Godaleich Pond on the island of Newfoundland in order to determine the acidity of precipitation on the island.

The samples were analyzed for pH, conductivity, sulphate, nitrate, ammonium, chloride, sodium, potassium, magnesium and calcium. Those samples which were obviously contaminated were discarded which left 60 samples in total. For these accompanying meteorological conditions were determined, namely weather type (i.e. history of the appropriate low pressure track), trajectory sector (from determination of 850 mbar. back-trajectories), antecedent rainfall duration, rainfall total and rainfall intensity. The combination of rainfall totals and precipitation chemistry results enabled the calculation of deposition values of SO_4^{2-} , NO_3^- and H^+ - factors considered most important with respect to precipitation acidity. From these results the influence of meteorological variables was determined from subjective and objective analyses in the form of basic and multiple correlation.

Although in a study of precipitation chemistry variability this sampling period was too short to negate the effects of natural variability, certain patterns did emerge which appear to result from the influence of specific variables. Antecedent rainfall duration, weather type and trajectory sector were the most influential variables on precipitation chemistry, although it is difficult to separate them.

since they are interdependent to a large extent. The most acidic events both in chemical concentration and total deposition of SO_4^{2-} , NO_3^- and H^+ , were associated with lows that had arrived over the island via Labrador and Quebec. Trajectory Sector 2, which includes high emission areas north of the Great Lakes contained the most acidic events with respect to concentrations ($\text{SO}_4^{2-} 1.66 \text{ mg.l}^{-1}$, $\text{NO}_3^- 0.66 \text{ mg.l}^{-1}$, pH 4.55). However, Sectors 4 (41.6% H^+) and 3 (31.3% H^+) respectively, produced the highest overall deposition values due to the frequency of trajectories from those sectors.

Other possible factors influencing precipitation chemistry were site location with respect to local pollution at St. John's, variations in total rainfall receipt (affecting dilution of pollutants) and induced orographic precipitation. In addition, seasonal variations, for example summer anticyclonic conditions being most conducive to pollutant accumulation and spring being the season of least precipitation and therefore least dilution. It was not possible to determine if precipitation in Newfoundland is becoming more acidic due to the lack of long-term precipitation records. In fact, CANSAP data from 1977-81 indicate that 1981 concentration values of SO_4^{2-} and NO_3^- may be lower than usual due to higher precipitation totals.

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LIST OF ABBREVIATIONS

L/PQ Low	Labrador/Quebec Low
CL/E Low	Great Lakes/East Coast Low
GL Low	Great Lakes Low
Mar. Low	Maritimes Low
Sub-Trop. Low	Sub-tropical Low
TS	Tropical Storm
WT	Weather type
TS	Trajector sector
DP	Antecedent rainfall duration
IN	Rainfall intensity
	Rainfall total
St.J.	St. John's
CB	Cape Broyle
BF	Bishop's Falls
GL	Grand Lake
NP	Norris Point
SD	Salmon Dam
GP	Godaleich Pond

CHAPTER 1

INTRODUCTION: THE LONG-RANGE TRANSPORT OF AIR POLLUTANTS AND SUBSEQUENT DEPOSITION AS ACIDIC PRECIPITATION

1.1 The concept of LRATP and acidic precipitation

Although recent news articles (National Geographic, 1981; Time Magazine, 1982; Peterson, 1982) have heralded "acid rain" as North America's greatest environmental problem of the decade, the phenomenon of "acid rain" was initially recognized over 100 years ago from research conducted around industrial areas of Great Britain (Smith, 1872). Recent concern in North America has probably arisen due to the combined effects of greater environmental awareness since the 1960's, the realization that wilderness areas far away from pollutant source areas are being affected, and perhaps more pertinently that the tourist (especially in the form of fishing) and forestry industries may suffer financial losses.

The term, "acid rain", refers to liquid precipitation having a pH of less than 5.6, this being the pH for distilled water in equilibrium with atmospheric carbon dioxide (Odén, 1976). Precipitation acidity is a measure of the concentration of hydrogen ions present, and since the pH scale is logarithmic a change in pH from 5.6 to 4.6, for example, reflects a 10-fold increase in acidity. In fact, pH levels around 4.6 are common in eastern North America (Altshuller & McBean, 1979. For further detail see Ch. 2).

The four stages involved in the deposition of acidic precipitation at the surface are:

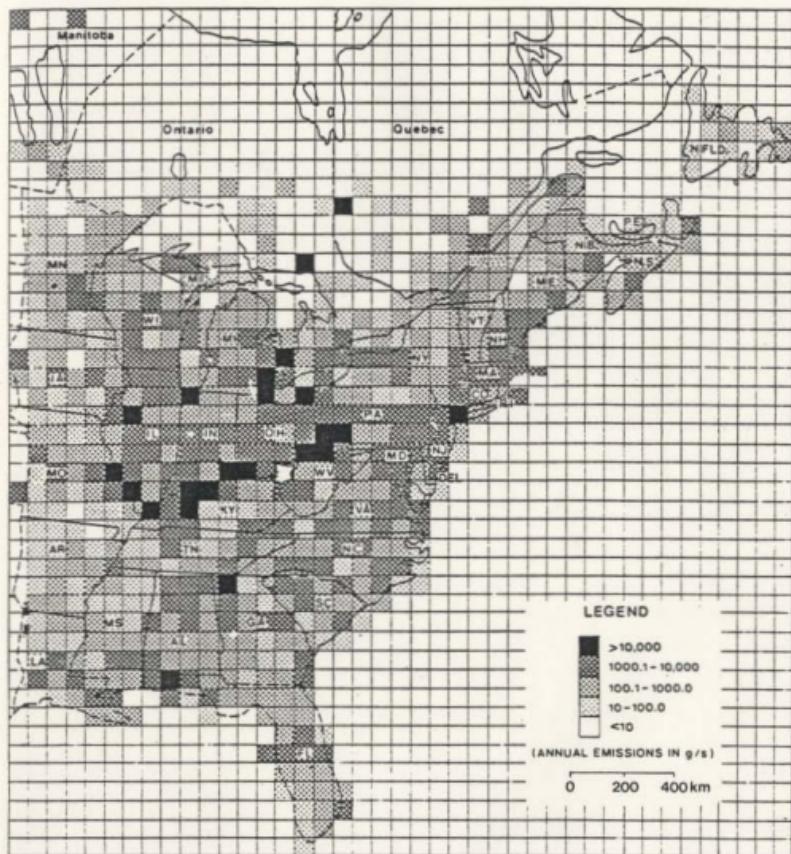
emissions
transportation
transformation
deposition

1.1.1. Emissions

There are a number of air polluting chemicals, including sulphates, nitrates, ozone, carbon monoxide and various organic gases and particulates that may undergo long-range transport (Altshuller & McBean, 1979). Long-range transport may be defined as the tropospheric transport of pollutants for sufficient time and/or distance to enable the original primary species (for example, sulphur dioxide, SO_2) and nitrogen oxides (NO_x) to transform to secondary compounds (sulphates (SO_4^{2-}) and nitrates NO_3^-). Although the acidity of wet deposition is dominated by sulphuric and nitric acids, smaller contributions come from hydrogen halide acids, Brønsted acids and other weak acids (Curtis, 1981).

Sulphur dioxide is in fact one of the few inorganic substances for which man-made emissions exceed natural levels—the former being 130 million tonnes globally, compared to only 4 million tonnes per annum from volcanoes (AES, 1979). More specific estimates show that natural sulphur emissions in Canada account for approximately 15% of national sulphur emissions, for Ontario only 7%, and for all of eastern North America, even lower at 5% (Curtis, 1981).

Anthropogenic sources of atmospheric pollution in North America occur approximately in the proportions of two-thirds sulphur and one-third nitrogen, with high emissions of both chemicals around the Great Lakes area, Ohio Valley, mid-west and east coast areas (see Figs. 1-1 and 1-2).

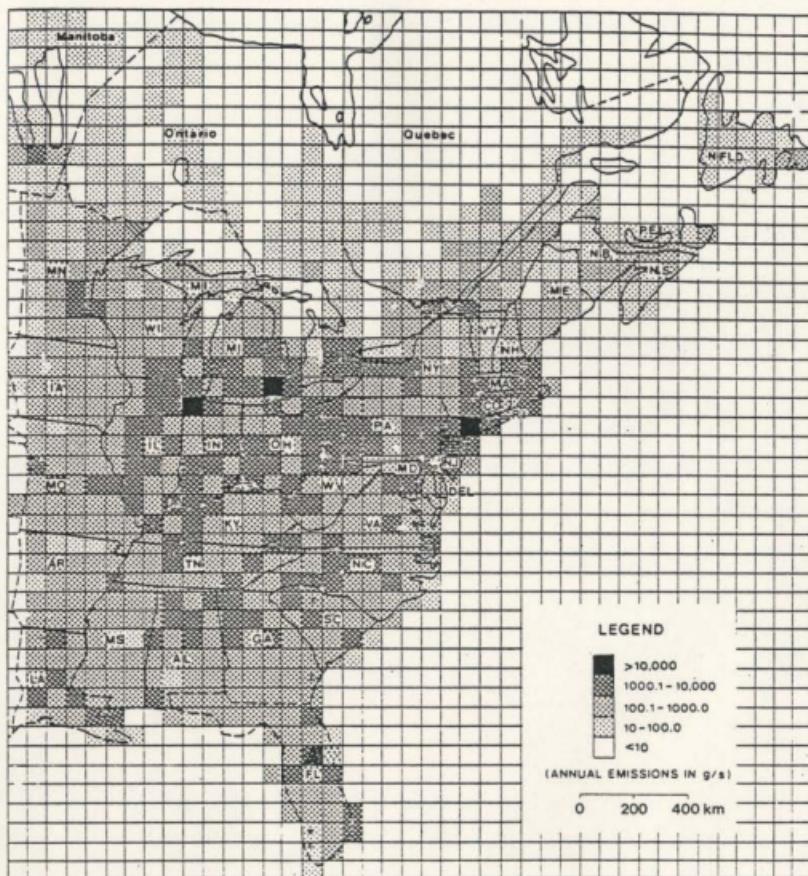


Source: Altshuller & McBean (1979)

Figure 1-1 SO₂ emissions for North America.

USA emissions from Sure II Data Base

Canadian emissions from Environment Canada



Source: Altshuller & McBean (1979)

Figure 1-2 NO_x emissions for North America.

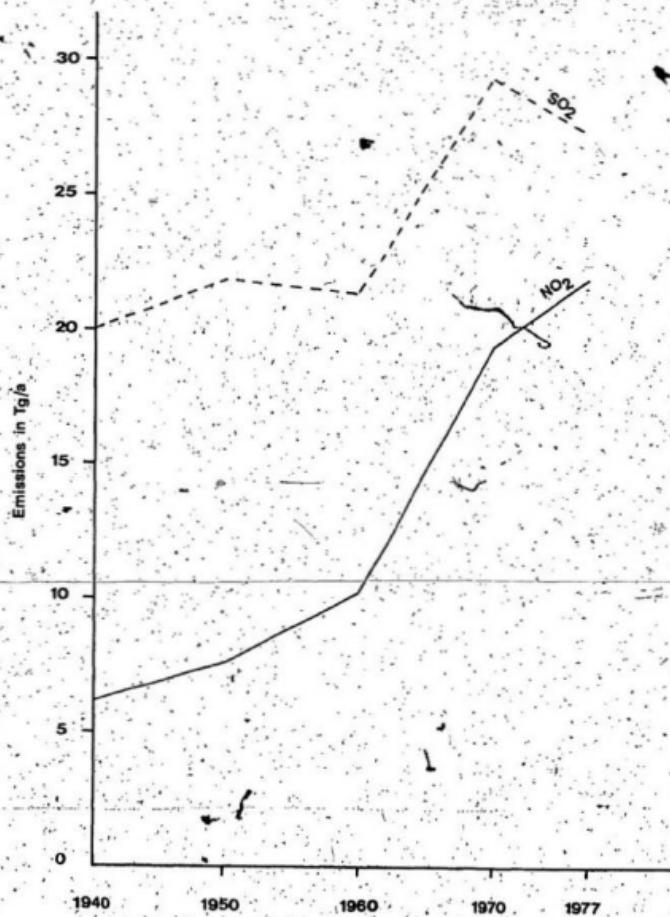
USA emissions from Sure II Data Base
Canadian emissions from Environment

Since industrial sources of sulphur and nitrogen differ between the United States and Canada, they will be referred to separately. SO₂ emissions within the United States come largely (see Table 1-1) from electrical generating plants, with other fossil fuel burning installations accounting for the remainder, whereas Canadian sources are mainly non-ferrous smelting industries, with power plants, other combustion sources and industrial processes contributing the rest. Regardless of industrial sources, Canadian emissions of SO₂ are one-fifth of her North American counterpart. Sources differ less with respect to NO_x emissions in that the major source for both countries is the transportation sector (see Table 1-2), followed by electric utilities and other combustion sources (Altshuller & McBean, 1979; Executive Summaries, 1983).

It is interesting to note that nitrogen compounds may play a more significant role in acidification of precipitation in the future, since trends (see Fig. 1-3) indicate that sulphur emissions may only increase moderately, while nitrogen emissions may increase significantly, due to increases from stationary fuel combustion sources and the transportation sector (Altshuller & McBean, 1979; Curtis, 1981).

1.1.2. Transportation

Although a regional pattern of "acid rain" was recognized in North America during the 1920's (Cogbill, 1976), the problem became more widespread during the 1950's with the legislative requirement for taller chimney stacks in industry. Whilst alleviating the problem of local pollution to a certain extent this increased the long-range transport of pollutants on a regional scale.



Source: Curtis (1981)

Figure 1-3 Historical trends in SO_2 and NO_x emissions in the United States (NO_x expressed as NO_2).

TABLE 1-1

Current SO₂ Emissions for the United States and Canada
Based on 1980 data (10⁶ tonnes/year)

	United States	Canada
Electrical Utilities	15.8	0.75
Industrial Fuel Combustion	2.4	0.62
Non-ferrous Smelters	1.4	2.13
Residential/Commercial	0.8	0.21
Other Industrial Processes	2.91	0.92
Transportation	0.8	0.16
Total	24.1	4.77

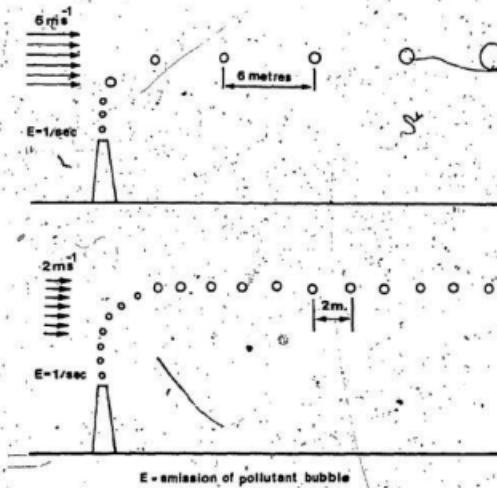
Source: Memorandum of Intent on Transboundary Air Pollution,
Executive Summaries (1983).

TABLE 1-2

Current NO_x Emissions for the United States and Canada
based on 1980 data (10⁶ tonnes/year)

	United States.	Canada
Electric Utilities	5.6	0.25
Industrial Fuel Combustion	3.5	0.30
Residential/Commercial	0.7	0.09
Non-ferrous Smelters		0.01
Other Industrial Processes	0.7	0.07
Transportation	8.5	1.11
Miscellaneous	0.3	
Total	19.3	1.83

Source: Executive Summaries (1983).



Source: Neiburger et al (1975)

Figure 1-4 The effect of wind speed on pollutant concentrations.

Once a pollutant has been released into the atmosphere, from either a high or low elevation, its concentration is governed by (1) the stability of the air as governed by the vertical-variation of temperature (which governs the mixing depth), and (2) the direction and velocity of the wind throughout the mixing layer. The mixing depth varies diurnally and with differing weather conditions. For example, during the day with a superadiabatic lapse rate (unstable conditions creating turbulence) vertical mixing may occur in a layer up to 3 kilometres deep. However, with a surface-based inversion, for example on a clear night under anticyclonic conditions (where the mixing height would be almost zero), or with the advance of a warm front (where the mixing height decreases with the approach of the front), greater stability prevents vertical mixing above a few hundred metres (Rodhe et al., 1982). In such instances dilution may only occur through horizontal dispersion (Neiburger et al., 1973). The effects of wind velocity on pollutant dilution are two-fold, by horizontal dispersion and vertical mixing. The effects of these are illustrated in Figure 1-4, showing that greater wind velocity increases both horizontal and turbulent mixing. Hence, in general, pollutant accumulation is most favoured with an inversion and light winds; whereas dispersion is most efficient with a large positive lapse rate (unstable conditions) and high wind velocity. After mixing and dispersion within the boundary layer the main reduction in pollutant concentration is by removal processes (Sciven & Fisher, 1975).

1.1.3. Transformation

Those pollutants which are not deposited near their source are likely to undergo some form of chemical transformation, from primary to

secondary pollutants. It should be noted that the processes involved are extremely complex and so at this stage will be simplified to a large extent. Much of the sulphur dioxide (SO_2) in the atmosphere oxidizes to sulphur trioxide (SO_3) which then reacts with water vapour to form sulphuric acid (H_2SO_4) mist. The sulphuric acid in the aerosol then reacts with other materials in the air to form sulphates, particularly ammonium and calcium sulphates (Haagen-Smit & Wayne, 1976 in Stern). Since research suggests that sulphate (SO_4^{2-}) particles of the order 1 μm diameter have smaller deposition velocities than SO_2 (Nriagu, 1978), conversion to SO_4^{2-} increases its lifetime up to three weeks (Env., Can., AES, 1979), and consequently the acidifying influence of emissions is extended to greater distances. The rate of transformation to SO_4^{2-} depends on the presence of catalysts, clouds, reactive photochemical products and ozone, and, as a result, may vary from 0.1% to 10% per hour. Not all SO_2 oxidizes to form acidic compounds, some being neutralized by alkaline substances, such as ammonia or calcite dust, and then oxidized to form the corresponding sulphates (Heuval & Mason, 1963).

Nitrogen oxides through conversion to nitrates can similarly stay in the atmosphere for days (Whelpdale, 1979); however, the oxidation processes to nitrate in the liquid phase are not fully understood (Rhode, Eliassen et al., 1982).

1.1.4. Deposition

Consideration will be given to both dry and wet deposition processes although wet deposition is generally regarded as the dominant long-range mechanism in eastern North America (Slinn, 1982). Measurements of the deposition velocity (that is, the ratio of the

rate of deposition per unit area to the concentration at a convenient height above the ground) of small SO_4^{2-} and NO_3^- ions made by Chamberlain (1966, in Friagu, 1978) indicate that removal rates by dry deposition are slow enough to enable long-range transport. Gaseous deposition occurs all the time the gas is in contact with the ground; this in itself is dependent upon the occurrence of small-scale turbulent eddies near the underlying surface (Rodhe et al., 1982).

Wet deposition occurs by one of two main processes, rainout or washout. The former involves the absorption of SO_2 within the cloud or, if in particulate form (SO_4^{2-}) greater than a few tenths μm radius, the pollutant may act as condensation nuclei for the formation of liquid cloud droplets. This is the most efficient in-cloud particle scavenging process (Rodhe et al., 1982). Removal may also occur within clouds as larger cloud droplets "capture" smaller particles as they fall. Washout refers to below cloud scavenging, largely by gravitational collision, a process similar to particle capture just described. Once again the effectiveness of this process is size dependent, since for raindrops of radius between approximately 50 and 2000 μm only particles of radius greater than 1 μm are readily captured (Junge, 1963). The processes involved with snow scavenging are less well known (Slinn, 1977). Suffice to say that with the large surface area to mass ratio of snow crystals, removal by interception should be quite efficient, but due to the crystalline surface gas absorption is very limited (Rodhe et al., 1982).

It should be noted at this point that although certain amounts of sulphate and nitrate are deposited with each wet precipitation occurrence (event), usually the main part occurs within a small number

of events. Such occasions are usually referred to as episodes. The exact definition of an "episode" appears somewhat arbitrary, but may, for example, refer to those individual events with the highest wet deposition, which, when summed, constitute at least 30% of the annual wet deposition total at a particular site (Rodhe et al., 1978).

1.2. Effects of acidic deposition

The main concerns relate to aquatic and terrestrial ecosystems, particularly the former where changes have been more readily observed. Although much of the research regarding aquatic ecosystems has concentrated on fish, all trophic levels are affected to some extent (Haines, 1981). For example, reduced rates of decomposition have been found in lakes (Hendrey et al. and Leivestad et al., 1976 in Haines, 1981) due to a change in dominance from bacteria to algae. Invertebrates, and amphibians may experience a reduction in the number of species and the dominance of different species, although this may be due to predator-prey relations (with reduced fish populations, as an indirect effect of acidification), rather than due to toxic metals released with increased acidification. Effects on fish include mortality (see Table 1-3), reproductive failure, reduced growth rate, skeletal deformities and increased uptake of heavy metals. In Norway fish populations, mainly brown trout, have been found to be sparse or absent at pH 5.5 or less (Haines, 1981).

Probably the most devastating effects on fish mortality come from the cumulative effects of particular events, either in the form of spring snow-melt or heavy autumn rains, termed acid "pulse" or acid "shock" (Harvey, 1978; Haines, 1981). Spring-melt is particularly destructive since embryos and fry are more sensitive to higher

TABLE 1-3

The Effects of Acidification on Various Fish Species

Family and Species		**pH at Which Population Ceased Reproduction,		
		Embryo	Fry or Adults*	Juveniles Declined or Disappeared
<u>Salmonidae</u>				
Rainbow trout	<i>Salmo gairdneri</i>	5.5	4.3	3.6-4.1
Lake trout	<i>Salvelinus namaycush</i>			4.4-6.8
Atlantic salmon	<i>Salmo trutta</i>	4.0	4.2	-
Arctic char	<i>Salvelinus alpinus</i>			5.0
Brown trout	<i>Salmo trutta</i>	4.0	5.0	-
Brook trout	<i>Salvelinus fontinalis</i>	6.5	4.4	4.5
Lake whitefish	<i>Coregonus clupeaformis</i>			<4.4
<u>Esoxidae</u>				
Northern pike	<i>Esox lucius</i>		5.0	4.2-5.2

*From laboratory experiments.

**From observation of natural populations.

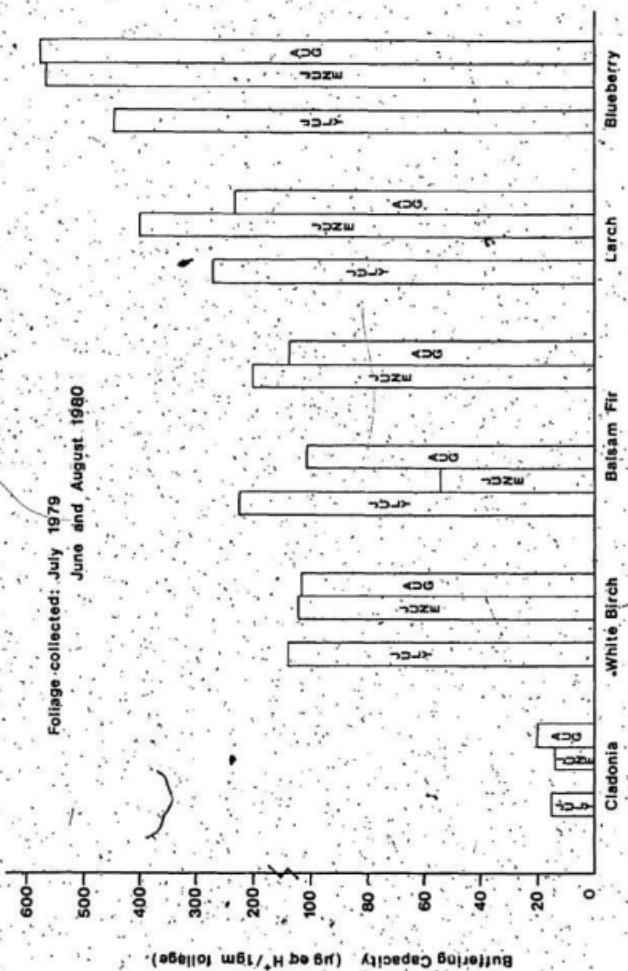
Source: Haines (1981).

acid and toxic (mainly aluminium) levels.

Effects on terrestrial ecosystems may be more complex because in some cases higher nitrogen levels can be beneficial to plant growth. However, acidification is generally harmful due to the loss of plant nutrients, reduction in soil exchange capacity, reduction in available phosphorus, and increase in the solubility of aluminium (McFee, 1979). The more direct impact of acid precipitation on plant foliage may accelerate the leaching of nutrients and increase the erosion of epicuticular waxes. Although it is more difficult to observe a direct correlation between reduced plant growth and acid precipitation (particularly since laboratory simulations are short term and the actual effects occur over long periods), analyses of forest growth in southern Sweden from 1896 to 1965 showed a 2-7% decrease in growth between 1950 and 1965. Jonsson and Sundberg (1972 in Galloway & Cowling, 1978) found no reason to attribute this to anything other than acidification.

With respect to Newfoundland, it has been estimated that with the present rate of deposition (10-20 kg. S/ha/yr. for the southwest and 5-10 kg. S/ha/yr. for the rest of the island (Sidhu, 1981 (from CANSAP data 1978)), forest production could be reduced at the rate of 1% per annum.

Sidhu also gives a sensitivity index for selected boreal species prevalent in the province (see Fig. 1-5), based on foliage tolerance or buffering capacity to acidification. However, these are only indirect estimates based on preliminary work. Lichen, some of which may also be used as an indicator of urban pollution, is the most sensitive species shown, and if significantly reduced in numbers may,



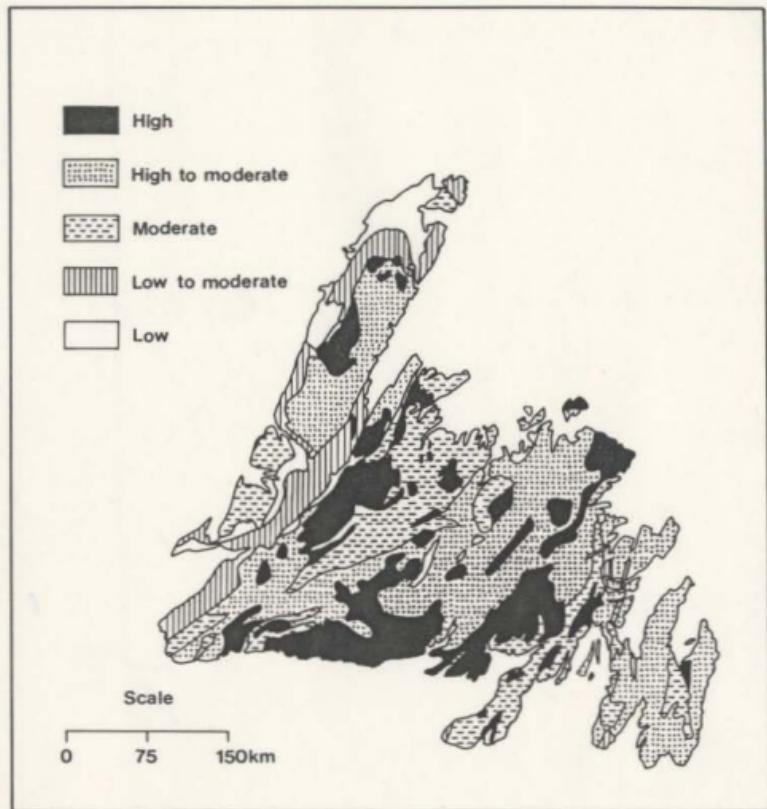
Source: Sidhu (1981)
Figure 1-5 Average buffering capacity of foliage from five boreal species in Newfoundland.

through the food chain, affect moose and caribou for which it is a major food source.

The susceptibility of certain areas to acidification, that is, their buffering capacity, is determined by the geochemistry, geomorphology and hydrodynamics of the system. These determine the capacity of soil and water to neutralize acids, resist pH change in water and absorb metal and organic compounds (Haines, 1981). Whilst an area still has some form of buffering (its alkalinity has not been totally eliminated), pH decline in surface waters may be negligible; but once alkalinity is removed increases in acidity can be rapid.

However, it should be noted that reductions in surface water alkalinity may also occur as a result of land use changes and may not always be attributable to acidic deposition. Reductions in alkalinity have been found in Great Britain, Scandinavia, Ontario, Quebec, Nova Scotia, Maine, New Hampshire, New York, New Jersey, North Carolina and Florida (Haines, 1981). Headwater lakes may undergo more rapid acidification than those lower in the watershed due to their higher flushing rate and lower buffering capacity of the drainage basin. As a result, fish are often lost from these lakes first and so require immediate attention (Harvey, 1978).

Although Newfoundland is geologically quite complex it is possible to make certain generalizations when delineating areas of differing buffering capacities. Much of the island consists of granitic (acidic) formations, apart from isolated limestone areas around the west coast, so that large areas are poorly buffered (see Fig. 1-6). This is further aggravated by extensive peatland areas with high humic and fulvic acid content.



Class	Relative sensitivity	Geology
1	Low	Extensive areas of limestone and dolomite
2	Low to Moderate	Sedimentary rocks, containing widespread calcium and magnesium carbonates
3	Moderate	Volcanic terrains; major mafic igneous complexes
4	Moderate to High	Quartz-feldspar gneisses; sedimentary rocks poor in calcium and magnesium carbonates
5	High	Granites and related rocks

Source: Nfld. & Lab. Dept. of Mines and Energy

Figure 1-6 Classification scheme for the sensitivity of areas of Newfoundland and Labrador based on regional geology.

Another means of determining the buffering capacity of water is by a Calcite-Saturation Index (CSI), where the higher the CSI number, the greater the sensitivity of the water. Although such values were calculated for Newfoundland recently (Clarke, Wittman & Whitlow, 1980), insufficient samples were taken from the interior, so that further sampling is required to complete the data. However, it is clear from sensitivity/buffering data that despite being situated well downwind of the major North American emission areas, Newfoundland may be susceptible to long-term adverse effects from relatively minor increases in precipitation acidity.

CHAPTER 2

STUDY OBJECTIVES AND RELATED RESEARCH

2.1. Study objectives

The aim of this research may be stated as follows:

- (i) to determine the acidity (as given by pH value), conductivity and chemical concentrations (SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , Ca^{++} , Mg^{++} , Na^+ , K^+) of individual precipitation events collected on the island of Newfoundland;
- (ii) to identify the degree of variability in selected precipitation chemistry values (that is, pH, SO_4^{2-} , NO_3^- and NH_4^+), according to synoptic meteorological conditions prevailing at and prior to specific precipitation events;
- (iii) to identify the degree of variability in precipitation chemistry between specific events as a function of particular meteorological variables, including precipitation duration prior to event at sampling site and the total precipitation and precipitation intensity at site during the event;
- (iv) to determine airflow back-trajectories for selected precipitation events from manual and computer techniques, in order to distinguish the distant source areas contributing to the most acidic (and consequently most polluted) precipitation events on the island;
- (v) to compare local and distant sources' contributions to precipitation acidity for selected sites and events.

2.2. Historical development of related research

Although reference will be made to initial research and work conducted in Europe, a more thorough examination will be made of precipitation and trajectory related studies recently conducted in North America. The intention is not to provide an extensive chronology of all acid precipitation research (see Cowling, 1982; Wisniewski & Kinsman, 1982), but a selection of material to examine how awareness of the concept progressed with respect to changing research aims and techniques.

2.2.1. Innovative research in Europe

Robert Angus Smith is generally regarded as pioneering acid precipitation research with his publication of "Air and Rain: The Beginnings of a Chemical Climatology," in 1872. In addition to actually coining the phrase "acid rain" Smith initiated some of its principal concepts, for some of which he receives little credit. Based on numerous precipitation samples collected at urban and rural sites in Britain, Ireland and West Germany, Smith showed that precipitation chemistry can be influenced by coal combustion, decomposition of organic matter, wind trajectories, proximity to the sea and the amount and frequency of rain or snow (Cowling, 1982). Smith also gives detailed descriptions of collection and analytical techniques, noting the importance of preventing dry deposition into a wet sample and strict requirements regarding site location. Of particular interest is his recognition of the changing chemistry of precipitation during an event, a fact which has greatly influenced the most recent sampling procedures (see Raynor & Hayes, 1982). Probably one of the first references to the long-range transport of

air pollutants came from another British scientist, Meetham, who in 1945 found that between 10 and 40% of sulphur dioxide in Leicester, England probably came from sources in the Ruhr Valley, Germany (Meetham, 1964).

Subsequently, the scientific awareness of acid precipitation came less from the analysis of precipitation samples but from limnology, agriculture and atmospheric chemistry. This is probably because there is less accurate historical data on precipitation chemistry, whereas data from other sources enabled better comparisons. For example, during the period 1950 to 1960 Eville Gorham conducted extensive studies of lakes in England and Canada and surmised that progressive acidification of lakes and subsequent loss of alkalinity was due to industrial emissions, mainly in the form of sulphur dioxide and its product sulphuric acid (Gorham & McFee, 1978; Cowling, 1982). One of the earliest precipitation networks, the European Air Chemistry Network (EACN) was established to obtain long-term precipitation chemistry data for agriculture and forestry in west and central Europe. Although data collection started in 1955, complete analysis was not available until 1968 and showed an area of acid precipitation centred on the Low Countries expanding throughout the collection period from 1955 to 1970 (Barnes, 1979). Average pH levels were as low as 4.0 and 3.8 in the central area with sulphate identified as the main cause of acidification. This was related to a doubling of European anthropogenic SO_2 emissions between 1950 and 1970; in addition, although not known at the time, NO_x emissions trebled during the same period.

Research on acid precipitation within the atmospheric sciences began largely in Sweden, initiated by Rossby and Eriksson who used precipitation data from EACN to test their theories of pollution transport and transformation (Cowling, 1982). However, the major contribution of Sweden's innovative work came from Svante Odén who, although being a soil scientist, integrated all aspects of acid-precipitation in his research. Odén's work includes analysis of the chemistry of rainfall events at several stations in Sweden, for which he then constructed 3-day back-trajectories at the 850 mbar. pressure level. Although details of the trajectory technique are not given his results indicate that trajectories passing over high emission areas have a lower pH and substantial increases in sulphur and nitrogen levels (Odén, 1976).

Odén also introduced the concept of "looping", whereby sulphur (and other chemicals) is deposited into the ground along its trajectory and then reintroduced into the atmosphere by diffusion processes, such as evapotranspiration. It is possible that this process may result in the underestimation of sulphur transport (Odén, 1975). Odén's research created much interest amongst scientists and in fact led to Sweden's contribution at the 1972 United Nations Conference on the Human Environment, entitled "Air Pollution Across National Boundaries: The Impact of Sulphur in Air and Precipitation". The report cited hundreds of lakes that had lost their ability to support fish life. For example, in southern Scandinavia during the period 1920 to 1940, only a few lakes had pH levels below 5.5, whereas in 1974, 40% of 155 lakes in southern Norway were below that level (Gorham & McFee, 1978). The report

also warned that "a similar situation might possibly exist within certain areas of Canada and the north-eastern part of the U.S.A.", and that a "detailed study of the likelihood of such a development is a matter of urgency" (Howard & Perley, 1982). Although the conference had little impact in North America, European interest was sufficient to initiate the establishment of the SNSP Project, the Norwegian Interdisciplinary Research Programme, "Acid Precipitation - Effects on Forest and Fish," from 1972 to 1980. In addition, a study of the long-range transport and deposition of atmospheric sulphur in Europe was commissioned by the Organization for Economic Co-operation and Development (OECD) from 1973 to 1975. The OECD findings showed that the area of acid precipitation covered virtually all of northwestern Europe. They also confirmed the concept of long-range transport, showing that each European country is measurably affected by emissions from the other European countries (OECD, 1977).

2.2.2 North American research

Preliminary research focused more on the local effects of sulphur dioxide and heavy metal deposition around metal smelting industries, particularly the effect of the International Nickel Company (Inco Ltd.) at Sudbury, Ontario. The initial realization that acid precipitation did exist in eastern North America came not from precipitation data, but from numerous lakes sampled in southern Ontario and Nova Scotia (Beamish & Harvey, 1972). For example, in 1966 4,000 pink salmon were introduced into Lumsden Lake in Killarney Park (La Cloche Mountain area of Ontario) and by 1968 not one of the fish could be found. Subsequent pH tests of

the water found a decline from 6.8 in 1961 to 4.4 in 1971—a hundred-fold increase in acidity (Howard & Perley, 1982). A survey conducted in the same area in 1971 revealed that of 150 lakes sampled, 33 had a pH below 4.5, termed "critically acidic" and 37 between pH 4.5 and 5.5 termed "endangered" (Beamish & Harvey, 1972). The subsequent disappearance of fish followed a similar pattern to those observed in Scandinavia (Haines, 1981). In 1972 Inco completed the building of their 400 metre "superstack" at Sudbury where local studies confirmed their objective to reduce sulphur levels in the surrounding area. However, emissions are now being injected higher into the atmosphere and as a result undergo long-range transport (and dilution) further east under the influence of the prevailing westerly winds.

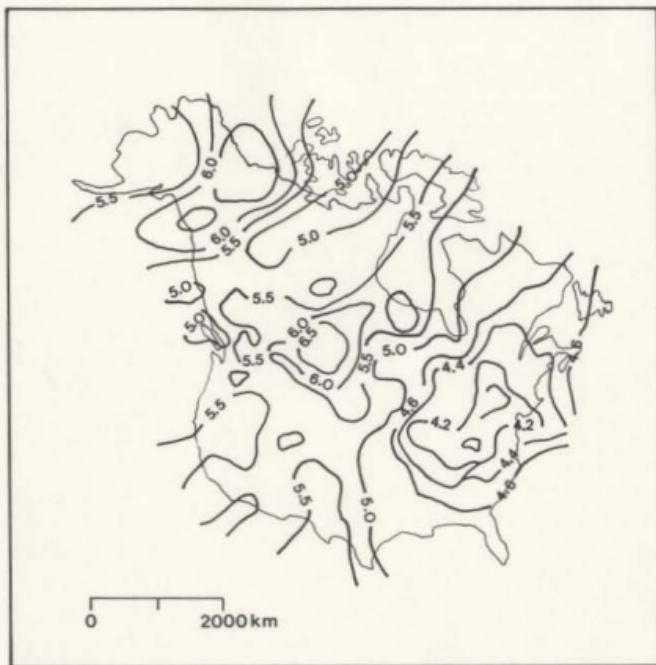
The realization that fish stocks and forests are threatened by acid precipitation led to the formation of a number of long-range programmes for analysis of precipitation by both American and Canadian governments.¹ Prior to 1977 the only Canadian precipitation network consisted of 10 stations established by the World Meteorological Organization (WMO) to monitor background air pollution. The Canadian Network for Sampling Precipitation (CANSAP) began in 1977 and its American counterpart, the National Atmospheric Deposition Programme, commenced in 1978. By 1981, 50 stations were operational in Canada and 93 in the United States (Cowling, 1982). Combined results from these programmes enabled

¹ Further information regarding these programmes may be found in: Melo, 1981; Cowling, 1982; Whelpdale & Barrie, 1982; and Wisniewski & Kinsman, 1982.

the construction of Figure 2-1, emphasizing that much of eastern North America, and to a lesser extent the west coast of British Columbia, received precipitation averaging below pH 5.0 during the sampling period.

The CANSAP programme involves collection of monthly samples of precipitation with samples analyzed for acidity and soluble major ions, including sulphate and nitrate (Bartie et al., 1980). However, it became apparent that chemical analysis of individual precipitation events was necessary to provide a greater understanding of the meteorological and source variables, and the "acid shock" effect mentioned previously (Ch. 1, p. 13). As a result the Canadian Air and Precipitation Monitoring Network (APN) was instigated in 1979 (see Fig. 2-2) to sample wet (only) precipitation events (with an automatic Sangamo sampler), suspended particulate matter and sulphur dioxide. Site requirements for this network are much more stringent than those for CANSAP (see Barrie et al., p. 4), particularly with regard to excluding local pollutants; for example, sites have to be at least 20 kms from population centres of 10,000 people or more. Various sites have also been established by provincial governments (see Fig. 2-2); those in Newfoundland will be referred to in Section (v).

It should be noted that major differences exist between precipitation sampling networks as to whether they collect bulk (wet and dry) or only wet depositions, and whether this is done as a monthly, weekly, daily event or sequential (usually hourly) sampling basis (Wisniewski & Kinsman, 1982). This is crucial when making comparisons between results for different areas and may



Source: Cowling (1982)

Figure 2-1 Average annual pH from Sept. 1979 to Oct. 1980:
based on data from NADP in the U.S.A. and
CANSAP in Canada.

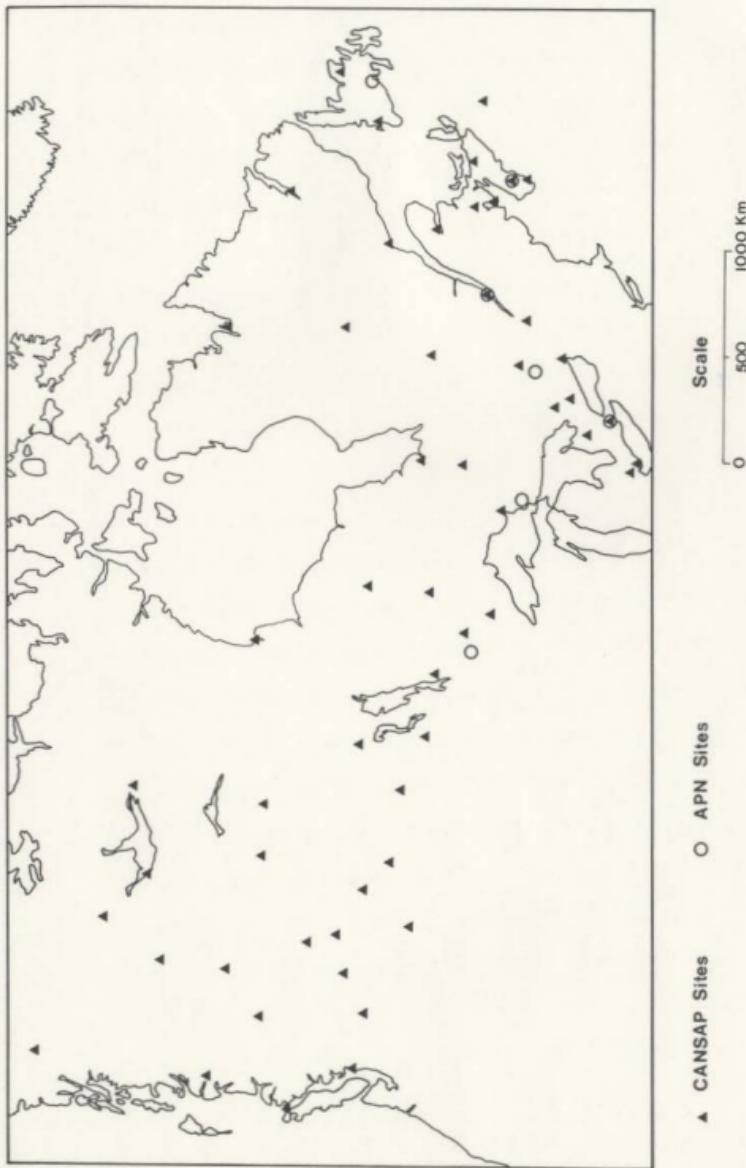


Figure 2-2 Location of CANSAP and APN monitoring sites in Canada.

lead to large errors when slightly different variables are compared. Such errors may arise when constructing historical pH isopleth maps which require data collected over several years, at various sites by different organizations. For example, recent research has questioned the validity of evidence (e.g., Cogbill & Likens, 1974) suggesting that rainfall acidity has increased in eastern North America significantly since the 1950's. Although Hansen and Hidy (1982) conclude that there probably has been an increase in precipitation acidity (this cannot be verified due to incomplete data), Stenstrand and Seignin (1982) interpret any apparent increase in acidity from the 1950's to 1970's as a result of unusually high pH values during the 1950's. This was inferred from the high levels of magnesium and calcium as a result of drought conditions during this earlier period. When these values are corrected there is little difference between precipitation values of the 1950's and those of the 1970's. However, it is important to remember that there also exist inherent problems with the use of correction values, so that it is virtually impossible to draw any firm conclusion from this data.

Other inaccuracies when comparing data may arise from changing collection and analytical procedures; although it is possible to make corrections for pH values taken several years ago, these are not totally satisfactory. Such problems even question the absolute validity of the EACN data with respect to data filing and chemical analysis (Paterson & Scorer, 1973). This, however, is not to the extent of invalidating their overall results for the spread of acid precipitation over Europe mentioned previously. In a detailed review of related problems Hansen and Hidy (1982) conclude

that at present there are no accurate means of relating source emissions to acidic deposition, and that meteorological variables should be given more attention, particularly with respect to the total ionic composition of precipitation.

In 1978, the governments of Canada and the United States formed a combined Research Consultation Group on the Long-Range Transport of Air Pollutants, in order to have better liaison between scientists on either side. The reports from this group (Altshuller & McBean, 1979 and 1980) identified two meteorological situations conducive to long-range transport in eastern North America, namely, the stagnation of summertime high pressure areas over the eastern portion of the continent followed by long periods of continuous brisk winds, enabling transportation of accumulated pollutants from source to receptor areas. Once pollution has collected within these warm, moist air masses, removal by precipitation is favoured with the convective showers typical of such air masses. In addition, when a stagnating anticyclone breaks down the leading edge of the advancing cooler air mass is often preceded by a frontal zone where precipitation is likely to occur (Altshuller & McBean, 1979).

Following the establishment of the Research Consultation Group in 1980, the two governments signed a Memorandum of Intent on Transboundary Air Pollution. This was a response to "actual and potential damage resulting from the long-range transport of air pollutants between countries and in recognition of the already serious problem of acid rain" (Phase II, Summary Report, 1981). The Memorandum covers all aspects of the problem including emissions, aquatic and terrestrial ecosystem effects, modelling of pollutant movements,

impact and emission control assessments. Although not all the results obtained are available in detail there are some rather conclusive findings which tend to negate any suggestions that acid precipitation poses no serious threat. Some of these are as follows:

- (1) Sulphuric acid has been identified as the dominant compound contributing to long-term surface water acidification.
- (2) Studies of lakes in eastern North America show higher sulphate levels than those expected from natural sources—these also occur in areas of high atmospheric deposition. For example, in Quebec SO_4^{2-} in surface waters decreases further east and north.
- (3) Sediment cores analyzed from lakes in Maine, Vermont, and New Hampshire show significant pH decline since the 1900's. This is reflected in lower metal levels in the sediment, since a low pH maintains metals in the water column and a change in the diatom population.
- (4) Long-term water quality data and sediment cores show that acidic deposition has caused long and short-term acidification of sensitive (low alkalinity) surface waters in Canada and the U.S.A. Any consequent loss of genetic fish stock would not be reversible.
- (5) Areas of low pH (<4.5) correspond with (a) regions of most intense emissions of SO_2 and NO_x and (b) regions immediately downwind of these.

It is interesting to note that the use of sediment cores may prove to be a useful tool for determining long-term changes in surface water pH, providing that any change in metal concentrations may not be attributable to other factors. Such results may in fact show that acidification has been occurring since the industrial revolution (c. 1900), but has become of more significance on the regional and continental scale with increased emissions and taller chimney stacks. With respect to this, since acid precipitation is experienced in "remote" locations, due either to very distant sources of anthropogenic emissions or to the relative absence of buffering substances (Ca^{++} and NH_4^+), it would be useful to determine a background or natural

acidity value (U.S.-Can. Exec. Summary, 1983). In other words, the value of pH 5.6 taken to indicate "clean" precipitation may not be very realistic.

Although this research also included transport modelling, few details have yet been published regarding techniques used or results obtained. However, "air trajectory analyses reinforce the conclusion that man-made emissions have a major influence on acidic deposition" (U.S.-Can. Exec. Summary, 1983). The use of transport models will now be discussed in more detail.

2.2.3. Application of long-range transport models

In addition to the establishment of numerous precipitation networks over Europe and North America a number of transport models have been formulated to relate pollutant deposition to source emissions. The three main types are (1) Lagrangian, dealing with the wet removal along an air mass trajectory; (2) Eulerian, involving a large number of emission sources and different release heights, within a fixed grid framework; and (3) statistical parameterization of advection and chemical processes (Altshuller & McBean, 1980). Models to estimate dry and wet depositions of pollutants include the OECD LRTAP study, the Sulphate Regional Study—SURE (Pack et al., 1978) and the Advanced Statistical Trajectory Regional Air Pollution Model—ASTRAP (Shannon, 1979). These models each incorporate emission data and estimations of dispersion and removal processes to give deposition data for specific receptor points. Although models may be applied on a monthly and annual basis (for example, with respect to transboundary fluxes) recent work has used data from individual storms due to significant variability between events.

With regard to trajectory transport models, three have been selected for referral--the Air Resources Laboratories' Model, the Heffler Interactive-Terminal Transport Model (a version of the ARL Model) and the Canadian Atmospheric Environmental Service Model, initiated as part of the LRTAP project in the mid-1970's.²

ARL Model. This enables the calculation of forward and backward trajectories at any level in the northern hemisphere. Precipitation sampling conducted in Hawaii (Miller, 1979) and Bermuda (Jickells et al., 1982) made use of this model. Not all samples collected in Hawaii were on an event basis due to the remoteness of some of the sites, and since automatic samples were not used, contamination by dry deposition may have occurred. Trajectories were constructed for the 3,000-5,000 metre layer from 1975 to 1977 and most were categorized into compass quadrants. Results indicate that the more acidic precipitation in Hawaii is associated with flow from the north and greater altitude, with pH 5.2 at sea level and pH 4.2 at 3,600 metres. The author suggests that the washout of alkaline aerosols may cause lower acidity on the coast; in addition, the site at 3,600 metres is above the level of maximum precipitation, so that less dilution may account for the lower pH at this altitude.

In Bermuda, all samples collected were on a wet deposition event basis except for a short period when bulk samples were collected. In this case only three trajectory sectors were chosen comprising (1) continental North America, (2) South America and tropical islands, and (3) the Atlantic Ocean east of Bermuda. The majority of the most

²Further reference will be made to both computer and manual trajectory techniques in Ch. 4. For further reading see Pack et al. (1978) and Walmsley & Maillet (1982).

acidic events ($\text{pH} < 4.5$) originated in continental North America and were found to occur during winter when frontal systems pass regularly.

Heffter Model. Wolff et al. (1979) collected precipitation event samples at sites within the New York Metropolitan area between 1975 and 1977, not only for the computation of back-trajectories but also to compare spatial, meteorological and seasonal variables. Once again some of the samples may have included dry deposition since automatic samplers were not used. Although the trajectory technique is not actually specified, it was conducted at the Brookhaven National Laboratory and so is assumed to be the Heffter Model used by Raynor and Hayes (1982). Trajectories were calculated with winds averaged from the surface to 1,000 metres for five days prior to the event and then divided into six sectors, the choice of which was not explained. However, results indicate that trajectories from the southwest and west (which includes Ohio, a high emission area) have the lowest pH values, and those from the north and east (Atlantic Ocean) the highest. Lowest pH values were also found to correspond with cold front and air mass (non-frontal) type precipitation events, which occurred more often in summer along the sulphate maxima. It is interesting to note that air mass type showers or thunderstorms generally occur within the poleward flow around the western side of a high pressure system, which has been documented as conducive to the accumulation of pollutants (see p. 30).

Using the same basic trajectory model (but with three as opposed to five days back in time) over selected height intervals, Raynor and Hayes (1982) were able to relate the chemistry of precipitation events (at Brookhaven National Laboratory, Upton) in New York to a number of meteorological parameters, including synoptic type, season

precipitation type and rate, wind direction and speed, and temperature. Results indicate that the lowest pH values occurred during the summer when precipitation amounts are lowest, and during cold front and squall line precipitation from relatively polluted air in warm sectors ahead of cold fronts. Wind direction indicates that higher pollutant levels occurred during westerly winds from the New York urban area. Trajectories for some of these events suggest that, the true source may be distant, from the Ohio Valley (Raynor & Hayes, 1982) reflecting the difficulty involved when attempting to distinguish between local and distant pollution sources. It is pertinent to note from these studies that meteorological parameters accompanying an event are equally as important if not more so than prior trajectory path, so that studies only considering the latter may be inadequate when explaining variability between events.

AES Model. Data on the AES Model with respect to wet deposition was only published very recently so reference will be made here to dry deposition data. Barrie et al. (1980) used 3-dimensional, 4-day back-trajectories at 1000 mbar. (surface) for daily particulate sulphate and gaseous SO_2 concentrations collected at a site in southwestern Ontario. For a trajectory from northern Canada on February 16 low concentrations ($0.76 \mu\text{gm.}^{-3}$ $\text{SO}_4^{=}$ and $1.1 \mu\text{gm.}^{-3}$ SO_2) were found. When the trajectory shifted south to the United States an increase of pollutants was found ($4-9 \mu\text{gm.}^{-3}$ $\text{SO}_4^{=}$ and $18-20 \mu\text{gm.}^{-3}$ SO_2 on February 18 and 19). Similarly, trajectories calculated by Chang (Clark, 1981) for Ontario Hydro indicate that air parcels from the south and southwest have higher concentrations of sulphate aerosol. For an event on 20 April, 1977 in southwestern Ontario values of $25-40 \mu\text{gm.}^{-3}$ $\text{SO}_4^{=}$ were

recorded, associated with a slower moving air mass from the southwest (twice the amount recorded by Barrie et al. for a southerly trajectory).

In contrast, strong northwesterly winds gave very low aerosol values (Melo, 1981). Desautels (1981) used the AES Model to determine the variation in air parcel trajectories over Quebec according to region, season and the presence or absence of precipitation, based on 1978 weather conditions. This and other research mentioned in this chapter will be referred to again in Chapter 4.

2.2.4. Application of manual trajectories

Although considerably time consuming and perhaps less accurate due to over-simplification of atmospheric processes (see Ch. 4, p. 73) some researchers still determine air trajectories manually. Kurtz and Scheider (1981), for example, collected wet precipitation events from sites in the Muskoka-Haliburton area of central Ontario between 1976 and 1979, and constructed sea level geostrophic trajectories from surface pressure maps to track air parcels back 48 hours to their "octant of origin." This is a similar method to that of Förlund (1972) except the latter chose six as opposed to eight sectors of origin. Since it was not always possible to collect single events Kurtz and Scheider conducted data analysis for both the entire data set and for single events. Both data sets showed that the majority of hydrogen ion, sulphate and nitrate deposited were associated with trajectories from the west and southwest octants. No further consideration was given to meteorological parameters in this study.

In a project conducted around Schefferville, Quebec, Lewis and Hrebenyk (1979) collected wet event samples (where possible) during July and August, 1978. From a synoptic classification of summer

'rainfall' events for Schefferville (not yet published), the authors identified three important storm parameters related to potential pollutant deposition episodes:

- (1) the position of the cyclonic storm track, in association with the 850 mbar. back-trajectory;
- (2) two or more days of anti-cyclonic weather in central and eastern North America immediately prior to event;
- (3) the number of hours precipitation was occurring within the storm prior to its arrival at Schefferville.

Trajectories were calculated at the 850 mbar level according to the method outlined in Pettersen (1956, Ch. 2, p. 27). Using these parameters to compare precipitation chemistry, the storm of 16 July travelled further north than the storm of 27 July, which came slowly along a track from western Ontario across James Bay into central Quebec. However, the trajectories for both storms are quite similar, passing near major point sources at Sudbury and Noranda. The slightly higher levels of sulphate and nitrate, and lower pH, on 27 July may then be attributable to a shorter period of removal, 30 hours of precipitation prior to reaching Schefferville, as opposed to 48 hours on 16 July. This study was, however, limited to only five single events, insufficient for reliable comparison of precipitation chemistry values.

Similarly, using the 850 mbar. level for trajectory calculation, Shaw (1980) sampled wet and dry precipitation events at St. Margaret's Bay, a rural site in Nova Scotia, during late 1978 and 1979. Wet deposition was measured with a Sangamo automatic sampler. Results are compared with monthly samples collected at CANSAP sites in Kejimkujik Park and Truro, and event samples collected at Dutch Settlement (situated between Truro and Halifax) and Kejimkujik to

determine the contribution of pollution from local and distant sources. When sulphate (St. Margaret's Bay 36.2 kg.ha^{-1} ; Kejimkujik 13.5 kg.ha^{-1}) and hydrogen ion (St. Margaret's Bay $64.3 \mu\text{eq.m}^{-2}$; Kejimkujik $17.1 \mu\text{eq.m}^{-2}$) levels at St. Margaret's Bay were found to be virtually treble those at Kejimkujik and Truro (140 and 100 kms, respectively, from Halifax), local surface wind data were used to determine if Halifax, 25 km east of the site at St. Margaret's Bay, was acting as a "local" source. Results suggest that approximately 50% of the annual wet deposition at St. Margaret's Bay is due to SO_2 emissions from Halifax. From this it is estimated that $29 \text{ kg SO}_4^{2-} \text{ ha}^{-1} \text{ yr}^{-1}$ in 1979 was from distant sources. Trajectories for distant source events were divided into three categories according to the region over which the air parcel had passed for 30 to 40 hours prior to the event (see Ch. 6, p. 120). However, it is important to note that the relative importance of each source region is largely governed by the frequency of precipitation events from each region. This in fact is the case for all studies relating the contribution of pollution from certain areas or sectors.

2.2.5. Research in Newfoundland

In comparison with other parts of eastern North America acid precipitation research in this province is quite limited, although more projects have been initiated in the last few years. Precipitation measurements started in 1977 with the installation of three CANSAP sites in the province at Goose Bay, Gander and Stephenville, collecting wet monthly samples. Although the validity of some of this data may be questioned (for example, the sampler at Gander was in close proximity to the aircraft hangars), this is the only substantial precipitation data available at present. Figure 2-3 illustrates

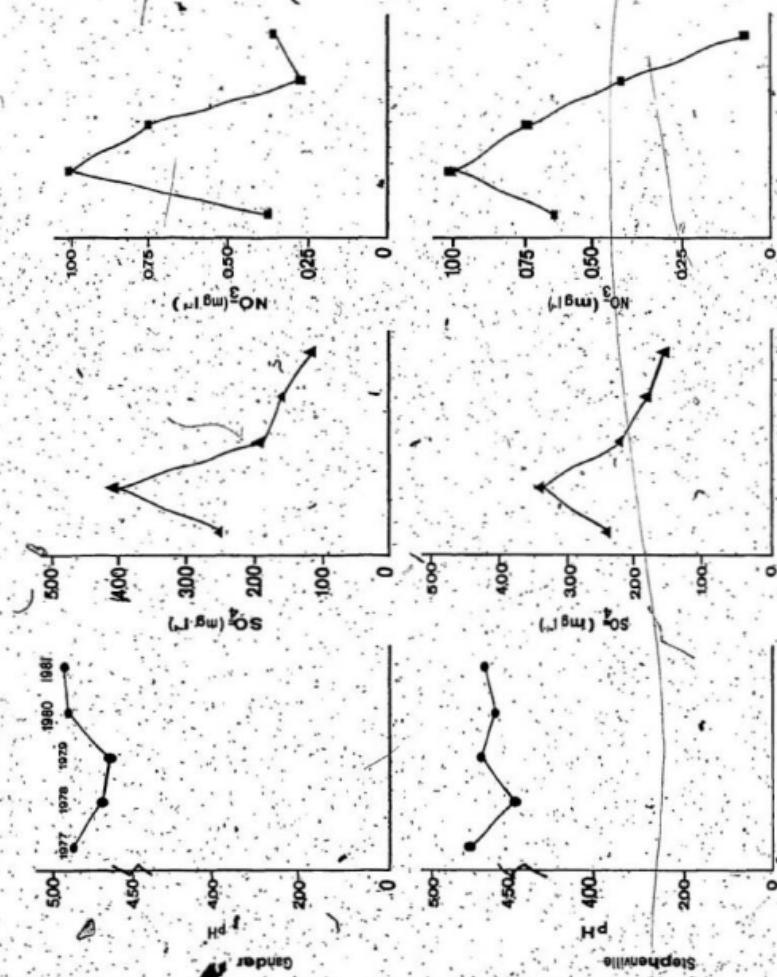


Figure 2-3. Mean CANSAP values of pH , SO_4 and NO_3 from 1977 to 1991 at Gander and Stephenville.

values for pH, SO_4^{2-} and NO_3^- for the island sites from 1977 to 1981, showing the large degree of variability in the data. The mean values for both sites are quite similar, with an overall mean pH of 4.79 at Gander and 4.67 at Stephenville and corresponding mean SO_4^{2-} values of 2.23 mg.l^{-1} and 2.30 mg.l^{-1} , respectively. The slightly higher acidity values at Stephenville may be due to its southwesterly position on the island, being in the immediate path of incoming cyclones from the mainland (so that washout levels of SO_4^{2-} and NO_3^- may be higher).

Comparisons of monthly values indicate that acidity levels are generally higher during summer months (from May to August/September (see Table 2-1) which would be expected with the accumulation of pollutants under summer anticyclonic conditions and less dilution and lower rainfall amounts overall. However, any interpretations from this should be made with caution since they are monthly figures taken over a five-year period, so that it is difficult to distinguish natural variability over such a short time, particularly where data is missing for several of these months. Comparison between CANSAP values for 1981 and values obtained from this study will be discussed in Chapter 6.

Following the installation of the CANSAP sites, the Newfoundland Department of the Environment located MIC samplers at Cape Broyle in September, 1980; Whitbourne in January, 1981; Bay D'Espoir in August, 1982 and Grandy's River (Port aux Basques) in October, 1982 to collect weekly wet precipitation samples. The Environmental Protection Service have a similar project with sites commencing at Terra Nova Park in February, 1981 and Gros Morne in 1982, both collecting wet precipitation samples on a weekly basis.

With the realization that individually sampled precipitation events as opposed to monthly or weekly samples are of more value when

TABLE 2-1
Mean Monthly CANSAP Values for Gander and Stephenville
from 1977 to 1981

	Gander			Stephenville		
	pH	$\frac{\text{SO}_4^{2-}}{(\text{mg.l}^{-1})}$	$\frac{\text{NO}_3^-}{(\text{mg.l}^{-1})}$	pH	$\frac{\text{SO}_4^{2-}}{(\text{mg.l}^{-1})}$	$\frac{\text{NO}_3^-}{(\text{mg.l}^{-1})}$
January	5.16	1.30	0.29	5.45	1.83	0.43
February	5.45	1.70	0.23	-	2.00	0.04
March	5.63	2.10	0.33	4.40	2.65	0.64
April	4.70	1.85	0.56	4.67	1.77	0.16
May	4.50	2.70	0.78	4.33	3.83	0.57
June	4.35	4.90	0.67	4.43	3.10	0.74
July	4.55	3.05	1.04	4.78	1.95	0.72
August	4.60	3.27	0.74	4.43	2.73	0.75
September	4.42	2.08	0.42	4.64	2.34	0.60
October	4.80	0.93	0.34	4.68	1.50	0.87
November	4.75	1.68	0.18	4.83	1.90	0.60
December	5.20	1.08	0.33	4.90	2.93	1.29

relating precipitation chemistry to meteorological variables; an APN site (see Ch. 2, p. 26) was installed at Bay D'Espoir in the late fall of 1981 to sample wet and dry deposits on a daily basis. This is the most sophisticated acid precipitation sampling network on the island at present, and should yield some interesting results. As yet there has been no sequential sampling on the island in relation to acid precipitation.

Since until very recently the only precipitation sampling on the island has been on a monthly or weekly basis the data obtained may only be used to determine any spatial and monthly variation at different sites, so that this study is the first to attempt to relate precipitation chemistry to meteorological variables and to the source areas of associated pollutants. Due to the lack of long-term data it is impossible to determine if there has been any change in precipitation acidity during the last 80 years (unless perhaps lake sediment cores are used, see Ch. 2, p. 31) in Newfoundland. However, CANSAP data does indicate that precipitation acidity is approximately 11 times greater than "clean" precipitation.

Other acid precipitation related projects have also been undertaken by the Department of Fisheries and Oceans (DFO) and the Canadian Forestry Service (CFS). In 1981 the DFO sampled 109 small headwater lakes in remote areas of the island; results from lake water, fish, phyto and zooplankton samples confirm the sensitivity maps based on geology—that lakes with the lowest pH occur on the southwest coast and on the eastern side of the Great Northern Peninsula. Another project involved the monitoring of 22 Atlantic salmon rivers from May, 1981 to May, 1982; results showed that pH values in certain rivers

may vary by two units in a given year and the pH may drop as low as 4.6 in certain areas, which is below the level at which many species become endangered (see Table 1-3). The research at CFS has already been mentioned in Chapter 1 (p.15), however other research includes the long-term effect of simulated acid precipitation on forest soils and any effects pertaining to seed germination.

As previously mentioned, acid precipitation research in Newfoundland is rather limited and biased towards the effect on surface waters with a noticeable gap with regards any relation to meteorology and transport. With this respect it is hoped that this project may be the first of similar work on a much larger scale, so that the advancements made in the field over the last century may be put to good use.

CHAPTER 3

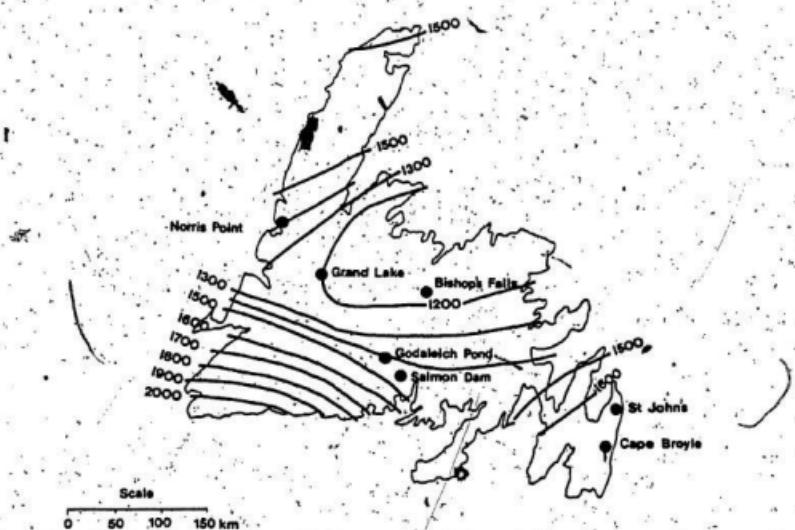
PRECIPITATION SAMPLING TECHNIQUES

3.1. Sampling areas and site locations

Ideally precipitation sampling sites for this study should be chosen to give the most spatially representative sample of precipitation events for the island of Newfoundland. This may be interpreted as either having sites spread equally over the island, purely in a spatial context, or that their location be representative of differing rainfall amounts experienced over the island. Although perhaps from an objective statistical viewpoint the former interpretation may be preferred, rainfall amount is an important variable in this study so that the latter intention may be equally valid (see Fig. 3-1). Since the rainfall collectors required close supervision (see Section 3.2(a)), another prerequisite for their location was that field workers have permanent access to them.¹ For this reason and those discussed previously sites were located and operated as follows:

<u>Site</u>	<u>Operator</u>
St. John's (Oxen Pond)	P. McCullough
Cape Broyle	Cape Broyle Forestry Station Staff
Bishop's Falls	Newfoundland and Labrador Hydro
Grand Lake	" " "
Norris Point	Dr. D. Belisle
Salmon Dam	Newfoundland and Labrador Hydro
Godaleich Pond	" " " "

¹ Due to the limited funds available for this study all collection of samples in the field was conducted on a volunteer basis.



● Location of sampling sites

Precipitation (mm) adjusted to be consistent with observed run-off

Source: Den Hartog and Ferguson (1975)

Figure 3-1: Map of annual precipitation for the island of Newfoundland with study sampling sites located.

The number of sites was limited to seven since this would not produce an excessive number of samples for analysis by arrangement with the Newfoundland Department of the Environment.

The actual site location of precipitation collectors should be such as to reduce as far as possible any direct effects from local pollution (i.e. nearby chimney stacks), contamination by dust or dry atmospheric deposition and through-fall from vegetation, which may be contaminated with organic matter and nutrients collected from leaves and branches. In addition, a collector sited close to a building or closer than one metre to the ground may receive less rainfall due to the effects of turbulence and/or shelter produced by the building and micro-topographical features respectively. This will be discussed further with reference to each site.

It was hoped originally to commence sampling at the beginning of July and continue for at least three months at all sites to obtain at least 10 samples for each site. However, due to problems with installation and the availability of field workers the commencement and duration of sampling varies at each site (these dates are given in the following section). Consequently, there is a significant difference in the number of samples collected at each site (see Table 4-1, p. 70), particularly since sampling at St. John's continued into December to compensate for samples lacking at other sites.

Individual site descriptions

3.1.1. St. John's (Oxen Pond)

In operation 28 July to 16 December, 1981. This site was located approximately 1 km west of the built-up area of St. John's in

Oxen Pond Botanical Park' (see Fig. 3-2), approximately 11 km east of the Conception Bay coastline and 6 km west of the Atlantic coast at St. John's harbour. The collector was situated on a grassy south-southwest facing slope clearing (angle of slope 25-30°), with the nearest building approximately 20 metres to the northwest and a coniferous forest area approximately 15 metres to the south and southeast (downslope). Local and regional sources of pollution include St. John's itself (although there are no large individual sources of air pollution in the city) and the Holyrood Thermal Generating Station point source 40 km to the southwest.

This part of the Avalon Peninsula comprises siltstone, arkose, conglomerate, slate and acidic to intermediate volcanic rocks and is classified as a moderate to high sensitivity area with respect to surface water acidification (see Fig. 1-6)..

3.1.2. Cape Broyle

In operation 28 July to 5 October, 1981. This site is located on a ridge of relatively higher ground (approximately 150 m above sea level) between Cape Broyle Harbour and Calvert Bay (see Fig. 3-3). The ridge itself is largely unforested, marshy in places and dotted with several small ponds. The nearest settlement is Cape Broyle, approximately 2½ km to the north-northwest. The collector was installed by the Newfoundland Department of the Environment at the Cape Broyle Provincial Forestry Station and was previously used for weekly precipitation sampling. It is located approximately 2 metres to the west of the low one-storey forestry building, with coniferous trees 4 metres further to the west, so that it is sheltered on both



Figure 3-2 St. John's site map.

Key for Figures 3-2 to 3-8

	Built-up area		Forest		Pond
	Location of collector				Main Road
Contours in metres a.s.l.					

Scale

0 0.5 1.0 1.5 km

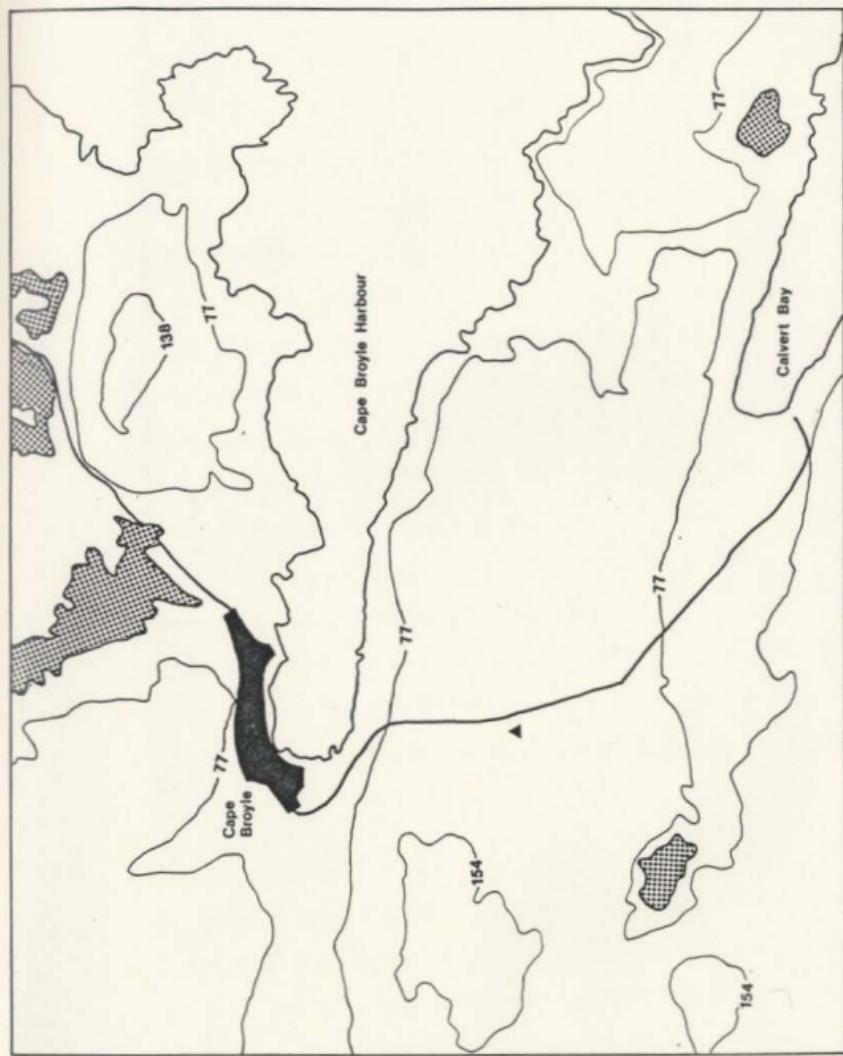


Figure 3-3 Cape Broyle site map.

es. The effect of this, if any, would be to slightly reduce the
receipt of precipitation and possible contamination from throughfall.
In St. John's the Cape Broyle area consists largely of slate, con-
glomerate and volcanic rocks which places it in a moderate to high
sensitivity category.

1.3. Bishop's Falls

In operation 7 August to 12 October, 1981. The site was
located on the premises of a Newfoundland and Labrador Hydro Depot on
an up-lying flat grassed area, approximately 25 metres from the nearest
buildings (see Fig. 3-4). This area lies between 8 and 15 metres from
the northern bank of the Exploits River approximately 10 km southwest
of the point at which it joins Norris Arm and the Bay of Exploits.

The area surrounding Bishop's Falls is gently undulating, rarely rising
above 200 metres a.s.l. Any local pollution affecting this site would
come from the town of Bishop's Falls 1½ km to the southwest, or Baker's
asphalt plant 3 km to the east.

The Bishop's Falls area constitutes part of the sandstones,
conglomerates and acidic volcanic rocks of the Botwood Group and
therefore falls within the moderate to high sensitivity category.

1.4. Grand Lake

In operation 3 August to 29 September, 1981. This site is
approximately 120 metres above sea level on the east shore of Grand
Lake (see Fig. 3-5) and on the north bank of Hind's Brook inlet. The
surrounding area is largely forested, although the immediate area
was cleared by Newfoundland and Labrador Hydro, so that there should
be no contamination from throughfall or dust since the soil appeared

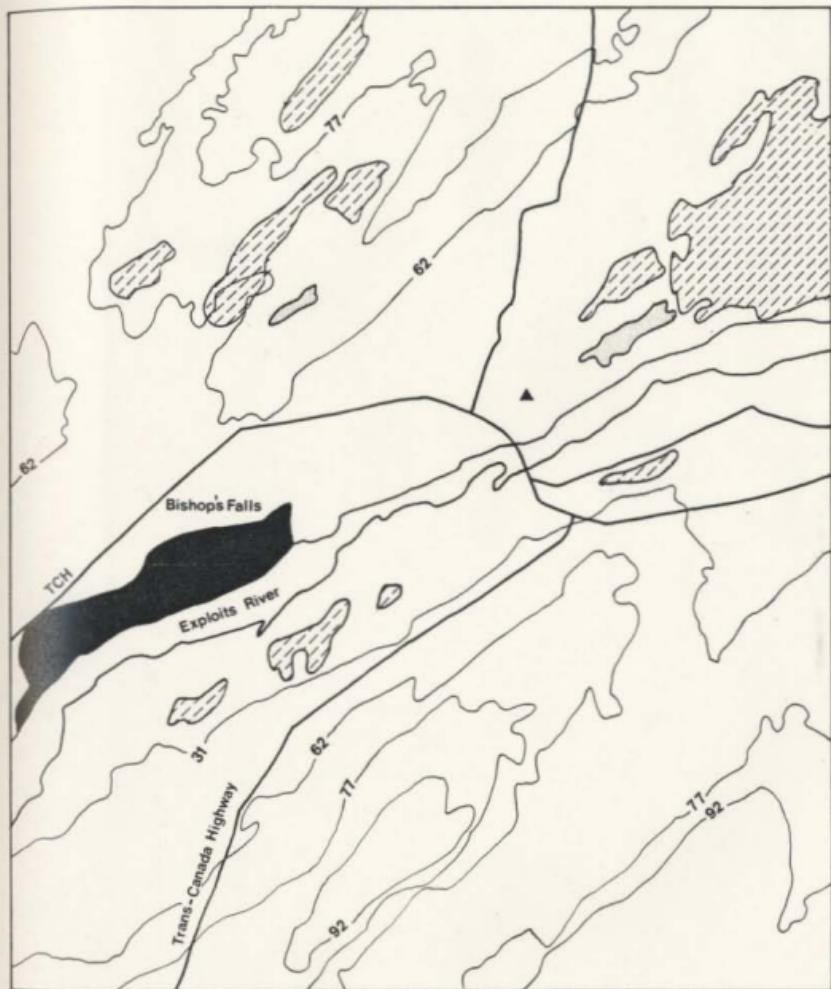


Figure 3-4 Bishop's Falls site map.

For this figure only all areas are forested unless marked otherwise



Marshy, unforested areas

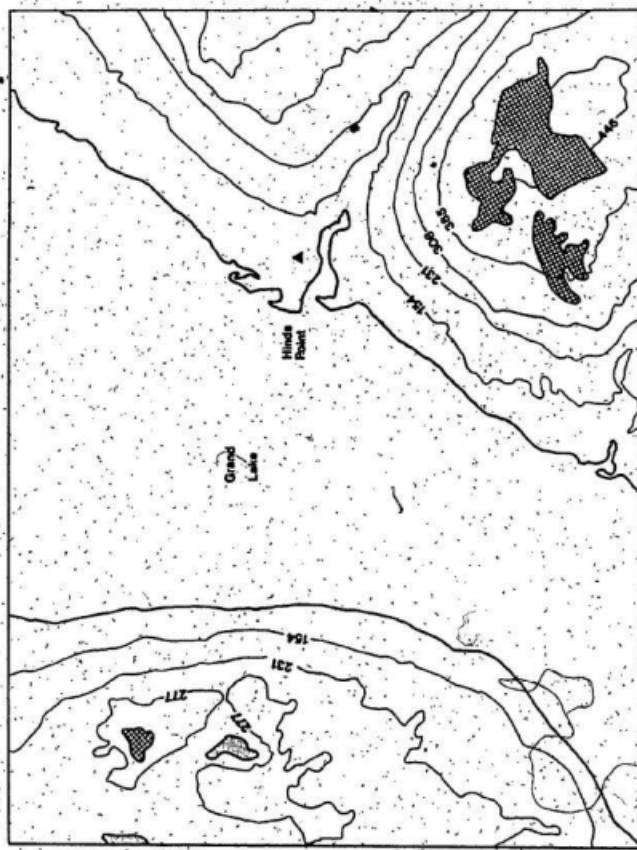


Figure 3-5 Grand Lake site map.

to contain sufficient clay to prevent wind blown deposits. The area west of Grand Lake consists largely of forest interspersed with ponds and a few marsh areas, rising in parts to over 300 metres. The relief on the east shoreline is more pronounced, particularly with the steep sides of the Hind's Brook Valley rising to nearly 500 metres. This area is also mainly forested except for certain areas cleared by Hydro mentioned previously. The nearest settlements are Howley 11 km to the northeast, Deer Lake 19 km to the northwest, and Corner Brook 69 km to the west-southwest.

The area contains various rock types including conglomerate, sandstone, shale and limestone of the Codroy Group which gives it a moderate to high sensitivity classification.

3.1.5. Norris Point

In operation 2 August to 29 September, 1981. The settlement is situated just above sea level on a small peninsula within the fjord inlet of Bonne Bay (see Fig. 3-6). The area is surrounded by high relief cut by steep-sided valleys, rising to over 600 metres on the southwest side of the inlet, and over 800 metres to the northeast in the vicinity of Gros Morne (although the immediate area to the north and northeast is below 200 metres). As a result, orographic enhancement of precipitation is likely to occur in this area and with considerable local variations in amount, intensity and duration of precipitation at times. Large areas of the north side of the bay are forested whereas the south side in this area is mainly unforested but with several small ponds. The orientation of Bonne Bay is such that it may act to accelerate onshore northwesterly winds but may reduce the

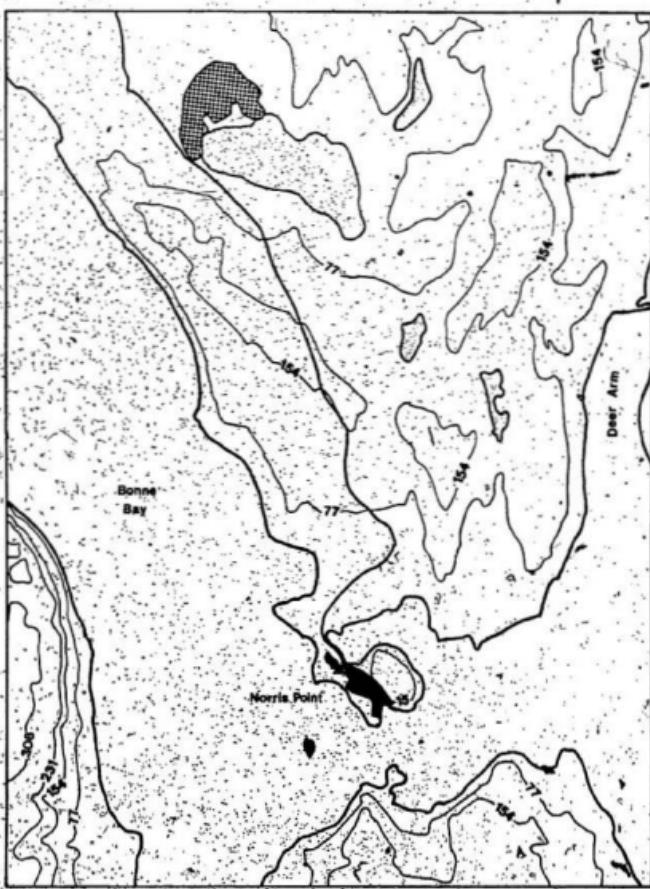


Figure 3-6 Morris Point site map.

strength of southerly winds. The collector itself was sited in a residential garden near the Cottage Hospital so that the proximity of surrounding buildings (the nearest one being approximately 6 metres away) may influence local wind flow, but probably not act to contaminate precipitation.

The geology of this area includes shale, sandstone, limestone and basic volcanic rocks which place it in the moderate to low sensitivity category.

3.1.6. Salmon Dam

In operation 2 August to 28 October, 1981. This is largely an area of moderate relief interspersed with numerous ponds and streams (see Fig. 3-7). The dam is situated on the Salmon River as it flows from Long Pond into an inlet of Bay D'Espoir, approximately 9 km northwest of St. Alban's and 40 km from the south coast. The area is forested to the east and along the Salmon River Valley, unforested to the south with water bodies to the north (Long Pond Reservoir) and northeast (Long Pond). The collector was located just off the constructed Hydro road which may have led to dust contamination. Although the creation of dust from heavy vehicles was observed at the time of collector installation, it was thought that precipitation would settle the dust prior to the collector opening. However, this may have been an overoptimistic assumption. St. Alban's is the nearest settlement but is unlikely to be a source of local pollution.

This area comprises intermediate to mafic volcanic rocks of the Bay D'Espoir Group placing it in the highly sensitive category.



Figure 3-7 Salmon Dam site map.

3.1.7. Godaleich Pond

In operation 2 August to 28 October, 1981. The collector was sited approximately 45 km northwest of Salmon Dam (see Fig. 3-8) on a level bog surrounded by a gently undulating upland area between 240 and 300 metres above sea level. Much of the area is forested with numerous lakes. The site was approximately 15 metres from the Hydro road and 50 metres from the nearest trees, so that contamination may have occurred from road dust, although this is less likely than at the other Upper Salmon site closer to the road.

Both south coast sites fall within the highly sensitive category due to the predominance of acidic to mafic volcanic rocks in the area.

3.2. Precipitation collection

The aim was to collect individual precipitation events at each site to be related to antecedent and accompanying meteorological conditions. Researchers appear to use the terms event and individual or single storm synonymously, but do not give a strict definition in either case (Lewis, 1978; Wolff et al., 1979; Shaw, 1980; Kurtz & Scheider, 1981; and Melo, 1981). However, it seems that in most cases the term "event" refers to a single continuous period of precipitation. This is assumed to result from a particular low pressure system, so that it is possible to have more than one event from the same low. This was also the case in this study but only when there was a significant break between periods of continuous precipitation. Consequently, an event will be defined here as precipitation associated with a single low pressure system (as determined

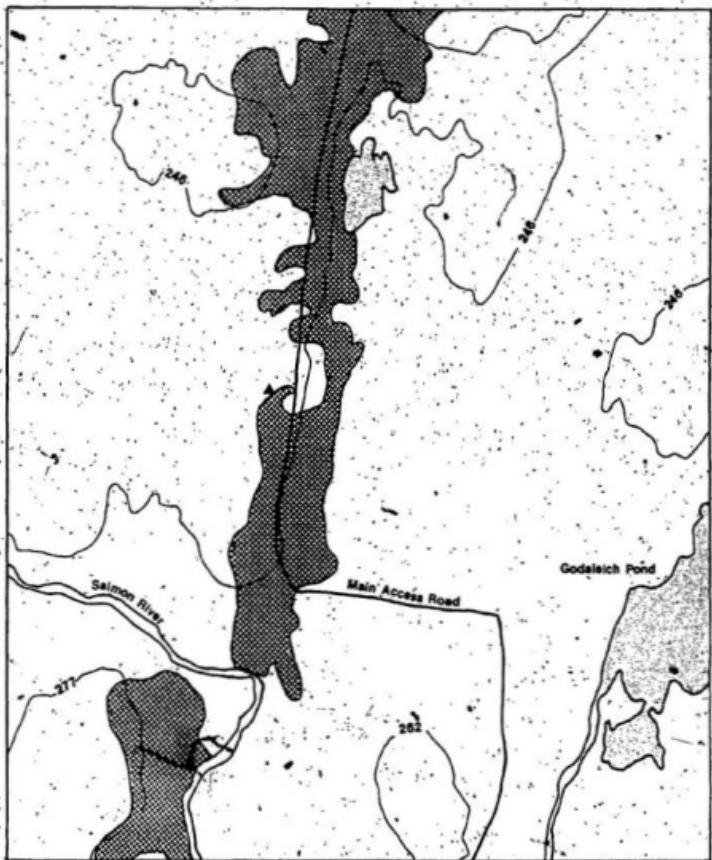


Figure 3-8 Godaleich Pond area map.

by surface analysis charts) in sufficient quantity for chemical analysis (in this case between 250 and 300 ml). It was not possible to collect samples from single air masses, that is, individually from both the warm and cold sectors associated with a frontal depression, due to the difficulties that would be involved in accurately timing frontal passages at each site and the possibility that it may occur during the night.

Event sampling was chosen since only monthly and weekly precipitation samples have previously been collected for the island and because it enables

- (i) determination of storm to storm variability in precipitation chemistry as a result of meteorological factors;
- (ii) determination of the effect of trajectory path on precipitation chemistry;
- (iii) comparison between the effects of (i) and (ii) and subsequently to identify the most important synoptic variables affecting precipitation chemistry;
- (iv) comparison between sites for the same event to determine the possible effects of differing amounts of washout (i.e. when precipitation commences earlier at one site than another), and site location, particularly the effect, if any, of relief;
- (v) the identification of the most polluted events (episodes²).

Since some low pressure systems were closely followed by another, not all the samples collected constitute events. However, of 72 samples analyzed from all sites only four have been identified as

² An episode refers to an event in which the highest concentrations of sulphates and nitrates occur.

composite samples (see Table 4-1, p. 70). As previously mentioned the discrepancy in the number of samples collected from each site result largely from differing sampling periods; additional factors include different precipitation event frequencies at the site, and samples mislaid on site (for example, at Bishop's Falls and the Upper Salmon sites). Consequently, there is less data available for between-site comparisons, particularly of the same event at different sites.

3.2.1. Collectors

Sampling precipitation events is usually conducted with automatic samplers which open at the onset and close at cessation of precipitation to prevent evaporation (Hansen & Hidy, 1982) and any collection of dry deposits. Two NIC (Model A) automatic samplers were made available courtesy of the Newfoundland Department of the Environment for use at the St. John's (Oxon Pond) and Cape Broyle sites. This sampler is able to collect both wet and dry deposits (see Fig. 3-9) although, in this case only wet deposits were collected. At the onset of precipitation a sensory plate activates a cover to expose the wet collector and cover the dry collector. When precipitation ceases, the sensory plate de-activates and the cover returns to the wet collector. The plate is extremely sensitive and requires little moisture to be activated; however, closure takes longer—approximately two minutes (this varies according to the evaporation rate as a function of wind speed, air temperature and humidity), but insufficient time for dry deposition contamination.

This type of collector was previously used with a bucket for sample receipt but for this study large polyethelene bags were used. This was to reduce any contamination that may occur through inadequate

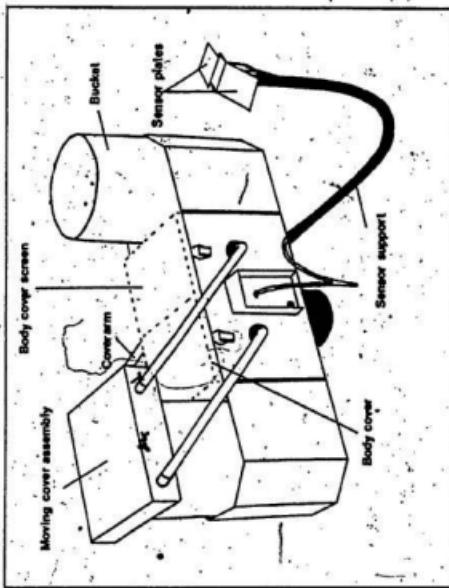


Figure 3-9
NTC sampler.

rinsing of buckets between samples and for easier handling. Precautions were taken when opening and closing the bags so that the inner area exposed to precipitation was not touched. The bags were closed by extracting as much air as possible and then making a tight knot, before careful labelling. Although all the bags were heat-sealed (by the manufacturer) prior to use, any contamination from the polyethylene was determined by keeping two bags of deionised water, refrigerated at c. 4°C for approximately six weeks before chemical analysis (results of which will be discussed in Ch. 4 and Appendix III).

Since only two MIC samples were available, additional collectors were constructed for use at all other sites (Fig. 3-10). The design involves a sheet of 3/8" masonite on which initial precipitation collects and is channelled (by shaping and slope on the masonite) into a tin, which when full, counterbalances a piece of lead-filled copper holding the lid down on the collector. Once the weight of water in the tin exceeds the weight of lead the lid opens. A small hole in the tin acts as a slow-drip mechanism, so that at cessation of precipitation, the weight of lead gradually exceeds that of the tin and the lid closes.

The amount of precipitation required to open the lid was estimated (from initial testing prior to assembly at sites) as 0.1 mm, but this, and the time required depends upon the rainfall intensity—the greater the intensity the faster the lid opens. Slightly less than 7.5 mm of precipitation in total is required to open the lid and provide a sufficient sample (250 to 300 ml) for chemical analysis. Once rain has stopped closure with the slow-drip mechanism takes approximately 10 minutes so that little contamination should occur.

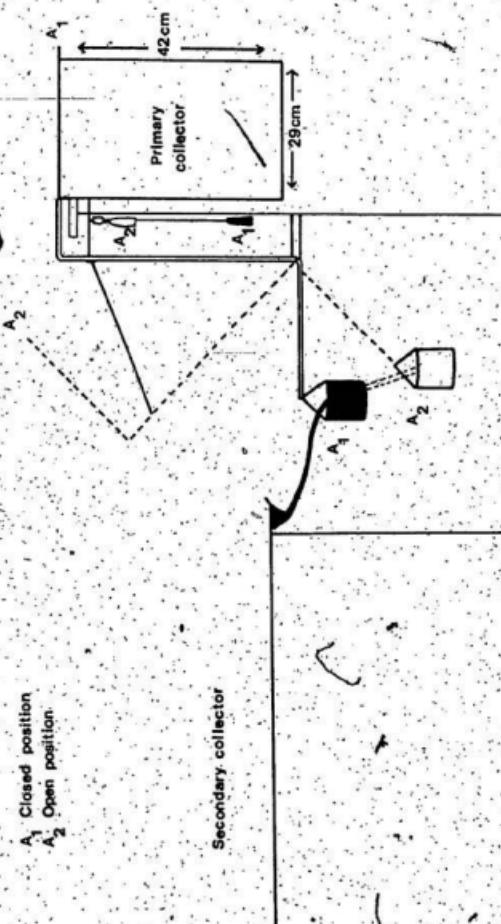


Figure 3-10 Constructed sampler.

Design contributors:
Ian MacCallum
Jim Everard

The constructed collectors were operated using the same polyethelene bags as for the automatic collectors. The bags were also used to cover the collector lids (also made from masonite) to increase rainfall run-off and to prevent dripping into the collector bag on closure. Collector buckets of both the MIC and constructed samplers were positioned at least one metre (but not over 1.5 metres) above the ground to reduce any influence from microtopography and enable easy operation.

Both the MIC and constructed collectors proved reliable for the majority of the sampling periods. The only problem with the MIC sampler involved the replacement of the sensory plate, which did not cause any events to be missed. Problems encountered with the constructed sampler were more easily rectified since they usually resulted from displacement of the lead weight (attached by nylon cord) on the pulley.

3.2.2. Information sheets

In order to make the keeping of precipitation time and date records simpler and uniform for each field worker an information sheet was compiled, an example of which is shown in Figure 3-11. Although field workers were not always precise when completing the sheets, it was always possible to approximate the times of precipitation with the aid of autographic raingauge data (from the gauge station nearest to a site), and whether or not any obvious contamination occurred.

The raingauge sites were as follows:

Site location	Sample Number	Date of collection	Time of collection	Approx. time of commencement	Approx. time of cessation	Duration	Date of shipment	Any leaves, insects etc?

Figure 3-11 Example of information sheet.

Collection Site	Nearest Autographic Raingauge Location	Approximate Distance in km
St. John's (Oxen Pond)	St. John's Airport	6
Cape Broyle	" "	50
Bishop's Falls	Gander Airport	67
Norris Point	Daniel's Harbour	80
Salmon Dam	St. Alban's	9
Godaleich Pond	"	54
Grand Lake	Deer Lake	17

It is likely that the distance between the collection sites and autographic raingauge sites and possible influence of intervening topography will have led to some inaccuracy in the timing of events and the total precipitation amounts which were also obtained from these records. However, with the limitations involved with this study this proved the most viable means of verifying and/or determining precipitation times, duration and amounts. It should be noted that all event times have been corrected to Greenwich Mean Time to correspond with synoptic chart times.

3.2.3. Storage and shipping

Samples were kept refrigerated at approximately 4°C (this inhibits biological growth) in the same polyethylene bags prior to shipping, which was as long as five weeks in some cases (Bishop's Falls, Grand Lake and Norris Point) due to transportation problems.

It is generally considered that the chemical composition of precipitation samples maintained at $1\text{--}5^{\circ}\text{C}$ for as long as seven months (particularly if $\text{pH} < 4.5$) remains stable although a slight increase in chloride may occur (Jacobson et al., 1976; Galloway & Likens, 1976). Although it is preferable to test pH immediately sufficient field meters were not available for this, so that all chemical analyses were conducted in the laboratory. Due to the limited funds available for this project it was not possible to arrange refrigerated transport,

therefore samples were shipped in polystyrene boxes fitted with "ice bags" in order to maintain a cool temperature during road transportation to St. John's. On arrival the samples were transferred to sterile vials by first cutting a corner of the bag and allowing some of the sample to wash the cut edge to prevent possible contamination from the scissors. The samples were then kept refrigerated before the chemical analysis, which will be discussed in Chapter 4.1.1.

CHAPTER 4

DATA ANALYSIS PROCEDURES

4.1 Precipitation chemistry

4.1.1 Chemical analysis of precipitation samples

All samples collected in the field were analyzed by the Chemical and Physical Analysis Laboratory, Newfoundland Forest Research Centre, Canadian Forestry Service, St. John's, by arrangement with the Provincial Department of the Environment.

Full chemical analysis determines pH, alkalinity (for pH > 5.4), conductivity and concentrations of potassium (K^+), sodium (Na^+), calcium (Ca^{++}), magnesium (Mg^{++}), chloride (Cl^-), ammonium (NH_4^+), sulphate (SO_4^{--}) and nitrate (NO_3^-). The laboratory procedures for these tests are given in Appendix I.

On receipt of the samples, the Laboratory Supervisor noted that they were clear with no obvious contamination from soil, organic matter or fungal growth. If any insects were found in samples they were carefully extracted on transfer from the polyethylene bags to vials to prevent decomposition and subsequent contamination.

The laboratory tests all incorporate specific quality control procedures described in Appendix I; however, generally every tenth sample is analyzed in duplicate. Samples may also be re-checked if there is a large discrepancy in the ion balance (there should be an equal number of cations⁺ and anions⁻), or the total

number of ions is low. There are no set values for warranting rechecking; it is a subjective decision made by the Laboratory Supervisor.

Table 4-1 illustrates the number of samples collected for each site and how many of those underwent full chemical analysis with results considered valid by the Laboratory Supervisor. Therefore a sample that missed even one test, or was insufficient in volume for rechecking, or produced an extremely uneven ion balance is not included in this category.

After analysis all samples were corrected for any ionic contribution from sea-salt, which is based on the amounts of sodium and chloride (see Appendix II). Seawater may be a significant source of Cl^- and $\text{SO}_4^{=}$, but makes an insignificant contribution to NO_3^- and H^+ concentrations.

(After correction the remaining anions are referred to as "excess" ions.)

The correction is made with the use of a computer programme which provides data in both ppm (g.l^{-1}) and milliequivalents. Although results were available in both units, analyses involving chemistry data were conducted in ppm to enable comparison with other data for eastern Canada (see Appendix IV). Since minor contamination from Cl^- and Na^+ was shown to have occurred from the polyethylene bags used (see Appendix III), over-correction of the sea-salt contribution to $\text{SO}_4^{=}$ and Cl^- may have resulted. Consequently the excess $\text{SO}_4^{=}$ and Cl^- values given may be very slightly lower than the actual values.

By providing the amount of total precipitation for each event (by measuring hourly rainfall amounts given with autographic gauge records) it was also possible to calculate deposition values (mg.m^{-2}) for $\text{SO}_4^{=}$, NO_3^- and H^+ .

4.1.2 Chemical relationships

It is pertinent at this point to briefly consider some of the chemical relationships that may be expected in precipitation. The

TABLE 4-1
Number of Samples Collected and Analyzed

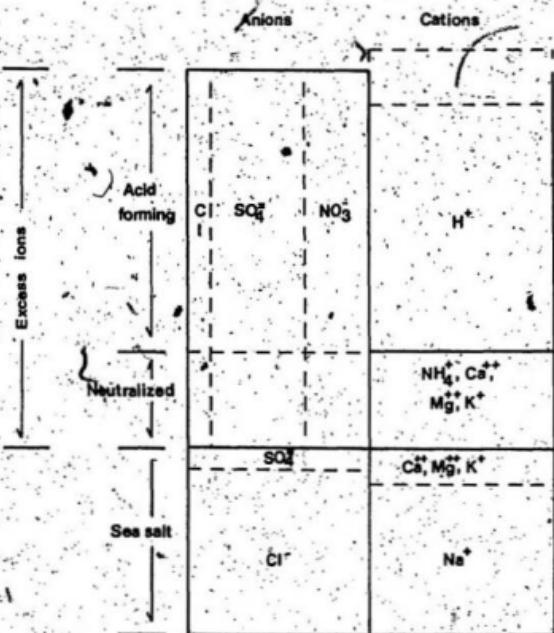
Site	No. of Samples Collected and Sent for Analysis	No. of Samples for Which Complete, Valid Chemical Analysis Conducted to Satisfaction of Chemist	No. of Composite Samples
St. John's	27	24	3
Cape Broyle	8	8	1
Bishop's Falls	7	7	0
Grand Lake	16	9	0
Morris Point	10	9	0
Selton Dam	2	2	0
Godaleich Pond	2	2	0
Total	72	61	4

Rationale for establishing a relationship between the amount of alkalinity (acid or base) and the elements in precipitation is that some of the elements were originally corresponding ions to hydrogen ions or base ions (Gránat, 1972). This is further illustrated in Figure 4-1 (Mogbill & Likens, 1974).

As previously mentioned excess sulphate and nitrate are the main causes of acidity in precipitation; chloride is another dominant anion but is unlikely to contribute to acidity since it is largely of marine origin (Fowler et al., 1982). The actual contribution of excess sulphate and nitrate to precipitation acidity is determined by their quantity and association with certain cations. Often there may be sufficient excess sulphate to account for all the acidity as sulphuric acid; however, since ammonium sulphate is an important component of aerosols, some of the excess sulphate is likely to be associated with ammonium. It has been estimated that, on average, nitric acid contributes 29% and sulphuric acid 71% to precipitation acidity in North America, Great Britain and Scandinavia (Fowler et al., 1982). Although excess magnesium, calcium and sodium also act to neutralize acidity to a certain extent, the main buffer is considered to be ammonium.

4.2. Back-trajectories

Back-trajectories are constructed basically to locate the previous successive positions of an air parcel, and are pertinent to air pollution studies in that they should be indicative of the emission areas over which the air parcel travelled. This method of transport modelling is considered numerically and conceptually very simple (Daggupaty et al., 1979) and consequently has been used by meteorologists for decades--for example, Pettersen (1940). It also



Source: Cogbill and Likens (1974)

Figure 4-1 Theoretical relationship between major chemical ions in precipitation.

provides the best evaluation for changes in air mass characteristics as they encounter different surfaces (Pack et al.; 1978). Until quite recently trajectories were calculated manually by determining the transport winds from weather charts; however, the use of computer models provides much more flexibility and enables the routine computation of hundreds of trajectories forward or backward in time (Pack et al., 1978).

4.2.1. Manual trajectory techniques

Basically there are two types of trajectories, those constructed on an isobaric surface and those constructed on an isentropic surface. The former refers to synoptic charts of constant pressure levels and the latter charts of constant potential temperature.¹ Isentropic trajectories are favoured in that they enable the calculation of vertical displacement by mapping the topography of chosen surfaces of constant potential temperature, and so producing 3-dimensional trajectories (Petterseen, 1956). It has been suggested that if vertical motions and the gradients of vertical motion are considerable, then isobaric and isentropic trajectories may differ horizontally by $\geq 1,000$ km in 12 hours, and the curvatures of the trajectories may be of the opposite sign (that is one cyclonic and the other anticyclonic) (Danielsen, 1974). Since isentropic trajectories are more time-consuming to construct and may not always be justified by greater accuracy (O'Neill, 1981) isobaric trajectories were constructed for this study. It was thought that by constructing

¹Potential temperature is the temperature an unsaturated air parcel attains if brought dry adiabatically to a reference pressure, usually 1,000 mbar. (Barry & Perry, 1973).

trajectories at three levels, namely surface, 850 mbar. and 700 mbar. and then selecting a "mean" path, that some of the inaccuracies inherent in purely horizontal trajectories may overcome. (This will be discussed further in Chs. 6 and 7).

However, it should be noted that the 850 mbar. level is usually recognized as being representative of the transport level at which many air pollutants are carried (OECD, 1977) and being representative of the lower "turbulent" boundary layer under a variety of summer meteorological conditions (Özkaynak et al., 1982). In addition, the strong stability of the lower layers of the atmosphere over Canada in winter makes use of the surface geostrophic wind inappropriate at this season (Smith & Hunt, 1978). Consequently, if major discrepancies occur between trajectories at different levels, the 850 mbar. level is often considered the most representative path. However, in some cases a near surface onshore flow layer may be the cause of precipitation (i.e. an onshore precipitation layer below the height of the 850 mbar. pressure level—1,100 metres a.s.l. on average) at an east coast site, so that trajectories need to be analyzed subjectively in conjunction with the charts at all levels.

The actual technique of trajectory construction was chosen for simplicity and accuracy. Within this limitation, since in excess of 180 trajectories were to be produced, One technique available is that of Petterssen (1956; Ch. 2, p. 27), which requires the mean of two estimations for each previous successive point from the observed wind taken at the first two approximations from the starting point, to obtain a final approximation. The aim is to account for any change in wind velocity (displacement) between points. This method was

tried but comparison with a more straightforward, less time-consuming approach (Shaw, 1980) revealed only slight differences in trajectory path and end-point. Following Shaw's procedure, the observed wind (as given on synoptic chart) was used whenever possible and, if not, the geostrophic wind was calculated using appropriate geostrophic wind scales. Hence the method proceeds as follows for upper air charts at 12-hour intervals:

- (1) Select the nearest chart prior to the time of onset of precipitation—for example, if precipitation started at 08:30 (GMT) start with the 00Z chart. This is considered important since initial precipitation may contain greater quantities of SO_4^- and NO_3^- as a result of below-cloud scavenging.
- (2) Starting at the sampling site in question (Point A), use the observed wind speed reported from the nearest station to plot the position of the air mass six hours earlier, following the wind direction as a mean path from the nearest station observation and the trend of the isobars. This is Point B.
- (3) Locate Point B on Chart 2 (i.e., 12 hours prior to Chart 1). Follow the same procedure using the information at Point B, to locate the position six hours previous to this: so that Point C therefore relates to $\Delta t = 12$ hours. Repeat the procedure at Point C to obtain Point D which should then be located on the chart 12 hours prior to this (Chart 3).

This method may be used at the surface level also except that only one point is plotted on each chart, since they are available every six hours as opposed to every 12 hours. Trajectories were continued back for 72 hours, although it may be considered that this increases trajectory error and that 48 hours is sufficient (Shaw, 1980). However, with the relatively distant position of Newfoundland with respect to the North American mainland it would be difficult to locate mainland source areas with shorter trajectories.

Apart from the exclusion of vertical motion variables, the main problem with the construction of trajectories involved relating the starting time of precipitation at a site to the corresponding start of the trajectory, that is the time of the first chart used. This was particularly the case with upper air charts since they are only produced every 12 hours. It is possible that this may account for some discrepancies that occur between trajectory path, associated meteorological conditions and associated precipitation chemistry, since the time involved is sufficient for quite a substantial change in airflow direction. Another source of error may have resulted from missing charts along a trajectory. When this occurred at the upper levels and additional six-hourly segment was plotted on the chart prior to and after the missing chart. With the surface charts a three-hourly segment was plotted on each corresponding chart. However, this occurred infrequently and was unlikely to be a major source of error.

4.2.2 Computer trajectory technique

In addition to the construction of manual trajectories it was also possible to have selected trajectories computed with the Canadian AES Trajectory Model. Unfortunately due to the limited funds and computer time available it was possible to compute trajectories for only six events. Events were selected to include various synoptic/weather type categories (see Section 4.3.1) with a complete chemical analysis available. The choice was limited to a further extent since AES requested that all the events occur within the same month. However, to incorporate each weather type two months were selected, August and October.

The information required to run the programme includes the exact starting location of the trajectory (latitude and longitude) and the starting date and time (to the nearest six hours). This was given as:

Site	Location	Starting Date and Time
Norris Point/Grand Lake ²	47.3 N 52.4 W	August 03 00Z 1981
" " "	47.3 N 52.4 W	August 04 06Z
" " "	47.3 N 52.4 W	August 18 06Z
St. John's	49.0 N 55.3 W	October 03 12Z
Bishop's Falls/ Godaleich Pond	49.0 N 55.3 W	October 09 06Z
	49.0 N 55.3 W	October 17 00Z

The computer model is quite complex but basically trajectories are run backwards for five days at six-hour intervals and at three levels in the vertical, 1,000 mbar., 925 mbar., and 850 mbar. (Olson, 1982). The model uses objectively-analyzed wind fields, with mountain and friction induced vertical motions being computed at the lowest level (Olson, Oikawa & Macafee, 1978). Winds at intermediate levels were previously computed with bi-linear interpolation (Olson, 1981), but the model now incorporates bi-cubic interpolation which is considered to achieve greater accuracy (Walmsley & Maillot, 1982). Further accuracy may be gained with a three-hour as opposed to six-hour timestep, however this is not yet available.³

Comparisons of results obtained from the manual and computer trajectories may perhaps reflect the inaccuracies associated with

² Due to the short distance between Norris Point and Grand Lake and similar latitude, when the same event occurred at both sites only one trajectory was constructed starting from a point equidistant to both sites. This was also the case for Bishop's Falls and the Upper Salmon sites.

³ Further information on the AES Trajectory Model may be acquired from Olson, Oikawa and Maillot (1978).

using a subjective manual technique which does not incorporate vertical wind motions.

4.3. Identification and classification of meteorological conditions accompanying precipitation events

In earlier precipitation studies emphasis was given to the relationship between precipitation chemistry and the source area of the associated air parcel. However recently, equal, if not more attention is given to the meteorological variables involved such as the synoptic/weather type, duration of precipitation prior to reaching the sampling point, total precipitation and precipitation intensity. Recent sequential sampling studies have provided a greater insight into atmospheric processes, using hourly data for changing chemistry throughout an event, together with wind direction, wind speed and temperature (Raynor & Hayes, 1980). However, due to the number of samples under consideration in this study and the nature of the sampling (that is, event, as opposed to sequential) consideration was given to only the following meteorological variables.

4.3.1. Synoptic weather type

At present there is no published classification of synoptic "weather" types for the island portion of Newfoundland; Barry's (1959) classification was developed for Labrador. Since all precipitation events in this study, with the exception of those associated with tropical storms, were associated with frontal-type low pressure systems, it was decided to make a classification according to the area over which cyclogenesis occurred and the subsequent track taken by the low prior to an event. These are often considered

important parameters for synoptic/weather type classifications (Lewis & Hrebenyk, 1978; Wolff et al., 1979), although other classifications may include different frontal types (Raynor & Hayes, 1980).

From tracking the low pressure system at the 850 mbar. level associated with each precipitation event, six synoptic/weather types were classified.

- (i) Labrador/Quebec Lows: Usually originating around the Hudson Bay area and following an eastward path across Quebec and Labrador.
- (ii) Maritime Lows: May actually originate in the Great Lakes area but stagnate over a portion of the Maritime provinces for ≥ 36 hours.
- (iii) Great Lakes Lows: Moving northeast along the St. Lawrence Valley from the Great Lakes area.
- (iv) Great Lakes/ East Coast Lows: Originating south of the Great Lakes, tracking east across the Appalachians, and then northeast along the east coast.
- (v) Sub-tropical Lows: Originating in sub-tropics but not classified as Tropical Storms either
 - (a) continental in origin or
 - (b) maritime in origin.
- (vi) Tropical Storms: Originally Tropical Atlantic hurricanes, following an oceanic path northward. These are non-frontal storms, in contrast to the other categories.

Figure 4-2 illustrates a "typical" path for a low pressure system associated with each category.

4.3.2. Duration of precipitation prior to reaching sampling site

This is an important factor since initial precipitation has a greater potential for removing suspended particulate (SO_4^{2-} and NO_3^-) and gaseous pollutants (SO_2 and NO_x) below the cloud base. This has been illustrated with sequential sampling, where greater amounts of SO_4^{2-} ,

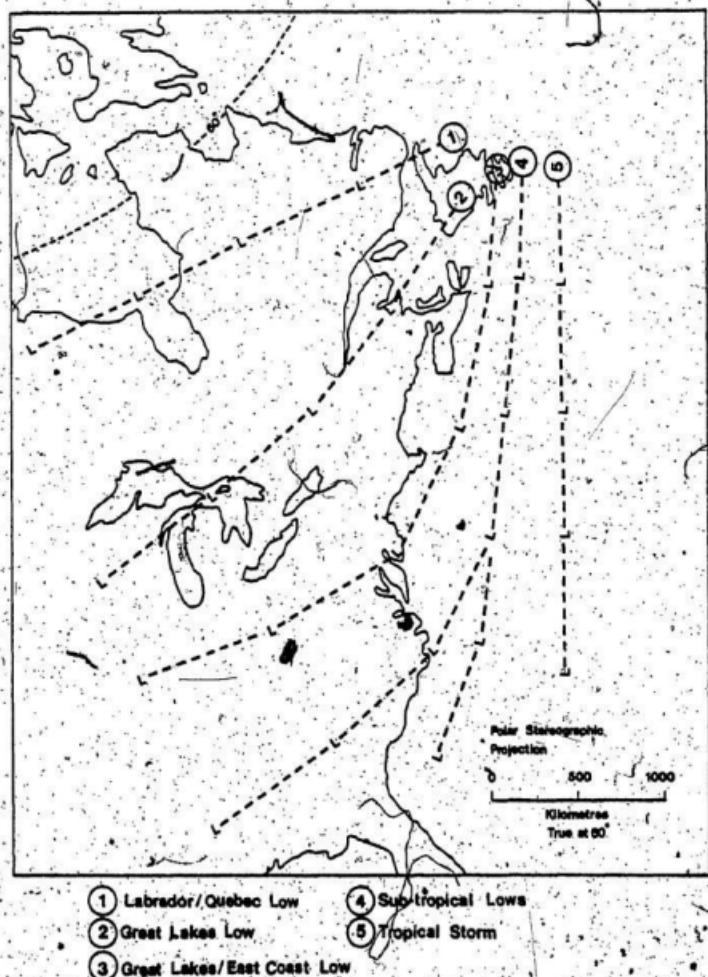


Figure 4-2 Typical path at the surface for lows associated with each weather type.

H^+ , and NO_3^- were found to occur within the initial four to five hours of an event at Brookhaven National Laboratory, New York (Raynor & Hayes, 1982). Amounts of SO_4^{2-} decreased from 195 $\mu eq.l^{-1}$ to less than 20 $\mu eq.l^{-1}$ over a five-hour period. NO_3^- decreased more rapidly which may indicate that nitrate is removed more readily than sulphate or is not replenished as quickly. Lewis and Hrebenyk (1979) also found that events with similar trajectory paths but different pollutant concentrations could be explained by different durations of washout prior to reaching the site (see Ch. 2, Section 2.2(iv)).

The duration of precipitation prior to reaching a sampling site was determined from surface analysis charts. Beginning with the time of the onset of a sampled event, the associated precipitation area was traced back as far as possible. The number of hours of precipitation prior to each event also includes stations registering frequent showers in addition to shaded areas of continuous precipitation, so that in some cases prior duration exceeds 72 hours.

4.3.3. Total preprecipitation and precipitation intensity

Although these variables are interdependent it may be necessary to consider them individually, particularly since the relationship between them and precipitation chemistry is not always clear. However, research suggests that precipitation of moderate to high intensity (resulting in high total precipitation) can lead to a high pH, probably as a result of greater dilution of the available acids. In some instances though high intensity may result in a low pH when associated with convective summer air masses which are more polluted (Wolff et al., 1979; Raynor & Hayes, 1980). Conversely, low intensity values

associated with light rain and drizzle may also result in a low pH due to less dilution. The effect of these variables, however, is more meaningful when discussed with respect to other meteorological aspects, such as synoptic/weather type, duration of precipitation prior to reaching the sampling site and the source area of the associated air parcel. Total precipitation (mm) and intensity (mm hr.^{-1}) were determined from autographic raingauge records; the former by measuring hourly amounts and then dividing this by the number of hours over which precipitation occurred to obtain the intensity. Some inaccuracies resultant from use of these records (as mentioned in Ch. 3) may have been overcome by measuring the volume of each sample on arrival; however, this was not considered at the time.

4.4. Statistical analysis.

Appendix IV presents results from 60 events which were considered of sufficient value for analysis,⁴ however due to a number of missing values only 43 were available for statistical analysis. Also, due to the large number of interrelated variables involved (11 dependent chemical concentration variables, 3 dependent deposition variables and 5 independent meteorological variables) the data set may not be sufficiently large to provide conclusive results. Within the three groups of variables referred to above individual correlations were made (see Appendix V), that is, one variable correlated with another single variable; for example, pH with SO_4^{2-} or pH with weather type. This produced a correlation coefficient (r), the significance of which was determined by means of an F-test. In addition, a multiple

⁴ Events for which chemistry values were not obviously affected by contamination.

correlation (r^2) was conducted in order to correlate the relationship between a single variable and a group of variables, for example, the effect of weather type on precipitation chemistry as a whole, the significance of which is given by the p-value. Any correlations referred to in the text are shown in the correlation matrices in Appendix V.

CHAPTER 5

PRECIPITATION CHEMISTRY AND METEOROLOGICAL VARIABLES

The significance of the findings of this study will be assessed both objectively with the use of basic correlation and multiple correlation analysis, and more subjectively from interpretation of simple graphs and tables. It should be noted that with the large number of independent variables involved more conclusive statistical results would require the sampling of several hundred precipitation events. Nevertheless, some interesting patterns have emerged which will be discussed in this and two subsequent chapters.

This chapter has been subdivided into six sections corresponding with the number of variables to be discussed, these being: precipitation chemistry, wet deposition of H^+ , SO_4^{2-} and NO_3^- , antecedent rainfall duration, precipitation total and intensity, weather type and temporal variation. Initially, patterns within each group will be considered and then the meteorological and temporal variations will be related to precipitation chemistry and wet deposition.

5.1. Chemical relationships

As is apparent in Appendix IV¹ there is quite a large degree of variability in the data which would be expected with so many influential variables and a relatively small sample number of 60. Although a complete chemical analysis is presented discussion will be

¹All chemical concentrations referred to from this study are "excess" ions. Wet deposition was also derived from these.

restricted to what are considered the most important variables with respect to acidic precipitation, namely SO_4^{2-} , NO_3^- and NH_4^+ (see Ch. 4, p. 71). pH will also be referred to, but should be regarded cautiously since its instability (particularly since field measurements were not possible) makes it less reliable.

Table 5-1 shows the means and range of values for these variables at all sites indicating the overall mean pH value of 4.78, which is almost 10 times more acidic than the base value of 5.6 for "clean" precipitation. This also corresponds with the mean monthly CANSAP pH values of 4.79 and 4.67 at Gander and Stephenville, respectively, over the period 1977-81. Comparison with CANSAP data may only be regarded in a very general sense due to the differences in sampling techniques (monthly as opposed to event), sampling periods (annually as opposed to August to December) and locations; however, at present this data provides the only means of comparison for the island. Perhaps more importantly CANSAP data enables comparison of 1981 data with previous years' precipitation chemistry data in order to determine if 1981 was a "typical" year. Consequently, Figure 5-1 illustrates mean bi-annual (August to December, corresponding with the St. John's sampling period) values of pH, SO_4^{2-} and NO_3^- from 1977 to 1981. These values were calculated as averages from data at Gander and Stephenville in an attempt to give more of an overall view for the island, and also to lessen the uncertainty from having several missing values at each site. It is apparent that there is quite a large degree of variability from year to year, although pH only fluctuates between 4.5 and 5.0. This type of variability is not unusual (see Raynor & Hayes, 1982) and is in fact one of the major drawbacks of short-term sampling, whether for

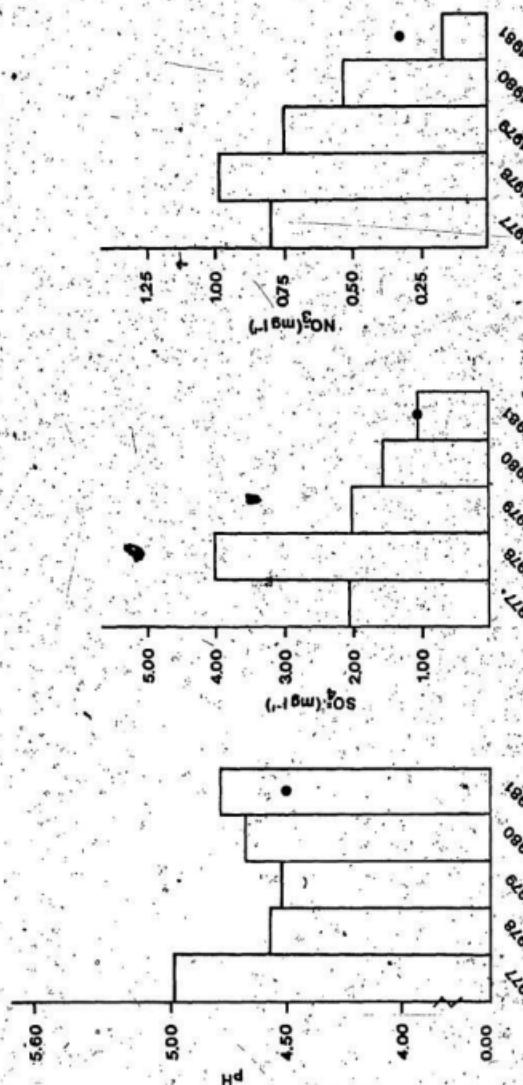


Figure 5-1 • Mean values for St. John's site
precipitation values averaged
for Gander and Stephenville,

TABLE 5-1
Mean, Maximum, and Minimum Values of Selected Chemistry
Values for all Sites Combined

	Mean	Maximum	Minimum
pH	4.78	5.80	4.03
SO_4^{2-} mg. \cdot $^{-1}$	1.05	4.96	0.03
NO_3^- mg. \cdot $^{-1}$	0.52	2.10	0.00
NH_4^+ mg. \cdot $^{-1}$	0.15	0.54	0.00

five months or five years; a much longer period is required in order to distinguish between natural variability (that is, meteorological factors) and changes due to anthropogenic influences. However, it is interesting to note that both $\text{SO}_4^{=}$ and NO_3^- CANSAP values for 1981 are the lowest over the five-year period, with St. John's values corresponding quite closely. This suggests that acidity levels were lower in 1981 than recent years, so that results from this study may reflect lower acidity concentrations than those usually experienced in Newfoundland.

Since $\text{SO}_4^{=}$ and NO_3^- are regarded as the main source of precipitation acidity, strong correlations would be expected between these variables and pH. This is illustrated in Figures 5-2 and 5-3 with a correlation of negative -0.717 for $\text{SO}_4^{=}$ and pH and only negative -0.516 for NO_3^- and pH (see Appendix VA), suggesting perhaps that $\text{SO}_4^{=}$ contributes more to precipitation acidity than NO_3^- as would be expected. Although the correlations between both NH_4^+ and pH and NH_4^+ and $\text{SO}_4^{=}$ are weak, 0.290 and 0.314, respectively, Figure 5-4 illustrates that there does appear to be a slightly positive relationship indicating that acidity caused by $\text{SO}_4^{=}$ may be buffered to a certain extent due to its association with ammonium, so that NO_3^- accounts for the remaining acidity. However, this relationship is not totally clear and should not be overstressed.

5.2. Wet deposition

Being a function of both chemical concentration and precipitation total, wet deposition is particularly valuable since it reflects the total amount of acidic compounds entering an ecosystem. In more recent research deposition values are referred to equally if not more

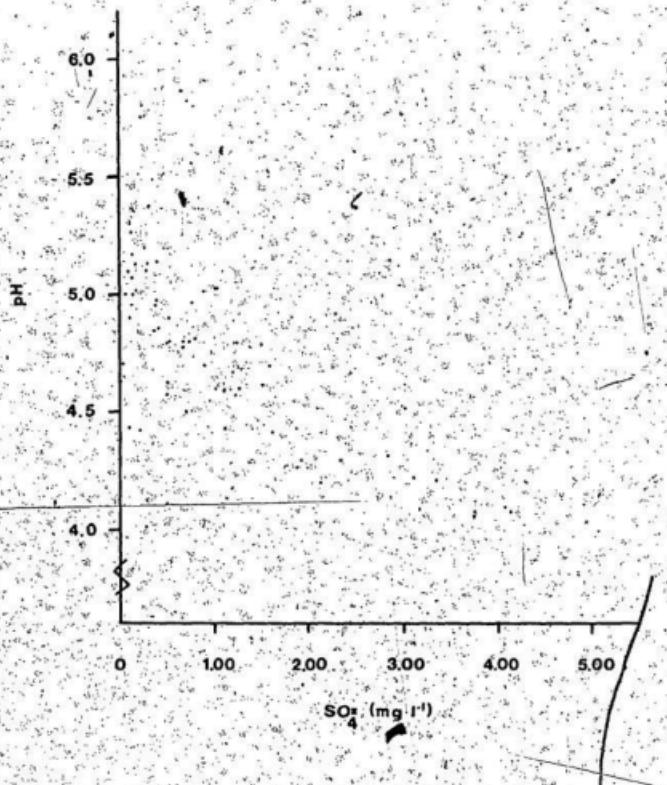


Figure 5-2. Graph of SO_4^{2-} v. pH.

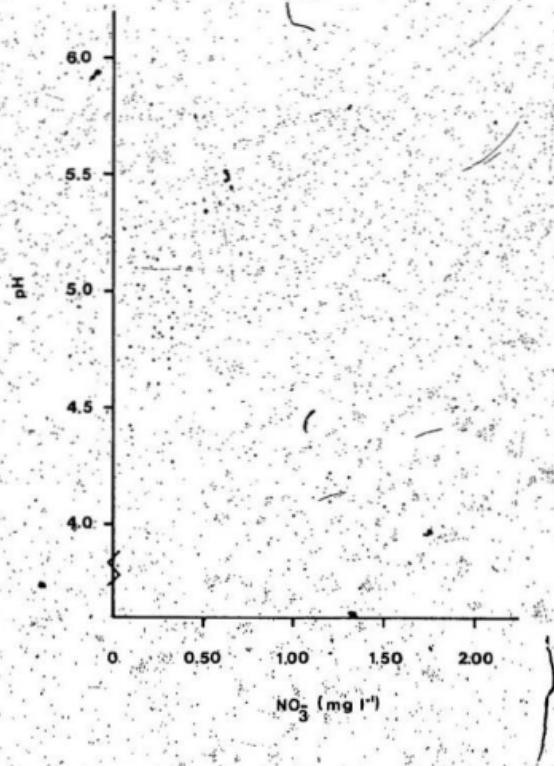


Figure 5-3. Graph of NO_3^- v pH.

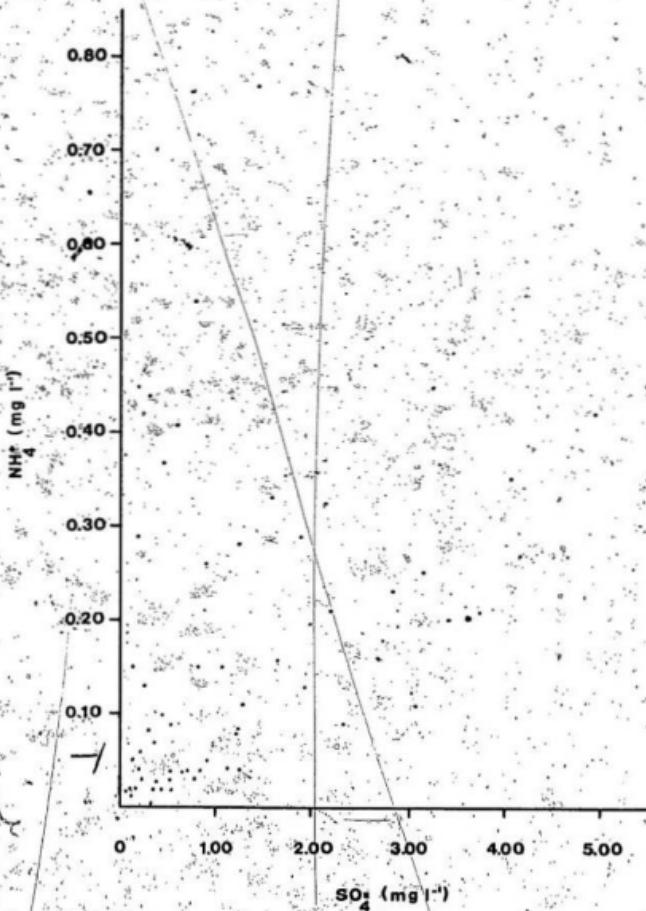


Figure 5-4 Graph of NH_4 v SO_4

than concentration values since they are considered more pertinent (Shaw, 1980; Kurtz & Scheider, 1981; Whelpdale & Barrie, 1981; Raynor & Hayes, 1982; Wilson & Mohnen, 1982; and Executive Summary, 1983).

Although it is often assumed that greater amounts of precipitation cause greater dilution of SO_4^{2-} and NO_3^- concentrations, the overriding effect is to increase the total wet deposition value. Consequently, it is necessary to identify not only which variables result in greater concentrations of acidic compounds, but which meteorological conditions result in a greater overall deposition—in other words, what conditions are conducive to high concentrations and high precipitation amounts. Since results indicate that precipitation event totals have a much broader range (0.6–129.2 mm) than chemical concentrations ($0.03\text{--}4.96 \text{ mg.l}^{-1}$) it would appear logical that in this study precipitation amount was the more influential of the two variables on the resultant deposition value. However, statistical analysis shows that this is not the case with a correlation of 0.714 for SO_4^{2-} and SO_4^{2-} deposition and only 0.434 for precipitation total and SO_4^{2-} deposition (see Table 5-2). A similar situation exists for H^+ and NO_3^- deposition, showing that in fact chemical concentration is the dominant variable of the two variables here contrasted in determining deposition values. Wet deposition will be referred to again in subsequent sections and in Chapters 6 and 7.

5.3. Antecedent rainfall durations

As mentioned in previous chapters, the significance of the number of hours of precipitation duration prior to reaching a sampling site relates to the amount of available pollutants removed from the atmosphere by rainout and more particularly, washout. For all events

TABLE 5-2

Precipitation Total and Chemical Concentration
Correlated with Wet Deposition Values

SO_4^{2-}	with SO_4^{2-}	$\Delta = 0.714$	PT with SO_4^{2-}	$\Delta = 0.434$
NO_3^-	NO_3^-	$\Delta = 0.646$	PT	$\text{NO}_3^- \Delta = 0.432$
H^+	H^+	$\Delta = 0.579$	PT	$\text{H}^+ \Delta = 0.356$

 Δ = wet deposition (mg.m^{-2})

PT = precipitation total (mm).

at all sites durations ranged between 12 and 88 hours, with approximately 20% in a category of 0-24 hours, 40% between 25 and 60 hours and 40% over 60 hours. Since synoptic station information from surface analysis charts (including the occurrence of showers) was taken to indicate prior precipitation, in addition to the shaded areas of precipitation, the durations are probably higher than might be expected in some cases.

Although squared multiple correlation (see Ch. 4, pp. 82-3 and Appendix V for correlation matrix) showed that precipitation duration prior to an event was more related to chemical concentrations ($p = 0.0095$, significant at the <0.01 level) than weather types ($p = 0.091$, significant at the <0.1 level) it would seem that the two meteorological variables are also related, although not to a statistically significant level (correlation 0.201). Table 5-3 indicates the mean, maximum and minimum number of hours of precipitation prior to an event for each weather type. The number of cases for each weather type is also given to show the probable unreliability of some of these means based on only a few examples. The significance of these results will be discussed in Section 5.5.

5.4. Total precipitation and precipitation intensity

5.4.1. Total precipitation

Precipitation totals for all events at all sites ranged between 0.6 mm and 129.2 mm, with 37% between 0.1 and 10.0 mm, 49% between 10.1 and 40.0 mm and 14% between 40.1 and 130.0 mm. No significant relationship (see Appendix VB) was found between chemical concentration and precipitation total, although there was a correlation

TABLE 5-3
Antecedent Rainfall Duration in Hours

	L/PQ	E/GL	GL	Mar.	TS	Sub.
Mean	38.9	57.8	68.7	36.8	54.0	33.3
Max.	76.0	88.0	88.0	82.0	100	54.0
Min.	12.0	18.0	42.0	18.0	29.0	24.0
No. of Cases	19	15	11	6	5	3

with wet deposition (as previously mentioned) which will be discussed further in Section 5.5.

Monthly precipitation totals for each site (Salmon Dam and Godaleich Pond were combined) were calculated from AES Monthly Climate Summaries for St. John's Airport, Cape Broyle, Bishop's Falls, Woody Point (for Norris Point), Grand Lake and Bay D'Espoir Generating Station (see Table 5-4) to determine site to site variation, and also to compare these values to long-term means (see Fig. 5-5 a and b). Table 5-4 shows that for July-December, 1981 the east Avalon and south coasts received almost twice the amount of precipitation than the west and more central parts of the island (particularly from September to November) which would result in significantly higher deposition values since there is no indication of lower concentration values on the east and south coasts. Due to the inconsistency in sampling periods at the different sites it is difficult to substantiate this statement other than comparing the September H^+ deposition values at St. John's (on Avalon site) and Grand Lake (west-central) which were 5226.1 and $431.3 \text{ meq.metre}^{-2}$, respectively (i.e. over 12 times as high at St. John's).

Figure 5-5 shows the variation of 1981 monthly precipitation values from the long-term means at each site. The east coast and south coast values for 1981 are higher than the normal for September, October and November, with the October value higher at all sites except Norris Point. This may have resulted in higher deposition values than would normally occur during this period at St. John's, Cape Broyle and the south coast sites, although further comparison between sites is limited since only St. John's was sampled over a

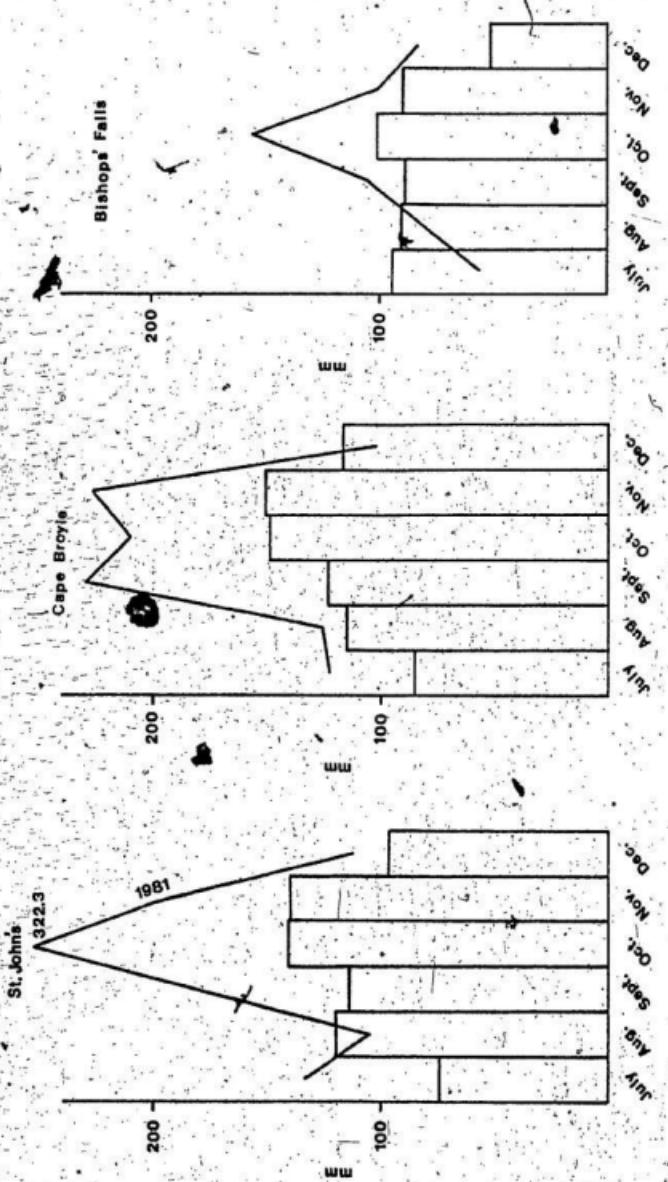


Figure 5-5(a) Monthly precipitation normals for July to December for St. John's, Cape Broyle and Bishop's Falls.

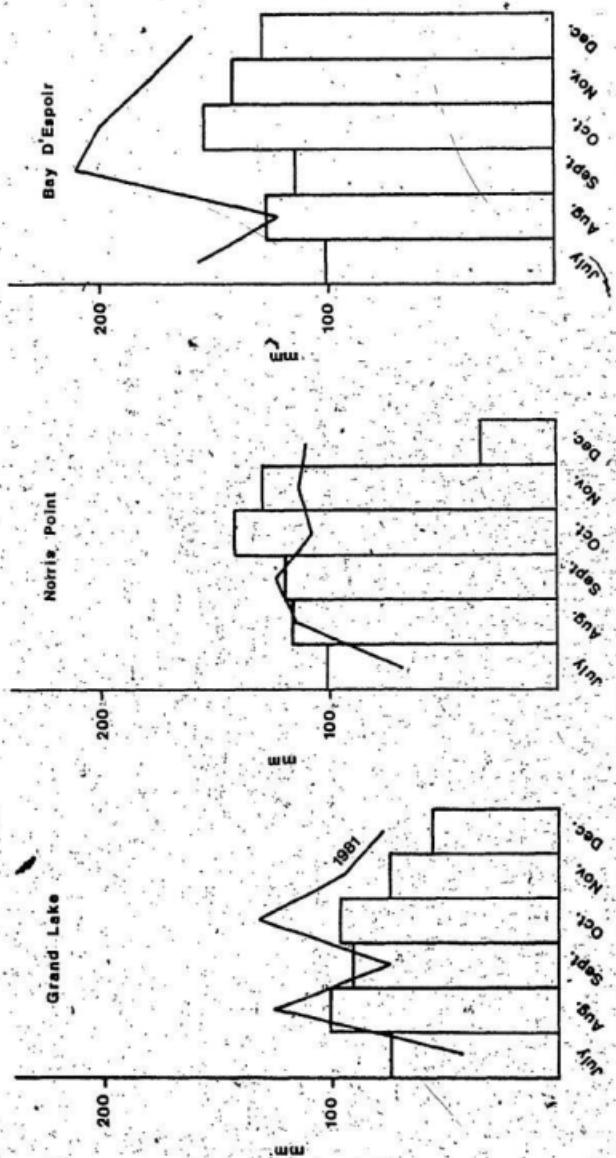


Figure 5-5 (b) Monthly precipitation normals for July to December for Grand Lake, Norris Point, and Bay D'Espoir.

TABLE 5-4

Monthly Precipitation Totals July-December, 1981, At All Sites

	St. John's Airport (Oxen Pond)	Cape Broyle	Bishop's Falls.	Grand Lake	Woody Point (Norris Point)	Bay D'Espoir Generating Stn. (Salmon Dam/ Godaleich Pond)
July	133.3	122.8	57.0	43.0	68.8	156.8
August	106.0	127.0	81.4	126.6	115.8	123.3
September	186.9	230.0	106.4	75.0	123.5	211.0
October	322.2	210.4	158.6	132.8	108.9	201.2
November	192.3	227.2	102.2	95.0	114.4	179.2
December	112.4	102.4	84.2	78.5	111.8	159.7
Mean	175.5	170.0	98.3	91.8	107.2	171.9
Total	1054.1	1019.8	589.8	558.9	643.2	1031.2

Source: Environment Canada, AES. Monthly Climate Summaries for July to December, 1981.

Brackets indicate precipitation event sampling stations.

Precipitation measurements in mm.

five-month period.

5.4.2. Precipitation intensity

Hourly values of precipitation intensity during events ranged between 0.20 and 4.28 mm hr^{-1} with 28% between 0.01 and 1.00 mm hr^{-1} , 46% between 1.01 and 2.50 mm hr^{-1} and 26% between 2.51 and 4.50 mm hr^{-1} . From extensive research at the Brookhaven National Laboratory in New York (Raynor & Hayes, 1982) findings suggest that low precipitation intensity produces the highest concentrations of all chemicals due to minimal dilution of available atmospheric compounds. Although in this case no significant correlation was found between mean hourly precipitation intensity during an event and chemical concentrations (see Appendix IVB), correlations of 0.515 for NO_3^- , 0.455 for SO_4^- and 0.428 for H^+ were found with respect to wet deposition (see Appendix VC). Since there is also a strong correlation of 0.654 (significant beyond 0.01, see Appendix VA) between precipitation total and intensity this relationship may also result from precipitation total, which has a direct effect on the wet deposition values. No further comment upon precipitation intensity will be made since this information was derived from meteorological stations which were not always located adjacent to sampling sites (as previously mentioned in Ch. 3, p. 66).

5.5. Weather type

Table 5-5 illustrates the total number of cases of each weather type for all events (a), by site (b), month (c), and season (d). It is apparent from (a) that Labrador/Quebec Lows occurred most frequently during the study period, followed by Great Lakes/East Coast

TABLE 5-5

Weather Type

See p.xii for abbreviation key

	L/PQ	GL/E	GL	Mar.L	TS	Sub.L	
Total Cases	19	15	11	7	5	3	= 60
<u>By Site</u>							
Cape Broyle 01	4	1	1	1	1	0	= 8
St. John's 03	3	7	6	3	4	1	= 24
Grand Lake 04	8	3	3	1	0	0	= 15
Norris Point 05	4	2	1	0	0	0	= 7
Bishop's Falls 06	0	1	0	2	0	1	= 4
Godaleich Pond 08	0	1	0	0	0	1	= 2
<u>Sampling period</u>							
<u>month</u>							
July (from 29th)	1	0	0	0	0	0	= 1
Aug.	15	4	7	3	2	0	= 31
Sept.	3	4	0	0	3	0	= 10
Oct.	0	4	2	3	0	2	= 11
Nov.	0	2	2	0	0	0	= 4
Dec. (up to 16th)	0	1	0	1	0	1	= 3
<u>By Season</u>							
Summer (end of							
July to Sept.)	9	8	7	3	5	0	= 42
Autumn (Oct. & Nov.)							
Winter (Dec. 1-16)	0	6	4	3	0	2	= 15
	0	1	0	1	0	1	= 3

Lows and Great Lake Lows. It should be emphasized that Maritime Lows (which were fourth in order of frequency) do not actually originate over the Maritimes, but are Great Lakes/East Coast or Great Lakes Lows that have stagnated over the Maritimes for approximately 36 hours or more. This is important since cyclone tracks would indicate many more cyclones tracking east and northeast from the Great Lakes area than are reflected in this table. Although Labrador/Quebec Lows predominated overall, Table 5-5(b) elucidates this, showing that these lows were only dominant at the west coast sites of Norris Point and Grand Lake, since the mean path of Labrador/Quebec Lows (see Fig. 4-2) associated precipitation may not affect the eastern half of the island. In fact, only 15% of events at St. John's constituted Labrador/Quebec Lows whereas over 50% on the west coast were of this type. It is also important to note that Table 5-5 is somewhat misleading since sampling on the west coast was only conducted during August and September, the period during which Labrador/Quebec Lows were most prevalent during 1981 according to low pressure centre tracks from July to early December (Climatic Perspectives, July to December, 1981, and AES, 500 mb charts for same period). This is largely a reflection of the northward shift of the subtropical high in the upper troposphere so that during summer months the main areas of cyclonic activity are further north than at other times of the year (see Bryson & Hare, 1974, p. 28). This should also explain the greater frequency of Sub-tropical Lows from October to December when the circulation is much stronger (consequently the lows travel greater distances) and the subtropical high has shifted equatorward.

TABLE 5-6
Mean Chemistry Values by Weather Type
(for all sites)

pH	L/PQ	4.58	
	Mar.L	4.64	lowest
	TS	4.70	
	CL/E	4.71	
	GL	4.92	
	Sub.L	5.45	
SO_4^-	Mar.L	1.70	highest
	L/PQ	1.47	
	TS	1.45	
	CL/E	1.00	
	Sub.L	0.43	
	GL	0.39	
NO_3^-	L/PQ	0.70	highest
	TS	0.59	
	Mar.L	0.57	
	CL/E	0.40	
	Sub.L	0.34	
	GL	0.25	

Abbreviations: Labrador/Quebec Lows
Great Lakes/East Coast Lows
Great Lakes Lows
Maritime Lows
Tropical Storms
Sub-tropical Lows

L/PQ
GL/E
CL
Mar.L
TS
Sub.L

Although the squared multiple correlations with all chemistry values (see Appendix VB) showed weather type to be only weakly related to precipitation chemistry with a p-value of 0.0919 (at < 0.1 level), definite patterns emerged which will be discussed with possible explanations. As Table 5-6 illustrates, Labrador/Quebec Lows produced the most acidic precipitation events with a mean pH of 4.58, $\text{SO}_4^{=}$ 1.47 and NO_3^- 0.70 mg.l^{-1} closely followed by Maritime Lows and Tropical Storms. This may be due to the more southerly track of some Labrador/Quebec Lows which would incorporate air from the industrial areas on the northern shores of the Great Lakes, including the point sources of Sudbury in southern Ontario and Noranda in southwestern Quebec. However, lows tracking further north would pass over no high emission areas which, under similar meteorological conditions, would result in lower acidity levels. Evidence for this contrast was also found for events sampled at Schefferville, Quebec (Lewis & Hrebenyk, 1979). In addition, Labrador/Quebec Lows appear to occur most frequently during summer months when the accumulation and long-range transport of air pollutants is most favoured. The relatively short period of prior precipitation duration (Table 5-6) associated with this weather type may also be a contributing factor to greater concentrations of $\text{SO}_4^{=}$ and NO_3^- .

The high acidity levels, particularly $\text{SO}_4^{=}$ (mean of 1.70 mg.l^{-1}) associated with Maritime Lows may result from a combination of several factors, since this category includes weather types originally classified as Great Lakes/East Coast Lows and Great Lakes Lows which stagnated over the Maritimes for ≥ 36 hours. This would enable the prior incorporation of pollutants from the Great Lakes area and/or the east coast. In addition, further pollutants may have been

jected into the circulation of the stationary low from Nova Scotia and the east coast of the U.S.A. Consequently, the passage and subsequent stagnation of Maritime Lows may account for their relatively high pollutant levels, particularly since the mean antecedent rainfall duration associated with these lows is only 36.8 hours, providing a short period for pollutant removal in the form of wet deposition.

Although not as high as those associated with Maritime Lows, the relatively high acidity levels (pH 4.71, SO_4^{2-} 1.00 and NO_3^- 0.40 mg.l^{-1}) produced by Great Lakes/East Coast Lows may result from their frequent passage over high emission areas of both the southern Great Lakes area (including Ohio) and the conurbations of the east coast. The disparity between this and the mean SO_4^{2-} value for Great Lakes Lows (0.39 mg.l^{-1}) is questionable when both associated lows would pass over high emission areas, although the former to a greater extent (see Figs. 4-1 with relation to Figs. 1-1 and 1-2). The most plausible explanation for this results from the difference in the average number of hours of precipitation prior to events associated with the two weather types; being 57.8 hours for Great Lakes/East Coast Lows and 68.7 hours for Great Lakes Lows--virtually 11 hours longer. This was shown on surface analysis charts where precipitation associated with Great Lakes Lows was often evident for in excess of 24 hours over the Great Lakes area before progressing east towards Newfoundland. Conversely, lows originating south of the Great Lakes may initially contain less moisture (and therefore would produce less precipitation) and may dry out further on descending the leeward side of the Appalachians; with fronts then being rejuvenated on reaching the east

coast. Although some pollutants may have been washed and rained out prior to arrival at the east coast, a major incorporation of pollutants over the latter area at this time in conjunction with less prior removal due to lack of moisture may account for the discrepancies between precipitation acidity (particularly with respect to SO_4^{2-}). for these weather types. This will be referred to again in Chapter 6.

Although Tropical Storms had a similar mean pH to Great Lakes/ East Coast Lows (4.70 and 4.71, respectively) higher acidity levels are reflected by the SO_4^{2-} value of 1.45 mg.l^{-1} and NO_3^- value of 0.59 mg.l^{-1} . This does not correspond with the premise that due to the relatively unpolluted area in which cyclogenesis occurs, and the large amounts of precipitation associated with such storms (and consequent dilution) that Tropical Storms would have comparatively low SO_4^{2-} and NO_3^- concentrations. Unfortunately, there are few related examples to cite other than a hurricane sampled in New York with a mean precipitation pH of 5.16, which was the least acid of the different weather types sampled (Wolff et al., 1979). However, further research is required to substantiate this statement since it is equally plausible that the Tropical Storms sampled over Newfoundland had relatively high acidity levels due to the incorporation of pollutants from the eastern seaboard while progressing northeast, and their rapid conversion to secondary pollutants in a warm, moist air mass. Alternatively, high acidity levels may have resulted from pollutants carried by preceding air masses from the west, despite the fact that precipitation was associated with onshore easterly winds extending from the Tropical Storm.

The smallest in number and least acidic of the weather type groups were the Sub-tropical Lows with a mean pH of 5.45. Only three of these were sampled in total, one continental, originating in the Texas and Gulf coast area, and two maritime originating just north of Florida. These differ from Tropical Storms in that they are frontal and may originate over continental areas, are not as intense, and are most frequent during late autumn and winter when the sub-tropical high has shifted equatorward. It is interesting to note that the low of continental origin has approximately double the mean SO_4^{2-} concentration of the maritime Sub-tropical Lows (0.73 mg.l^{-1} compared with only 0.28 mg.l^{-1}). This may result from greater pollution sources and catalysts over the land area, or to the greater dilution-rate associated with maritime Sub-tropical Lows having a mean precipitation total of 88.5 mm.

The relationship between weather type and wet deposition is illustrated in Table 5-7 showing both mean and total values. To a certain extent these exhibit a similar pattern to those previously discussed for concentration values, however significant differences occur with respect to total deposition values. When comparing these values it is important to note the number of cases for which precipitation data was unavailable, since the total wet deposition associated with these weather types should be higher than the figures given.

Labrador/Quebec Lows accounted for almost triple the total deposition of H^+ , SO_4^{2-} and NO_3^- compared with other weather types, values (for Labrador/Quebec Lows) which would in fact have been higher if all data were available. Although total deposition is also a function of concentration value, the discrepancy between this and total deposition

TABLE 5-7

Mean and Total Wet Deposition Values by Weather Type
(for all sites)

	Mean	Total
<u>H⁺</u>		
TS	781.4	L/PQ 8737.8
L/PQ	582.5	TS 3907.0
Mar.L	334.8 meq.m^{-2}	CL/E 2708.1 meq.m^{-2}
GL/E	313.4	Mar.L 2543.7
GL	207.5	GL 1660.0
Sub.L	146.00	Sub.L 292.0
		1 missing
		3 missing
<u>SO₄</u>		
TS	35.8	L/PQ 376.6
L/PQ	26.9	GL/E 210.6
Sub.L	24.4 mg.m^{-2}	TS 178.8 mg.m^{-2}
GL/E	16.2	Mar.B 112.0
Mar.L	16.0	GL 80.6
GL	8.1	Sub.L 48.7
		highest
<u>NO₃</u>		
L/PQ	15.8	L/PQ 221.2
Sub.L	13.3	TS 66.0
TS	13.2 mg.m^{-2}	Mar.L 63.7 mg.m^{-2}
Mar.L	9.1	CL/E 63.6
GL/E	5.3	GL 47.0
GL	4.7	Sub.L 26.6

for say Maritime Lows which had similar concentration values to Labrador/Quebec Lows (see Table 5-6) is due to a much greater number of Labrador/Quebec Lows occurring during the sampling period. This also explains the higher deposition than concentration values for Great Lakes/East Coast Lows which constitute the second largest number of events and highest rainfall total, although without any missing values it is probable that Labrador/Quebec Lows would have the highest precipitation total. This is further illustrated in Table 5-8 showing the individual, mean, high, low and total precipitation for each weather type. It is significant that Tropical Storms yielded the second highest total deposition values of both H^+ and NO_3^- , and third highest total deposition of SO_4^{2-} considering that there were only five of these events with precipitation totalling only 80.3 mm. This probably results from consistently high concentration values in conjunction with moderate precipitation totals (with 3.4 mm being the lowest). However, it should also be noted that missing values in all but this and the Maritime weather types would also make the Tropical Storm deposition totals appear comparatively higher, so that the overall Tropical Storm deposition value is quite high. In addition, the Maritime Lows which had slightly higher concentration values than Tropical Storms have relatively low precipitation totals (see Table 5-8) (with the exception of one event having 129.2 mm) resulting in lower deposition values.

Great Lakes Lows and Sub-tropical Lows follow a similar pattern for total wet deposition as for concentration values. However, the mean deposition of SO_4^{2-} and NO_3^- for Sub-tropical Lows is much higher comparatively due to the exceptionally high precipitation totals

TABLE 5-8
Precipitation Values According to Weather Type

	L/PQ	E/GL	G/L	Mar.	TS	Sub.
Total	231.1	232.5	155.6	187.1	80.3	177.0
Mean	16.5	21.1	17.3	23.4	16.1	88.5
Max.	43.0	77.1	49.6	129.2	35.5	88.5
Min.	0.8	0.8	1.2	0.8	3.4	88.5
Missing Values	5	3	1	0	0	1

Precipitation measurements in mm.

associated with these two events (see Table 5-8). This results in a biased view of the mean deposition values, so that with this study, total wet deposition values are a better indication of the impacts of different weather types.

5.6. Temporal variations

Determination of temporal variations is limited since sampling was conducted from August to mid-December at St. John's but for shorter periods at other sites during this time. Consequently, temporal variations will relate largely to monthly (August to November) variations of concentration and more particularly deposition values at St. John's only. Reference will also be made to seasonality with a greater emphasis on the patterns found by CANSAP.

Table 5-9 gives the mean and total wet deposition values of H^+ , $SO_4^{=}$ and NO_3^- from August to November for the events at St. John's.¹ It is apparent that both mean and total deposition values were highest during September; in fact, H^+ and $SO_4^{=}$ deposition values were almost double those for any other month. It is surprising that the deposition figures for August are so low; however, this is undoubtedly a consequence of the below average precipitation during that month (see Fig. 5-5) and the above normal values for September, October and November. This is further illustrated when comparing the $SO_4^{=}$ concentration values (see Table 5-10) with the deposition values since August has the third highest mean concentration. These results are also a reflection of the temporal variation of weather types since

¹N.B. Total wet deposition values for the months of August and November are lower than actual figures due to missing values.

TABLE 5-9

Total and Mean Wet Deposition Values by Month for St. John's

	Aug.	Sept.	Oct.	Nov.
H ⁺ Δ μeq.m ⁻²	57.6 296.4 74.6 53.5 67.2	1970.1 (TS) 53.5 1765.1 (TS) 1164.5 (GL/E) 272.9	407.8 391.5 2031.5 (Mar.L) 7.7 157.7	491.1 788.2 1280.3 640.15
Total	549.3	5226.1	2996.2	
Mean	109.86	1045.2	599.24	
SO ₄ ²⁻ Δ mg.m ⁻²				
Total	32.26	231.3	114.4	46.3
Mean	6.45	46.26	22.88	23.15
NO ₃ ⁻ Δ mg.m ⁻²				
Total	39.8	78.0	54.6	29.9
Mean	2.82	15.6	10.9	15.0
Missing Values	2	0	0	3

Bracketed weather types indicate "episodes."

TABLE 5-10

Mean SO_4^{2-} and NO_3^- Concentrations by Month for St. John's

	Aug.	Sept.	Oct.	Nov.	Dec.
SO_4^{2-} mg. l^{-1}					
Mean	1.26	1.69	0.66	0.85	1.36
NO_3^- mg. l^{-1}					
Mean	0.41	0.64	0.20	0.23	0.55

three of the five events in September were Tropical Storms associated with high concentration and wet deposition values. The monthly contrasts for NO_3^- are similar to those of SO_4^{2-} with the exception that the mean concentration for December is slightly higher due to the presence of snow in some of the precipitation (see Raynor & Hayes, 1982). Monthly variations will not be interpreted further due to the small number of examples for each month and the missing values which may significantly influence the results.

It is interesting to note that a few events contribute a large proportion of the acidity. For example, three events (the Tropical Storm mentioned previously) occurring in September constitute 18% of the events sampled at St. John's but contain 49% of the H^+ total deposition. When combined with a Maritime Low event in October (see Table 5.9) the H^+ deposition rises to 69%, from 25% of the events at this location. These events may be termed "episodes" since although few in number they contribute a large part of the total wet deposition. Some of these will be discussed in more detail in Chapter 7.

Discussion is further limited with respect to seasonality since only two seasons were sampled at St. John's—summer and autumn. Comparisons between CANSAP data from 1978 to 1981 and with data from this study was made by averaging SO_4^{2-} and NO_3^- concentration values from Gander and Stephenville for the following seasons:

April to June	- spring
July to September	- summer
October to November	- autumn
December to March	- winter

Although these seasons are not entirely conventional, it was considered that a late spring, shorter autumn and longer winter (particularly since snow frequently occurs in March) was more appropriate for Newfoundland. These results (see Fig. 5-6) show a general trend of highest concentrations during spring, declining during summer and decreasing further in autumn. The high concentrations in spring may result from the combined effects of the period of lowest precipitation (AES Canadian Climate Normals, 1981) and the frequency of low pressure systems from the polluted areas of the Great Lakes and eastern seaboard (Hare & Thomas, 1974, p. 71). In winter SO_4^- tends to rise slightly and NO_3^- declines further in most years which does not correspond with the fact that NO_3^- concentrations are usually higher in snow.

Although not closely corresponding with 1981 CANSAP values, the concentration values from this study follow the same trend for summer and autumn, with a mean SO_4^- concentration of 1.45 mg.l^{-1} in summer and only 0.63 mg.l^{-1} in autumn. Total deposition values of SO_4^- also correspond, with 263.5 mg.m^{-2} in summer and 160.3 mg.m^{-2} in autumn, which suggests that higher precipitation amounts during the latter month dilute the acidic compounds to the extent of reducing the overall wet deposition.

From this discussion it is apparent that all the variables discussed affect the chemistry of precipitation to a greater or lesser extent. Despite the inconclusiveness of these results (largely due to a short sampling period and consequently few samples) some patterns have emerged although not always statistically significant. Generally, it would appear that weather type (i.e. previous history of low track)

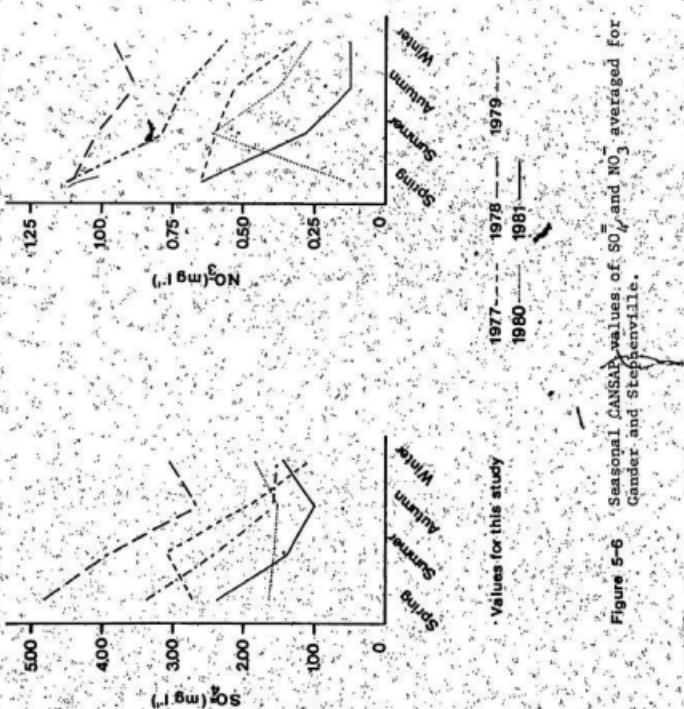


Figure 5-6 Seasonal CANSA values of SO_4^{2-} and NO_3^- averaged for Gander and Stephenville.

is one of the most influential variables, however this is only the case because each weather type has certain specific characteristics with respect to other meteorological and temporal variables. For example, Labrador/Quebec Lows were found to produce the most acidic events (with respect to pH and NO_3^-) overall, probably because the associated lows (may) pass over highly polluted areas with comparatively little time for washout and rainout before reaching Newfoundland. Also, this weather type is most prevalent during summer months when the long-range transport of pollutants is most conducive, with more prolonged anticyclonic conditions enabling their accumulation and subsequent advection northeast. Precipitation total and intensity are also important as previously mentioned, but are more variable within each weather type.

CHAPTER 6

AIR PARCEL TRAJECTORIES AND SOURCE AREAS

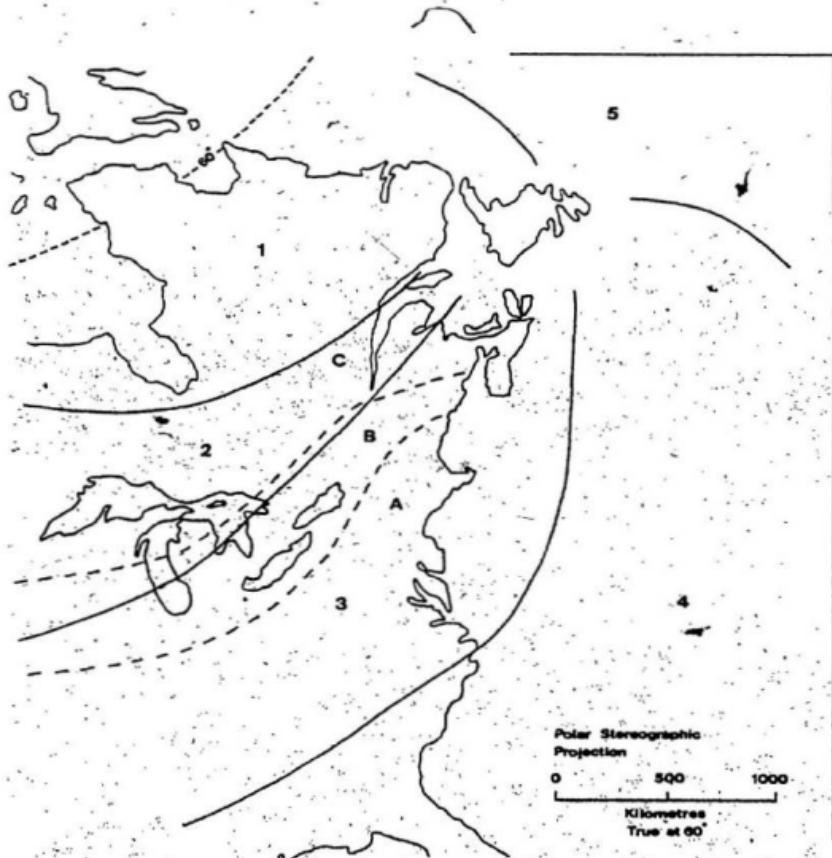
6.1. Classification of trajectory sectors

As explained in Chapter 4 back-trajectories were constructed for events¹ in order to relate precipitation chemistry to the track of the associated air parcel. Unfortunately, constructing trajectories at the surface, 850 and 700 mbar, levels in order to incorporate a vertical dimension (by choosing a mean path) did not prove successful due to often major differences in the tracks at different levels (this will be discussed further in Section 6.4). Consequently, the 850 mbar, track (mean elevation approximately 1100 m) was taken to be the most representative layer for the long-range transport of atmospheric pollutants. Since the inaccuracies inherent in using single trajectories are well known (Rodhe, 1974; Smith & Jeffrey, 1974; OECD, 1977; and Shaw, 1980) trajectory paths were divided into five sectors. Although from an objective point of view sectors should be chosen according to compass quadrants or octants (for example, Förlund, 1972; Millér, 1979; Kurtz & Scheider, 1981; Desautels, 1981; and Raynor & Hayes, 1982), subjectively chosen sectors (Wolff et al., 1979; Shaw, 1980; and Jickells et al.,

¹For similarly timed events at (a) St. John's and Cape Bröyle, (b) Grand Lake and Norris Point, and (c) Bishop's Falls and Salmon Dam one trajectory was constructed starting at an equidistant point between the two sites in each case.

1982) enable delineate areas to follow a similar isobaric curvature-- in this case the 850 mbar. curvature. Since few trajectories follow a straight line, compass sectors would result in several trajectories passing through more than one sector, a problem which is not entirely overcome by curved sectors (see Section 6.3). In addition, subjectively chosen sectors enable certain known high and low emission areas in both Canada and the United States to be distinguished.

Consequently, five sectors were chosen as illustrated in Figure 6-1. Sector 1 represents a low emission area including Labrador, Quebec and part of northern Ontario. Sector 2 represents an area of higher emissions which includes the point sources at Sudbury (1350×10^3 tonnes SO₂ p.a.) and Noranda (630×10^3 tonnes SO₂ p.a.) (Lewis & Trebenyuk, 1979), the commercial and industrial centres of Montreal, Ottawa, Quebec City and Trois Rivières along the St. Lawrence, in addition to emissions from some industrial areas just within the United States border. Sector 3 contains all the remaining high emission areas south of the Great Lakes, including Chicago, Detroit, Cleveland (and other areas of Ohio) in addition to the large industrialized conurbations of the eastern seaboard. Sector 4, although largely oceanic may incorporate emissions from both the United States and Canada due to its close proximity to the east coast, particularly since the cyclonic flow around a low pressure centre off the east coast would bring in air from the west and northwest. Although Sector 5 is illustrated in Figure 6-1 it is largely to provide more distinct boundaries for Sectors 1 and 4, and since only two trajectories occurred here it was unrealistic to calculate mean precipitation chemistry values for the sector.



Sectors A, B, C (850mbar) Shaw (1980)
Sectors for this study 1, 2, 3, 4, 5 (850mbar)

6-1 Trajectory sector delineation.

The sectors chosen by Shaw (1980) are also illustrated in Figure 6-1 to enable comparison when results are discussed in Section 6.3. The reasoning for this choice of sectors is not entirely clear but is presumably related to the grouping of the 850 mbar. trajectories.

Before discussion of the precipitation chemistry associated with the trajectory sectors and corresponding source areas a brief description of the 850 mbar. trajectories for each weather type will be given.

6.2. Trajectory sector according to weather type

For this discussion all back-trajectories were included regardless of whether they occur in a particular sector or if a complete chemical analysis were available. Statistical analysis showed a correlation of 0.445 between trajectory sector and weather type, the significance of which should become apparent.

(i) Labrador/Quebec Lows. Over 50% of Labrador/Quebec Lows followed a track through Sector 2 (see Fig. 6-2) which may be expected due to the fact that the general eastward track of the associated lows was to the south of Ungava Bay then east across the northern tip of Newfoundland (see Fig. 4-1). Variations from this general path depend on the isobaric curvature and wind speed, related to the intensity of the associated low pressure system. The two trajectories which do not conform to the general trend (B10 and N8) result from a more northerly position of the associated low at the onset of precipitation.

(ii) Great Lakes/East Coast Lows. There is a greater diversity of trajectory paths within this group with several having a greater

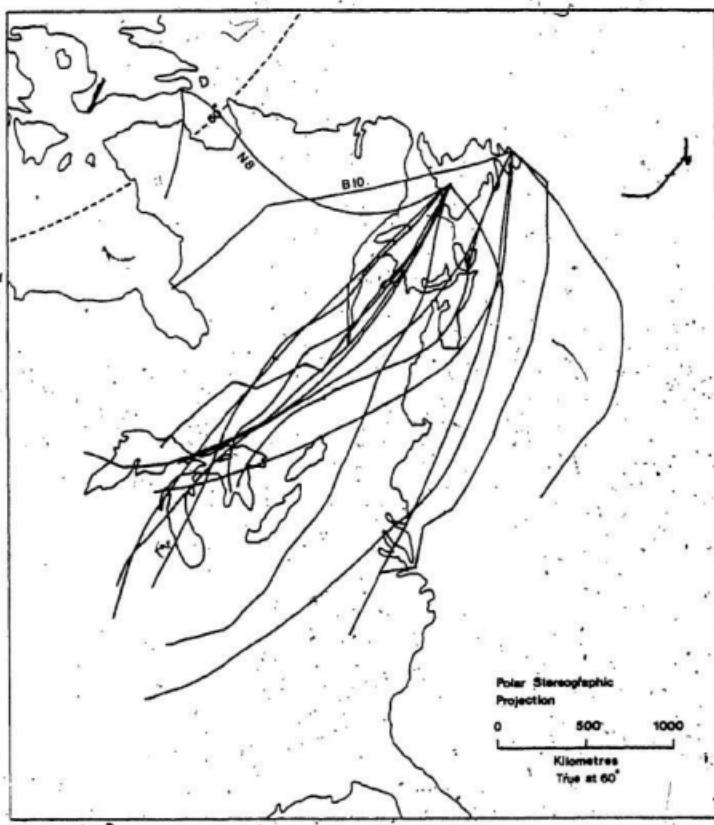


Figure 6-2 850 mbar, Labrador/Quebec Lows.

isobaric curvature and a more oceanic path. The greater isobaric curvature may result from a combination of more intense lows travelling up the east coast and from the associated low centres passing closer to the island. The trajectories within this group following a more northerly path again result from the northeasterly position of associated lows at the onset of precipitation. As Figure 6-3 illustrates the majority of E/GL trajectories occur in Sectors 2, 3 and 4 other than the three exceptions in Sector 1 referred to above (N17, E3 and N4).

(iii) Great Lakes Lows. Generally these trajectories take a more southerly path to the mid-east coast of the U.S.A. then tracking west across to locations just south of the Great Lakes area (see Fig. 6-4). Although some of these terminated over the Atlantic, they would probably track well south of the Great Lakes area of continued back in excess of 72 hours. The majority of these occur in Sectors 3 and 4 with the anomalies in Sector 1 terminating in Quebec.

(iv) Maritime Lows. These trajectories bear similarities to both E/GL and GL Lows largely following a path via the Sable Island area to the east coast between Cape Cod and Cape Hatteras, then west to the Great Lakes but with a stronger isobär curvature more characteristic of E/GL Lows (see Fig. 6-5). The majority of these occur in Sector 4 although the greater curvature of some trajectories results in partial occurrence in Sector 3.

(v) Tropical Storms. As would be expected these have southwesterly oceanic trajectories falling in Sector 4 (see Fig. 6-6). The exception to this again results from the northerly position of the relevant TS at the onset of precipitation.

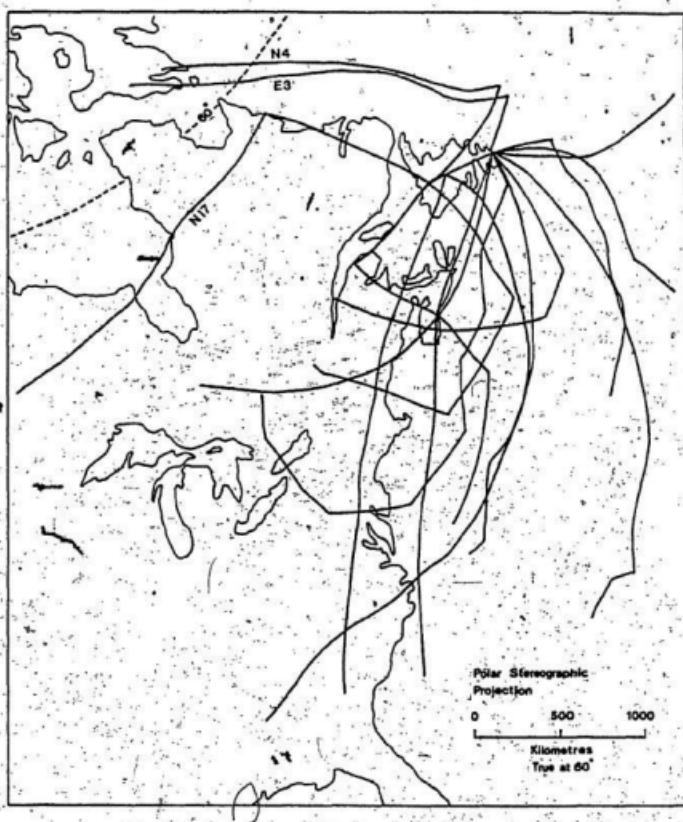


Figure 6-3 850 mbar. Great Lakes/East Coast Low.



Figure 6-4 850 mbar, Great Lakes Lows.

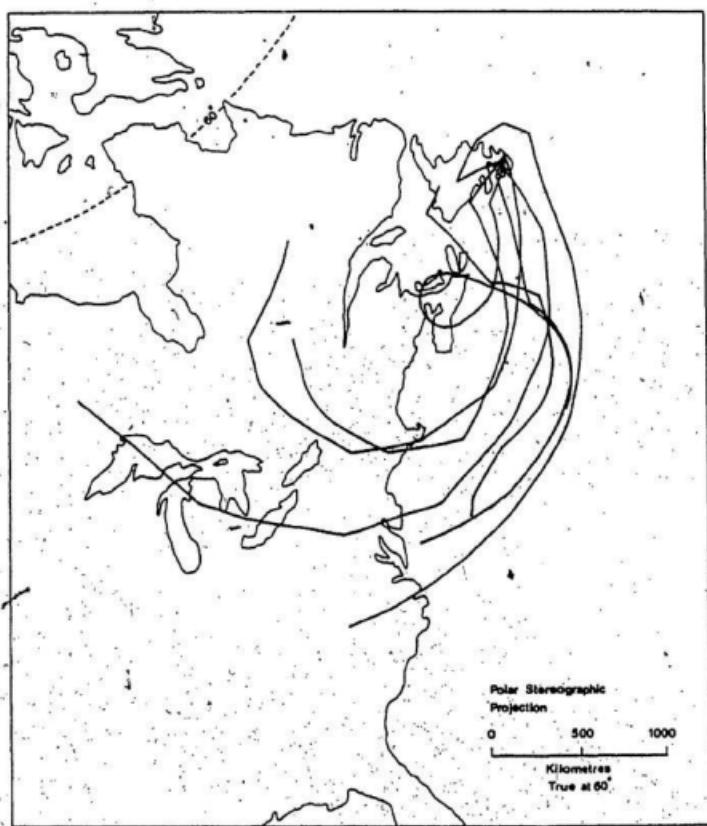


Figure 6-5 850 mbar. Maritime Lows.

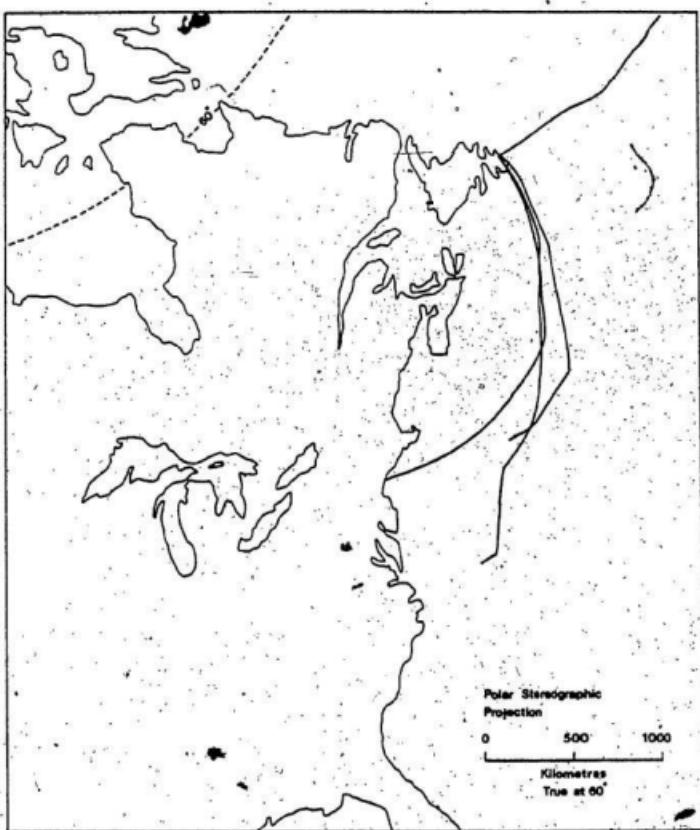


Figure 6-6 850 mbar. Tropical Storm.

(vi) Sub-tropical Lows. The two trajectories within this category correspond to the oceanic and continental tracks of their associated low pressure centres (see Fig. 6-7), occurring in Sectors 4 and 2 respectively. Generally then, there are certain relationships between weather type and trajectory path although anomalies may occur due to the position of the low centre at the onset of precipitation and variations depending on the intensity and precise track of the low.

6.3. Trajectory sectors and precipitation chemistry

Figure 6-8 illustrates the 850 mbar. trajectories for which complete chemical analysis was available and in which no contamination occurred. Since several trajectories occurred in more than one sector a trajectory which occurred in one sector for approximately 75% of its length was designated to that sector. Even so, 13 trajectories could not be included in this analysis since they appeared in two or more sectors with no particular predominance in any one sector. To avoid exclusion of these trajectories, additional or subsectors could have been created but this would have reduced the reliability (by making one sector too specific) in any determination of source areas.

For each sector the mean and total values of pH, SO_4^{2-} , NO_3^- , SO_4^{2-} deposition, NO_3^- deposition and H^+ deposition were calculated for each event associated with the respective trajectories. In cases where only one trajectory was constructed for say an event at both Norris Point and Grand Lake, both sets of precipitation chemistry data were included. These are illustrated in Table 6-1.

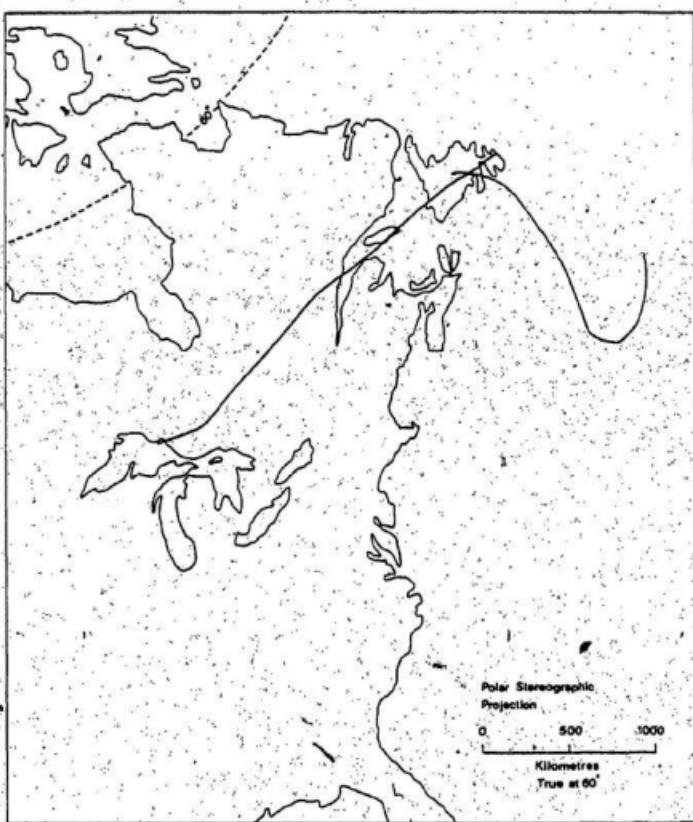


Figure 6-7. 850 mbar. Sub-Tropical Lows.

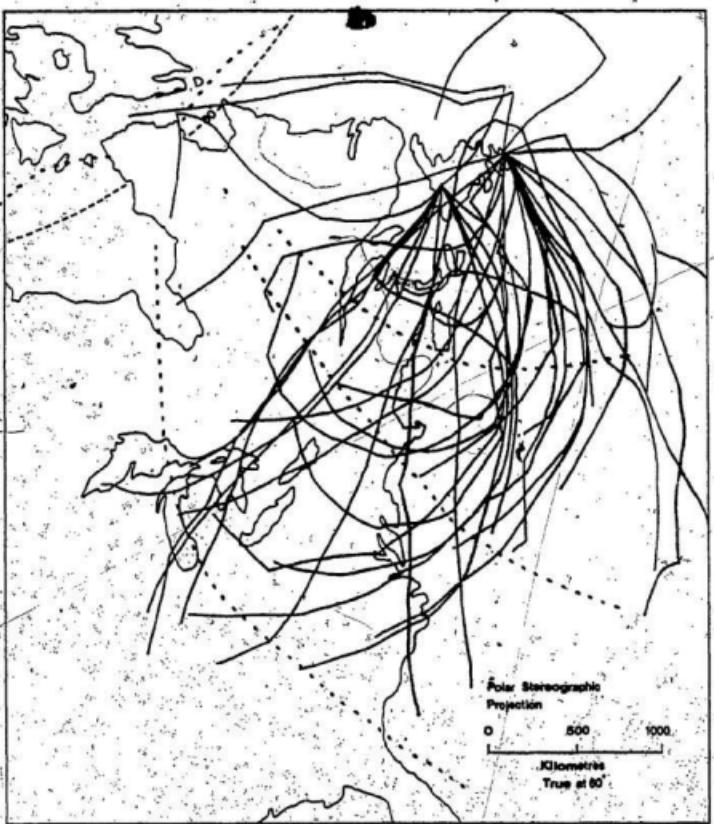


Figure 6-8 850 mbar, trajectories within sectors.

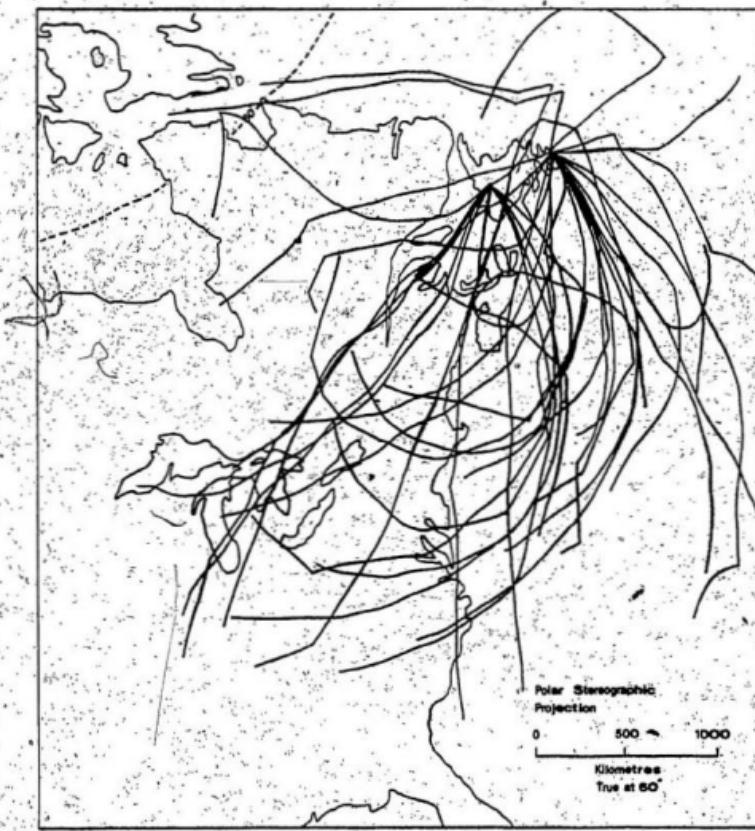


Figure 6-8 850 mbar, trajectories within sectors.

--- Sectors

TABLE 6-1
Concentration and Deposition Values by Trajectory Sector

	<u>SECTOR</u>			
	1	2	3	4
Mean pH	7.71	4.55	4.69	4.97
Mean $\text{SO}_4^{=}$ mg.l ⁻¹	1.04	1.66	1.12	0.84
Mean NO_3^- mg.l ⁻¹	0.68	0.69	0.44	0.37
Mean $\text{SO}_4^{=}$ Dep. mg.m ⁻²	11.2	25.2	23.6	15.5
Mean NO_3^- Dep. mg.m ⁻²	5.62	11.24	18.46	7.94
Mean H^+ Dep. $\mu\text{eq.m}^{-2}$	213.76	570.9	471.7	312.8
Total $\text{SO}_4^{=}$ Dep. mg.m ⁻²	56.0	151.2	256.9	325.6
% $\text{SO}_4^{=}$ Dep.	7.1%	19.1%	32.5%	41.2%
Total NO_3^- Dep. mg.m ⁻²	28.1	56.2	147.5	158.8
Total H^+ Dep. $\mu\text{eq.m}^{-2}$	1068.8	3425.3	5188.8	6881.0
% H^+ Dep.	6.5%	20.7%	31.3%	41.6%
No. of Cases	7	10	12	23
Missing values for deposition	2	4	1	1

Although total values have been included in this table, they may be misleading due to the inconsistency in sampling periods and numbers at different sites. In addition, trajectory path varies according to the location on the island, which is related to the frequency and seasonality of particular weather types (discussed in Ch. 5), so that these results are biased since they only include samples collected from the end of July (mainly August) to mid-December.

Although squared multiple correlation (see Appendix VB) indicated that trajectory sector was only weakly related to precipitation chemistry, with a p-value of 0.0967 at the <0.1 level some interesting relationships are apparent. It is perhaps surprising that Sector 2 produced the most acidic precipitation events (see Table 6-1) reflected in mean concentration and deposition values, with those for Sector 3 being somewhat lower, since Sector 3 contains the majority of high SO₂ emission areas (see Fig. 1-1, SO₂ em. p. 3). This would suggest that trajectory path alone is not responsible for the resultant precipitation chemistry. In addition, over 50% of trajectory weather types within Sector 2 were L/PQ Lows with a relatively short trajectory path with relatively less time for pollutant removal, so that this could be a major contributing factor. This situation may also reflect the sampling period (since L/PQ Lows were most prevalent during the summer) and because these were mainly associated with west coast sites where pollutant removal time would be shorter. However, this is not to imply that pollutant concentrations should not generally be higher from Sector 2 since Sudbury and Noranda are major point sources of SO₂ within this area.

It is interesting to note that in fact NO_3^- deposition values are highest in Sector 3, which may result from the more even distribution of NO_x emissions (see Fig. 1-2, NO_x em. p. 4) in several areas south and east of the Great Lakes. In contrast SO_2 emissions result from more specific point sources, some of which occur in the immediate vicinity of the Great Lakes and were likely to affect trajectories in Sector 2. The total deposition values for this are biased due to the greater number of missing precipitation data values for Sector 2. Nevertheless, the total H^+ deposition value of 5188.8 mg.m^{-2} for Sector 3 indicates that this area is also a major contributor to precipitation acidity, particularly with respect to NO_3^- .

Sector 4 trajectories produced the lowest concentrations of SO_4^{2-} and NO_3^- , the third highest mean deposition values and the highest total deposition values. This may result from the predominantly oceanic path of these trajectories resulting in moderate to high precipitation amounts in combination with relatively low concentrations, since the only emission areas would be air along the eastern seaboard incorporated into a system travelling northeast. Although the mean values from this sector are relatively low, the number of trajectories associated with the category results in the highest H^+ deposition overall (6881.0 mg.m^{-2}). However, these values may be considerably different on an annual basis and some researchers may consider that the impact of episodes rather than total acid loading is more detrimental to the environment, so that trajectories from Sector 2 may be more harmful.

Trajectories from Sector 1 have the lowest mean and total deposition values which may result from it being the lowest emission sector with few instances. The slightly higher concentration values

may be due to lower precipitation totals than, for example, trajectories from Sector 4 with a largely oceanic path.

When comparing these results with those of Shaw (1980) it is apparent that the mean concentration values in Newfoundland are considerably lower than those measured in Nova Scotia, where mean $\text{SO}_4^{=}$ values of 5 mg.l^{-1} were obtained for Sector A, 4 mg.l^{-1} for Sector B and 8 mg.l^{-1} for Sector C, compared with a maximum of 1.66 mg.l^{-1} for Sector 2 in this study. However, since emissions from Halifax were calculated to contribute 50% of this deposition it is perhaps more realistic to halve these figures when considering long-range transport. The overall pattern for source areas is similar in that the sector incorporating largely Canadian emissions north of the Great Lakes (i.e. Sudbury and Noranda) was found to produce the highest mean concentration of $\text{SO}_4^{=}$ in both studies (Sector C for Shaw, Sector 2 in this study²). However, due to the greater frequency of events from Sectors 3 and 4 total H^+ deposition (as a percentage of the total H^+ deposition for all sectors) percentages are highest for these areas, 31.3% and 41.6%, respectively, with a combined total of 72.9% (73.7% for $\text{SO}_4^{=}$ deposition). This is comparable with the same area as Shaw's Sectors A and B which together contributed 96% (65% for A and 31% for B) of the total deposition. The fact that Sectors 1 and 2 were found to contribute 27.2% of H^+ deposition (26.2% for $\text{SO}_4^{=}$ deposition) compared to only 4% at St. Margaret's Bay in Nova Scotia would be indicative of the infrequency of events from this direction in Nova Scotia, which is

²Shaw's Sector C would also incorporate Sector 1 but it is unlikely that trajectories from this sector would significantly influence Nova Scotia.

apparent from both the paths of the trajectories (see Fig. 6-8) and the track of L/PQ Lows which are most prevalent within these sectors.

Before summarizing these findings it should be noted that due to the inconsistency in sampling periods at all sites, because values for a number of sites were included and due to some missing deposition values, these results are tentative, particularly when comparing them with a single site in Nova Scotia. Nevertheless, two important assertions can be made:

(1) The sector producing the highest mean concentration and wet deposition (i.e. Sector 2) of SO_4^- , NO_3^- and H^+ does not necessarily coincide with the area of greatest SO_2 and NO_x emissions. This is probably due to the intervening influence of a number of meteorological variables, particularly the amount of pollutant removal before reaching the sampling site--dependent upon the duration of precipitation prior to the event and the presence of catalysts aiding the transformation to secondary pollutants. In addition, since trajectory paths are related to the synoptic flow (and weather types) which varies seasonally, this too would influence the results.

(2) Sectors producing the highest deposition values are not necessarily synonymous with those producing the highest total concentration values, but are more a function of the frequency of trajectories from that sector (and consequently the amount of precipitation) as was the case with Shaw's study.

This emphasizes the fact that although emissions influence the amount of available pollutants in the atmosphere, the resultant chemistry of precipitation occurring at a point, say 1800 km downwind of this is equally if not more dependent on certain meteorological

variables. These include:

- (a) the amount of diffusion and consequent dilution (by vertical and horizontal mixing) occurring at and following the time of pollutant injection into the atmosphere;
- (b) the amount of dry deposition prior to and following transformation to secondary pollutants;
- (c) the number of available catalysts for this conversion; and
- (d) the amount and type of precipitation, which affects removal efficiency, falling prior to and on reaching the sampling site. As discussed in Chapter 5 some of these variables are related to weather type with respect to the area over which cyclogenesis occurred and the track of the resultant low (with respect to direction and trajectory duration).

6.4 Comparison of computer and manual trajectories

Figures 6-9 to 6-14 illustrate the paths of both computer and manual trajectories for six selected events referred to in Ch. 4.2.2. The computer paths were plotted from six-hourly latitude, longitude and height positions for each event calculated by the AES model. This information was incorporated into a computer mapping programme set at the same scale and stereographic projection as those shown here. This produced six-hourly points along trajectories at each pressure level, namely 1000, 925 and 850 mbar. The exact orientation of these plots onto the base maps was determined by a cross on the computer maps at the intersections $60^{\circ}\text{N } 65^{\circ}\text{W}$ and $30^{\circ}\text{N } 65^{\circ}\text{W}$. It is fairly apparent from the resultant computer and manual paths that in certain cases there are major discrepancies between the trajectories. However, before

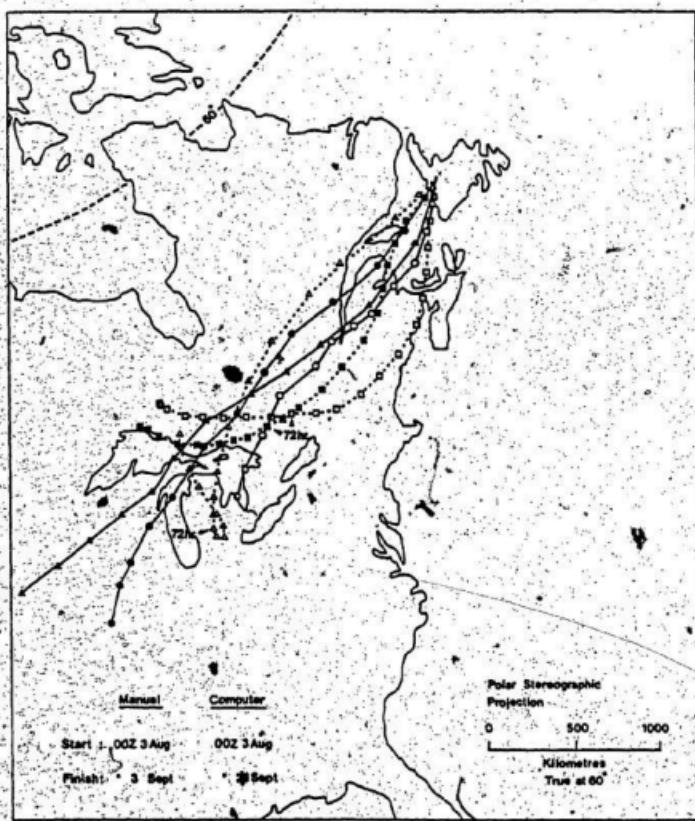


Figure 6-9 Computer and manual trajectory paths for Grand Lake event 34 starting 00Z 03 August.

Key for Figures 6-9 to 6-14

Manual	○ Surface	Computer	□ 1000 mbar	6-hourly positions for all trajectories
	● 850 mbar			■ 925 mbar	
	△ 700 mbar			▲ 850 mbar	

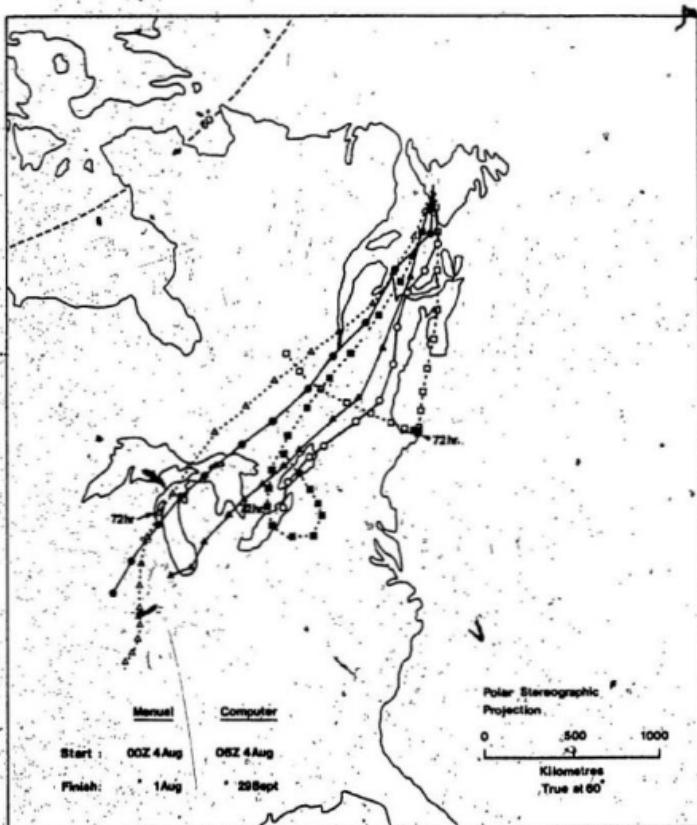


Figure 6-10 Computer and manual trajectory paths for Grand Lake event 35 starting 00Z 04 August.

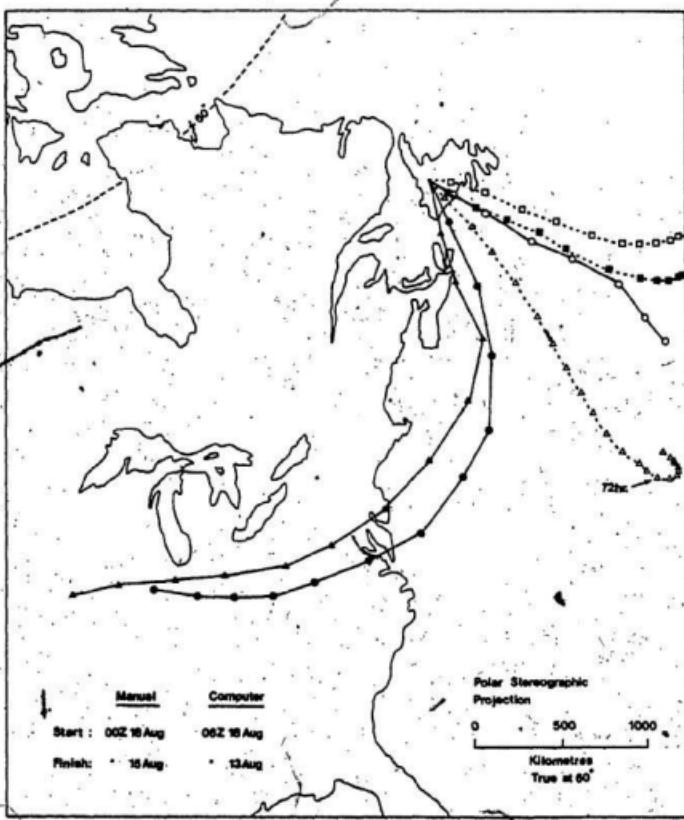


Figure 6-11 Computer and manual trajectory paths for Grand Lake event 42 starting 00Z 18 August.

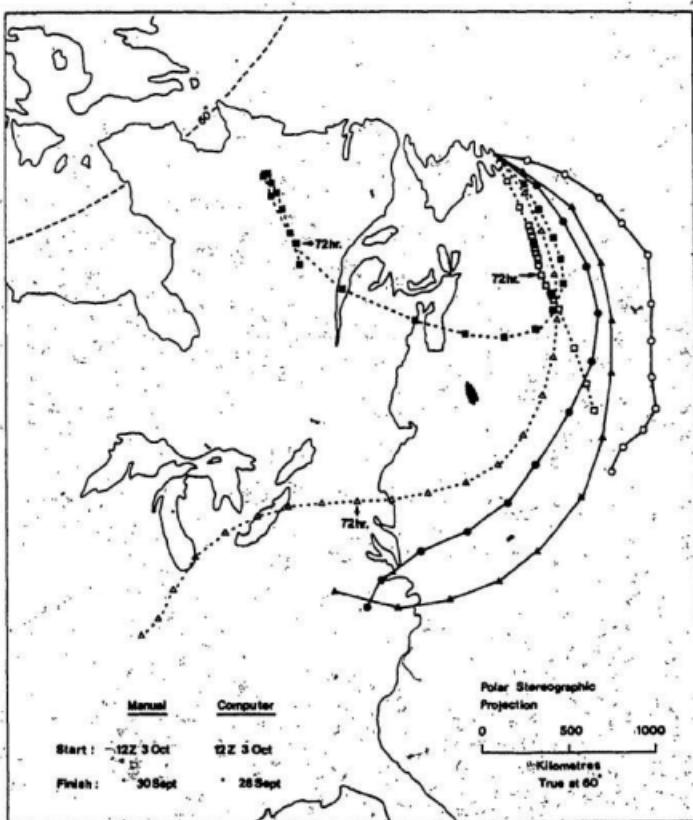


Figure 6-12 Computer and manual trajectory paths for St. John's event 21, starting 12Z 03 October.

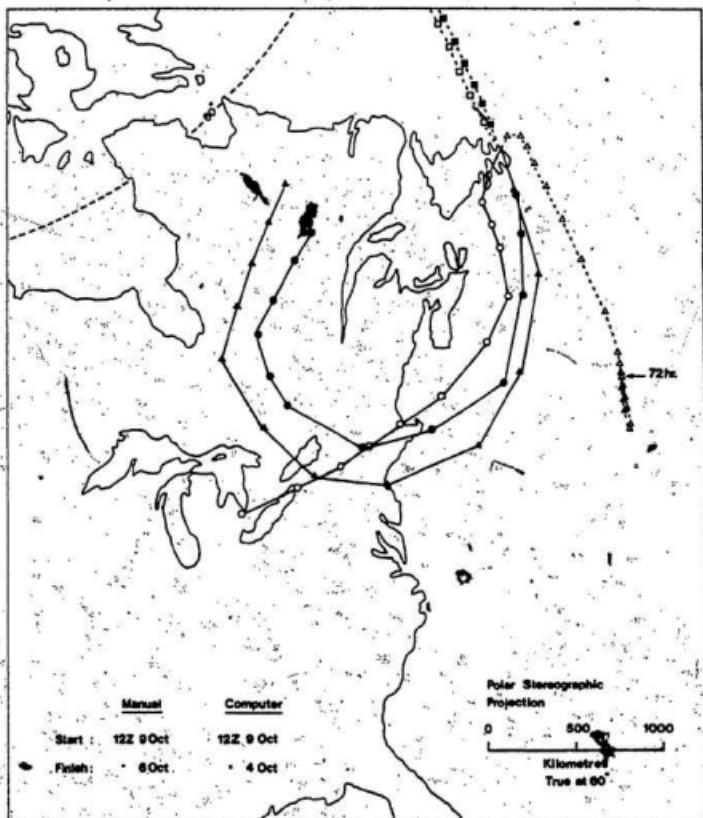


Figure 6-13 Computer and manual trajectory paths for St. John's event 22 starting 12Z 09 October.

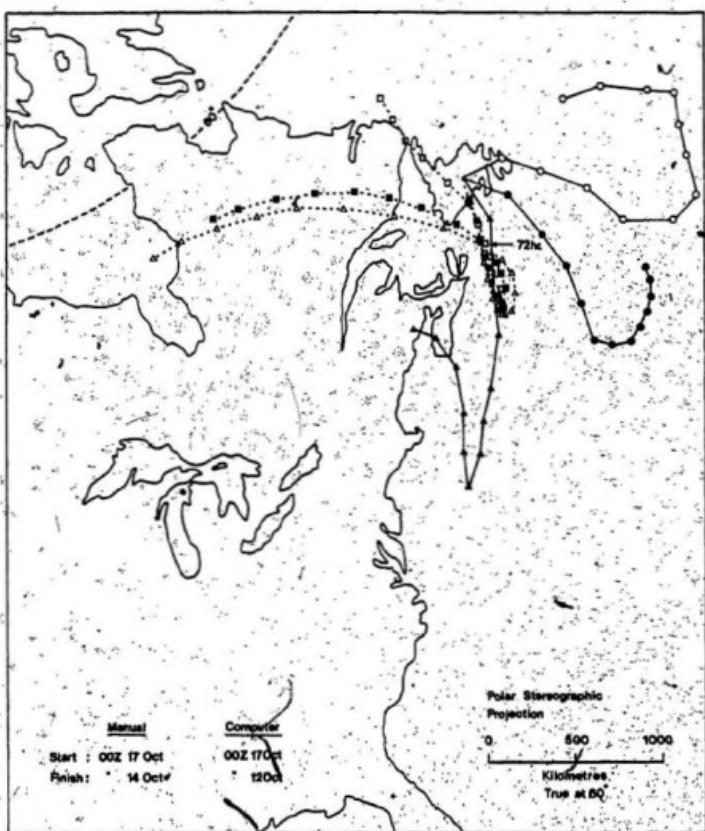


Figure 6-14 Computer and manual trajectory paths for Bishop's Falls event 57 starting 00Z 17 October.

considering possible causes for this certain differences of the AES computer model and the manual methods should be noted.

(1) The pressure levels for which calculations were made do not entirely correspond, with the AES model levels at 1000, 925 and 850 mbar., and manual levels at surface, 850 and 700 mbar. For this reason it may be more realistic to ignore the 700 mbar. tracks indicated on the figures.

(2) The AES model computed trajectories at six-hourly intervals from start to finish at all levels, whereas the manual method only did this for surface trajectories, with upper air trajectory starting times based on 12-hourly charts.

(3) As a result of this the AES method often enabled trajectories to start nearer to the time of an event, as indicated on Figures 6-9 and 6-10.

(4) The AES model constructed trajectories back for five days as opposed to three; so that for better comparison 72 hours duration is marked on each computer trajectory.

(5) The AES model also incorporates a vertical component which may, in some synoptic situations, greatly affect the direction and speed of a trajectory.

Trajectory tracks illustrated in Figures 6-9 and 6-10 show strong similarities of computer and manual trajectory paths, particularly those at the 850 mbar. level. It is interesting to note that for these and in fact all the computer plots, tracks at different pressure levels often exhibit greater variance than that resulting solely from differences in isobaric curvature. From this it would appear that computer trajectories may not overcome the difficulties this presents.

when trying to locate source areas, other than choosing the most representative layer for the transport and removal of air pollutants.

Trajectory paths in Figures 6-11 to 6-14 not only exemplify the different tracks that may be obtained from computer and manual methods but also two other notable differences. These are the distance travelled over three-day periods for both trajectories and the apparent oversimplification of the paths portrayed by the manual technique. At least in part these inconsistencies probably result from the absence of a vertical wind component with the manual method in conjunction with subjectively analyzed wind data. However, this should not act to totally condemn the manual methodology, since when restricted to three days the general track of the 850 mbar, trajectories is quite similar. This tends to favour the approach of classifying events into trajectory sectors to lessen possible errors when relating precipitation chemistry and deposition values to a single trajectory path. In addition, restricting the duration of a manual trajectory to three days reduces errors that may result from the oversimplified interpretation of wind data. So that within these criteria this manual technique for constructing back-trajectories may prove useful in cases where a computer model is not available. However, due to the absence of vertical wind data more realistic manual trajectories may be attained by reducing the trajectory speed calculated from the geostrophic wind velocity. For example, the trajectory paths compared here suggest that a reduction to approximately 80% may be in order.

CHAPTER 7

CASE STUDIES

Chapters 5 and 6 presented results and discussions for meteorological and trajectory sector variables for the data set as a whole. Although this is useful for making generalized statements as to the relative importance of certain variables in this study, reference to specific examples, relating the most pertinent variables, should enable a better understanding of the resultant precipitation chemistry in each case. This should also help identify cases where the relationship is not clear, possibly due to complex atmospheric processes which are not yet fully understood (Raynor & Hayes, 1982).

The choice of examples was limited to those for which a full chemical analysis was completed and all meteorological variables were known as far as possible. In addition, cases were chosen to exemplify all weather types and trajectory sectors, excluding Sector 5, and coincident events at St. John's and Cape Broyle to determine the possible effects of local pollution. Similarly, comparison of events (sampled at various sites) associated with the same low pressure system will be made, to determine any significant differences in precipitation chemistry and offer possible explanations. Some of these are the same events for which computer trajectories were calculated, so that reference in these instances will be made to both trajectory paths.

7.1. (a) Events GL 33 and NP 48; GL34; and GL 35¹.

The chemical and meteorological variables associated with these events are given in Table 7-1. Although there are missing precipitation data (and subsequently missing deposition data) for GL 33 it was still included since it was coincident with NP 48 where all values were available. These four events will be considered together since on a temporal basis they occur consecutively and from surface synoptic analysis observation they appear to result from the same L/PQ Low tracking across the north of Ungava Bay and across northern Quebec (see Fig. 7-1, 7-2 and 7-3). Events NP 48 and GL 33 occurred virtually simultaneously; however, more representative autographic raingauge records from locations nearer the sampling sites would probably have indicated that precipitation occurred earlier at Norris Point due to its coastal location with respect to the precipitation incoming from the west. Although this temporal difference is not shown in the hours of precipitation prior to the event (due to approximations from surface analysis charts) it is reflected in the precipitation chemistry values with slightly higher acidity levels at Norris Point. Further examples to substantiate this are lacking due to a number of contaminated samples from Norris Point, and due to the more frequent collection of samples at Grand Lake which prevents valid comparison with accumulated samples at the former. However, the only other example of coincident events associated with the same (L/PQ) low, for events NP 52 and GL 44 (see Table 7-1) show significantly higher concentrations and deposition

¹ Abbreviated terms for sites are as follows: CB = Cape Broyle; St.J. = St. John's; GL = Grand Lake; NP = Norris Point; BF = Bishop's Falls; and SD = Salmon Dam.

TABLE 7-1
Tabulated Results for Case Studies

Event	Date	Precip. Duration (mm)	Precip. Duration (hours)	pH	$\text{SO}_4^{=}$ (mg.l ⁻¹)	NO_3^- (mg.l ⁻¹)	H^+ Dep. ($\mu\text{eq.m}^{-2}$)	WT
(NP 48) (GL 33)	2 Aug. 2 Aug.	1.4 MD	26 26	4.21 4.32	3.16 2.49	1.20 1.40	86.2 MD	1 1
GL 34	3 Aug.	10.8	12	4.09	4.19	1.50	877.1	1 6.2
GL 35	4 Aug.	16.5	18	4.44	0.16	0.00	598.5	1 6.2
(CB 02) (St.J.09)	5 Aug. 5 Aug.	8.2 8.2	56 56	5.13 5.15	0.22 0.46	0.24 0.34	60.7 57.6	5 5
(CB 03) (St.J.10)	7 Aug. 7 Aug.	14.2 14.2	73 73	4.81 4.68	0.83 1.25	0.28 0.28	218.2 296.4	2 2
(GL 36)	7 Aug.	0.8	80	4.80	1.90	0.71	12.7	2
(CB .04) (St.J.11)	9 Aug. 9 Aug.	0.8 0.8	24 24	4.31 4.03	2.34 4.96	1.10 1.00	38.9 74.6	4 4
(GR 37)	9 Aug.	1.4	38	4.80	1.29	0.49	*22.0	4
(St.J.13)	18 Aug. (an)	21.5	72	5.08	0.17	0.23	53.5	
(GL 41)	17 Aug. (pm)	14.1	53	5.00	0.13	0.43	140.9	
(St.J.14) (GL 42)	18 Aug. 18 Aug.	9.5 3.9	88 75	5.15 5.00	0.32 0.20	0.17 0.30	67.2 38.7	
(St.J.23) (BF 55)	9 Oct. 9 Oct.	129.2 3.1	64 62	4.80 4.97	0.56 0.28	0.28 0.15	2031.5 33.2	

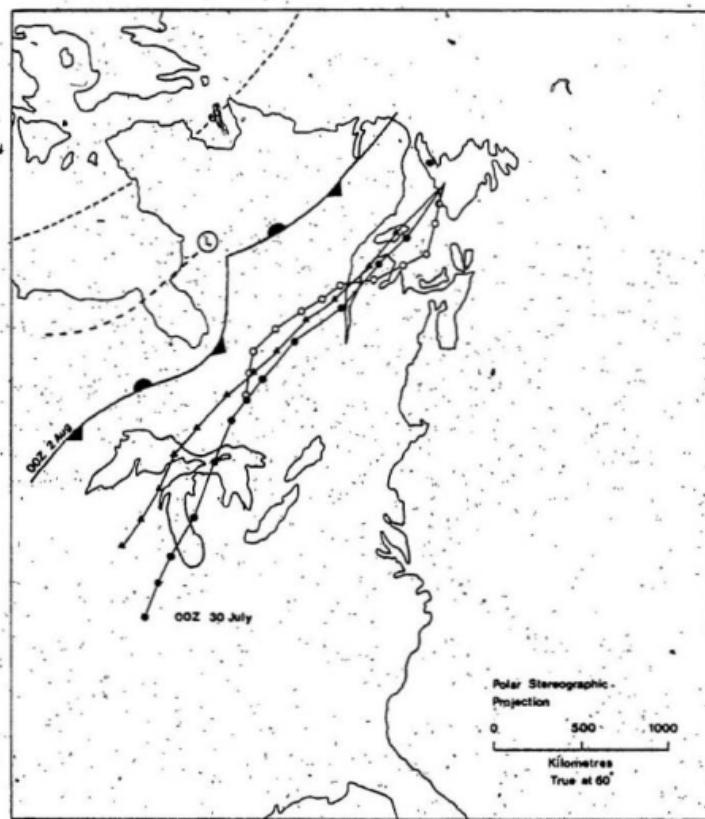


Figure 7-1 Trajectories at 3 levels for Grand Lake event 33 and Norris Point event 48.

Key for Figures 7-1 to 7-14 Case Studies

- (L) - Position of associated low centre at and prior to onset of event
- - 6-hourly position at surface
- - 850mbar
- ▲ - 700mbar
- Position of front at onset of event

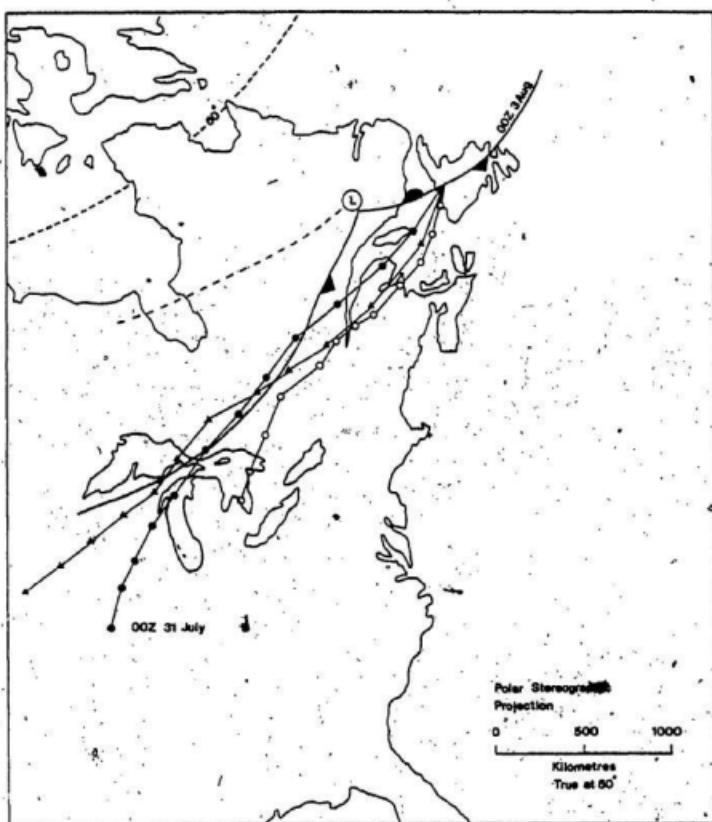


Figure 7-2 Trajectories at 3 levels for Grand Lake event 34.

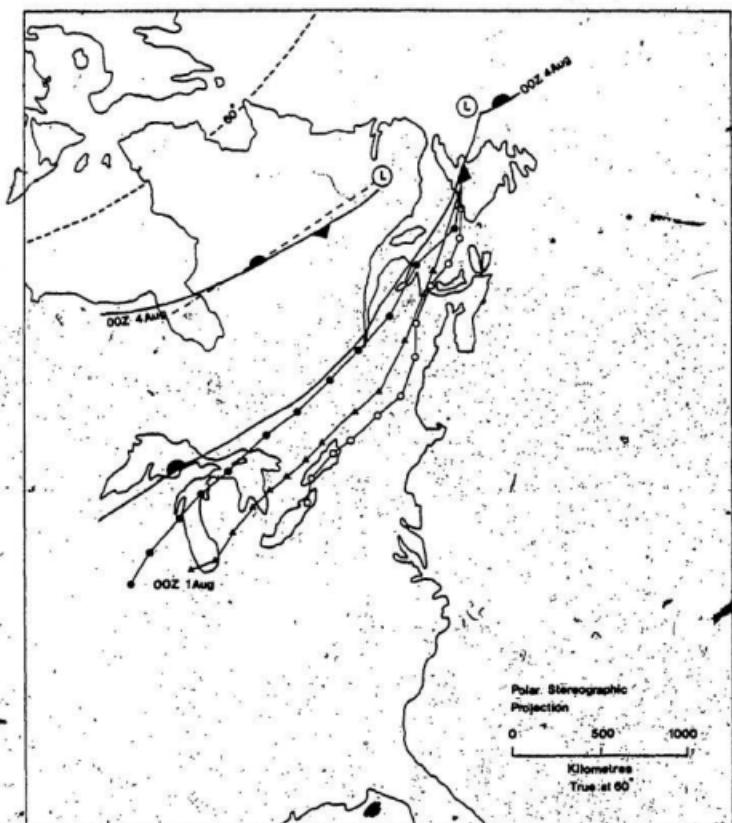


Figure 7-3. Trajectories at 3 levels for Grand Lake event 35.

values at Norris Point. The higher precipitation total at Norris Point for this and other events (see Fig. 5-5, p.97-8) suggests that orographic rainfall may induce pollutant removal (by washout and rainout), and reduce acidity levels at Grand Lake since it lies in the rain shadow area of the Long Range Mountains during precipitation associated with winds from westerly points.

The air parcel trajectories associated with NP 48 and GL 33 (see Fig. 7-1) indicate that although the associated low had a northerly track characteristic of L/PQ Lows, the trajectories passed over some high emission point sources including Sudbury and Noranda, producing relatively high acidity levels. This may have been further enhanced by a short period of prior precipitation and low precipitation total.

Events GL 34 and GL 35 were initially thought to be associated with the same L/PQ low pressure system (see Figs. 7-2 and 7-3) as NP 48 and GL 33. However, the high acidity levels associated with GL 34 (pH 4.09, SO₄²⁻ 4.19, NO₃⁻ 1.50, 877.1 H⁺ deposition) suggest that at the time of the event polluted air may have been incorporated from a GL low positioned south of the St. Lawrence at the time of the first event. Surface analysis charts do not clarify this and further confusion is caused by a large frontal system across the island at this time. Since the trajectories for GL 34 and 35 are extremely similar for both computer and manual techniques (see Figs. 6-8 and 6-9), the greater acidity of GL 34 may also be due to less removal of pollutants prior to the event in conjunction with a lower precipitation total. It should also be noted that trajectories at all levels for these low events are very similar suggesting that these paths are a fairly accurate representation of the actual tracks of the associated air parcels.

(b) CB 02 and St.J. 09

These events were associated with Tropical Storm Cindy which was positioned south of the Avalon Peninsula at the onset of precipitation (see Fig. 7-4). The 850 and 700 mbar. trajectories indicate that polluted air may have been incorporated from the east coast as the storm tracked northeast, but the 56 hours of prior precipitation would probably have led to a significant amount of removal of SO_4^- and NO_3^- . The surface trajectory indicates onshore easterly winds at the time of precipitation, which may also contribute to the low acidity levels.

Comparison of precipitation chemistry data for the two sites shows slightly higher SO_4^- and NO_3^- concentrations at St. John's which may be attributed to local pollution. However, it may also have resulted from lower precipitation levels at St. John's (although the St. John's autographic rain gauge readings were used for both sites) since Cape Broyle generally receives greater precipitation amounts (see Fig. 5-5, p.97-8), which would also account for the slightly higher H^+ deposition at Cape Broyle in this example.

(c) CB 03, St.J. 10 and GL 36

Although precipitation at the east coast sites and Grand Lake was associated with the same GL/E Low on this date, precipitation on the east coast occurred approximately 36 hours earlier (see Figs. 7-5 and 7-6). This is related to both the movement of the front associated with the low and the track of the low itself, since as the low was moving further northeast the front was moving further west, so affecting the Avalon first. Precipitation chemistry values at all sites are moderate to low, with values at St. John's again being slightly higher than those at Cape Broyle (see Table 7-1). With the track of the

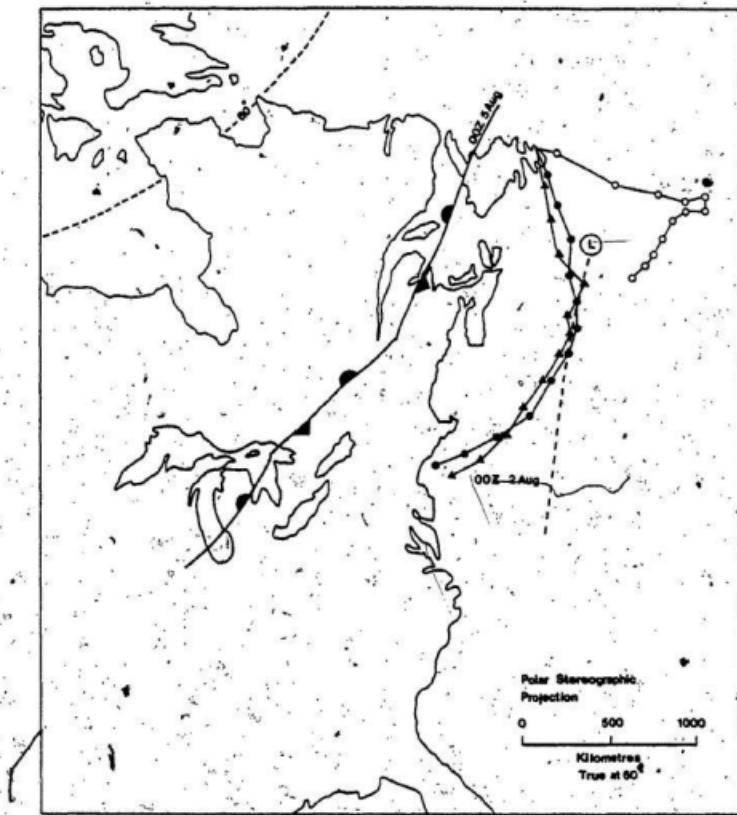


Figure 7-4 Trajectories at 3 levels for St. John's event 9 and
Cape Broyle 2.

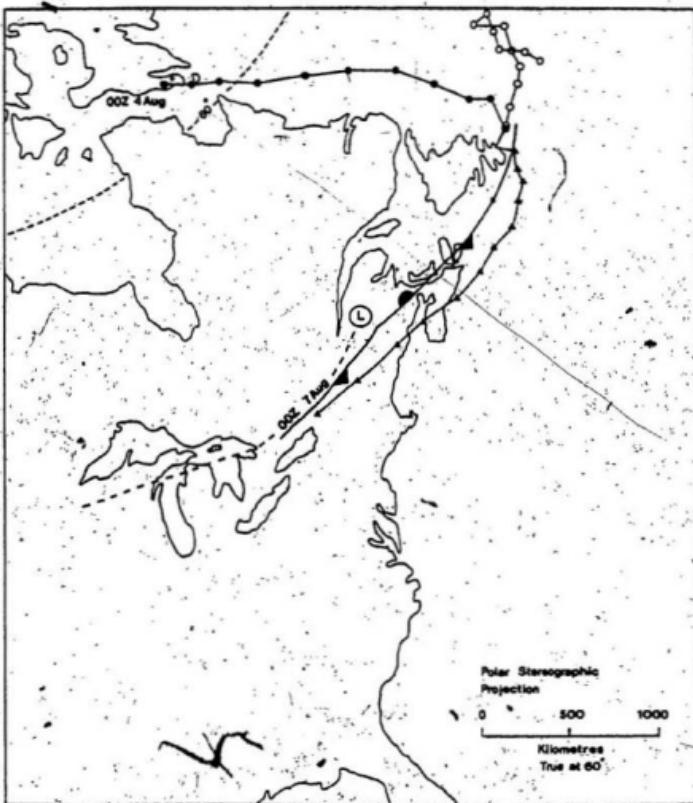


Figure 7-5 Trajectories at 3 levels for Cape Broyle event 3 and St. John's event 10.

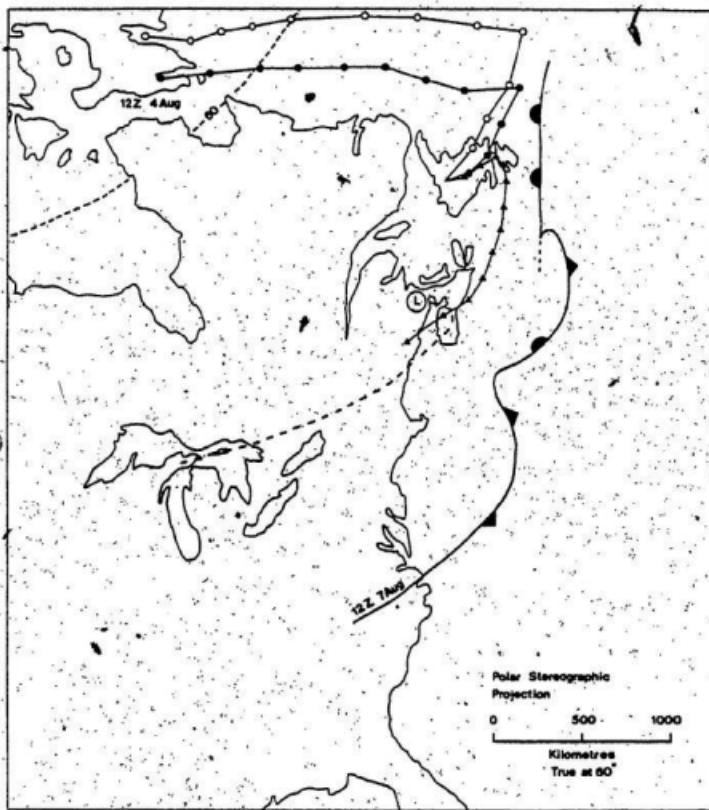


Figure 7-6 Trajectories at 3 levels for Grand Lake event 36.

associated low passing from the Great Lakes across Nova Scotia acidity levels might have been higher. However, the prolonged pollutant removal prior to the event or the incorporation of relatively unpolluted air from the northwest as indicated by the surface and 850 mbar. trajectories, probably reduced the acidity. Although the event at Grand Lake occurred after those on the east coast the higher SO_4^- and NO_3^- concentrations at the former may result purely from the low precipitation total of 0.8 mm. Trajectories for east coast and west coast sites are similar with the 700 mbar. path conforming most to the low track, suggesting that the 850 mbar. and surface lows were positioned further north at the onset of precipitation.

(d) CB 04, St.J. 11 and GL 37

All these events were associated with a low pressure system which originated in the Great Lakes area then stagnated over the Maritimes for approximately 36 hours before progressing further northeast across Newfoundland. Acidity levels at St. John's and Cape Broyle are high, particularly the former suggesting again that local pollution may increase acidity levels. Trajectory paths indicate that emission areas along the east coast and St. Lawrence (see Figs. 7-7 and 7-8) were encountered, which in conjunction with only 24 hours of prior precipitation would enhance precipitation acidity.

It is perhaps surprising that acidity levels at Grand Lake are lower, particularly since precipitation occurred here 12 hours earlier. Greater dilution and the incorporation of air from the northwest (see Fig. 7-8) may partially explain this. In addition, further incorporation of pollutants into the low while stagnant over the Maritimes may have occurred just prior to the events on the east coast.

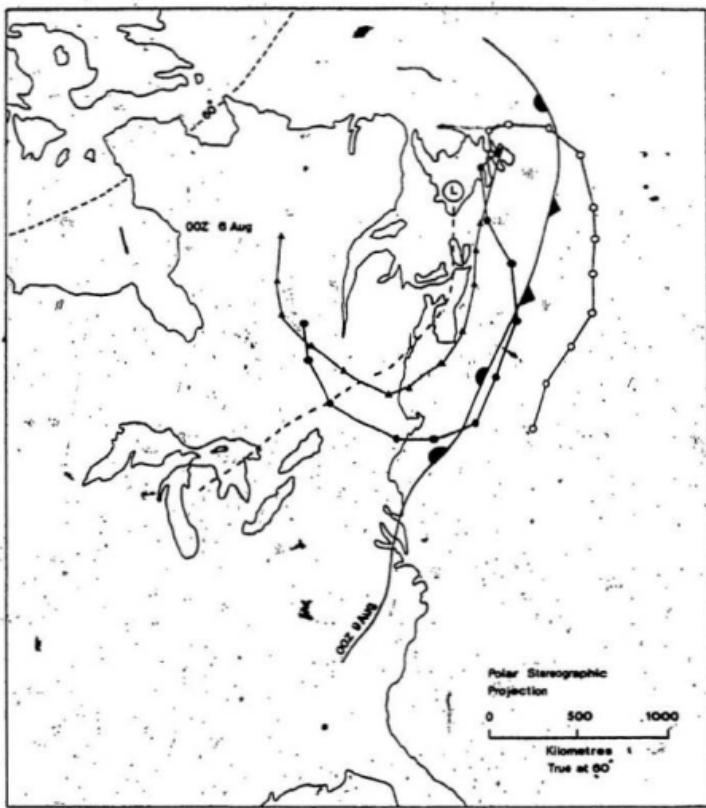


Figure 7-7 Trajectories at 3 levels for Cape Broyle event 4 and St. John's event 11.

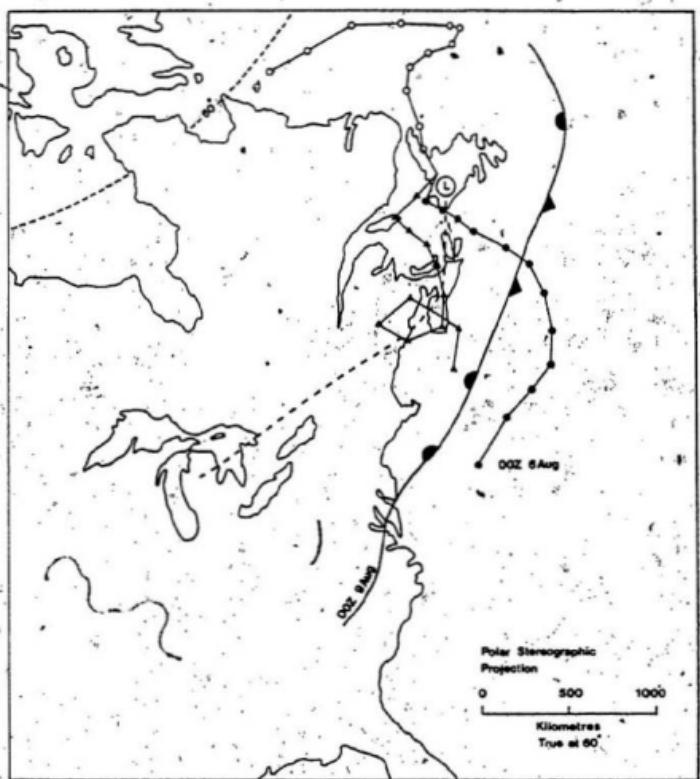


Figure 7-8 Trajectories at 3 levels for Grand Lake event 37.

(e) St.J. 13 and GL 41; St.J. 14 and GL 42

All of the above results were associated with a low pressure system from the northern Great Lakes area. St.J. 13 corresponds with GL 41, although precipitation occurs first at the latter which may partly explain the slightly higher acidity levels at Grand Lake. In addition, the trajectory path for GL 41 passes south of the Great Lakes (see Fig. 7-10) whereas the St.J. 13 and GL 42 computer trajectories are totally oceanic (see Fig. 7-9 and Fig. 6-11). The St.J. 14 and GL 42 acidity levels (pH) are much the same as the earlier events (see Figs. 7-11 and 7-12) although the SO_4^{2-} concentrations are slightly higher. This may result from less dilution due to lower precipitation totals. It is surprising that the concentration values for all these events are not higher with respect to the low track and trajectory paths; however, the long duration of prior precipitation may account for this in conjunction with a more oceanic track as indicated by the computer model trajectory.

(f) St.J. 23 and BF 53

The low pressure system associated with these events originated just north of the Great Lakes and remained over the Maritimes for approximately 36 hours. The SO_4^{2-} and NO_3^- concentrations at both sites were moderately low which may partly result from the 850 mbar. and surface trajectories (see Figs. 7-13 and 7-14) passing over southern Quebec and the northern St. Lawrence low emission areas. However, deposition at St. John's was extremely high ($2031.5 \mu\text{eq.m}^{-2}$) for this event (classifying it as an episode), probably due to the precipitation total of 129.2 mm over >48 hours. This may have resulted from the passage of the low centre directly over the Avalon. The slightly higher SO_4^{2-} and

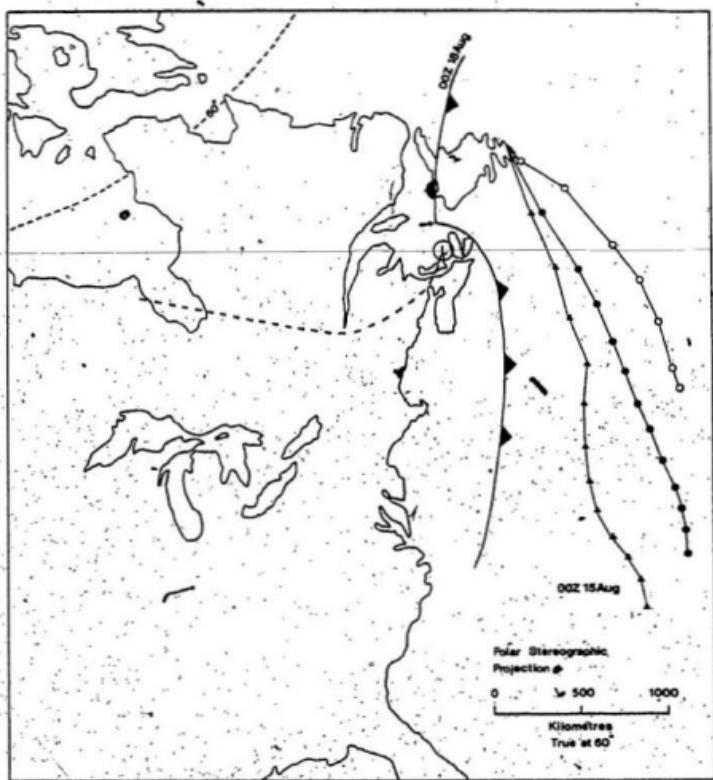


Figure 7-9 Trajectories at 3 levels for St. John's event 13.

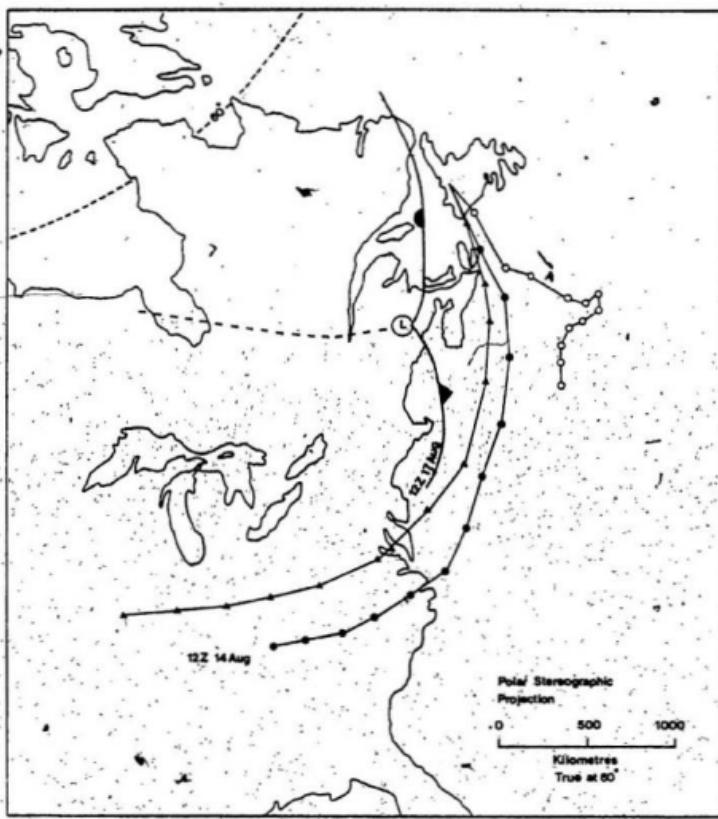


Figure 7-10 Trajectories at 3 levels for Grand Lake event 41.

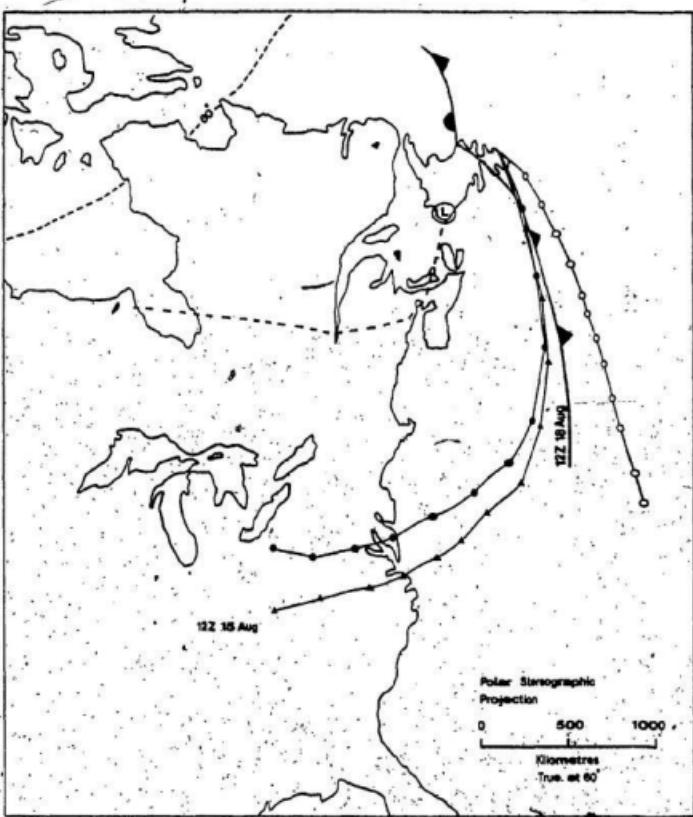
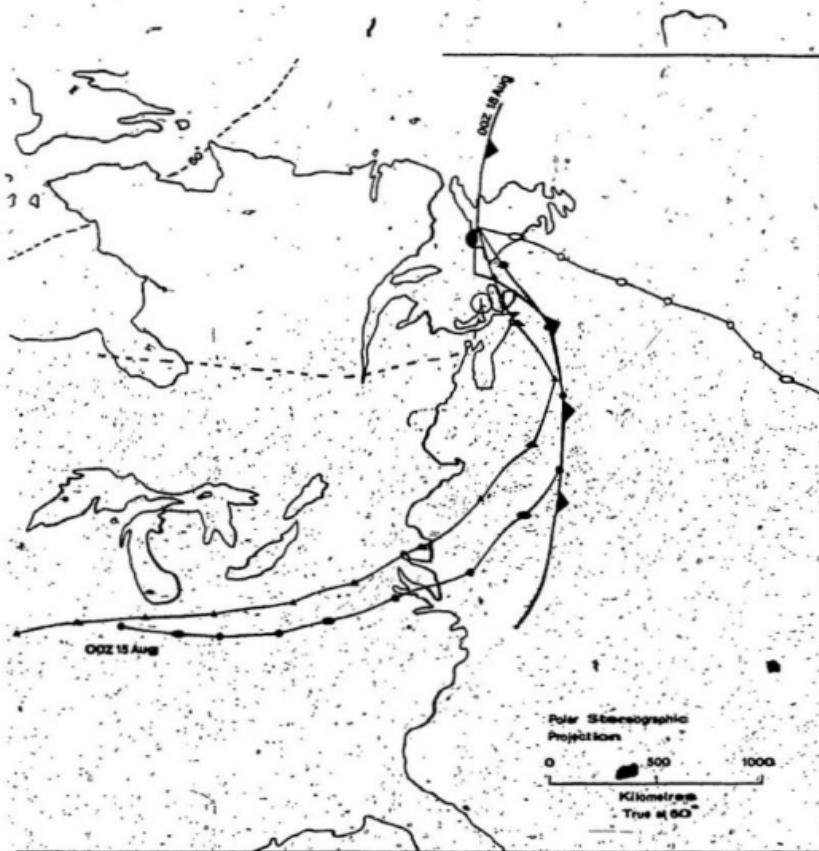


Figure 7-11 Trajectories at 3 levels for St. John's event 14.



7-12 Trajectories at 3 levels for Grand Lake event 42.

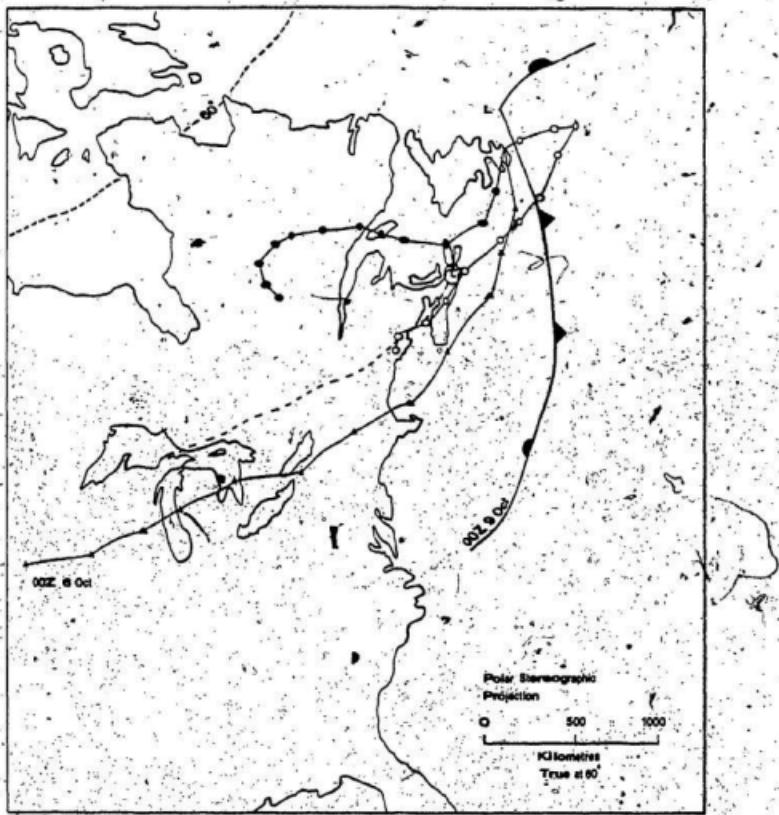


Figure 7-13 Trajectories at 3 levels for St. John's event 23.

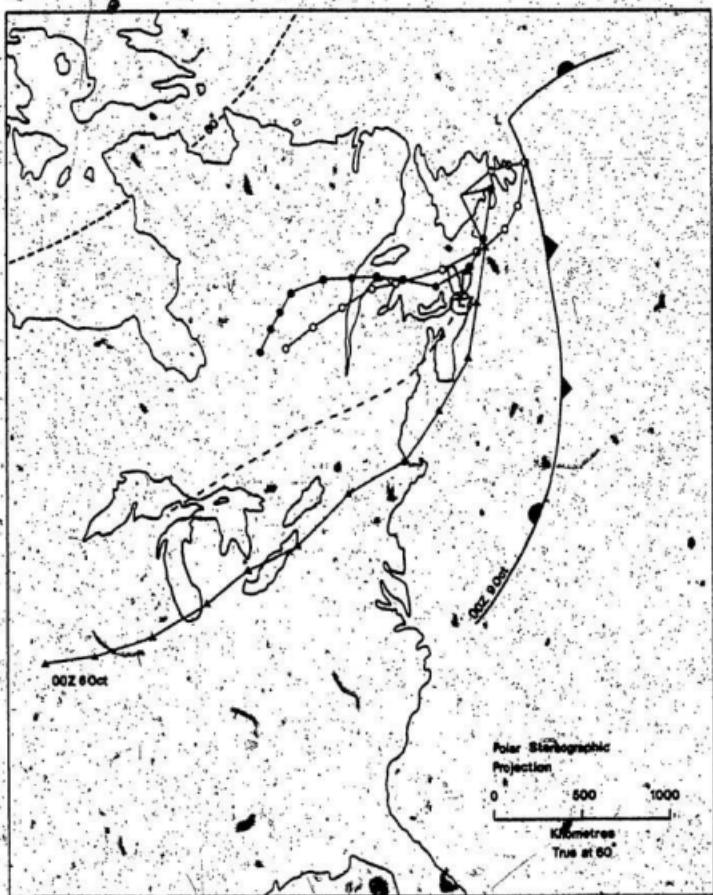


Figure 7-14 Trajectories at 3 levels for Bishop's Falls event 55.

NO_3^- concentration values at St. John's may once again be due to the influence of local pollution since Bishop's Falls is not close to any significant SO_2 emissions.

7.2. Summary

Analysis of these case studies reveals that:

(i). SO_4^{2-} and NO_3^- levels in precipitation at St. John's may well be increased slightly by local emissions--however alternately, by comparison with Cape Broyle this may only result from less dilution at St. John's since precipitation levels are generally higher at Cape Broyle (see AES Canadian Climate Normals, 1981);

(ii). SO_4^{2-} and NO_3^- concentrations and H^+ deposition at Norris Point appears to be higher than at Grand Lake. This could be partly explained by orographically induced precipitation and removal of pollutants at the former, whereas with westerly airflow the latter falls in the rain shadow of the Long Range Mountains, so that overall deposition values are also lower here;

(iii) inconsistencies between trajectories at different levels may act to increase or reduce the acidity of the resultant precipitation--for example, an easterly or northwesterly surface wind in conjunction with a southwesterly 850 mbar. trajectory;

(iv) associating precipitation with a single frontal system or low pressure system is not always possible since air may be incorporated from another adjacent pressure system, which may act to increase or reduce precipitation acidity levels.

CONCLUSION

It is apparent from the last three chapters that, to a large extent this study fulfilled its main objectives outlined in Chapter 2. However, due to the inconsistency of sampling periods at various sites it has been extremely difficult to identify spatial variations in the acidity of precipitation on the island of Newfoundland. Comparisons of precipitation chemistry from the events associated with the same low pressure system at St. John's and Cape Broyle, and Norris Point and Grand Lake indicate that the former of the east and west coast sites received precipitation of slightly higher acidity. In the case of the Avalon sites this may result from local pollution at St. John's and/or greater dilution at Cape Broyle due to higher precipitation levels (as indicated by monthly climate summaries (Env. Can., AES, 1981). Whereas on the west coast earlier removal of pollutants induced by orographic rainfall, may account for higher acidity levels at Norris Point than Grand Lake. However, it is important to note that these observations are based on a small number of samples and as such are inconclusive. The remaining aims of this study yielded some interesting results which will be summarized below.

All the meteorological variables considered have to a greater or lesser extent influenced the resultant precipitation chemistry sampled on the island. Due to the interdependency of these variables it may not be practical to single out any one variable as being the most influential. For example, although Labrador/Quebec Lows were found to produce the most acidic events, this may have resulted from

the characteristic short period of antecedent rainfall and the trajectory path associated with those lows. However, the importance of trajectory sector, i.e. the source area of an event, should not be overstressed, since although determining the amount of available pollutants incorporated into an air mass, the following variables determine the degree of acidity of the resultant precipitation events:

- (1) The amount of diffusion and consequent dilution occurring at and following the time of pollutant injection into the atmosphere;
- (2) the amount of dry deposition prior to and following transformation to secondary pollutants;
- (3) the number of available catalysts for this conversion to secondary pollutants;
- (4) the amount and type (with respect to intensity) of precipitation falling prior to and on reaching the sampling site;
- (5) the association of sulphate and nitrate—to what extent they are in the less acidic form of ammonium sulphate and ammonium nitrate than in the strongly acidic form of sulphuric and nitric acid;
- (6) the influence of the surrounding relief, whether to induce precipitation orographically or create a rainshadow area;
- (7) increased acidity from dry fall-out of pollutants from local emissions; and
- (8) the time of the year, for example, during the summer when accumulation of pollutants under anticyclonic conditions is most conducive.

Results from this study proved reasonably comparable with those from CANSAP data for 1981; some differences would be expected due to incompatibility of sampling methodologies. Due to the lack of any long-term precipitation chemistry data for the island it was not possible to determine if precipitation acidity has increased over recent years. Comparison and analysis of CANSAP data from 1977 indicates that acidity levels for 1981 were lower than those for the last

four years, possibly due to higher precipitation totals. This underlines the fact that short-term precipitation sampling studies do not provide conclusive results due to the inherent variability in precipitation chemistry from year to year.

In conclusion, it appears from this and similar studies that the processes involved in atmospheric chemistry are extremely complex and require further research. In this respect, the need for event and sequential sampling is self-evident in that they enable the determination of the influence of meteorological conditions accompanying such events. Projects of this nature have been established in Ontario and Nova Scotia, and it is hoped that the daily precipitation sample from the APN site at Bay D'Espoir may also be used for similar studies until an event sampling programme is established in the province.

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APPENDIX I

Chemical Analysis Procedures Conducted on Precipitation Samples¹

(1) pH (Potentiometric Method)

The glass electrode in combination with a fast-flow calomel reference is used. The glass membrane of the pH electrode forms a partition between two liquids of differing hydrogen ion concentration and a potential is produced between the two sides of the membrane that is proportional to the difference in pH between the liquids. Ideally, a change of 1 pH unit produces an electrical change of 59.1 mV at 25°C.

(2) Specific Conductance

The conductance of an aqueous solution is the reciprocal of its electrical resistance: $K = \frac{1}{R}$

Since electricity is carried in the solution by migration of the solute ions, the conductivity is related to the total ionic concentration of the solution. The principle of the conductivity meter is similar to that of an ohmeter in which resistance is measured in ohms. Conductance is expressed in mhos.

(3) Potassium (Atomic Absorption Spectrophotometry)

Potassium (in solution) is aspirated into an air-acetylene flame where it is converted into its atomic state. Radiation from

Further detail of these methodologies may be obtained from the Chemical and Physical Analysis Laboratory, Nfld. Forest Research Centre, Canadian Forestry Service, P.O. Box 6028, Pleasantville, St. John's, Nfld. A1C 5X8

a hollow-cathode lamp is passed through the atomized sample and the amount of light absorbed at a pre-selected wavelength is determined by a spectrophotometric detection system. Under optimum operating conditions the amount of light absorbed is directly proportional to the concentration of potassium in solution.²

(4) Sodium (Atomic Absorption Spectrophotometry)

Sodium (in solution) is aspirated into an air-acetylene flame where it is converted into its atomic state. Procedure then continues as (3).

(5) Calcium (Atomic Absorption Spectrophotometry)

Calcium (in solution) is aspirated into an air-acetylene flame where it is converted into its atomic state. Procedure then continues as (3).

(6) Magnesium (Atomic Absorption Spectrophotometry)

Magnesium (in solution) is aspirated into an air-acetylene flame where it is converted into its atomic state. Procedure then continues as (3).

(7) Ammonia (Automated Colourimetric)

Following reaction of ammonia with sodium salicylate, sodium nitroprusside and sodium hypochlorite in a buffered alkaline medium (pH of 12.8-13.0) an emerald-green coloured ammonia-salicylate complex is formed. This complex is measured colourimetrically at 660 nm.

² Metals referred to are in ionic form, i.e., K^+ , Na^+ , Ca^{++} , Mg^{++} , etc.

(8) Chloride (Ion Chromatography)

Chloride is determined by conductance following its separation on an ion exchange resin and suppression of the eluent background conductance by means of a fibre suppressor in contact with a dilute solution of sulphuric acid.

(9) Nitrate (Ion Chromatography)

Procedure as (8).

(10) Sulphate (Ion Chromatography)

Procedures as (8).

APPENDIX II

Correction for Sea-Salt

Cl^-/Na^+ in seawater = 1.166 (epm) conversion from ppm to epm on following page.

Total epm is first calculated for each anion and cation from analytical result put in computer.

Equivalent amounts of Na^+ , K^+ , Ca^{++} , Mg^{++} , Cl^- (NO_3^- varies) are calculated based on the ratio above $\text{Cl}^-/\text{Na}^+ = 1.166$.

The difference between total ions and salt ions are referred to as "excess" ions. In other words, $\text{Cl}^-/\text{NO}_3^-/\text{SO}_4^{=2-}$ exist in two forms-- neutralized or acid but in both cases in the same proportion to one another. The neutralized forms are calculated from NH_4^+ and excess K^+ , Ca^{++} and Mg^{++} .

APPENDIX II (cont'd.)
Seawater Chemistry and LRTAP

Ions	ppm to epm
H ⁺	0.99209
K ⁺	.02558
Na ⁺	0.04348
Ca ⁺⁺	0.04990
Mg ⁺⁺	0.08224
NH ₄ ⁺	0.05544
Cl ⁻	0.02821
F ⁻	0.05264
NO ₃ ⁻	0.01613
NO ₂ ⁻	0.02174
SO ₄ ⁼	0.02082
CO ₃ ⁼	0.03333
HCO ₃ ⁻	0.01639

Major Elements Present in Sea Water
(in solution)

Ions	ppm	epm.
Cl ⁻	18,980	535.4
Na ⁺	10,561	459.2
Mg ⁺⁺	1,272	104.6
S	884	
Sas SO ₄ ⁼	2,648	55.1
Ca ⁺⁺	400	20.0
K	380	9.7
Br	65	0.8

APPENDIX III

Determination of Possible Contamination from Polyethelene
Bags Used in Precipitation Collectors

Chemical analysis of two bags of dionised water (from MUN
Chemistry Dept.) kept at c. 4°^oC for approximately six weeks.

Each sample was transferred into two clean vials so that analysis on
each polyethelene bag sample was repeated. The results were as follows:

Sample No.	Cond. (4 mhos.)	K ⁺	Na ⁺	Ca ⁺⁺ (mg.l ⁻¹)	Mg ⁺⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	
1A	6.18	2.6	<.01	.37	.10	<.005	<.02	<.10	<.03	.034
1B	5.81	3.3	<.01	.11	.044	<.008	<.02	.41	<.03	.034
2A	NSM	NSM	<.01	.32	.086	<.005	<.02	1.8	<.03	.042
2B	5.82	1.8	<.01	.11	.044	.006	<.02	.10	<.03	.034

Although the levels of Cl⁻ and Na⁺ from the polyethelene bags were not sufficient to seriously contaminate the precipitation samples over-correction for sea-salt contribution may have resulted.

APPENDIX IV
Chemical Concentrations (mg.l^{-1})

Date	Event Number	Site	pH	Cond. (mhos)	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+	H^+	Cl^-	SO_4^{--}	NO_3^-
28 July	1	1	5.01	12.8	0.14	0.11	0.08	0.03	0.26	0.01	0.00	0.90	0.41
04 & 05 Aug.	2	1	5.13	4.5	0.01	0.01	0.04	0.00	0.04	0.01	0.03	0.22	0.24
06 & 07 Aug.	3	1	4.81	19.0	0.12	0.01	0.00	0.01	0.04	0.02	0.00	0.83	0.28
08 & 09 Aug.	4	1	4.31	19.0	0.05	0.03	0.03	0.03	0.09	0.05	0.00	2.34	1.10
13 Aug.	5	1	4.51	18.0	0.06	0.53	0.21	0.04	0.12	0.03	0.00	3.02	2.10
N.R. Aug.	6	1	4.85	5.2	0.00	0.01	0.04	0.00	0.02	0.01	0.01	0.37	0.23
18 Aug.	7	1	5.01	4.0	0.00	0.01	0.04	0.01	0.03	0.01	0.06	0.22	0.14
N.R. Aug.	8	1	4.42	16.8	0.05	0.01	0.03	0.01	0.16	0.04	0.00	1.63	0.72
04 & 05 Aug.	9	3	5.15	4.8	0.02	0.01	0.03	0.02	0.10	0.01	0.00	0.46	0.34
06 & 07 Aug.	10	3	4.68	20.5	0.08	0.02	0.01	0.04	0.08	0.02	0.47	1.25	0.28
09 Aug.	11	3	4.03	35.4	0.00	0.03	0.03	0.00	0.42	0.09	M	4.96	1.00
N.R. Aug.	12	3	4.83	4.8	0.00	0.01	0.04	0.01	0.02	0.01	0.05	0.41	0.33
18 Aug (am)	13	3	5.08	31.3	0.00	0.01	0.04	0.01	0.03	0.01	0.05	0.17	0.23
18 Aug (pm)	14	3	5.15	2.6	0.00	0.04	0.08	0.01	0.00	0.01	0.11	0.32	0.17
N.R. Aug.	15	3	4.59	22.9	0.04	0.01	0.01	0.00	0.04	0.03	0.00	1.28	0.54
07 Sept.	16	3	4.10	43.0	0.48	0.15	0.14	0.04	0.35	0.08	0.00	4.09	1.20
11 Sept.	17	3	4.80	6.3	0.12	0.12	0.06	0.01	0.04	0.02	0.00	0.55	0.34
12 Sept.	18	3	4.30	17.0	0.04	0.21	0.11	0.00	0.13	0.05	0.00	1.94	0.84
24 & 25 Sept.	19	3	4.60	25.0	0.00	0.16	0.07	0.01	0.04	0.03	0.11	1.12	0.26
29 & 30 Sept.	20	3	4.50	17.0	0.11	0.01	0.13	0.01	0.04	0.03	0.00	0.73	0.56
04 Oct.	21	3	4.70	10.0	0.20	0.09	0.03	0.02	0.05	0.02	0.00	0.92	0.21
08 Oct.	22	3	4.60	20.0	0.00	0.02	0.06	0.01	0.11	0.03	0.63	1.27	0.20
Oct.	23	3	4.80	6.8	0.03	0.24	0.02	0.00	0.02	0.02	0.02	0.00	0.28
25 Oct.	24	3	5.19	6.9	0.00	0.01	0.09	0.00	0.02	0.01	0.22	0.18	0.11
28 Oct.	25	3	4.96	3.5	0.00	0.04	0.10	0.01	0.03	0.01	0.18	0.48	0.22

APPENDIX IV (cont'd.)

Event Number	DEPOSITION			METEOROLOGICAL VARIABLES				
	SO ₂ (mg m ⁻²)	NO ₂ (mg m ⁻²)	H ⁺ (µEq.m ⁻²)	Precipitation Total (mm)	Precipitation Intensity (mm hr ⁻¹)	Antecedent Precip. (hours)	Weather Type	Trajectory Sector
1	0.7	0.3	7.8	0.8	0.20	42	1	4
2	1.8	2.0	60.7	8.2	1.03	56	5	4
3	11.8	4.0	218.2	14.2	0.84	73	2	1
4	1.9	0.9	38.9	0.8	0.27	24	4	4
5	94.1	65.5	956.5	31.2	3.10	36	1	3
6	M	M	M	M	M	60	1	2
7	6.6	4.2	292.9	31.0	1.94	75	3	4
8	M	M	M	M	M	12	1	1
9	3.8	2.8	57.6	8.2	1.03	56	5	4
10	17.7	4.0	296.4	14.2	0.84	73	2	1
11	4.0	0.8	74.6	0.8	0.27	24	4	3 & 4
12	M	M	M	M	M	60	1	2
13	3.66	4.9	53.5	21.5	1.64	72	3	4
14	3.1	1.6	67.2	9.5	3.17	88	3	4
15	M	M	M	M	M	12	1	1
16	102.0	30.0	1970.1	25.0	1.56	77	5	M
17	1.9	1.2	53.5	3.4	0.57	29	5	4
18	69.0	29.8	1765.1	35.5	2.73	52	5	4
19	51.8	12.1	1164.5	46.4	1.50	48	2	4
20	6.3	4.9	272.9	8.7	1.45	71	1	3
21	18.9	4.3	407.8	20.6	2.58	88	2	4
22	19.8	3.1	391.5	15.6	1.56	42	3	1
23	69.6	36.2	2031.5	129.2	2.75	M	4	M
24	0.2	0.1	7.7	1.2	1.20	57	3	4
25	5.9	3.2	157.7	M	M	71	2	3

APPENDIX IV (cont'd.)

Date	Event Number	Site	pH	Cond.	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	NH ₄ ⁺	H ⁺	Cl ⁻	SO ₄ ⁼	NO ₃ ⁻
7 & 8 Nov.	26	3	5.28	6.1	0.00	0.01	0.05	0.00	0.05	0.01	0.05	0.15	0.12
N.R. Nov.	27	3	4.43	12.0	0.01	0.01	0.05	0.00	0.08	0.04	0.00	1.22	0.00
22 Nov.	28	3	4.64	23.8	0.00	0.01	0.08	0.01	0.03	0.02	0.03	0.52	0.60
26 & 27 Nov.	29	3	4.99	9.1	0.00	0.03	0.03	0.01	0.37	0.01	0.04	0.46	0.22
N.R. Dec.	30	3	4.27	19.1	0.00	0.01	0.06	0.03	0.29	0.05	0.14	1.90	0.32
09, 10, 11 Dec.	31	3	7	18.7	0.00	0.04	0.02	0.01	0.77	0.10	0.11	1.46	1.10
16 Dec.	32	3	4.80	10.0	0.00	0.00	0.00	0.01	0.03	0.02	0.09	0.73	0.23
02 Aug.	33	4	4.32	20.6	0.03	0.02	0.04	0.02	0.23	0.05	0.00	2.89	1.40
03 Aug.	34	4	4.09	32.5	0.00	0.01	0.04	0.01	0.27	0.08	0.06	4.19	1.50
04 Aug.	35	4	4.44	16.0	0.00	M	0.28	0.05	0.15	0.04	M	0.16	0.00
07, 08 Aug.	36	4	4.80	17.0	0.00	1.77	0.25	0.02	0.54	0.02	0.91	0.71	1.90
08, 09, 10 Dec.	37	4	4.80	7.0	0.06	0.28	0.06	0.00	0.28	0.02	0.00	1.29	0.49
12, 13 Aug.	38	4	4.20	18.0	0.00	0.38	0.14	0.00	0.21	0.06	0.21	2.18	1.30
13, 14 Aug.	39	4	5.10	3.8	0.00	0.18	0.07	0.00	0.02	0.01	0.13	0.16	0.14
15, 16, 17 Aug.	40	4	5.10	7.6	0.00	0.07	0.13	0.00	0.44	0.01	0.59	0.32	0.82
17 Aug. (pm)	41	4	5.00	9.4	0.00	0.04	0.04	0.01	0.02	0.01	M	0.13	0.43
17, 18 Aug.	42	4	5.00	2.7	0.02	0.04	0.14	0.02	0.06	0.01	0.00	0.22	0.30
18, 19 Aug.	43	4	4.70	8.7	0.00	0.06	0.12	0.00	0.02	0.02	0.68	0.03	0.00
24 Aug.	44	4	4.60	10.0	0.03	0.03	0.09	0.01	0.15	0.03	0.00	1.04	0.64
21 Sept.	45	4	4.10	35.0	0.35	0.11	0.36	0.06	0.41	0.08	0.00	0.61	0.00
24, 25 Sept.	46	4	5.20	11.0	0.00	M	0.21	0.01	0.08	0.01	0.94	0.30	0.00
29, 30 Sept.	47	4	4.90	4.9	0.17	0.27	0.14	0.01	0.11	0.01	0.00	0.11	0.00
02 Aug.	48	5	4.21	24.7	0.00	0.00	0.03	0.00	0.25	0.06	0.06	3.16	1.20
10, 11, 12 Aug.	49	5	4.08	31.0	0.00	0.00	0.02	0.00	0.21	0.08	0.03	3.76	1.60
12, 13, 15, 16 Aug.	50	5	4.71	15.4	0.06	0.05	0.10	0.03	0.33	0.02	0.00	1.62	1.20
18, 19 Aug.	51	5	4.77	6.8	0.00	0.01	0.04	0.01	0.04	0.02	0.06	0.70	0.33
24 Aug.	52	5	4.21	28.8	0.26	0.02	0.09	0.05	0.20	0.06	0.00	3.37	1.20
13, 14 Sept.	53	5	4.42	17.1	0.00	0.05	0.17	0.02	0.29	0.04	0.10	0.22	0.10

APPENDIX IV (Cont'd.)

Event Number	SO_4^{2-} (mg m^{-2})	NO_3^- (mg m^{-2})	H^+ ($\mu\text{Eq. m}^{-2}$)	Precipitation Total (mm)	Precipitation Intensity (mm hr^{-1})	Antecedent Precip. (hours)	Weather Type	Trajectory Sector
26	M	M	M	M	M	66	3	4
27	M	M	M	M	M	48	2	3
28	11.1	12.9	992.1	21.5	1.43	68	3	M
29	35.2	17.0	788.2	77.1	4.28	24	2	3
30	M	M	M	M	M	18	2	M
31	27.6	20.8	0.10	18.9	1.65	82	4	4
32	M	M	M	M	M	54	6	2
33	M	M	M	M	M	26	1	2
34	45.3	16.2	877.1	10.8	2.7	12	1	2
35	2.6	0.0	598.5	16.5	3.3	18	1	2
36	0.6	1.5	12.7	0.8	0.27	80	2	1
37	1.8	0.7	22.0	1.4	0.2	18	4	4
38	41.0	24.4	1185.1	18.8	3.76	28	1	2
39	0.2	0.28	8.7	1.1	0.37	54	1	2
40	6.1	15.5	150.0	18.9	1.45	76	1	1
41	1.8	6.1	160.9	14.1	2.82	53	3	4
42	0.8	1.2	38.7	3.9	0.78	75	3	4
43	0.3	0.0	183.4	9.2	1.15	80	3	3
44	11.6	7.1	216.6	11.1	1.23	44	1	2
45	0.4	0.0	47.3	0.6	0.3	48	2	3
46	3.3	0.0	69.3	11.0	1.1	74	2	4
47	2.8	0.0	314.7	25.2	2.1	72	1	1
48	4.4	1.7	86.2	1.4	0.47	26	1	2
49	23.3	9.9	515.2	6.2	0.89	28	2	M
50	69.5	51.6	831.8	43.0	1.79	28	1	1
51	35.0	26.4	841.6	49.6	3.31	80	3	3
52	87.1	31.0	1578.2	25.8	1.84	44	1	2
53	4.4	2.0	752	19.8	2.2	18	1	2
54	0.5	0.4	26.6	M	M	26	2	3

APPENDIX IV (cont'd.)

Date	Event Number	Site	pH	Cond. (mhos.)	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+	H^+	Cl^-	$\text{SO}_4^{=}$	NO_3^-
20 Sept.	54	5	5.27	17.6	0.07	0.06	0.22	0.02	0.02	0.01	0.00	0.11	0.08
09 Oct.	55	6	4.97	10.5	0.00	0.00	0.03	0.02	0.15	0.01	0.26	0.78	0.15
10 Oct.	56	6	6.90	6.9	0.00	0.01	0.04	0.00	0.09	0.01	0.12	0.52	0.31
17,18 Oct.	57	6	5.76	6.5	0.00	0.07	0.05	0.00	0.13	0.00	0.08	0.28	0.09
28,29 Oct.	58	6	4.89	5.1	0.00	0.04	0.04	0.00	0.07	0.01	0.07	0.35	0.32
17,18 Oct.	59	8	5.80	5.7	0.00	0.10	0.12	0.02	0.13	0.00	0.06	0.27	0.21
28,29 Oct.	60	8	4.85	16.5	0.19	0.51	0.42	0.04	0.29	0.01	0.00	1.27	0.46

Key

Site Number: 1 = Cape Broyle
 3 = St. John's (Oxen Pond)
 4 = Grand Lake

5 = Norris Point
 6 = Bishop's Falls
 8 = Godaleich Pond

N = Missing value

NR = No record of precipitation

APPENDIX IV (cont'd.)

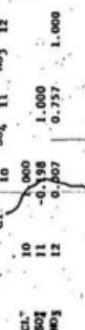
Event Number	S_0 (mgm^{-2})	H_0 ($\mu\text{Fg m}^{-2}$)	Precipitation Total (mm)	Antecedent Precip. (hours) (mm hr $^{-1}$)	Weather Type	Trajectory Sector
55	0.9	0.5	33.2	3.1	0.26	M
56	6.0	3.5	143.4	11.4	1.14	4
57	24.6	8.0	153.7	88.5	2.68	4
58	7.2	6.6	286.4	20.7	1.29	6
59	24.1	18.5	139.3	88.5	2.68	2
60	34.2	13.4	409.2	20.7	1.29	3

Key

- Weather Type: 1 = Labrador/Quebec Low 4 = Maritime Low
 2 = Great Lakes/East Coast Low 5 = Tropical Storms
 3 = Great Lakes Low 6 = Sub-tropical Low

APPENDIX VA
Correlations

	H _T	13	14	BP	15	MET	-16	TS	PW	COND.	3	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	6	Na ₄ ⁺	H ₄	8
H _T	13	1.000																	
H _T	14	-0.454	1.000																
BP	15	-0.229	0.013	1.000															
MET	16	0.381	0.194	0.201	1.000														
TS	17	0.103	0.188	0.060	0.445	1.000													
PW	1	0.360	0.132	0.155	0.395	0.033	1.000												
COND.	2	-0.088	-0.148	-0.195	-0.089	0.078	-0.773	1.000											
Na ⁺	3	-0.095	-0.124	-0.175	-0.094	0.378	-0.426	0.568	1.000										
K ⁺	4	-0.116	-0.167	-0.194	-0.113	-0.082	0.051	0.056	-0.031	1.000									
Ca ⁺⁺	5	-0.095	-0.124	-0.175	-0.113	-0.082	0.051	0.056	-0.031	1.000									
Mg ⁺⁺	6	-0.085	-0.138	-0.117	-0.034	-0.023	-0.159	-0.277	0.281	0.536	1.000								
NH ₄ ⁺	7	-0.035	-0.117	-0.020	0.010	0.043	-0.347	0.360	0.643	0.472	0.351	1.000							
H ⁺	8	0.039	-0.143	-0.259	-0.148	-0.174	-0.290	0.481	0.285	0.353	0.353	0.368	1.000						
Cl ⁻	9	-0.202	-0.107	-0.284	-0.224	-0.106	-0.895	0.467	0.486	-0.063	0.154	0.154	0.160	1.000					
SO ₄ ²⁻	10	-0.175	-0.194	0.307	-0.055	-0.291	0.110	-0.024	-0.337	0.609	-0.184	-0.161	-0.160	-0.160	1.000				
NO ₃ ⁻	11	-0.031	0.310	-0.339	-0.265	0.129	-0.717	0.770	0.371	-0.021	0.353	0.316	0.316	0.316	0.316	1.000			
NO ₂	12	-0.079	0.025	-0.232	-0.235	-0.095	-0.516	0.486	0.106	0.216	0.158	0.247	0.470	0.508	0.470	0.470	0.470	1.000	



APPENDIX VB

Squared multiple correlations of each variable in the first set with all variables in the second set.

Variable	B-regressed	Adjusted R-squared	F Statistic	Degrees of Freedom	p-value
13 RT	0.331690	0.121645	1.53	11	.31
14 TH	0.177750	-0.114615	0.61	11	0.2096
15 DP	0.568399	0.415115	3.71	11	0.6934
16 WT	0.427016	0.223780	2.10	11	0.0095
17 TS	0.424626	0.220662	2.08	11	0.0919
				31	0.0947

First set refers to weather variables, second set to chemistry variables.

APPENDIX VC Correlations

SOD	2	NOD	3	HD	4	RT	5	TN	6	DP	7	TR	8	TS	9
SO ₄ ²⁻	2		1.000												
NO ₃ ⁻	3		0.885		1.000										
H ⁺	4		0.899		0.698		1.000								
RT	5		0.34		0.432		0.356		1.000						
IN	6		0.455		0.515		0.428		0.654		1.000				
DP	7		-0.176		-0.236		-0.120		-0.229		0.013		1.000		
WT	8		0.004		-0.144		-0.025		0.381		0.194		0.201		1.000
TS	9		0.208		0.029		0.228		0.103		0.188		0.060		0.445

APPENDIX VD

Squared multiple correlations of each variable in the second set with all variables in the first set.

Variable	R-squared	Adjusted R-squared	F Statistic	Degrees of Freedom	p-value
5 RT	0.200267	0.138749	3.26	3	.39
6 IN	0.298274	0.244795	5.53	3	.39
7 DP	-0.060573	-0.011691	0.84	3	.39
8 WT	0.159667	0.095026	2.47	3	.39
9 TS	0.159921	0.095299	2.47	3	.39

