A STABLE ISOTOPIC STUDY OF NATURAL AND ANTHROPOGENIC SULPHUR IN PRECIPITATION IN EASTERN CANADA

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by

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ABSTRACT

Event rain samples were collected at three sites in eastern Canada in an attempt to characterize the sources of sulphate in precipitation utilizing the isotopic signatures of sulphur and oxygen. Both continental and marine sites were chosen providing an opportunity to compare these different environments. Sulphur isotopes are useful tools for source tracing because they undergo little fractionation subsequent to emission to the atmosphere. Oxygen isotopes are useful for examining processes of oxidation which occur during transport and deposition of sulphur. A unique feature of this study is the incorporation of trace metal and meteorological data along with isotopic evidence to further aid source identification.

Three sites were chosen for this study representing marine/urban (St. John's, NF), marine/rural (Seal Cove, NF), and continental/rural (Nepean, ON) environments. The sulphur isotopic results at both marine sites are best described by two end-member mixing between a seaspray end-member (+21‰) and a low $\delta^{34}S$ end-member (≈ +5‰). The low $\delta^{34}S$ end-member likely represents a mixture of long-range transported continental and local anthropogenic sources. Oxygen values also reflect a seaspray end-member (+9.5‰) and a continental end-member (+10 to +12‰), however the St. John's data contain a significant ^{18}O-enriched pollution input. Despite its proximity to a thermal generating station, the Seal Cove site is apparently free from a strong local pollution source, but some locally oxidized secondary sulphate is evident from the correlation between $\delta^{18}O_{SO4}$ and

$\delta^{18}O_{H2O}$. The Nepean site has a very different character because of its continental nature. It exhibits a constant isotopic signature with an average $\delta^{34}S$ value of +4.4‰ and an average $\delta^{18}O_{SO4}$ value of +14.7‰. Local oxidation is not important at this site. Since the region is relatively unpolluted, primary sulphates must have been transported from other areas. The average $\delta^{34}S$ value for Nepean is the same as the low $\delta^{34}S$ end-members of St. John's and Seal Cove, suggesting that eastern North America may be the source of the continental/anthropogenic signal seen at the coastal sites.

A significant contribution of this study has been the measurement of extremely high $\delta^{18}O_{SO4}$ values (+42‰) at St. John's; much higher than those measured in other studies. These ^{18}O-enriched sulphates are in samples with elevated metal concentrations (Ni, V, Mo, Co, Cu, Mn) and represent primary sulphates formed by the high temperature processes associated with combustion in the power plant located near the site. Previous researchers predicted that primary sulphates would exhibit extremely high oxygen isotopic compositions, and this work is the first to confirm this in natural rain samples.

This investigation has provided insight on how interaction between long-range transported continental, marine and local sulphur sources defines the character of individual sites. It has also demonstrated how isotopic and chemical data can be successfully combined to give a complete picture of the sources of sulphur affecting a particular.

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INTRODUCTION

1.1 Scope and Objectives

Atmospheric sulphur has been a subject of environmental concern for a number of years now. Its role in acid rain and global warming has generated widespread interest in the study of the sulphur cycle and the processes that govern it. The involvement of sulphur in the acidification of rain with its devastating effects on the environment have caused concern in both the scientific community and the public at large. In 1972, Lovelock *et al.* discovered the sulphur compound dimethyl sulphide (DMS) in the oceanic atmosphere. It has been postulated that one oxidation product of this compound (SO_4) may act as cloud condensation nuclei, which would influence the Earth's albedo in such a way as to counteract CO_2 warming (Charlson *et al.*, 1987).

The objective of the present study is to characterize sources of sulphur to the atmosphere at three sites in eastern Canada using the properties of stable isotopes. Each of these locations represents a different environment with different potential sulphur sources. St. John's, Newfoundland, was chosen as a marine/urban location while Seal Cove, Newfoundland, represents a marine/rural area. These marine sites will be compared with Nepean, Ontario, which was chosen as a continental site. Nepean can be viewed as a principally rural location with an adjacent urban influence. This study will utilize the variations in stable isotopic values to identify and quantify the sources to these environments and to provide a comparison of the sites and the processes that affect sulphur in these environments.

Östlund (1959) made the first isotopic measurements of atmospheric sulphur. Since that time, researchers have explored the advantages of using stable isotopes for the study of the atmospheric sulphur cycle (e.g. Mizutani and Rafter, 1969; Cortecci and Longinelli, 1970; Grey and Jensen, 1972; Nriagu and Coker, 1978a and 1978b; Wakshal and Nielsen, 1982; Nriagu *et al.*, 1991; Wadleigh *et al.*, 1996). Sulphur isotopes have been recognized as a powerful tool for tracing sulphur sources to the atmosphere because each source has a specific isotopic signature, which is not significantly changed during transport through the atmosphere. Sulphur isotopic signatures can therefore be used to determine the relative importance of various sources.

While sulphur isotopes are generally more useful for source studies, oxygen isotopes have gained favour for tracing the atmospheric transformation processes of sulphur compounds. Oxygen isotopes are fractionated during these processes, leading to sulphates with characteristic isotopic signatures. These signatures can be used to examine the oxidation processes and their contributions to the sulphur cycle.

A unique feature of this study is the incorporation of trace metal and meteorological data along with stable isotopes. This type of data has often been used independently for the study of pollution sources, but it has not yet been combined with the information provided by stable isotopes.

1.2 Background

1.2.1 Sulphur

Sulphur is an important element in nature. It occurs in a number of valence states ranging from sulphate (+6) to sulphide (-2). It is present in a wide range of environments and is also important biologically. This behaviour makes sulphur a good candidate for tracing natural processes. Sulphur has four stable isotopes (^{32}S,^{33}S,^{34}S,^{36}S) with natural abundances of 95.02%, 0.75%, 4.21%, 0.02% respectively.

Natural processes lead to the fractionation or segregation of light and heavy isotopes between reservoirs, which gives these reservoirs different isotopic signatures.

The usual way of expressing sulphur isotopic values is the delta notation:

$$\delta^{34}S = \left[\frac{R_{Sample}}{R_{Standard}} - 1\right] x\ 10^3$$

where R represents the ratio of the minor isotope to the major isotope (i.e. $^{34}S/^{32}S$) for the sample and standard respectively. This is expressed in units of parts per thousand or permil (‰). The isotopic reference for sulphur is Canyon Diablo troilite (CDT), which is an iron sulphide from the Canyon Diablo meteorite and is thought to represent a primordial value with a $^{34}S/^{32}S$ of 1/22.22 (Hoefs, 1987).

Sulphur isotopic compositions in nature have been found to vary between -65‰ and +90‰, although most samples lie between -40 and +40‰, as illustrated in Figure 1.1 (Nielson, 1979; Hoefs, 1987). This range is the result of various organic and inorganic fractionation processes which will be discussed below.

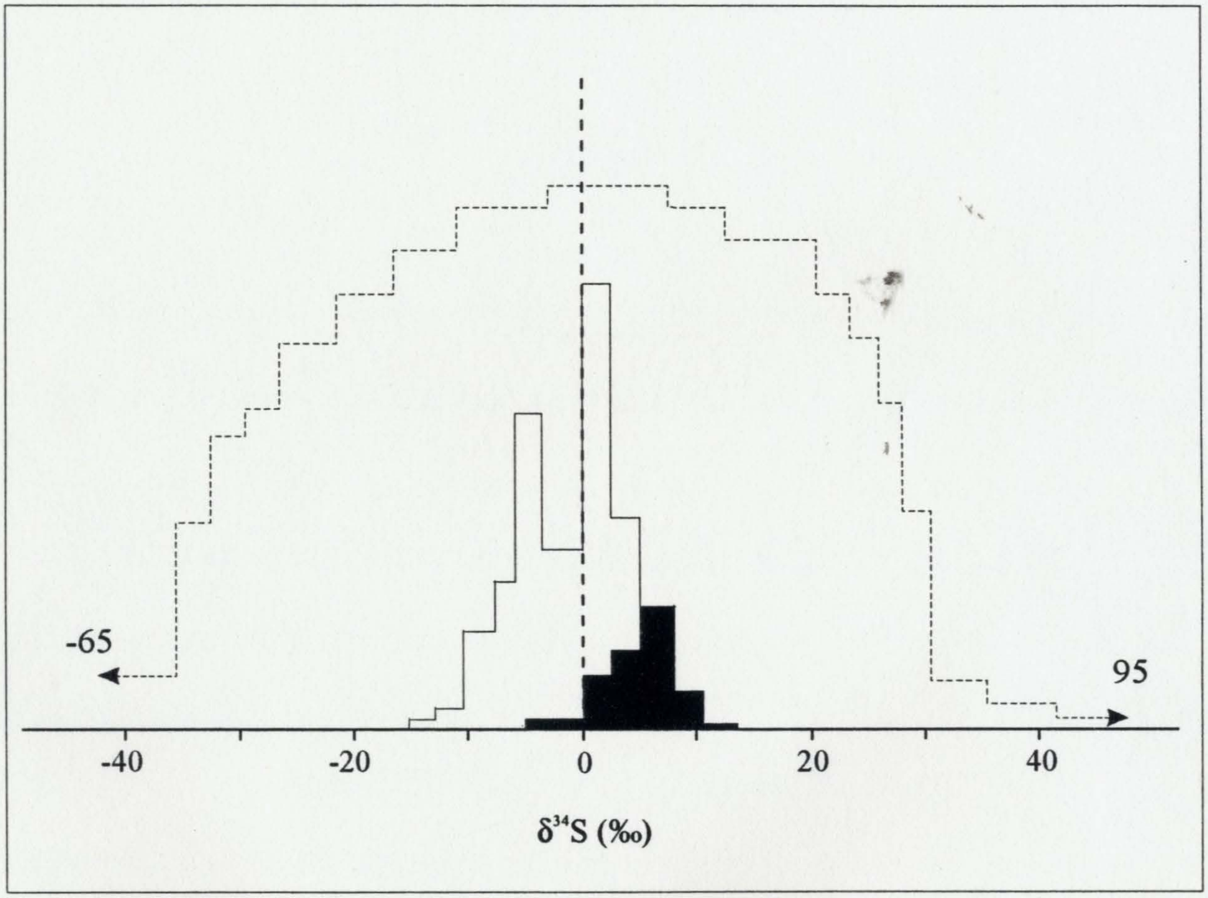

Figure 1.1 Histogram comparing the $\delta^{34}S$ distribution of volcanic sulphur (shaded area represents samples from Santorini volcano) with other terrestrial sulphur (dotted line) (Nielsen, 1974).

1.2.1.1 Fractionation Mechanisms

Isotopic fractionation occurs because of the mass differences between isotopes. Heavier isotopes have lower zero-point energies which means that they tend to be bonded more strongly, and thus react less readily, than light isotopes (Hoefs, 1987). Fractionation is represented by the symbol alpha (α) which can be written as:

$$\alpha_{A\text{-}B} = \frac{R_A}{R_B}$$

where R_A and R_B are the ratios of isotopes (e.g. $^{34}S/^{32}S$) in substances A and B respectively. Fractionation processes can result from equilibrium isotope effects or kinetic isotope effects.

Equilibrium isotope effects involve the exchange of isotopes between substances, phases, or molecules in a system at chemical equilibrium. An example is the exchange between H_2S and SO_2 which can be written as:

$$H_2{}^{34}S \quad + \quad {}^{32}SO_2 \quad \longleftrightarrow \quad H_2{}^{32}S \quad + \quad {}^{34}SO_2$$

Equilibrium constants can be utilized to quantify the fractionation associated with these reactions as:

$$K = \frac{({}^{34}S/{}^{32}S)_{SO2}}{({}^{34}S/{}^{32}S)_{H2S}}$$

which is equivalent to $\alpha_{SO2\text{-}H2S}$. These calculations are only valid if isotopic equilibrium is actually attained (Thode, 1991).

Kinetic isotope effects occur during fast, incomplete or unidirectional reactions. Since lighter isotopes react more quickly, these reactions tend to give products depleted in the heavy isotopes (Hoefs, 1987). Fractionation factors for kinetic reactions can be calculated from reaction rate constants. An example is the reduction of sulphate to hydrogen sulphide which can be represented by two reactions:

$$^{32}SO_4 \longrightarrow H_2{}^{32}S \qquad k_1$$

$$^{34}SO_4 \longrightarrow H_2{}^{34}S \qquad k_2$$

where k_1 and k_2 are rate constants. The fractionation factor will be equal to the ratio of the rate constants (k_1/k_2).

The most important factor affecting fractionation is temperature. With increasing temperature the difference in reactivity between the isotopes is reduced and the amount of fractionation decreases. Other influencing factors include the availability of reactants and whether the system is open or closed. As well, reactions can involve many steps and intermediate species and may involve both equilibrium and kinetic effects. This makes the calculation of expected fractionations much more complicated and dependent on the system being considered.

Inorganic processes may lead to fractionations of 25‰ (Nielson, 1974), but the actual range of $\delta^{34}S$ values found in nature is much greater (Figure 1.1). Inorganic fractionation of sulphur isotopes is inhibited by slow reaction rates at temperatures below 100°C (Nielson, 1974; Hoefs, 1987). It has therefore become evident that biologically mediated reactions are the most important agents of sulphur fractionation under normal surface conditions. Organisms catalyze these reactions, allowing them to proceed under normal surface conditions, which leads to the wide range of $\delta^{34}S$ values found in nature (Thode, 1949; Ault and Kulp, 1959; Nielson, 1974). Detailed discussions of fractionation mechanisms can be found in a number of sources including Hoefs (1987), Valley *et al.* (1986), and Kyser (1987).

1.2.2 Atmospheric Sulphur

Sulphur exists in many different forms in the atmosphere including hydrogen sulphide (H_2S), carbonyl sulphide (COS), dimethyl sulphide (DMS; CH_3SCH_3), sulphite (SO_3^{2-}), sulphur dioxide (SO_2), and sulphate (SO_4^{2-}) (Newman *et al.*, 1991). The more reduced sulphur compounds are ultimately oxidized to SO_2 and eventually to SO_4. Table 1.1 lists the atmospheric residence times for some of these sulphur compounds.

Figure 1.2 is an illustration of the atmospheric sulphur cycle as proposed by Brimblecombe *et al.* (1989). A number of authors have put forward their own estimations of these fluxes, but since only limited measurements have been carried out on a global scale, uncertainties still exist regarding the complicated processes governing this cycle (e.g. Kellogg *et al.*, 1972; Friend, 1973; Ryaboshapko, 1983; Möller, 1984; Berner and Berner, 1987; Bates *et al.*, 1992).

1.2.2.1 Sources

Sulphur contributions come from two broadly divided regions of oceanic and continental sources. In general, it is possible to differentiate these source regions based

Table 1.1 Residence times (τ) and transport distances for different sulphur compounds in the atmosphere (Brimblecombe *et al.*, 1989).

	Planetary boundary layer		Free troposphere		
	τ (days)	transport distance (10^3 km)	τ (days)	transport longitudinal (10^3 km)	distance latitudinal (10^3 km)
H_2S	1	0.5	2	4	1
DMS	<0.5	<0.2	<1	<2	<0.5
COS	500	global	500	global	global
CS_2	10	5	20	global	5
SO_2	1	0.5	10	synoptic	3
SO_4^{2-}	4	2	15	global	4

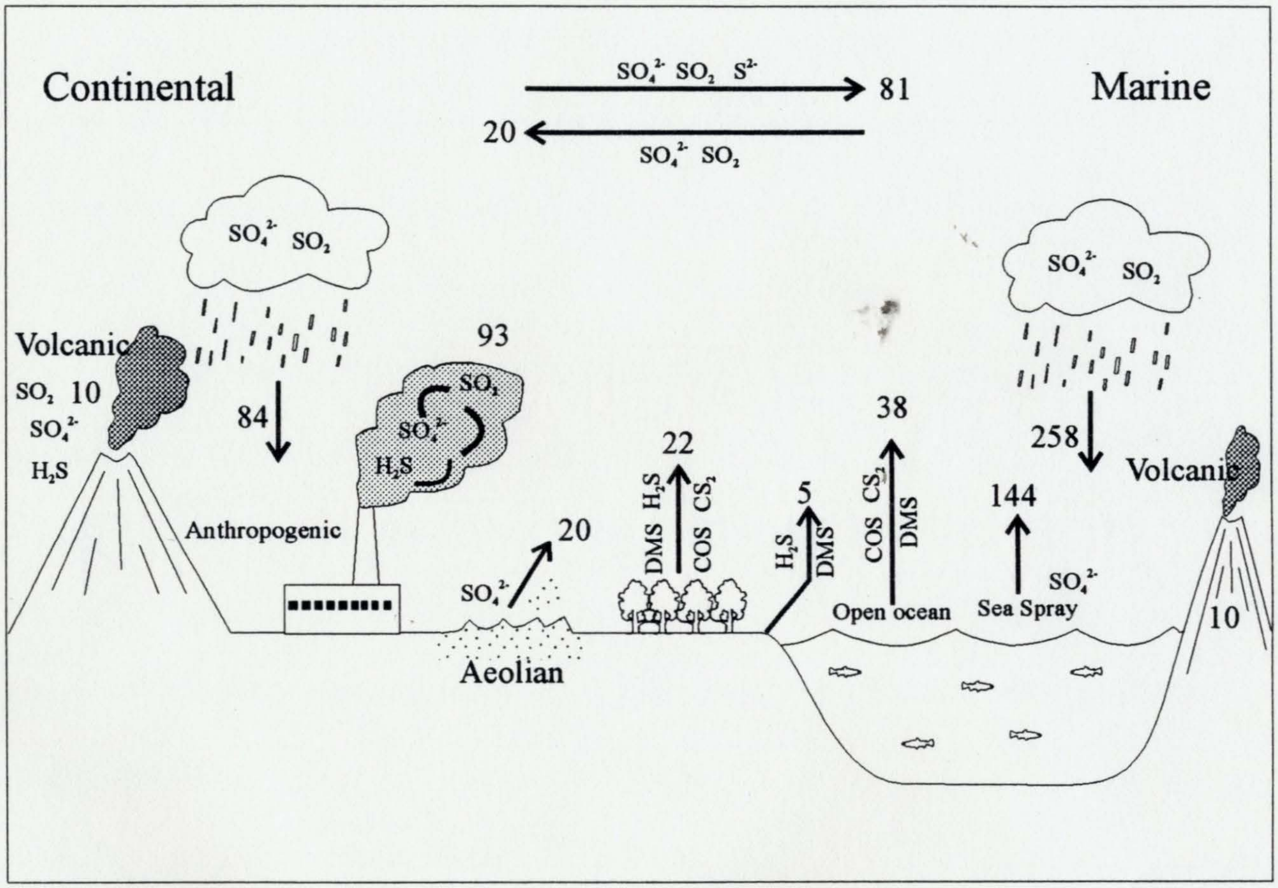

Figure 1.2 Atmospheric sulphur cycle (after Brimblecombe *et al.*, 1989). All fluxes in Tg (S) a^{-1}

upon their isotopic signatures. Figure 1.3 illustrates the ranges of $\delta^{34}S$ values found for some important atmospheric sulphur sources.

1.2.2.1.1 Oceanic

The major sources of sulphur to the marine atmosphere are seaspray and biogenic emissions. These provide sulphate and reduced sulphur compounds to the oceanic atmosphere. Andreae *et al.* (1983), Andreae (1985 and 1986), Berresheim (1987), and Toon *et al.* (1987) provide reviews of the marine sulphur cycle.

Seaspray particles are formed when air bubbles from breaking waves burst, forming droplets that are thrown up into the atmosphere. The water evaporates leaving seasalt particles that are generally 2 to 20 µm in size (Berner and Berner, 1987; Andreae, 1986). Seawater sulphate has a fairly well known and constant isotopic value of +21‰ (Rees *et al.*, 1978). Little fractionation is thought to occur during the formation process, and therefore the seasalt particles should maintain the isotopic signature of their seawater source (Luecke and Nielsen, 1972). Most of this seaspray is deposited back to the ocean, but approximately 10% is transported to the continents where it is generally deposited along the coast, with little penetrating into the continents (Andreae, 1986).

There are two main biological methods of producing volatile reduced sulphur compounds: assimilatory and dissimilatory sulphate reduction. Volatile sulphur compounds produced by these processes are released to the atmosphere as by-products by living cells or through the decomposition of organic matter (Andreae, 1985). Assimilatory

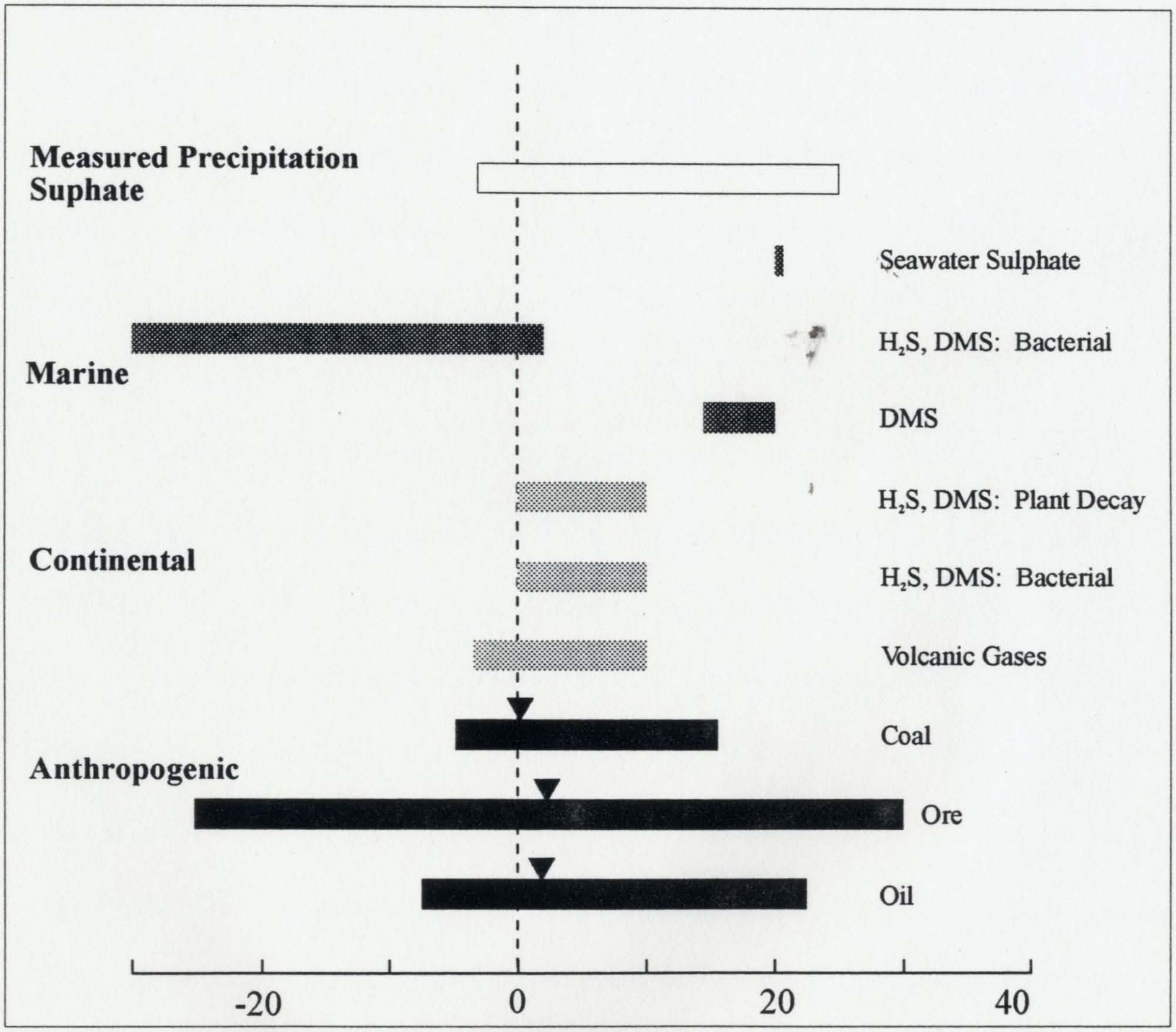

Figure 1.3 $\delta^{34}S$ values of various atmospheric sulphur sources. (Some values from Nielsen (1974) and Newman *et al.* (1991)).

sulphate reduction involves the synthesis of organosulphur compounds which organisms require for the production of proteins essential to life (Andreae, 1986). While animals and protozoans must acquire these from food sources, bacteria and plants have the ability to take in sulphate and reduce it to form these compounds (Andreae, 1986). The isotopic fractionation associated with this process is expected to be small since there is little fractionation during the uptake of sulphate by organisms (Kaplan and Rittenberg, 1964; Mekhtiyeva and Pankina, 1968). As an example, Kaplan and Rittenberg (1964) found fractionations of -0.9 to -2.8‰ during the uptake of sulphate by three different types bacteria.

The main source of reduced sulphur over the open ocean is the production of dimethyl sulphide (DMS) during assimilatory sulphate reduction by phytoplankton (Andreae *et al.*, 1983; Andreae, 1986). The isotopic composition of DMS has not been measured directly, but should be equal to the sum of the fractionations accompanying its formation and subsequent emission to the atmosphere. Since little fractionation accompanies the assimilation of sulphate by organisms, and fractionation is not expected to occur during the transfer between seawater and the atmosphere (Calhoun and Bates, 1989), the isotopic value for DMS should not be very different from seawater sulphate. Calhoun *et al.* (1991) measured the isotopic composition of the excess sulphate in aerosols, over the remote south Pacific ocean, which they believed represented sulphate produced by DMS oxidation, and they reported a value of +15.6 ± 3.1‰.

Dissimilatory sulphate reduction becomes the dominant source of atmospheric sulphur in coastal areas where the main product is H_2S. This process is utilized by microbial organisms in anoxic environments as a means of obtaining energy, and therefore it is generally found in areas where restricted circulation/mixing conditions exist (Andreae, 1985). Although this process is globally responsible for the production of large amounts of H_2S (70 Tg S/yr) (1 Tg = 10^9 kg), little actually escapes to the atmosphere (5 Tg S/yr) because H_2S is readily oxidized in the presence of oxygen (Andreae, 1985; Brimblecombe *et al.*, 1989). Sulphide oxidizing bacteria thrive at the anoxic/oxic interface where they are very efficient at oxidizing the H_2S. Isotopically this process produces much larger fractionations than assimilatory reduction. The steps in the process can be represented as:

$$\underset{\text{external}}{SO_4^{2-}} \xleftrightarrow{1} \underset{\text{internal}}{SO_4^{2-}} \xleftrightarrow{2} \text{APS} \xleftrightarrow{3} SO_3^{2-} \xrightarrow{4} S^{2-}$$

where APS stands for Adenosine-5'-phosphosulphate (Thode, 1991). A number of laboratory studies have attempted to measure the fractionation associated with dissimilatory sulphate reduction (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Nakai and Jensen, 1964). A number of factors were found to influence the amount of fractionation, but the main factor appears to be the rate of reduction. Temperature has an indirect effect because it affects the rate of reduction (Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979). Sulphate concentration has little effect except when it is very low. In general, the magnitude of fractionation varies inversely with the reduction rate.

Fractionation effects from +3 to -46‰ have been observed, but larger values are seen in nature (Chambers and Trudinger, 1979; Thode, 1991). For example, a value of -62‰ was measured by Kaplan *et al.* (1963) in pyrite from sediments off California. This implies a very large fractionation from seawater. The overall fractionation will be the sum of the fractionations associated with each step in the process. Some of the steps (1, 2 and 3) are reversible and this allows further fractionation. The specific conditions of a system will determine the rates of the different steps and the overall fractionation. In general, steps one and two are thought to result in only a few permil fractionation, while steps three and four result in much larger fractionations of up to -25‰ (Thode, 1991). There is still some uncertainty in these values though, and the fact that these mechanisms operate in restricted environments can add a further complication to this picture. In this type of environment, closed system conditions may be approached and the reduction of sulphate gives a progressively heavier sulphate source and sulphide product. If all the sulphate is eventually reduced, the sulphide should have the same isotopic composition as the original sulphate. Chambers and Trudinger (1979) review the processes of bacterial reduction, the isotopic fractionations involved, and the environmental factors that may affect them.

In the study of a salt marsh environment by Hitchcock and Black (1984) $\delta^{34}S$ values ranging from -9.44 to +2.10‰ were measured for atmospheric non-seaspray sulphate, believed to be primarily a result of H_2S oxidation. This is consistent with the isotopically light values expected for this source.

1.2.2.1.2 Continental

Continental sources of sulphate include biogenic, volcanic, and aeolian emissions as well as anthropogenic emissions. Discussions of these sources can be found in Andreae (1985) and Berner and Berner (1987).

Biogenic sources include emissions from soils and vegetation in many different environments. These emissions involve similar biogenic reduction processes as marine sources. Unlike the marine environment though, continental sulphate sources are more likely to vary in their isotopic composition as well as their availability. This leads to greater variability in the sulphur products. Nielson (1974) has speculated that the $\delta^{34}S$ of continental sulphate could be taken as being close to 0‰ because the sulphate available to continental organisms will often come from dissolved rock constituents and could be expected to be fairly homogenized.

Measurements made by Nriagu *et al.* (1987) in remote Canada suggest that continental biogenic emissions have an $\delta^{34}S$ of approximately -2.4‰. They also found that there was a seasonal variation in the $\delta^{34}S$ of atmospheric sulphate of approximately 2‰ with lighter values found in the summer. They believed this resulted from increased input of depleted biogenic sulphur during the summer. Caron *et al.* (1986) also found a seasonal variation in atmospheric sulphates measured in Quebec, but they concluded that change in temperature was the controlling factor.

Volcanic emissions are thought to account for approximately 6% of total sulphur emissions (Brimblecombe *et al.*, 1989). Gases emitted include SO_2, H_2S, COS, and CS_2, although SO_2 is generally dominant. Particulate sulphate is also emitted, although some of this may result from SO_2 oxidation within the volcanic plume (Andreae, 1985). These emissions are episodic in nature, although volcanoes emit gases continuously between eruptions. During violent eruptions, sulphur can be injected into the stratosphere (Bates *et al.*, 1992).

The $\delta^{34}S$ of volcanic emissions will generally cluster around 0‰, but can vary by as much as 15‰. Nielson *et al.* (1991) has given an estimate of approximately +5‰ for total volcanic sulphur although individual sulphur compounds can vary. A fairly uniform value of +2.6 ± 0.3‰ was found by Castleman *et al.* (1974) for stratospheric sulphur between eruptions, but after violent eruptions the values fluctuated between +16‰ and -24‰.

Other more localized sources of atmospheric sulphur include aeolian dust and biomass burning (Berner and Berner, 1987). Aeolian dust is generally in the form of $CaSO_4$ and is really only important in arid areas and these compounds are often insoluble. These sources would be expected to reflect the composition of the source rock and would generally be enriched.

Anthropogenic sources have become as important as natural sources to the global sulphur cycle. Brimblecombe *et al.* (1989) have estimated a flux of 93 Tg S/yr for anthropogenic SO_2 and SO_4. A global anthropogenic contribution of 76% was estimated by Bates *et al.* (1992) while the northern hemisphere was responsible for 90% of all anthropogenic emissions. These emissions result from activities such as fossil fuel combustion, ferrous and non-ferrous ore smelting, oil refining, sulphuric acid production, and minor inputs from transportation and biomass burning (Ryaboshapko, 1983; Berner and Berner, 1987). The relative importance of these sources is given in Table 1.2. Most of these emissions are in the form of SO_2, which is ultimately oxidized to SO_4.

The burning of fossil fuels is the largest anthropogenic source of sulphur to the atmosphere (Ryaboshapko, 1983). Coal and oil, which form from organic matter, can have a wide range of $\delta^{34}S$ compositions and therefore, so can the atmospheric emissions that result from their combustion. Coal contains sulphur mainly in the form of pyrite inclusions while oil and gas contain sulphur bearing organic compounds as well as H_2S.

Coal exhibits a considerable variation in $\delta^{34}S$, even within one deposit (Nielson *et al.*, 1991). In general, the $\delta^{34}S$ for coal has been found to range between -30 and +30‰. Oil and gas on the other hand, tend to have very uniform $\delta^{34}S$ values within reservoirs or provinces of the same age although between oil fields there can be a large range from -5.2 to +28.2‰ (Nielson *et al.*, 1991).

A study of the isotopic composition of fuels used in power plants in the northeast United States was carried out by Krouse *et al.* (1991). An average $\delta^{34}S$ value of +5‰ was found for fuel oil combustion, with a range of -1 to +9‰. The variations for coal combustion were much greater and it is difficult to give an average value, but variations as high as 6‰ were found from day to day. Over longer periods the variation of two oil burning plants was found to be 3‰ while for a coal burning plant it was 9‰.

Ore deposits form by many different processes in different environments and therefore the smelting of ores can lead to SO_2 with large variations in $\delta^{34}S$. Nielson *et al.*

Table 1.2 Relative importance of anthropogenic sources (from Berner and Berner, 1987).

Source	**Tg S/yr**	**Percent of Total**
Coal burning	45.4	70
Oil burning	5.5	8
Industrial (smelting and oil refining)	13.6	21
Transportation	0.4	1
Total	64.9	100

(1991) have given an average value of +3.4‰ for sulphide ore bodies, but a large range of -25 to +25‰ can be found (Newman *et al.*, 1991).

Sulphur dioxide from most of these anthropogenic sources are depleted in ^{34}S, however sulphur from sour gas processing exhibits much higher $\delta^{34}S$ values of approximately +20‰ (e.g. Krouse, 1980).

Anthropogenic contributions vary over time and from place to place for reasons such as energy demand fluctuations. Assessing these contributions will depend on the particular circumstances in the area being studied.

1.2.2.2 Atmospheric Transformations

The expected isotopic compositions of the various atmospheric sulphur sources have been discussed, but it is important to establish how these isotopic signatures are affected by atmospheric transformation processes. Most reduced sulphur compounds emitted to the atmosphere have relatively short residence times (Table 1.1). They are quickly oxidized to SO_2 and eventually most of this is oxidized to SO_4. The mechanisms of oxidation of reduced sulphur compounds have been studied quite extensively, but still many uncertainties exist about the exact paths and products.

The oxidation of DMS is believed to yield a number of products including SO_2, methane sulphonic acid (MSA), dimethyl sulfoxide (DMSO), and dimethyl sulfone ($DMSO_2$), although SO_2 and MSA are believed to be the main products (Saltzman *et al.*, 1983b). A recent study by Barnes *et al.* (1994) has indicated that carbonyl sulphide (COS) may also be a product of DMS oxidation. The dominant mechanism for DMS oxidation is believed to be reaction with the OH radical (Hynes and Wine, 1989; Plane, 1989). At night, however, as concentrations of OH drop, reaction with NO_3 is expected to dominate. A study by Barnes *et al.* (as cited by Plane (1989)) reported a production of 70% SO_2 from DMS oxidation by OH, however the relative proportions of SO_2 and MSA may be temperature dependent (Plane, 1989). MSA may also react with OH to produce additional SO_4^{2-} (Saltzman *et al.*, 1983b).

H_2S oxidation is also thought to be dominated by reaction with OH. The reaction can be written as:

$$OH + H_2S \rightarrow H_2O + HS$$

Little fractionation is expected to accompany these reactions and therefore the sulphate produced by the oxidation of reduced sulphur compounds should generally reflect the isotopic composition of the source (Newman *et al.*, 1991). As discussed above, Calhoun *et al.* (1991) found that NSS sulphate, thought to be formed by DMS oxidation had $\delta^{34}S$ values consistent with a fractionation of approximately 5‰ from seawater sulphate.

Sulphur dioxide can be oxidized by gas-phase (homogeneous) or aqueous-phase (heterogeneous) processes. Homogeneous oxidation involves the oxidation of SO_2 in the gas phase and subsequent dissolution (oxidation-hydrolysis), but during heterogeneous oxidation, the SO_2 is first dissolved and then oxidized (hydrolysis-oxidation). The reactions involved in these two pathways can be summarized as follows:

Heterogeneous oxidation:

$$SO_{2\,(g)} + H_2O_{(l,\,g)} \longrightarrow SO_2{\cdot}H_2O \tag{1}$$

$$SO_2{\cdot}H_2O \longrightarrow HSO_3^-{}_{(aq)} + H^+ \tag{2}$$

$$HSO_3^-{}_{(aq)} \longrightarrow HSO_4^-{}_{(aq)} \tag{3}$$

Homogeneous oxidation:

$$SO_{2\,(g)} + OH \longrightarrow HOSO_2 \tag{4}$$

$$HOSO_2 + O_2 \longrightarrow SO_{3\,(g)} + HO_2 \tag{5}$$

$$SO_{3\,(g)} + H_2O \longrightarrow H_2SO_{4\,(l)} \tag{6}$$

A kinetic isotope fractionation is associated with each of these processes during the oxidation of HSO_3^- (steps 3 and 6). Saltzman *et al.* (1983a) measured an $\alpha_{SO4\text{-}SO2}$ value for this process of 0.996 showing that the sulphate is depleted in ^{34}S with respect to the initial SO_2.

The heterogeneous oxidation pathway involves an equilibrium fractionation as well. The dissociation of $SO_2{\cdot}H_2O$ to HSO_3^- and H^+ (step 2) results in a large equilibrium fractionation ($\alpha_{HSO3\text{-}SO2}$= 1.0165 at 25°C) which enriches the HSO_3^- (Saltzman *et al.*, 1983a). This, combined with the smaller depletion of the kinetic fractionation step, leaves the resultant SO_4^{2-} heavier than the initial SO_2. Homogeneous oxidation, which involves only the kinetic fractionation, should result in SO_4^{2-} that is lighter than the initial SO_2.

This difference in isotopic signature should allow the use of sulphur isotopes to determine the relative contributions of the homogeneous and heterogeneous pathways. Saltzman *et al.* (1983a) measured the $\delta^{34}S$ of SO_2 and aerosol sulphates at the Hubbard Brook Experimental Forest in New Hampshire, U.S. The values of $\delta^{34}S_{SO4}$ were intermediate between the expected compositions for homogeneous and heterogeneous oxidation and therefore they concluded that both mechanisms were operative. However, they found that homogeneous processes were dominant, although heterogeneous gained in importance during the winter. Overall, oxidation decreased during the cooler winter months.

A number of authors have studied the oxidation mechanisms in the plumes of power plants utilizing these properties of sulphur isotopes (Newman *et al.*, 1975; Forrest and Newman, 1977a and 1977b; Newman, 1981). The $\delta^{34}S$ values of SO_2 in these plumes has been found to decrease with increasing distance from the source plant as oxidation occurs. It was believed that heterogeneous oxidation processes were operative in these cases, however it is likely that both processes are operative (Newman, 1981).

1.2.3 Source Tracing Using Sulphur Isotopes

A number of studies have been discussed in which isotopes have been successfully employed to determine source contributions and to elucidate atmospheric processes. Table 1.3 summarizes data from a number of these studies to illustrate the range of measured values for atmospheric sulphate, which is approximately -2.5 to +22‰.

In the perfect scenario, a study area would only be affected by two or three sources with well known, and widely separated, isotopic compositions. The study by Grey and Jensen (1972) was a fortunate case where circumstances allowed the comparison of pollutant vs. non-pollutant sulphur in the same area. They were studying the $\delta^{34}S$ of

Table 1.3 $\delta^{34}S$ values for sulphate in precipitation.

Region	Range	Mean	Reference	Comments
Shelburne, Nova Scotia	+2.0 - +16.2‰	+8.3‰	Wadleigh *et al.*(1996)	event samples higher winter values higher summer values for NSS sulphate
Sudbury, Ontario	+2.0 - +6.8‰	+4.7‰	Nriagu and Coker (1978a)	bulk precipitation samples higher winter values (2-3‰)
Great Lakes Basin				
urban	+3 - +9.3‰	+6.0‰	Nriagu and Coker (1978b)	bulk deposition samples
rural & remote	+1.9 - +8.2‰	+4‰		higher winter values (4‰)
northern Ontario				
summer	+1.9 - +3.4‰		Nriagu *et al.*(1987)	weekly bulk precipitation samples
winter	+4.5 - +5.3‰			seasonal difference of 2.4‰
Quebec	+3.1 - +6.7‰	+5‰	Caron *et al.*(1986)	bulk deposition samples higher values in winter
Ontario				
Plastic Lake	+2.9 - +5.0‰	-	Van Stempvoort *et al.*(1991)	
Paris	+7.1	-		
Alberta				
urban	+8.4 - +20.4‰	+15.4‰	Norman (1991)	event samples
rural Crossfield	+10.5 - +22.4‰	+16.1‰		
Fortress Mountain	+5.5 - +10.5‰	+7.8‰		
Bermuda	+6.1 - +19.1‰	+14.7‰		
Chicago	+3 - +8‰	+5‰	Holt *et al.* (1972)	event samples

Table 1.3 (Cont.) $\delta^{34}S$ values for sulphate in precipitation.

Region	Range	Mean	Reference	Comments
Salt Lake City, Utah				
polluted	-1.5 - +5.3‰	+2.2‰	Grey and Jensen (1972)	
unpolluted	+4.7 - +6.5‰	+6.0‰		
Pisa, Italy	-2.5 - +7.1‰	+1.1‰	Cortecci and Longinelli (1970)	event samples
Venice, Italy	-0.2 - +8.3‰	+3.0‰	Longinelli and Bartelloni (1978)	12 hr precipitation samples
Sweden	+3.2 - +8.2‰	+5.9‰	Östlund (1959)	event samples
Sweden	+3.9 - +6.4‰	+4.6‰	Andersson *et al.*(1992)	bulk samples
Israel				
coastal	+5.3 - +14.3‰	+9.5‰	Wakshal and Nielson (1982)	
inland	+4.5 - +5.9‰	+5.3‰		
Israel	0.0 - +15.3‰	+6.5‰	Herut *et al.*(1995)	decreasing values away from coast
Japan				
industrial	+3.2 - +7.3‰	+6.0‰	Jensen and Nakai (1961)	event samples
non-industrial	+12.3 - +15.6‰	+14.1‰		
Gracefield, New Zealand	-1.5 - 19.4‰	+10.9‰	Mizutani and Rafter (1969)	event samples
New Zealand				
inland (geothermal)	+6.6 - +10.1‰	+8.5‰	Spedding and Cope (1984)	
coastal	+15.9 - +17.2‰	+16.3‰		

atmospheric sulphur in Salt Lake City, Utah. During their study, the local copper smelter was shut down by a strike, and there was a marked drop in $\delta^{34}S$ from an average of +6‰ before the strike to +2.2‰ afterwards (Figure 1.4).

Krouse (1980) discusses the use of mixing models to represent various potential source situations. These types of models are useful, but will not always apply depending on the particular situation in the area being studied. When an area has many sources with overlapping sulphur isotopic signatures, differentiating between them may be impossible. This is generally why localized studies are much more useful than regional or global studies.

Although complications arise, some generalizations about source regions can be made. It can be seen that oceanic areas will, in general, be heavier than continental areas. This feature can be useful, especially in coastal areas where the effects of both should be seen. Studies in coastal regions have found linear mixing trends representing mixing between the seaspray source (+21‰) and a low $\delta^{34}S$ source (Mizutani and Rafter, 1969; Cortecci and Longinelli, 1970; Wadleigh *et al.*, 1994 and 1996; Wakshal and Nielsen, 1982; Herut *et al.*, 1995; McArdle and Liss, 1995). The low $\delta^{34}S$ source is often interpreted as a continental or anthropogenic end-member.

The incorporation of other types of data may also prove helpful, especially for the discrimination of anthropogenic and natural sources. In this study, oxygen isotopes as well as chemical data will be utilized in addition to sulphur isotopes.

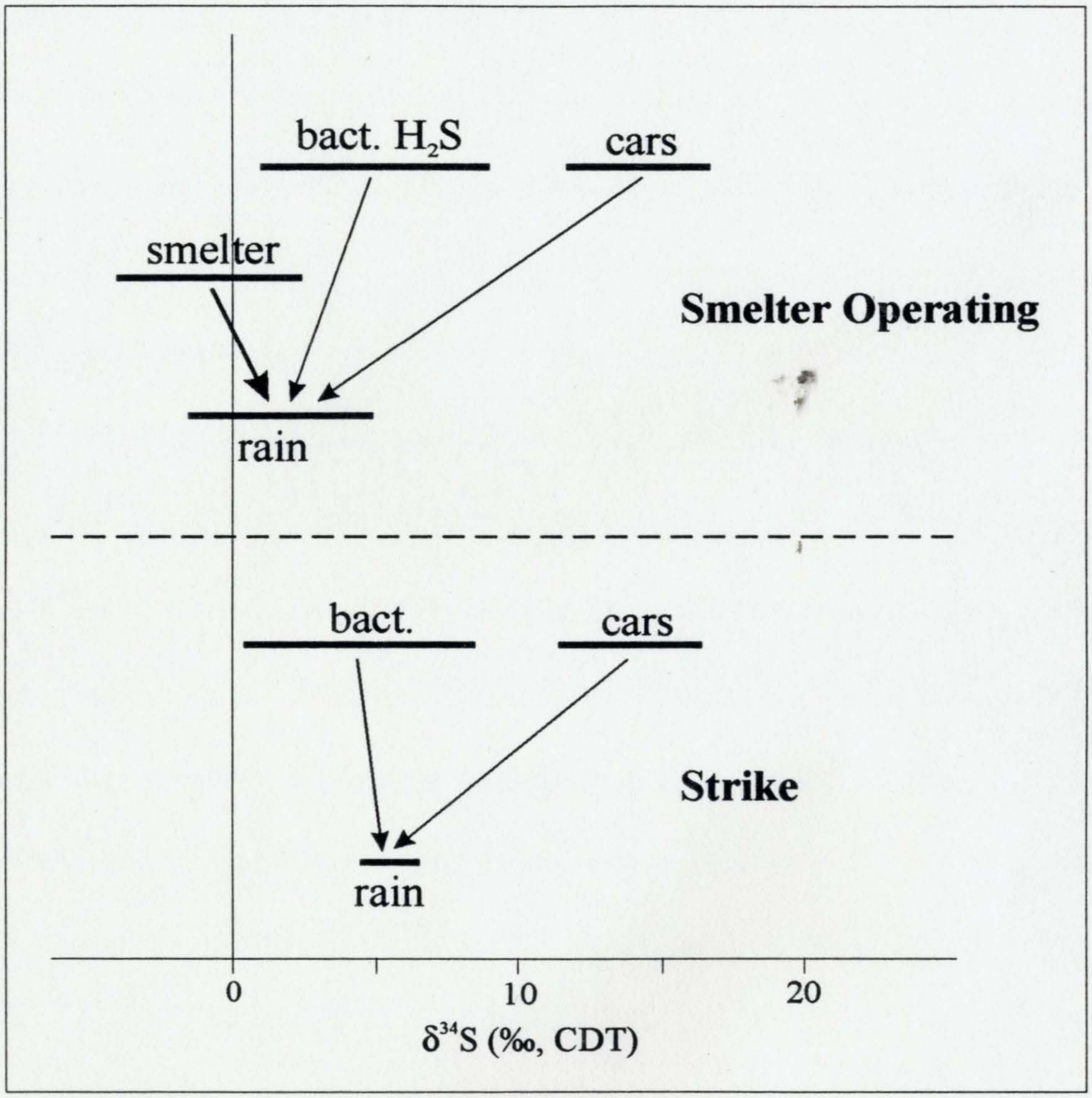

Figure 1.4 Results of the study by Grey and Jensen (1972) of the $\delta^{34}S$ for rainwater sulphate in Salt Lake City, Utah (figure after Nielsen, 1974).

1.3 Oxygen Isotopes

Although sulphur isotopes have been used to study transformations of atmospheric sulphur compounds, oxygen isotopes have proved most valuable for this type of study. Oxidation causes only small fractionations in sulphur isotopes, but it causes much larger changes in the oxygen isotopic values. Sulphur isotope studies may also be complicated by source variations, but the $\delta^{18}O$ of sulphate is completely determined by the process of oxidation and therefore oxygen isotopes may be used to gain insight into these processes.

Oxygen isotopic values are also reported in the standard delta notation (see Section 1.2.1) as $\delta^{18}O$ where R represents the ($^{18}O/^{16}O$) ratios of the sample and standard. Oxygen isotopes are measured with respect to Vienna Standard Mean Ocean Water (VSMOW). Figure 1.5 illustrates oxygen isotopic compositions relevant to atmospheric studies. A number of researchers have measured the $\delta^{18}O$ of precipitation sulphates and these results are summarized in Table 1.4. A range of values from +3 to +26‰ have been measured.

There are several features that make oxygen isotopes very useful for tracing the transformations of sulphur in the atmosphere. Rapid equilibration occurs between SO_2 and associated water (liquid or vapour) and therefore the SO_2 retains none of its initial oxygen isotopic signature. During oxidation, the isotopic composition will be determined by the particular pathway (homogeneous or heterogeneous) utilized. Since the oxidants involved in these different pathways have quite different isotopic compositions, they will produce sulphate of different $\delta^{18}O$ compositions. Once formed, the sulphate will retain the isotopic

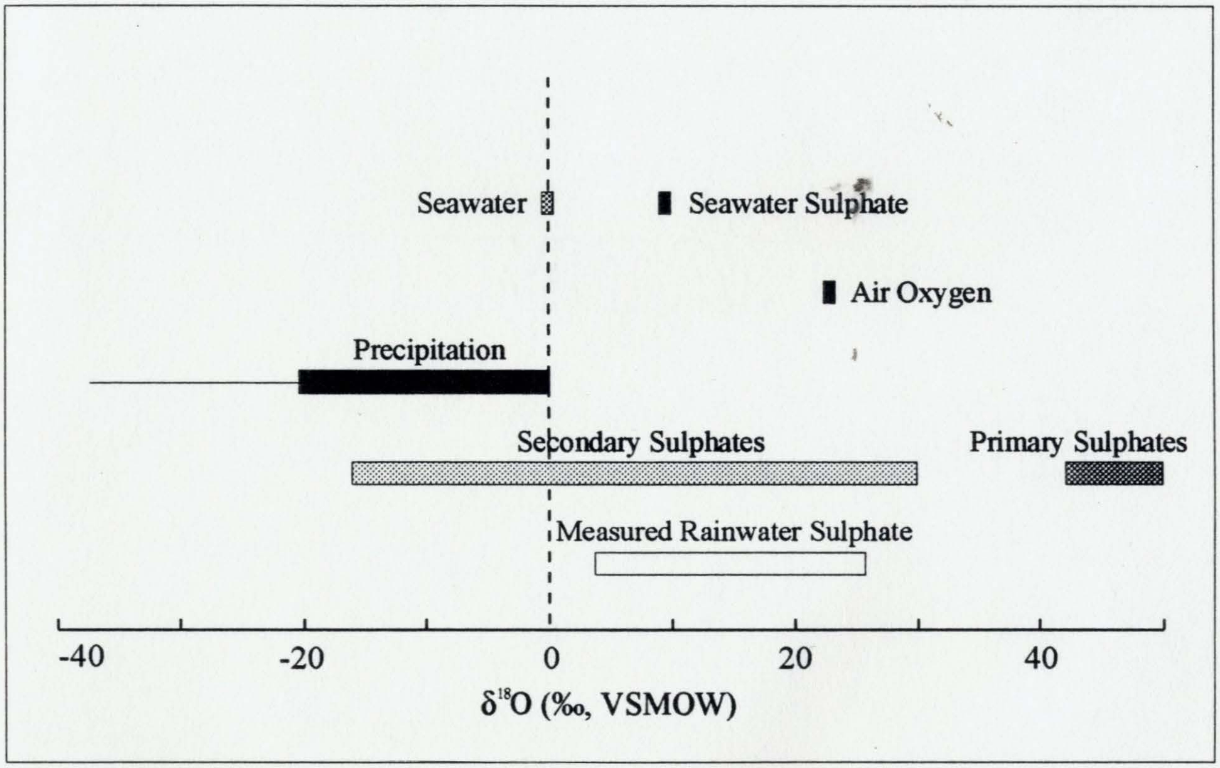

Figure 1.5 $\delta^{18}O$ values for some important atmospheric constituents.

Table 1.4 Measured $\delta^{18}O$ values of sulphate in precipitation.

Region	**Range**	**Mean**	**Reference**	**Comments**
Nova Scotia	+5.7 - +13.8‰	+9.5‰	Wadleigh *et al.* (1996)	event samples
Quebec	+8.3 - +13.4‰	+11.5‰	Caron *et al.* (1986)	bulk deposition samples decrease in winter values
Argonne, Illinois	+8 - +26‰	+14.3‰	Holt *et al.* (1979)	event samples decrease in winter values
Argonne, Illinois	+3.1 - +21.1‰	+12.4‰	Holt *et al.* (1981a)	event samples decrease in winter values
Pisa, Italy	+6.5 - +17.6‰	+12.3‰	Cortecci and Longinelli (1970)	event samples decrease in winter values
Venice, Italy	≈ +10 - +19‰	-	Longinelli and Bartellioni (1978)	12 hr precipitation samples
Gracefield, New Zealand	+7.6 - 14.1‰	+10.2‰	Mizutani and Rafter (1969)	event samples

signature of its formation mechanism since sulphate is very stable and undergoes no subsequent exchange (Lloyd, 1968).

1.3.1 Sulphur Dioxide Oxidation

As mentioned above, SO_2 undergoes rapid isotopic equilibration with associated water. Holt *et al.* (1979) noted a slope of ¾ for $\delta^{18}O_{SO4}$ vs $\delta^{18}O_{H2O}$ from samples collected near Chicago, Illinois. They proposed that three of the four oxygen atoms in the sulphate were controlled by ambient water and one by air. Further laboratory studies were carried out to confirm this finding (Holt *et al.*, 1981b; Holt *et al.*, 1983). Under both aqueous and non-aqueous conditions and with different oxidants, the slopes conformed with this hypothesis.

The two main oxidation pathways for SO_2 were discussed in Section 1.2.2.2 with respect to sulphur isotopes. Again the oxidation processes can be heterogeneous (hydrolysis-oxidation) or homogeneous (oxidation-hydrolysis).

During heterogeneous oxidation, $SO_{2(g)}$ is equilibrated with water during its dissolution, which can be represented as:

$$SO_2 + H_2O \longleftrightarrow HSO_3^- + H^+$$

Sulphates formed in this manner should exhibit a correlation between $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$.

The $\delta^{18}O$ value for water is affected by a number of factors including temperature, latitude, altitude and the amount of rain (Daansgard, 1964; Hoefs, 1987; Welhan, 1987). The $\delta^{18}O$ of sulphate formed by this heterogeneous process is expected to vary accordingly. Cortecci and Longinelli (1970), Longinelli and Bartelloni (1978), Holt *et al.* (1979), and Holt *et al.* (1981a) have all noted this type of variation in their studies of atmospheric sulphates.

Homogeneous oxidation involves oxidation in the gas phase where the $SO_{2\,(g)}$ is oxidized by atmospheric gases such as O_2, O_3, H_2O_2, and OH. The isotopic composition will depend on the composition of the oxidant. In general, this should lead to higher $\delta^{18}O$ values than heterogeneous oxidation as atmospheric oxygen has a constant $\delta^{18}O$ value of +23.5‰ (Kroopnick and Craig, 1972) while precipitation values tend to be much lower (Figure 1.5) (Holt *et al.*, 1978).

By understanding the compositions expected from these processes, it should be possible to determine the relative importance of these pathways. Figure 1.6 illustrates the curves constructed by Holt *et al.* (1981b), Holt *et al.* (1983) and Holt and Kumar (1984) for the various homogeneous, heterogeneous and high temperature oxidation reactions carried out during laboratory studies. In practice things become much more complicated. Atmospheric sulphates probably form by a combination of these processes and sulphates can travel over very long distances before being deposited. During this time, mixing can occur, obscuring the isotopic signatures. Precipitation sulphate can be a complicated mixture of local and distant sources formed by different oxidation mechanisms.

One important result to come from the work of Holt and his coworkers has been the idea that sulphate from combustion sources (primary sulphates) can be differentiated from sulphate formed in the atmosphere by heterogeneous and homogeneous oxidation

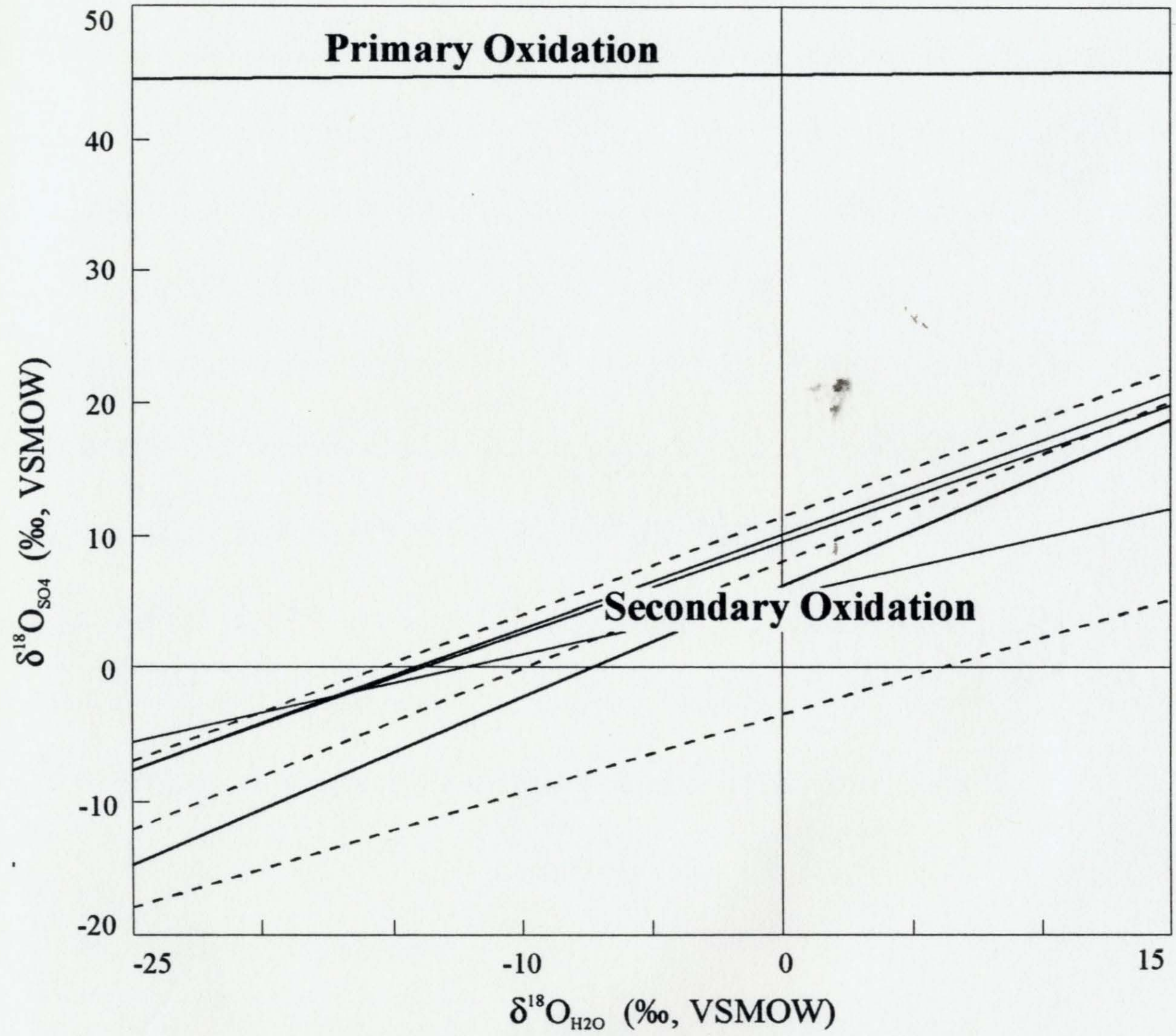

Figure 1.6 Relationship between $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$ for different primary and secondary oxidation reactions (Holt *et al.*, 1981b; Holt *et al.*, 1983; Holt and Kumar, 1984). The solid lines represent homogeneous reactions while the dotted lines represent heterogeneous reactions.

(secondary sulphates) on the basis of $\delta^{18}O$ values (Holt *et al.*, 1982). Sulphates formed under the high temperatures of combustion sources (e.g. power plants, smelters etc.) have very high oxygen isotopic signatures (>+40‰). This is because of the complicated equilibration reactions that occur between atmospheric oxygen, water vapour, and $SO_{3\,(g)}$ at high temperatures. Holt and Kumar (1984) carried out a study of these processes by looking at the various equilibration reactions involved. The conversion of $SO_{2\,(g)}$ to $SO_{4\,(s)}$ occurs in a number of steps. Initially the $SO_{2\,(g)}$ is oxidized by air oxygen to form $SO_{3\,(g)}$. Water vapour undergoes exchange with air oxygen under the high temperature conditions and its $\delta^{18}O$ is enriched, approaching that of the air oxygen (+23‰). During hydration to H_2SO_4, the $SO_{3\,(g)}$ exchanges with the water vapour and this results in very heavy $\delta^{18}O_{SO4}$ values. Values of $\delta^{18}O$ measured from sulphates in a power plant plume were also reported in this study, supporting the laboratory findings. It does not appear that any other workers have measured these types of values in actual rain samples.

Knowing the expected $\delta^{18}O$ value for primary sulphates allows the percent contribution to be calculated from:

$$x\delta^{18}O_P \;+\; (100 - x)\delta^{18}O_S \;=\; 100\delta^{18}O_m$$

where the subscripts stand for the primary, secondary and measured sulphates respectively. Primary sulphate can be assumed to have a $\delta^{18}O$ of +40‰ and the composition of the secondary sulphate can be calculated from the known isotopic composition of the water using curves such as those provided by Holt *et al.* (1981b) and Holt *et al.* (1983).

In marine influenced areas, oxygen isotopes may also be useful for identifying the influence of seaspray. Mizutani and Rafter (1969) compared the $\delta^{18}O_{SO4}$ with the amount of seaspray influence for precipitation samples from Gracefield, New Zealand. They found that the $\delta^{18}O_{SO4}$ values converged on the isotopic composition of seaspray (+9.5‰) at higher seaspray contributions.

1.4 Chemical Composition of Precipitation

Sulphur isotopes are very useful for source tracing but the incorporation of chemical data in an isotopic study may enhance the ability to identify particular sources. Chemical composition has been used in many studies to identify natural and anthropogenic sources using the characteristic chemical signatures of these sources.

Rainwater is basically a dilute solution of ions such as Na^+, Cl^-, and Ca^{2+}. As with sulphur, the sources of these elements can be broadly divided into marine and continental. Table 1.5 shows the typical composition of marine and continental rains. Typically, marine rain is dominated by Na^+ and Cl^- from seawater while continental rain is dominated by soil derived elements such as Ca^{2+}. These elements are not exclusive to these sources however, as Na^+ is often found in high concentrations in arid regions where it is derived from soil and sand (Berner and Berner, 1987). These elements can also result from anthropogenic sources. Chlorine, for example, can result from anthropogenic HCl emissions. Typically concentrations can be found in the order:

$$\underbrace{Cl^- = Na^+ > Mg^{2+} > K^+ > Ca^{2+} > SO_4^{2-} > NO_3^- = NH_4^+}$$

Marine Continental

Table 1.5 Typical concentrations of major ions in continental and marine rain (from Berner and Berner, 1987).

Ion	Continental Rain	Marine and Coastal Rain
Na^+	0.2 - 1	1 - 5
Mg^{2+}	0.05 - 0.5	0.4 - 1.5
K^+	0.1 - 0.5	0.2 - 0.6
Ca^{2+}	0.2 - 4	0.2 - 1.5
NH_4^+	0.1 - 0.5	0.01 - 0.05
H^+	pH = 4 - 6	pH = 5 - 6
Cl^-	0.2 - 2	1 - 10
SO_4^{2-}	1 - 3	1 - 3
NO_3^-	0.4 - 1.3	0.1 - 0 5

when moving from a marine to a continental environment (Berner and Berner, 1987).

The proportion of seaspray in rain has often been of interest to researchers studying sulphur isotopes, and they have utilized a parameter known as percent seaspray (PSS) after Mizutani and Rafter (1969) (e.g. Cortecci and Longinelli, 1970; Wakshal and Nielson, 1982; and Wadleigh *et al.*, 1994 and 1996). PSS is calculated using the known ratios of conservative ionic species in seawater. Generally Cl, Na, and Mg are used for these calculations and the formula for PSS is written as:

$$\mathrm{PSS} = \left[\frac{\left(\frac{\mathrm{SO4}}{\mathrm{X}}\right)_{\mathrm{Air}}}{\left(\frac{\mathrm{SO4}}{\mathrm{X}}\right)_{\mathrm{Seawater}}} \right] \times 100$$

where X is the concentration of the reference species. The seawater ratios are 0.14, 0.25, and 2.10 for Cl, Na, and Mg respectively (Drever, 1982). Non-seaspray sulphate (NSS) or excess sulphate must represent sulphate from other natural and/or anthropogenic sources. Ratios may also be used for other elements as well, to determine their seaspray component.

This type of calculation involves some assumptions. All of the reference species must be from seaspray. As well there can be no fractionation between the reference species and the sulphate during formation of the particles and their injection into the atmosphere or during their subsequent incorporation into precipitation (Keene *et al.*, 1986). Duce and Hoffman (1976a) have speculated that Cl^- may be removed from seasalt particles through the formation of HCl gas. This would cause PSS calculations to underestimate the seasalt contribution. Keene *et al.* (1986) have suggested that it is best to calculate PSS from each of the reference species and decide which is best for a particular site using objective criteria (e.g. Wadleigh, 1994).

Trace metals are also found in rainwater, and although they are often thought of as pollutants, they can be of either natural or anthropogenic origin. Metals occur in the atmosphere mainly in the particulate phase, although some such as Hg, Pb, Sn, As, Se, and Tl may be in a gaseous form (Puxbaum, 1991). A number of estimates have been made of the global emissions of metals by both natural and anthropogenic sources, but a lack of direct measurements of these fluxes and uncertainties about the cycles governing atmospheric metals has led to discrepancies between these estimates. Table 1.6 compares some estimates of natural and anthropogenic emissions on a global scale.

Although natural emissions are thought to dominate globally for some metals such as Se, Hg, and Mn, anthropogenic emissions dominate for most metals (Pacyna, 1986a). Metal processing and smelting, various industries, and the burning of fossil fuels are responsible for most of these anthropogenic emissions. Studies of ice cores and long term atmospheric measurements have confirmed the increasing influence of anthropogenic emissions through time (Cawse, 1982; Galloway *et al.*, 1982).

There are also natural sources for metals, which include windblown dust, volcanoes, forest fires, biogenic emissions, and seaspray. Table 1.7 summarizes emissions for a number of metals from these sources. Dust and volcanic emissions are the most important and widely studied of these sources, but generally natural sources have not been well studied (Pacyna, 1986b).

Table 1.6 Comparisons of global natural and anthropogenic emissions from two studies (10^6 kg) (after Paxbaum, 1991)

	Natural		Anthropogenic	
	Pacyna (1986b)	Salomons (1986)	Pacyna (1986b)	Salomons (1986)
As	8	21	24	78
Cd	1	0.3	7	6
Co	5	7	-	5
Cu	19	58	56	94
Cr	9	19	-	260
Hg	0.2	25	-	11
Mn	520	610	-	320
Ni	26	28	47	98
Pb	19	4	450	400
Se	0.4	3	1	14
V	66	65	-	210
Zn	45	36	310	840

Table 1.7 Global emissions of trace metals from natural sources (Pacyna, 1986b).*

	Windblown dust	**Volcanic Particles**	**Forest wild-fires**	**Vegetation**	**Seasalt**	**Total**
Global production ($\times 10^{-9}$) (kg/y)	6 - 1100	6.5 - 150	2 - 200	75 - 1000	300 - 2000	
As	0.24	7	0.16	0.26	0.14	7.8
Cd	0.25	0.5	0.01	0.2	0.002	0.96
Co	4	1.4				5.4
Cu	12	4	0.3	2.5	0.1	18.9
Cr	50	3.9				8.9
Mn	425	82		5	4	516
Ni	20	3.8	0.6	1.6	0.04	26
Pb	10	6.4	0.5	1.6	0.1	18.6
Se	0.3	0.1				0.4
V	50	6.9		0.2	9	66.1
Zn	25	10	0.5	10	0.02	4
Hg	0.03	0.03	0.1		0.003	0.16

*NOTE: all units in $\times 10^{-6}$ kg except where indicated.

Dust from the Sahara has been found to travel very long distances into Europe and across the Atlantic where studies have detected its input to the atmosphere over Bermuda and South America (Chen and Duce, 1983; Prospero, 1990). Volcanoes continuously emit gases to the atmosphere, but the intensity and composition varies both between different volcanoes and with time, and therefore it is more difficult to make precise estimates of the amounts. The sea also contributes a share of trace metals to the atmosphere through seaspray and gas exchange, but this contribution is small in terms of the overall trace metal cycle (Pacyna, 1986b).

Anthropogenic emissions have seriously impacted atmospheric trace metal cycles, although certain elements are effected more than others. As stated above, some elements may still be largely natural on a global scale. A number of methods have been used to study the impact anthropogenic emissions of trace metals (Cawse, 1982; Galloway *et al.*, 1982). These have included historical studies using ice cores or sediments, comparisons of present day natural and anthropogenic emissions (mobilization factors), and the calculation of enrichment factors.

Enrichment factors (EF) are similar to PSS in that calculations using known crustal ratios are used to estimate the contribution of crustal sources to the atmosphere. An enrichment factor (EF) is calculated using the formula:

$$EF_{Crust} = \frac{\left(\frac{X}{R}\right)_{Air}}{\left(\frac{X}{R}\right)_{Crust}}$$

where X is the element of interest and R is the reference species. Usually Al and Sc are the best reference species but sometimes Fe, Si, Ba, or Mn (Cawse, 1982) are used. An enrichment factor near unity indicates that the element is of a crustal origin while an enrichment factor greater than unity must indicate that some other source is present. There are some uncertainties however, such as the fact that crustal composition varies from place to place, therefore EF values of up to 10 can be taken to indicate a natural origin. Certain volatile elements may become enriched through oceanic emissions or through high temperature volcanic processes (Pacyna, 1986b; Church *et al.*, 1990). Another problem is the fact that some anthropogenic emissions, such as fly ash, can have compositions that are indistinguishable from crustal material, allowing underestimation of anthropogenic contributions (Church *et al.*, 1990).

Table 1.8 shows the relative impact of anthropogenic activities on various metals determined using mobilization factors, historical techniques as well as enrichment factors. From this data it can be seen that elements such as Cd, Pb, Cu, An, and Sn are usually highly enriched compared to natural levels while elements such as Co, Mn, and Ni are usually impacted to a lesser extent. These types of calculations are generally only valid on a larger scale. On the local scale, the relative importance of sources will of course vary from place to place, especially with the inputs of local point sources.

Emission factors are another way of estimating the impact of different sources. They show the amount of a metal that should be emitted from a source for a particular unit of production. These values have been compiled for a number of anthropogenic sources by Pacyna (1986a). The emission factors for oil combustion, wood combustion, and waste incineration are given in Table 1.9. This table should be used to see the relative

Table 1.8 Impact of anthropogenic emissions on trace metal concentrations in the atmosphere estimated through different techniques (Galloway et al, 1982).

	Expected enrichment			
Technique	**Low**	**Moderate**	**Large**	**No data**
Mobilization factor	Co, Mn, Hg	As, Cr, Ni, Se, V	Ag, Cd, Cu, Mo, Pb, Sb, Se, Sn, Zn	Be, Te, Tl
Enrichment factor	Co, Mn, Ni	Cr, V	Cd, Cu, Pb, Sb, Se, Zn	Ag, As, Be, Hg, Mo, Sn, Te, Tl
Historical factor	Co, Mn, Ni, Be	Cr, V, Cu, Ag, Zn, Se	As, Cd, Pb, Sb	Mo, Sn, Te, Tl, Hg

*NOTE: Low ≤ 2x enrichment; moderate = 2 to 4x; and large ≥ 4x

Table 1.9 Emission factors for a number of anthropogenic sources (Pacyna, 1986a)*

	Oil-fired Power plant (European) (μg/MJ)	**Oil Combustion - Commercial & Residential (g/ 10^3 L)**	**Wood Combustion (wood stove) (g/ t of wood)**	**Municipal Incinerators (g/ t refuse)**
As	24	0.6	0.5	0.52
Cd	12	0.3	0.3	2.25
Co	130	3.4		0.01
Cr	43	1.1		1.1
Cu	174	4.6	19	3.7
Mn	41	1.1		1.6
Mo	28	0.7		
Ni	1,020	27	4.7	0.33
Pb	126	3.3	7	17.6
Se	18	0.5		0.08
V	3,700	98		
Zn	89	2.3	58	260

*NOTE: these numbers are not for direct comparison, but for evaluation of the metals most affected by each process.

importance of a source for a particular metal, but not for direct comparison between these sources. The composition of fine aerosols from automobile emissions have also been listed in Table 1.10. This type of data must be taken as an average, and will vary from place to place. For example, power plants emissions will vary depending on the technology used, the oil source, and the temperature of combustion (Pacyna, 1986a).

Certain trace metals may be seen as characteristic of certain anthropogenic sources. Vanadium as an example is mainly emitted as a result of oil combustion and can be used to trace the emissions of oil burning power plants (Duce and Hoffman, 1976b). In the past, lead was often diagnostic of automobile emissions because it was added as an antiknock agent in gasoline (Ewers and Schlipköter, 1991). As it was realized that Pb was dangerous to health, it was replaced. By 1990, Pb had been completely removed from gasoline in Canada and replaced by compounds of Mn. It has been speculated that Mn may now become a tracer for automobile emissions (Loranger and Zayed, 1994).

Most metals, however, are emitted by a number of sources, and it becomes more valuable to examine patterns of behaviour for a number of metals in combination. Statistical techniques such as factor analysis can become useful in such studies to reveal correlations between the variables, especially with large data sets.

A problem for studying the trace metal composition of wet deposition is the fact that a large proportion of the literature on atmospheric metals deals with aerosols. Some difference in opinion exists as to what impact solubility has on metal concentrations, but it seems likely that there is some difference (Gatz and Chu, 1986). Galloway *et al.* (1982)

Table 1.10 Chemical composition of fine aerosol emissions from highway vehicles (%) (Pacyna, 1986a).

	Gasoline Autos and trucks (leaded	Automobile (unleaded fuel)	Diesel Engine	Tire tread	Brake lining	Highway composite
Al	0.043	0.12	0.34			0.074
Br	8.2		0.031			4.98
Ca		0.17	0.84		5.5	0.86
Cl	5.4		1.69			3.51
Cu	0.004	0.024	0.73			0.1
Fe	0.25	0.11	1.32			0.333
Pb	21.1		0.095			12.8
Mg					8.25	1.12
Mn		0.015	0.027			0.0039
Ni		0.015				0.0002
K		0.044				0.001
Si	0.075	0.51	0.17		15.4	2.17
Na			0.37			0.05
V			0.01			0.0014
Zn	0.021	0.08	0.23	1		0.151
sulphates	0.213	50	4.2			1.4
nitrates			0.72			0.1
carbon	54.5	39	70	87	28.3	56.2

have compiled the results of the few studies on metals in wet deposition and the results are presented in Table 1.11.

A number of reviews have been published discussing atmospheric trace metals. These include Galloway *et al.* (1982); Cawse (1982); and Nriagu and Davidson (1986).

1.5 Atmospheric Removal Processes

Atmospheric particles and gases are eventually removed by the processes of dry and wet deposition. Dry deposition involves gravity settling and the capture of particles and gases by surfaces. Wet deposition includes those processes that occur during the formation and subsequent descent of rain. It is through deposition that pollutants are eventually brought into contact with the environment. This study is concerned solely with wet deposition events, but other studies have used different sample types. Bulk samples containing both wet and dry deposition may be collected or wet depositions may be collected on a weekly or monthly basis. This is important to remember when comparing the results of various studies.

Rainout is the removal of materials within the cloud during the formation of rain drops while washout describes the removal that occurs as the rain drops fall through the atmosphere below the cloud. Figure 1.7 illustrates the processes involved in wet deposition.

During the formation of rain, water vapour condenses on particles known as cloud condensation nuclei (CCN) to form cloud drops. Generally, it is the larger, hygroscopic

Table 1.11 Median values and ranges for trace metal concentrations in wet deposition (Galloway et al, 1982). *

	Urban		**Rural**		**Remote**	
	Median	**Range**	**Median**	**Range**	**Median**	**Range**
Sb	-	-	-	-	0.034	0.034
As	5.8	5.8	0.286	0.005 - 4	0.019	0.019
Cd	0.7	0.48 - 2.3	0.5	0.08 - 46	0.008	0.004 - 0.639
Cr	3.2	0.51 - 15	0.88	<0.1 - 30	-	-
Co	1.8	1.8	0.75	0.01 - 1.5	-	-
Cu	41	6.8 -120	5.4	0.4 - 150	0.06	0.035 - 0.85
Pb	44	5.4 - 147	12	0.59 - 64	0.09	0.02 - 0.41
Mn	23	1.9 - 80	5.7	0.2 - 84	0.194	0.018 - 0.32
Hg	0.745	0.002 - 3.8	0.009	0.005 - 2.2	0.079	0.011 - 0.428
Mo	0.2	0.2	-	-	-	-
Ni	12	2.4 - 114	2.4	0.6 - 48	-	-
Ag	3.2	3.2	0.54	0.01 - 0.48	0.007	0.006 - 0.008
V	42	16 - 68	9	0.13 - 23	0.163	0.016 - 0.32
Zn	34	18 - 280	36	<1 - 311	0.22	0.007 - 1.1

* All values in ppb.

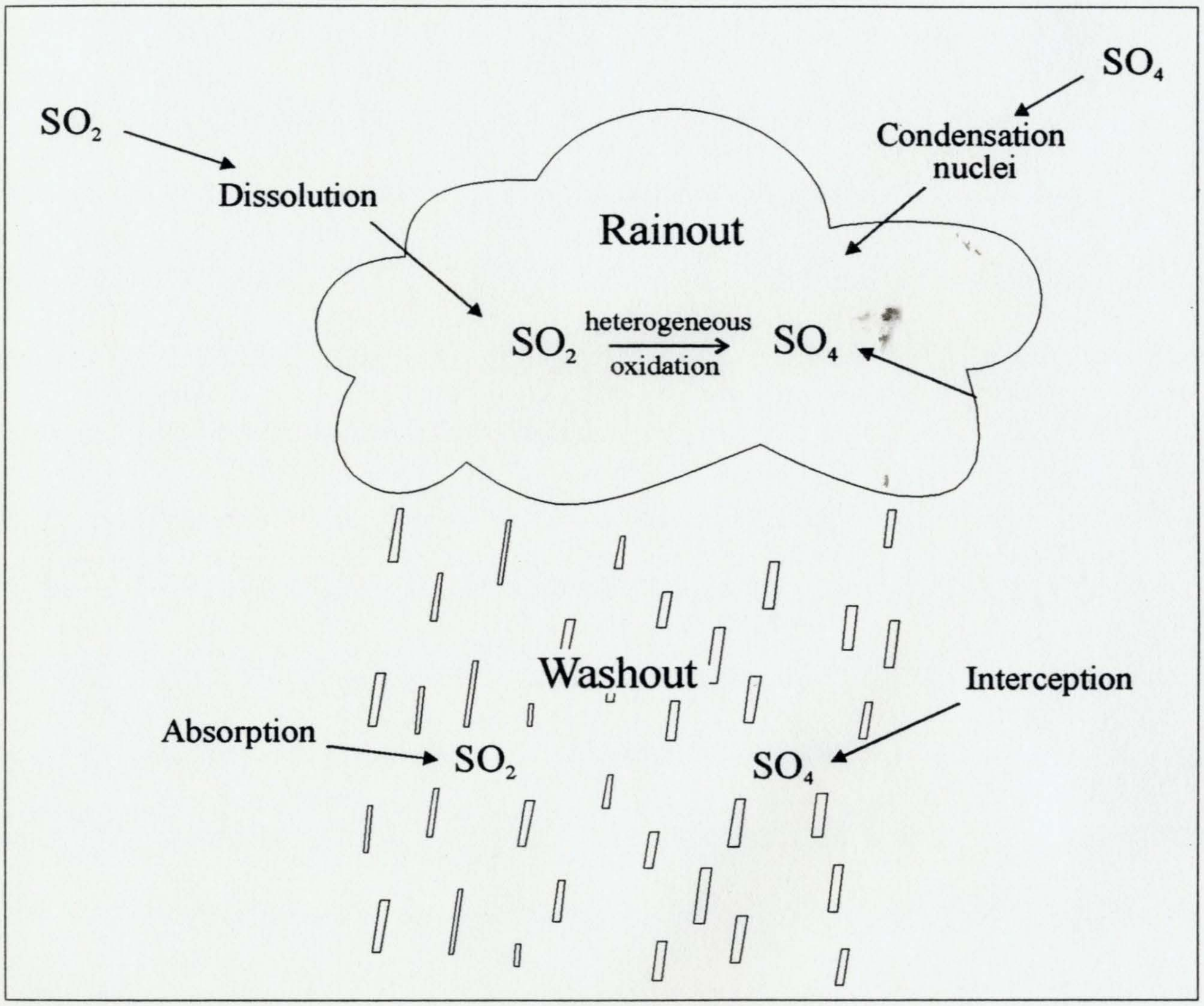

Figure 1.7 Illustration of the processes of wet deposition.

aerosols such as seasalt, H_2SO_4, and HNO_3 that are favoured in this process (Berner and Berner, 1987). Aerosols are solid or liquid particles in the atmosphere that form through the direct emission of particles to the atmosphere or through the condensation of gases. The composition of these aerosols is chiefly determined by the environment in which they form. Over the continents, they are mainly soil particles while over the oceans, seasalt is dominant. The composition of the rain is in turn largely determined by the aerosols that become CCN. This is why continental rain is dominated by Ca^{2+} and other soil related elements, while marine rain is dominated by Na^+ and Cl^- (Berner and Berner, 1987). The solubility of aerosol constituents will also influence rain chemistry meaning that rain will not always exactly reflect aerosol chemistry.

A large portion of the sulphate in the atmosphere is removed during rainout. Sulphate particles tend to make good CCN because of their size and hygroscopic nature (de Pena, 1982). SO_2 may also be removed during rainout as it is absorbed by the cloud drops and oxidized to form sulphate. This is the process of heterogeneous oxidation discussed in Sections 1.2.2.2 and 1.3.1. The efficiency of absorption will depend on a number of factors including the concentration of SO_2, the temperature, and the pH (de Pena, 1982).

Cloud drops must acquire a size large enough to allow them to escape from the cloud and fall as rain. Washout occurs during the time it takes for the drops to fall through the atmosphere. The time of this fall is quite short and therefore washout tends to be less effective than rainout. Particles may be removed as they are intercepted by the falling rain drops, although this removal will be more efficient for larger particles. Gases may also be absorbed during this time, but because the time is very short, rainout is generally more efficient for removing SO_2.

A number of important observations have been made concerning the effectiveness of these processes in proximity to pollution sources. The concentrations of various elements that may act as catalysts (particularly Mn and Fe) in the oxidation of SO_2 are higher near pollution sources, and as well, the concentrations of SO_2 are higher (Beilke and Gravenhorst, 1978). This means that washout processes may tend to be more important close to pollution sources. Faster oxidation of SO_2 will allow it to be incorporated into rain drops more easily.

Although it is not considered in this study, dry deposition is still an important process for removing particles and gases from the atmosphere. As stated above, dry deposition may be more important in less polluted regions where oxidation of SO_2 is not favoured. Many studies have attempted to calculate the relative importance of dry and wet deposition. It has been found though, that this varies over time depending on such things meteorological conditions and the local environment (Hicks *et al.*, 1989). A study carried out in Eastern Canada by Sirois and Barrie (1988) estimated that 22% of sulphate was being dry-deposited with a range of 37% to 78%.

1.6 Meteorological Data

This study will also incorporate meteorological data to augment the isotopic and chemical data already discussed. Air mass back trajectories show the path of the air mass responsible for a particular event, for five days prior to the event, thus showing the type of source areas that the air mass traveled over.

These trajectories are computed using models that utilize measured meteorological data to predict the position of an air mass at a particular point in time (Olsen *et al.*, 1978). The trajectories used in this study are computed for the 850 mb pressure level where a significant amount of transport is thought to occur.

CHAPTER 2

METHOD

2.1 Sample Sites

Three sites were chosen for this study: St. John's, Newfoundland; Seal Cove, Newfoundland; and Nepean, Ontario. The locations of these sites are shown in Figure 2.1. The St. John's and Seal Cove sites represent coastal environments while the Nepean site represents a continental environment.

2.1.1 St. John's, Newfoundland

The collector at St. John's was located on the campus of Memorial University of Newfoundland (MUN). St. John's is located on the east coast of the island of Newfoundland (Figure 2.2), and the city and its surrounding area has a population of approximately 160 000 people. Its location, directly on the coast, was expected to provide a strong marine influence and therefore this site represents a marine/urban location. There is not much industry in Newfoundland in general, and St. John's is not directly affected by any large point sources. A large oil refinery is located at Come-by-Chance about 100 km from St. John's (Figure 2.2).

The collector itself was placed in a weather station located on the west side of campus near a small oil-fired power station (Figure 2.3). The power station operates year round to provide heat and emergency power to the campus and nearby hospital. The

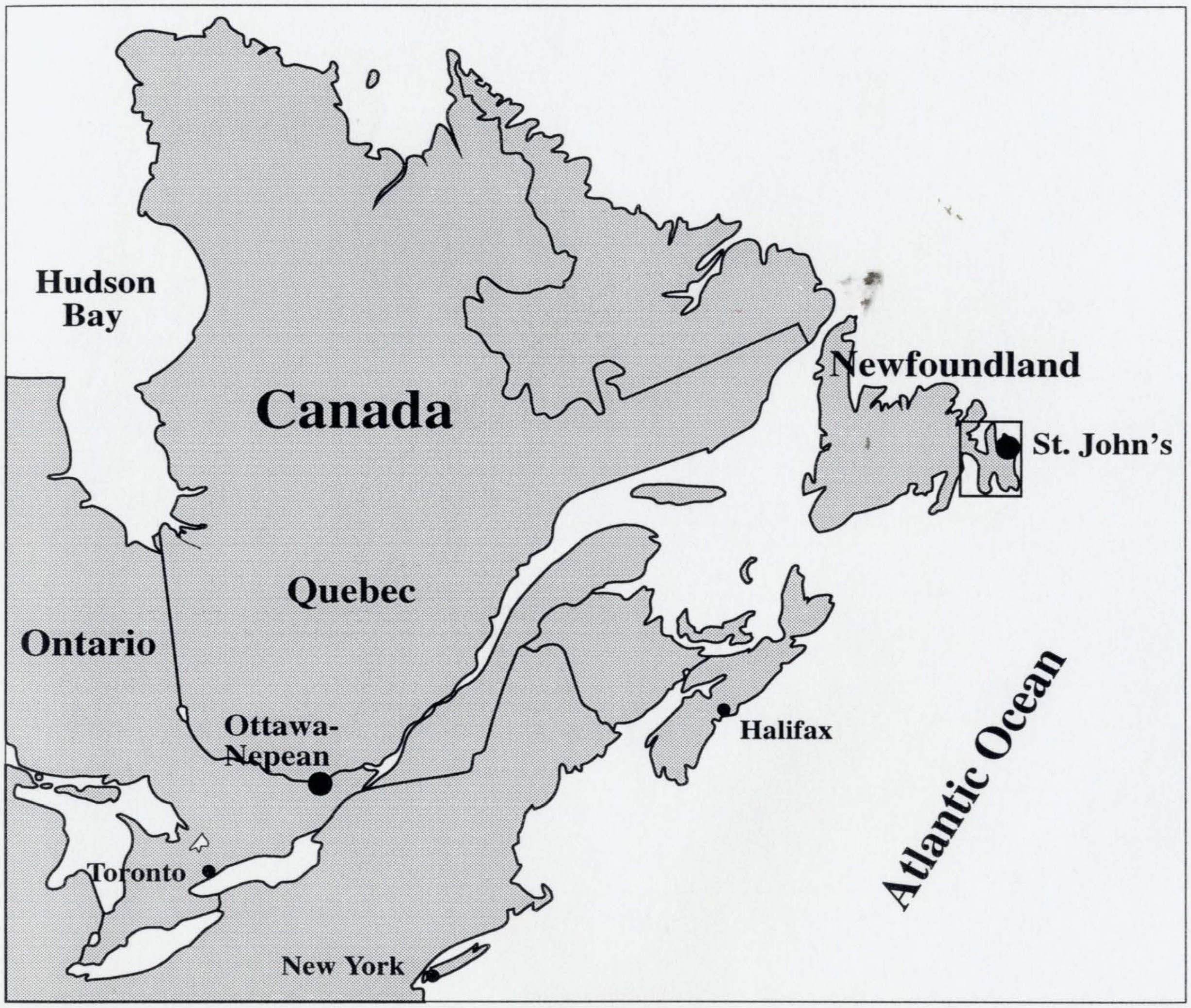

Figure 2.1 Map of eastern Canada showing the location of the three study sites. Seal Cove, Newfoundland, is located in the outlined area.

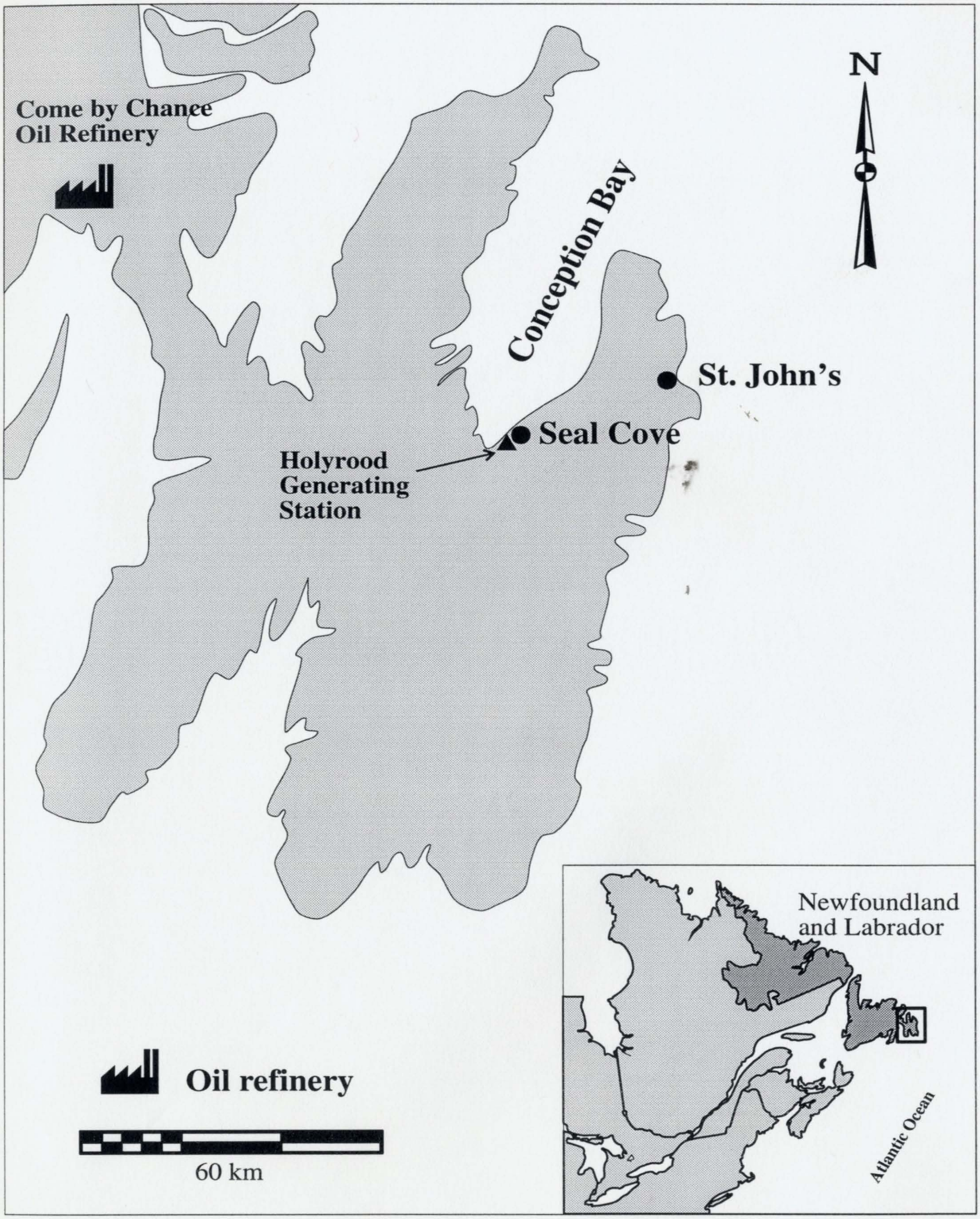

Figure 2.2 Location map for the St. John's and Seal Cove sites on the Avalon Peninsula, Newfoundland.

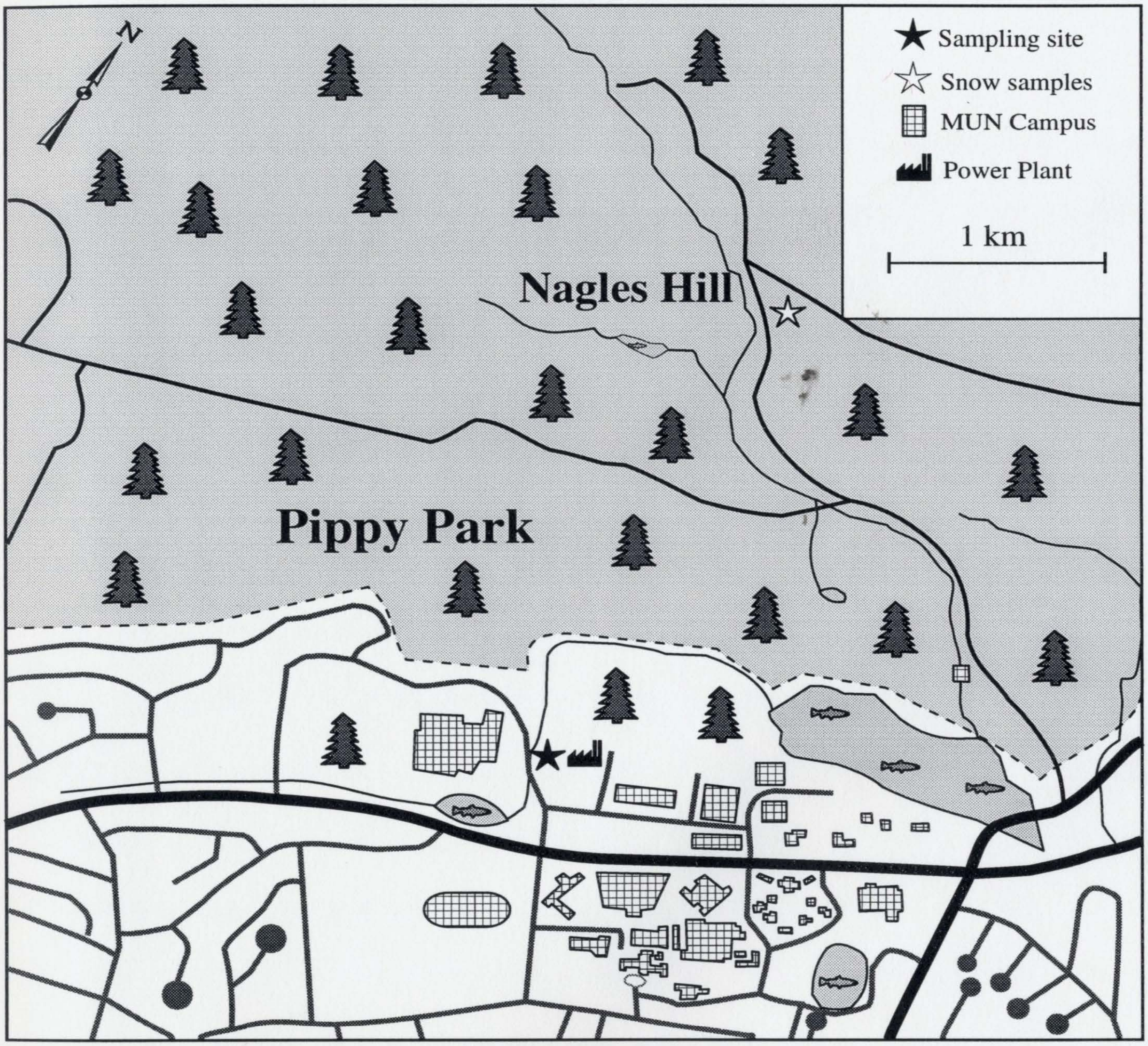

Figure 2.3 Map of the St. John's, Newfoundland study area.

station burns approximately 2 million gallons of Bunker C oil each year. The site is also located close to a major roadway and some automobile pollution is expected. Behind the collector is a wooded area which extends back approximately 3 or 4 km as part of C.A. Pippy Park.

Another site, located approximately 1 km from the MUN collection site (Figure 2.3), was chosen as a comparison with the main site for the collection of snow samples. This site was located in Pippy Park behind the MUN collector, near a golf course. There are only a few houses in this area, and although the samples were collected close to a road, this area is not heavily travelled.

2.1.2 Seal Cove, Newfoundland

Seal Cove is part of the community of Conception Bay South, located on the Avalon Peninsula, 30 km Southwest of St. John's (Figure 2.2). Seal Cove has a small population of less than 500, although Conception Bay is surrounded by dozens of small communities which run almost continuously around its coast. The community is located directly on the coast and should, like St. John's, have a strong marine influence. This site is considered to represent a marine/rural environment. The collector was located in the community itself, approximately 1 km from the sea (Figure 2.4). A large oil-fired power station is located approximately 2.5 km from this site. The Holyrood Generating Station generally operates only in the winter when the demand for power is higher. During this time it can produce large amounts of smoke over the area from the burning of Bunker C

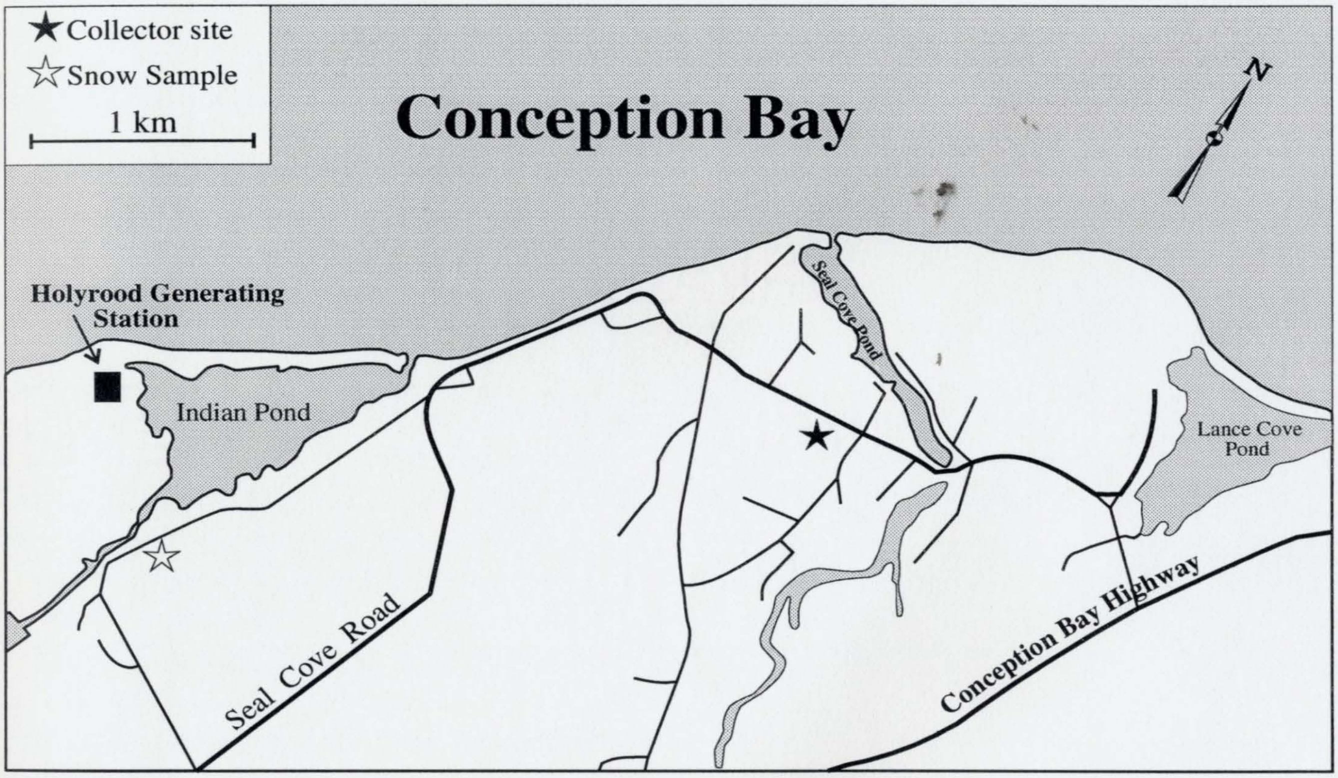

Figure 2.4 Map of Seal Cove, Newfoundland study area.

oil and represents a potential source of anthropogenic contamination. Other sources of potential pollution may be home heating by wood burning, and as well there is a gravel and sand operation located within 1 km of the site which may increase dust levels.

2.1.3 Nepean, Ontario

Nepean is a city of approximately 83 000 surrounding the west and south sides of the city of Ottawa. The sampling site was located in a quiet residential area with no major pollution sources in the immediate vicinity.

Ottawa is a fairly large city of approximately 300 000 people, but is not heavily industrialized. The most likely pollution sources are automobile exhaust and other domestic sources such the burning of fossil fuels and wood for home heating. A road is located approximately 20 m from the collector, but is not a major thoroughfare. A pulp and paper mill is located approximately 30 km from the site at Gatineau, across the Ottawa River (Figure 2.5) and may represent a source of sulphur to the rain samples. The surrounding area is largely agricultural, with few local sulphur sources. The most likely sources of transported pollution to the area are from oil and coal fired plants in the United States and smelting operations in northern Ontario and Quebec.

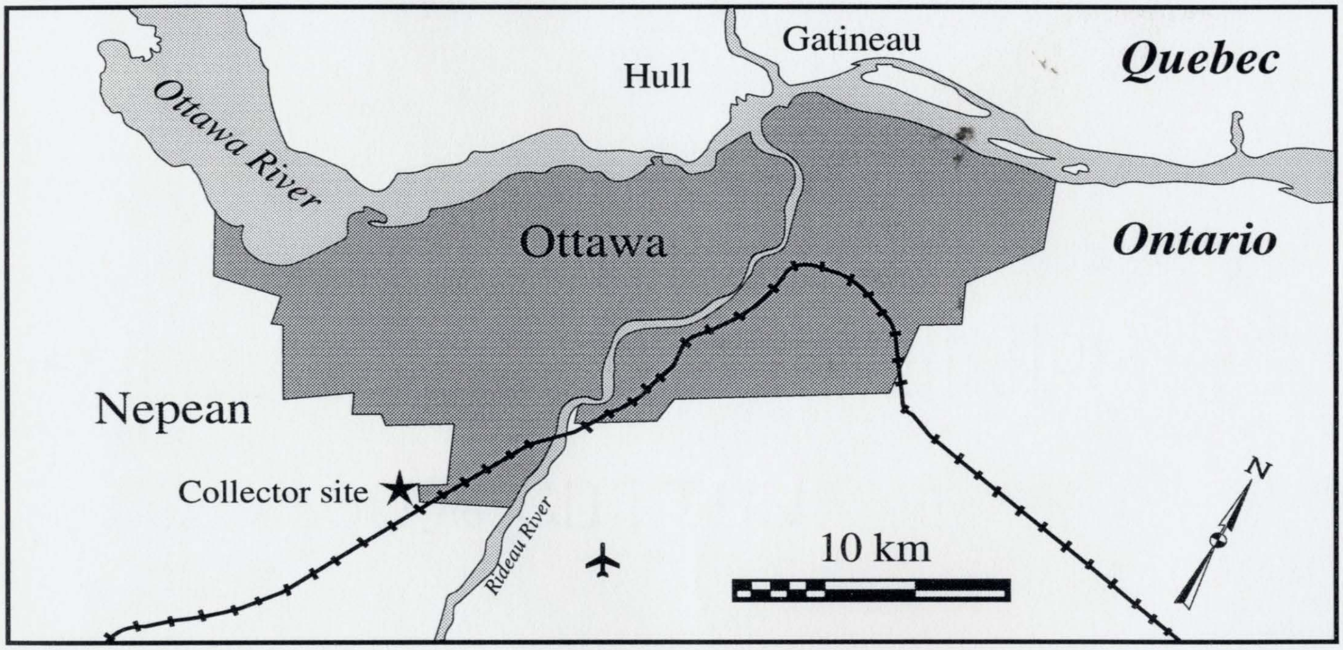

Figure 2.5 Map of the Nepean, Ontario study area.

2.2 Sample Collection

It was decided that event samples would be collected for this study. By sampling individual rain events, the sulphate and rainwater oxygen isotopes could be compared which would allow examination of atmospheric oxidation processes which was of interest.

Most collectors used in rain studies are small and designed to collect bulk precipitation. Collectors had to be built which could collect enough rain to ensure that isotopic analyses could be carried out. The collectors used in this study were designed to collect 1 L of sample for each mm of rain, and it was expected that this would allow collection of enough rain to provide sufficient sample for analysis. The collector, depicted in Figure 2.6, is constructed of wood and completely covered with 6 mil polyethylene sheeting to prevent contamination of the samples. A lid is also placed over the collector between rain events to prevent contamination by dry deposition. The lid is removed when rain is imminent and the collector is rinsed with deionized water. The rain flows down the collector, through a polyethylene covered funnel and into a clean 20 L polyethylene cubitainer.

The samples were shipped to Memorial University as soon as possible after collection. Upon arrival, pH and conductivity were measured and the samples were filtered, using a nitrogen pressured high volume filtration system, through 0.45 µm nitrate membrane filters. The samples were then refrigerated until analysis. An aliquot of each sample (250 - 500 mL) was removed and stored in a Nalgene polyethylene bottle for the analysis of chemistry as well as $\delta^{18}O_{H2O}$.

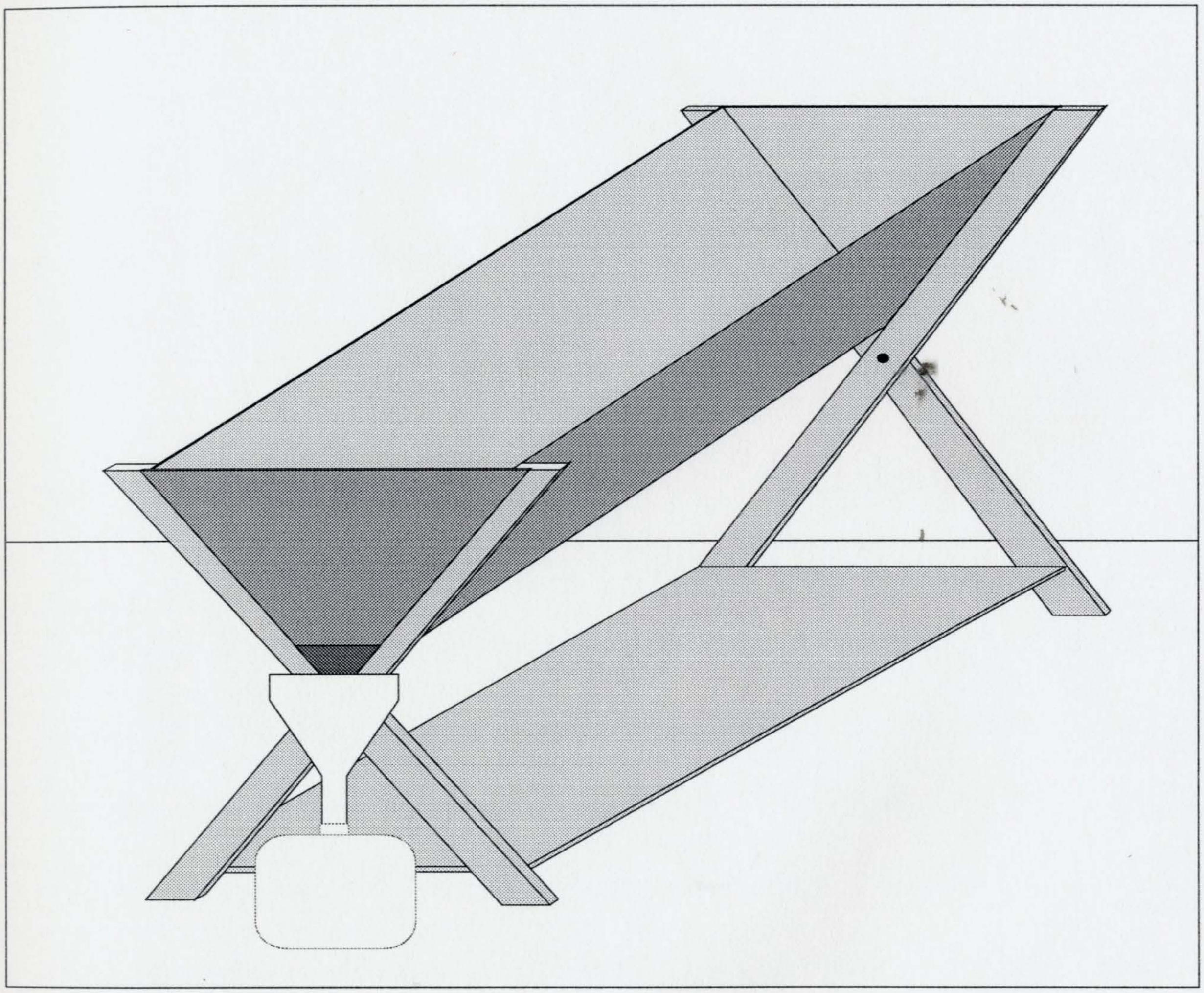

Figure 2.6 Event rain collector used in this study.

Collection of snow samples was carried out after the event. Plastic containers covered with 6 mil polyethylene sheeting were used for this purpose. Fresh snow was collected from the top layers and it was not difficult to differentiate the snow layer for each event as the previous snow hardened into a crust. These samples were allowed to melt at room temperature and were then treated in the same manner as the rain samples.

Figure 2.7 summarizes the analytical procedures followed for each sample and the methods used for each analysis. Tables 2.1 and 2.2 summarize the error involved in each method utilized.

2.3 Chemical Analysis

2.3.1 Inductively Coupled Plasma Mass Spectroscopy

Metal concentrations were measured using a SCIEX ELAN model 250 ICP-MS located at Memorial University of Newfoundland in the Department of Earth Sciences. Elements measured included Li, Be, Mg, Al, Si, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Br, Se, Rb, Sr, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Hg, Tl, Pb, Bi and U. About 10 mL of sample is placed in a clean test tube and 100 μL of distilled 8 N HNO_3 is added to acidify the sample.

Limits of detection are influenced by the operating conditions of the machine on any particular day. Background noise is used to calculate the limits of detection and this can vary between runs. Samples for this study were run on two separate occasions and

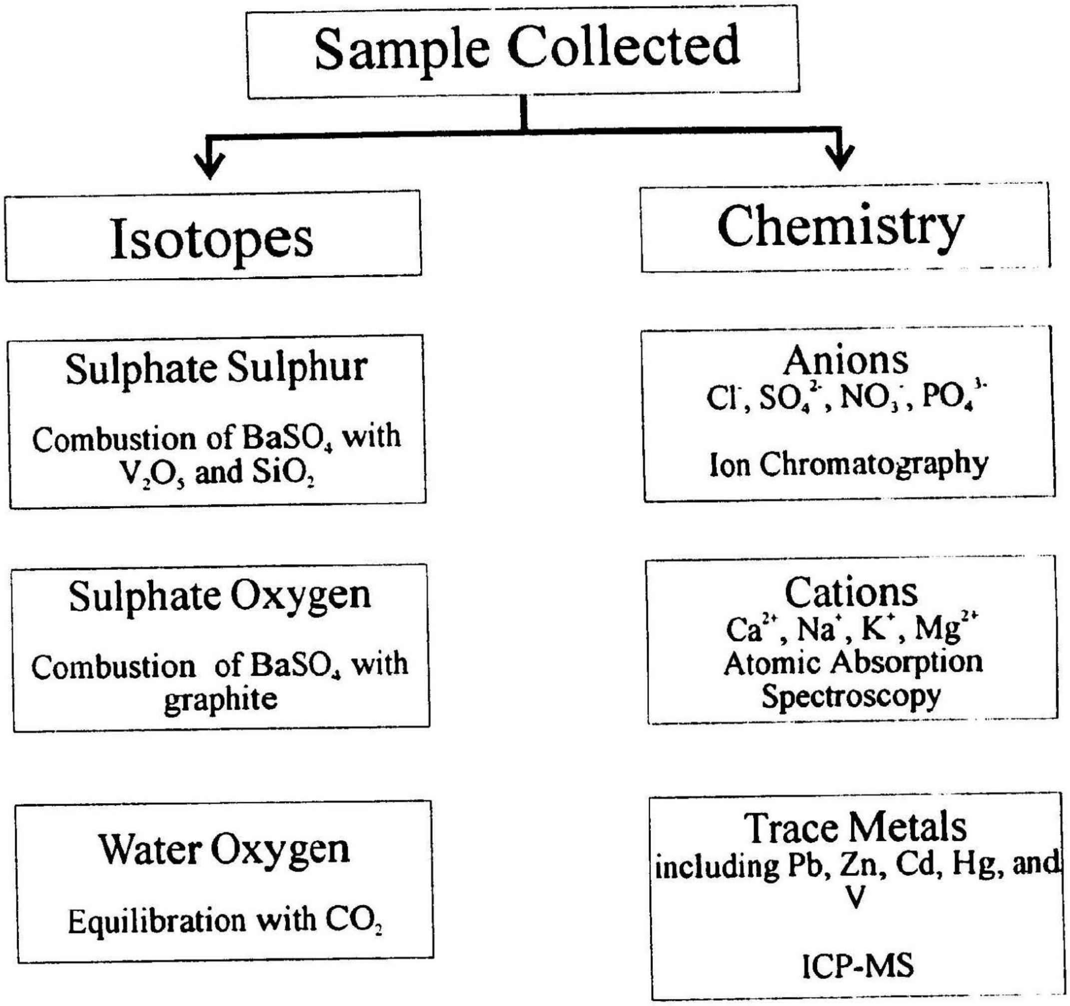

Figure 2.7 Summary of analytical procedures

Table 2.1 Error for ICP-MS analyses†.

Element	RSD*	Element	RSD*
Li	13.6	Zn	3.8 -178.8
Be	11.4 - 41.8	As	10.5
B	5.6 - 12.6	Se 77	31
Mg	9.5 - 74.6	Br	17.2
Al	5.7 - 7.4	Se 82	11.4 - 47.8
Si	6.8 - 7.5	Rb	5.9 - 24
P	41.2	Sr	3.8
S	6.6	Mo	2.9 - 139.5
Cl	5	Ag	7.4 - 9.8
Ca 42	4.3	Cd	3.6
Ca 43	4.1	Sn	31.8
Ti	44.5	Sb	4.5 - 29.1
V	3.9	I	58.6
Cr 52	3.2	Cs	56.5 - 154.5
Cr 53	12.6	Ba	3.1 - 3.6
Fe 54	6.7	La	29.8 - 56.7
Mn	4.1 - 57.9	Ce	30.6 - 53.4
Fe 56	16.3 - 38.8	Hg	31.1 - 166.4
Fe 57	51.2 - 53.1	Tl	64.8 - 149.4
Co	4.3 - 46.7	Pb	4.7 - 22.5
Ni	4.9 - 68.8	Bi	128.7
Cu	3.8 - 28.5	U	4.6 - 73.3

* Relative Standard deviation

† See Appendix II for dectection limits

Table 2.2 Error for various analytical procedures.

		Accepted	**Measured**	**Standard**
Ion Chromatography	Cl^-	2.66 ± 0.03 ppm	2.63 ± 0.09 ppm	M-110
	SO_4^{2-}	0.65 ± 0.07 ppm	0.64 ± 0.01ppm	M-110
Atomic Absorption	Ca^{2+}	0.74 ± 0.1ppm	0.78 ± 0.06 ppm	M-108
	Na^+	2.98 ± 0.04 ppm	3.19 ± 0.22 ppm	M-108
	K^+	0.099 ±0.002 ppm	0.06 ± 0.03 ppm	M-108
	Mg^{2+}	0.366 ± 0.003 ppm	0.40 ± 0.01 ppm	M-108
Isotopes	$\delta^{34}S$	+20.32 ± 0.36‰	20.4 ± 0.3‰	NBS-127
	$\delta^{18}O_{SO4}$	+9.4 ± 0.3‰	9.4 ± 0.4‰	NBS-127
	$\delta^{18}O_{H2O}$		±0.2 ‰	

thus the limits of detection for some elements vary between these runs depending on the conditions of each run.

Certain elements are determined by measuring two or more isotopes of that element and choosing one of these to calculate a total concentration. Elements calculated this way include Li, Ca, Cr, and Fe. Which isotope is used depends on the limit of detection for each isotope and any interferences affecting the measurement of each isotope. In this case, Ca^{2+} was measured by atomic absorption and the ICP-MS numbers were not used.

2.3.2 Ion Chromatography

Concentrations of the anions Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} were measured by ion chromatography on a Dionex DX-100 Ion Chromatograph utilizing an IonPac AS4A analytical column with an IonPac AG4A Guard column using suppressed conductivity detection. The eluent was a 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ solution.

Standards for calibration were prepared using NIST prepared standard solutions. Six standards were used in the calibration which is assumed to be linear over the range of interest. Accuracy and precision were checked during each run using USGS standard solutions (M-108, M-110, and M-112) diluted to suit the range of interest (1/100).

2.3.3 Atomic Absorption Spectroscopy

Measurements of cation concentrations (Ca^{2+}, Na^+, K^+, and Mg^{2+}) were carried out by atomic absorption spectroscopy (AA). Calibration was carried out using five standards prepared from NIST standard solutions. A diluted USGS standard solution was used to check for accuracy (M-108).

2.4 Stable Isotopes

2.4.1 Sulphate Extraction

Sulphate was preconcentrated using an ion exchange resin (Bio-Rad AG1-X8 chloride form). It was then precipitated as $BaSO_4$ by the addition of $BaCl_2$. The full procedure is outlined in Appendix I.

2.4.2 Sulphur Isotopes

To analyze the sulphur isotopic composition, approximately 5 mg $BaSO_4$ was converted directly to $SO_{2\,(g)}$ by combustion at 950°C with V_2O_5 and SiO_2 (in a ratio of 1:10:10) using the procedure of Yanagisawa and Sakai (1983). The gas was then analyzed by mass spectrometer. Most of the samples were analyzed at Memorial University using a VG Micromass 903. It was necessary to measure eight of the samples at the University of Ottawa, while fourteen of the samples were analyzed at the University of Waterloo.

$BaSO_{4(s)}$ samples were sent to the University of Ottawa for $\delta^{34}S$ analysis while prepared gases were sent to the University of Waterloo. When samples were analyzed at other institutions, known standards were also sent to ensure the accuracy of the results. NBS-127 $BaSO_4$, with an accepted $\delta^{34}S$ of +20.32 ± 0.31‰, and an internal standard (MUN-Pyrite), with an accepted $\delta^{34}S$ value of 1.26‰, were used for this purpose. At Memorial it was necessary to calculate a calibration curve and again NBS-127 and MUN-Pyrite were used.

2.4.3 Oxygen Isotopes (Sulphate)

The oxygen isotopic values for sulphate were measured by converting the $BaSO_{4\,(s)}$ to $CO_{2\,(g)}$ by combustion at 1000°C with 99.999% pure graphite powder as outlined by Rafter (1967). This reaction produces both $CO_{2\,(g)}$ and $CO_{(g)}$ and the $CO_{(g)}$ is converted to $CO_{2\,(g)}$ by passing a high voltage across two platinum electrodes. The $CO_{2\,(g)}$ was analyzed using a Finnigan MAT 252 mass spectrometer at Memorial University.

NBS-127 $BaSO_4$ was again used to ensure the accuracy of these analyses. The accepted $\delta^{18}O$ value of NBS-127 is +9.4 ± 0.3‰. An internal standard was also used and twenty-two analyses of this $BaSO_4$ yielded a precision of ± 0.36‰.

2.4.4 Oxygen Isotopes (Water)

Analysis of the rain water for oxygen isotopic composition could not be carried out at Memorial University and the samples were sent to two different facilities. Ten of the samples were analyzed at the University of Waterloo and the rest were analyzed at the University of Ottawa. The analysis is carried out by equilibrating a small sample of the water with $CO_{2\,(g)}$ of known isotopic composition. $CO_{2\,(g)}$ is added to a vessel containing the water sample, under vacuum, and the system is allowed to equilibrate in a water bath at 25°C for a number of hours. The isotopic composition of the $CO_{2\,(g)}$ is then measured and used along with the fractionation factor between the water and $CO_{2\,(g)}$ to calculate the isotopic composition of the water.

CHAPTER 3

RESULTS

A total of sixty-six samples of rain and snow were collected, of which thirty-four were from St. John's, fourteen from Seal Cove, and eighteen from Nepean. Sampling took place between May 1994 and May 1995 for the St. John's site, while the Nepean and Seal Cove sites both started sampling in July 1994. Complete tables of all analytical results can be found in Appendix II. Sample descriptions including the opening and closing date and time for the collector and the approximate volumes can be found in Tables II.1 to II.3.

3.1 Chemical Composition

Volume weighted mean (VWM) concentrations have been calculated for each variable measured. Since the snow samples were collected by a different method, precipitation amounts were obtained for each of the events sampled from Environment Canada. These were then used to determine the equivalent amount of rain which would have been collected using the event collector. These values were not available however, for the two snow samples collected at Seal Cove, and therefore these samples have been omitted from the calculation of VWMs. They have, however, been included in the concentration ranges reported for each element.

Some other important considerations must be made when examining this data. Not every rain event during the sampling period was collected. There is no way of knowing how much bias this may have introduced into the results although efforts were made to collect both small and large rain events. Nevertheless, the concentrations cannot be used to calculate total deposition at each site over the time of sampling because of these missing data. Only one sample was taken in some months, and if this was an unusually concentrated or dilute event, the monthly volume weighted means will be skewed. Seasonal volume weighted means have also been calculated, however the number of samples collected during winter and summer was not always the same, and this may cause some difficulty for comparisons.

3.1.1 pH and Conductivity

The pH and conductivity of each sample can be found in Tables II.4 to II.6. Variation in pH was found between the three sites and Nepean has the most acidic values with a volume weighted mean of 4.53. Seal Cove has the highest pH values with a mean of 5.48 and St. John's is intermediate with a mean pH of 4.82. While the mean values were different, the overall range of observed pHs was similar for each site.

There was also variation in the conductivities measured for each site. Nepean had the widest range of 8.0 to 158.6 μS/cm with an average of 43.3 μS/cm. Seal Cove had the lowest values ranging from 7.6 to 28.6 μS/cm with an average of 16.0 μS/cm. St. John's was again in the middle with an average conductivity of 24.9 μS/cm but with a large range of 5.6 to 66.2 μS/cm.

3.1.2 Major Ion Composition

Tables II.7 to II.12 give the anion and cation concentrations for each site while Table 3.1 gives the volume weighted mean and range for each ion at the three sites. Phosphate has been omitted from the anion tables as all the values were below detection.

Figure 3.1 is a representation of the relative proportions of anions and cations at each site (in equivalents) with the total equivalents listed at the bottom of the figure. There appears to be ion balance at the Seal Cove site, however discrepancies exist between anions and cations at the St. John's and Nepean sites. The discrepancy at St. John's is quite small, however at the Nepean site the anions are 3x more than the cations. Unfortunately, ammonium (NH_4^+) concentrations were not measured during this study, and this is most likely the species which would make up this difference. Ammonium concentrations tend to be much higher in continental environments (see Table 1.5), and therefore this would explain the larger discrepancy at Nepean.

Figure 3.1 quite clearly shows that the behaviour of the major ions at the St. John's and Seal Cove sites is similar. Both sites are characterized by high concentrations of Cl^-, Na^+, and SO_4^{2-}, although St. John's has higher concentrations of each, particularly SO_4^{2-} which is 2.5x greater at St. John's. The ranges for these ions are also quite large, but St. John's experiences the greater variation. The sites also have similar concentrations of Ca^{2+}, Mg^{2+}, K^+, and NO_3^- which are all present in fairly low concentrations. K^+ is the only species whose concentration is higher at Seal Cove and with a larger range than St. John's.

Table 3.1 Volume weighted means and ranges for major ions at each site (concentrations in ppm).

	St. John's		Seal Cove		Nepean	
	VWM	**Range**	**VWM**	**Range**	**VWM**	**Range**
Ca^{2+}	0.28	0.03 - 1.61	0.26	<ld - 1.43	0.50	0.05 - 1.71
Mg^{2+}	0.15	<ld - 0.50	0.12	<ld - 0.36	0.05	<ld - 0.20
K^+	0.04	<ld - 0.18	0.12	<ld - 0.69	0.04	<ld - 0.19
Na^+	1.49	0.12 - 6.98	0.99	0.07 - 2.12	0.19	0.02 - 1.01
Cl^-	2.30	0.17 - 7.36	1.60	0.07 - 3.42	0.13	0.03 - 0.78
SO_4^{2-}	2.19	0.20 - 10.36	0.64	0.13 - 2.90	2.62	0.31 - 9.41
NO_3^-	0.27	0.06 - 0.88	0.23	<ld - 1.75	1.73	0.30 - 6.38

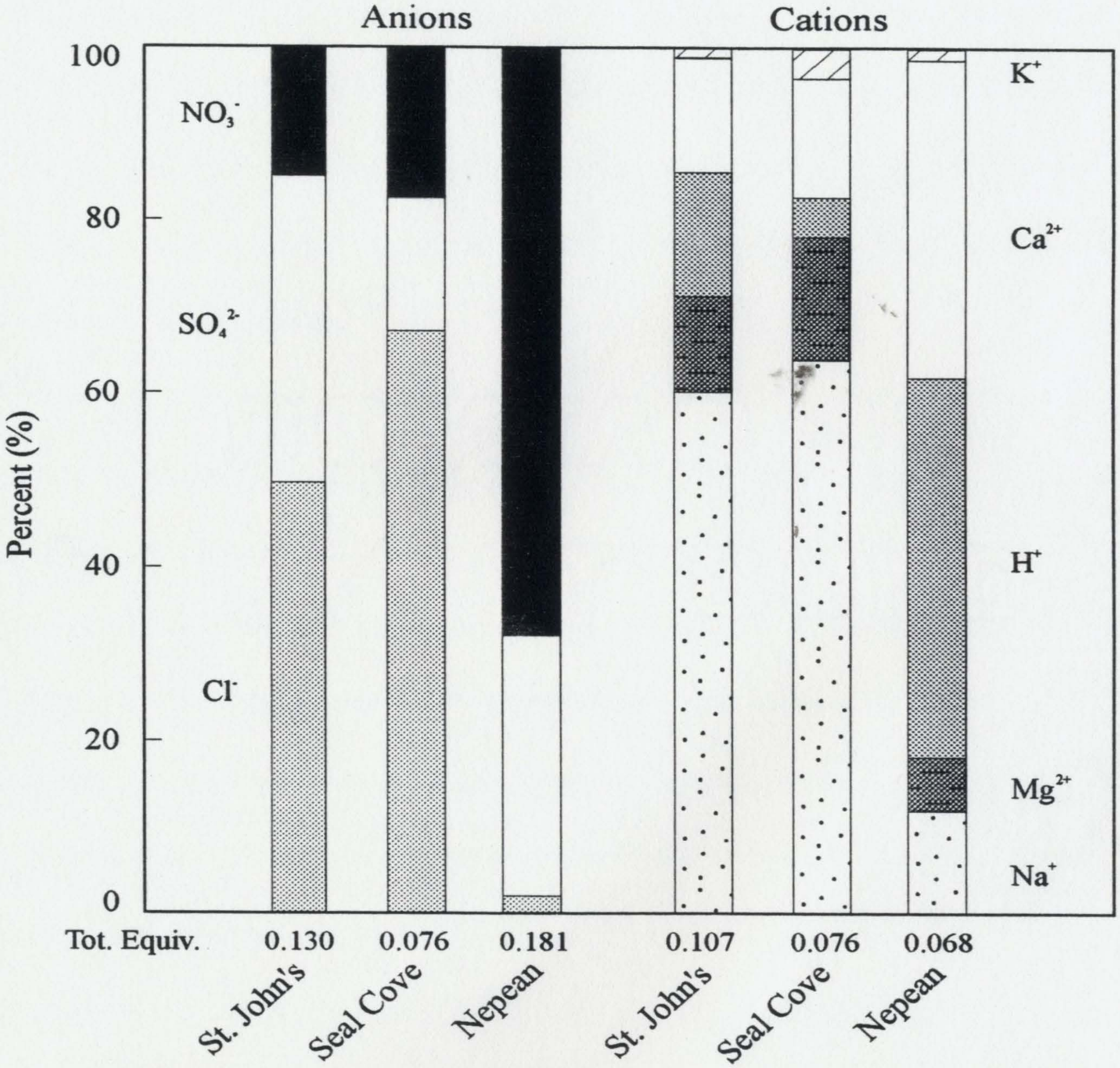

Figure 3.1 Relative proportions (in equivalents) of anions and cations for each site. These should not be taken to represent ion balances at each site (see text).

The Nepean site shows significantly different behaviour from the Newfoundland sites. Here the dominant ions are Ca^{2+}, SO_4^{2-}, NO_3^- and these ions are present in higher mean concentrations than at the other sites. The ranges for Ca^{2+} are similar at each site while the range for SO_4^{2-} is similar to St. John's but is much higher than Seal Cove. The NO_3^- range is much larger at Nepean than at either of the Newfoundland sites. Sodium and Cl^- which were dominant at the Newfoundland sites, are present in low concentrations at Nepean. Mg^{2+} is also present in lower concentrations while K^+ is similar to St. John's in both the mean and range values.

If the monthly volume weighted means are examined, a number of correlations can be found in the behaviour of the major ions. The most obvious at the St. John's and Seal Cove sites is the tendency for Na^+, Cl^-, Mg^{2+} and K^+ to correlate in their behaviour (Figures 3.2 and 3.3). This tendency can also be seen for Na^+ and Cl^- at the Nepean site, however the correlation is not as strong, and Mg^{2+} seems to correlate more with Ca^{2+} (Figure 3.4).

In terms of seasonal trends, differences are found between summer (April to September) and winter (October to March) volume weighted means. The seasonal VWM values for each site are given in Table 3.2.

Similarities can once more be found between the St. John's and Seal Cove sites, although some differences do emerge. At both sites, Na^+, Cl^- and Mg^{2+} have their highest values in winter. St. John's however has a marked winter high for SO_4^{2-} while Seal Cove shows no real difference. The opposite is true for NO_3^{2-}, Ca^{2+}, and K^+ which vary at Seal

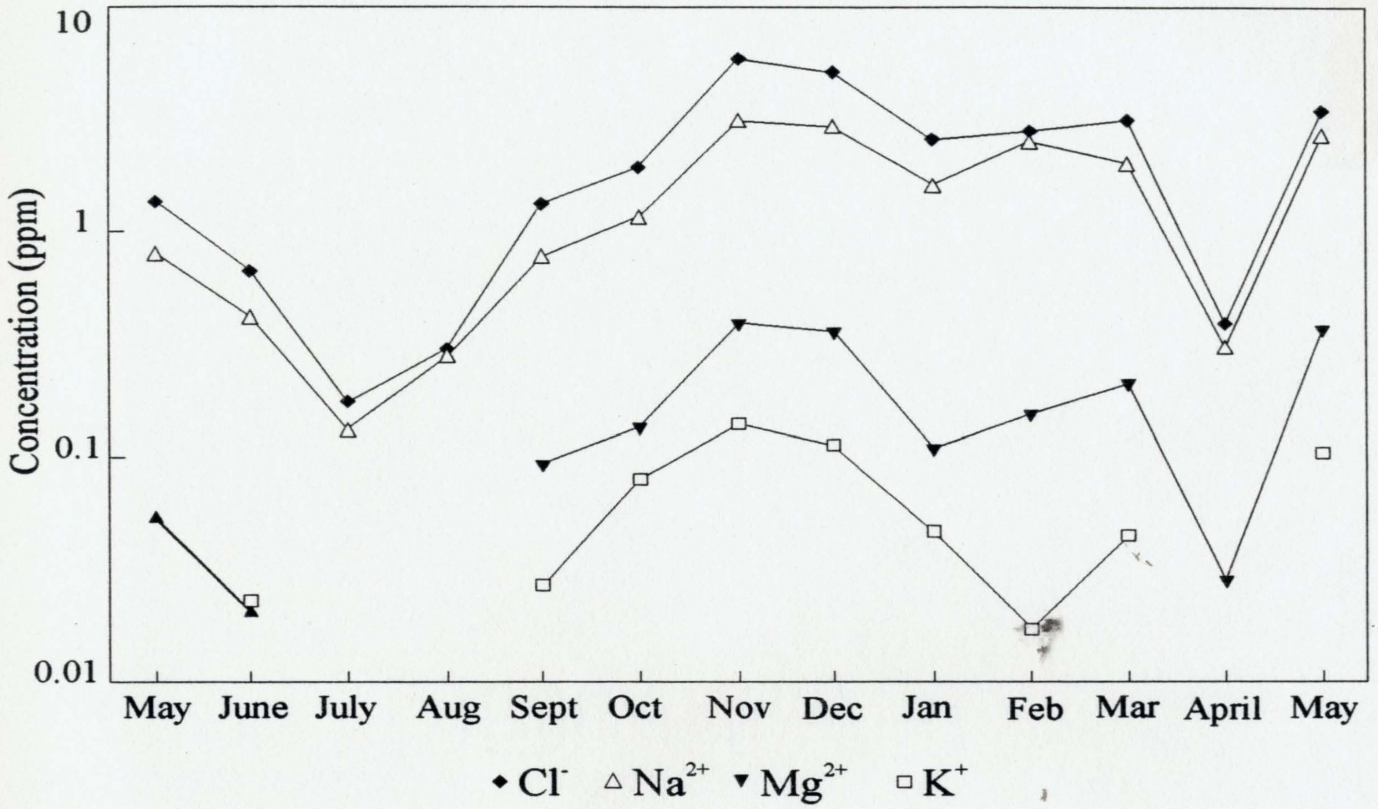

Figure 3.2 Monthly VWM concentrations for ions at St. John's.

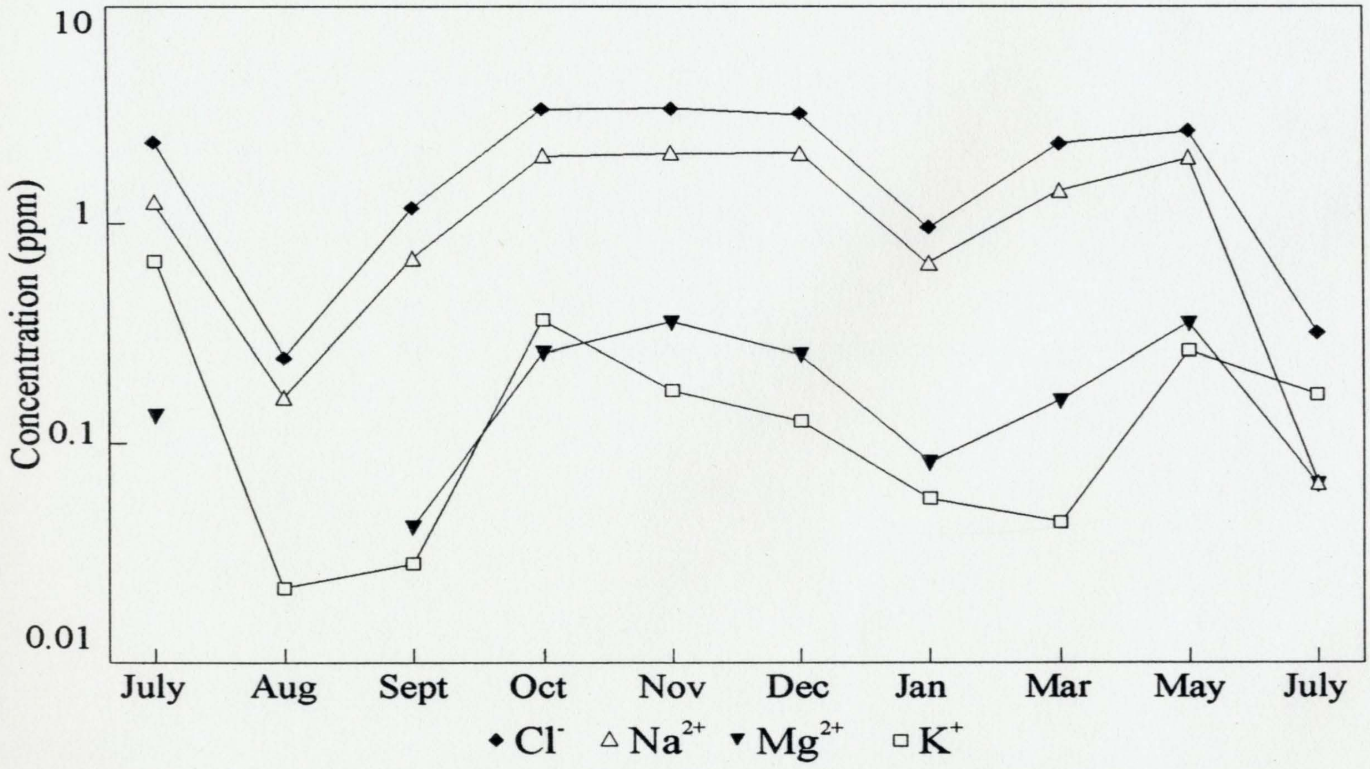

Figure 3.3 Monthly VWM concentrations for ions at Seal Cove.

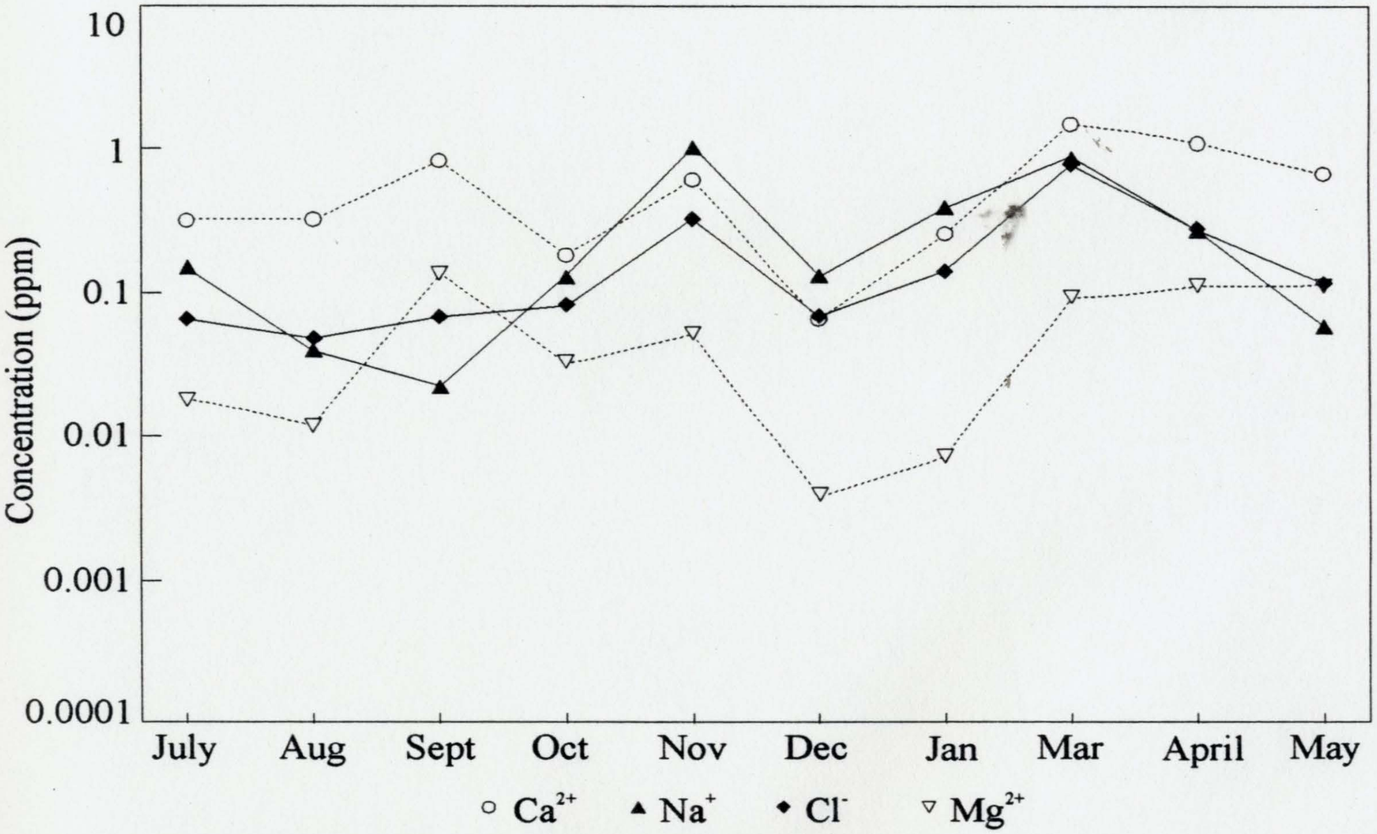

Figure 3.4 Monthly VWM concentrations for ions at Nepean.

Table 3.2 Seasonal VWM values for major ions at each site (concentrations in ppm).

	St. John's		**Seal Cove**		**Nepean**	
	Summer	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**
Ca^{2+}	0.29	0.28	0.17	0.39	0.57	0.32
Mg^{2+}	0.06	0.22	0.05	0.22	0.06	0.03
Na^{+}	0.61	2.31	0.50	1.64	0.13	0.33
K^{+}	0.02	0.07	0.08	0.19	0.03	0.06
Cl^{-}	0.95	3.55	0.87	2.59	0.11	0.17
SO_4^{2-}	1.28	3.03	0.61	0.67	3.10	1.48
NO_3^{-}	0.29	0.26	0.32	0.10	1.82	1.51

Cove while at St. John's they show no appreciable change. At Seal Cove, NO_3^- is highest in the summer while Ca^{2+} and K^+ are highest in the winter.

Like the Newfoundland sites, Nepean experiences winter highs for Na^+ and Cl^- although not for Mg^{2+} which shows little variation. Nepean also has summer highs for Ca^{2+}, SO_4^{2-}, and NO_3^-. K^+ seems to show little variation, similar to the St. John's site.

PSS values have been calculated using the formula shown in Section 1.2.2.1.1. For comparison, calculations were made using Cl^-, Na^+, and Mg^{2+} as the conservative tracer and the values are reported in Tables II.13 to II.15 and are summarized in Table 3.3 along with the range for each site. Although there are a few samples for which large discrepancies were found, it appears that either PSS_{Cl} or PSS_{Na} values can be used at each of the sites as overall there is no significant difference between the values ($R = 0.981$) (Figure 3.5). The values calculated using Mg^{2+} however, seen to deviate from those calculated with the other two species ($R = 0.932$ for PSS_{Mg} vs PSS_{Cl}) (Figure 3.6). Sulphur isotopic results may provide a clearer picture and will be reported in a later section.

The PSS values clearly reflect the strength of the marine source at each site. The Nepean continental site has extremely low PSS values ranging from 0.1% to 6.2%. The two marine sites exhibit much larger ranges with St. John's exhibiting an average PSS value of 23.4% and Seal Cove an average of 42.6%.

If the other ions are examined and compared with the bulk seawater Cl^- ratios some interesting features emerge. Table 3.4 summarizes these ratios. St. John's and Seal Cove

Table 3.3 Summary of average PSS values for each site.

	St. John's	**Seal Cove**	**Nepean**
PSS_{Cl}	23.4	42.6	1.2
Range	1.0 - 79.4	9.0 - 85.1	0.1 - 6.2
PSS_{Na}	27.1	46.3	3.9
Range	1.4 - 90.2	4.9 - 92.6	0.1 - 30.7
PSS_{Mg}	20.4	41.1	4.8
Range	1.7 - 74.1	11.3 - 92.1	2.4 - 13.9

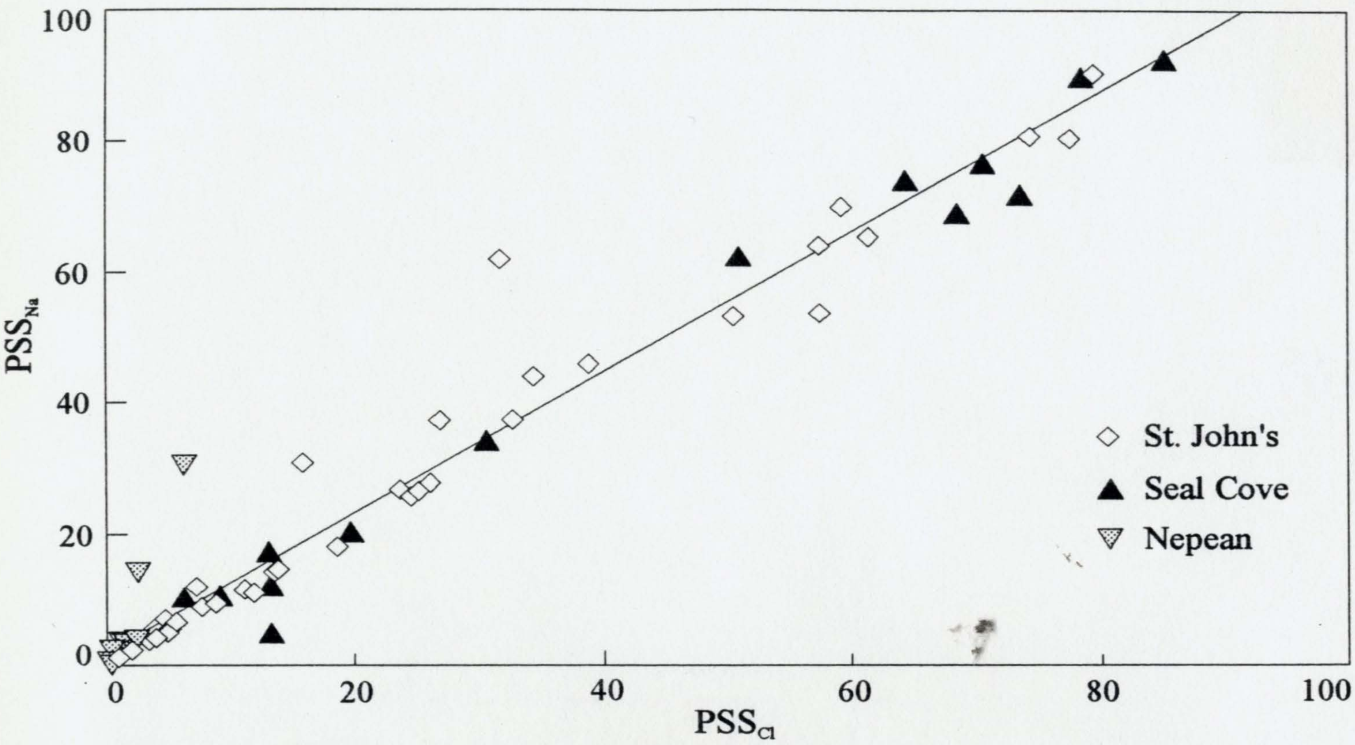

Figure 3.5 PSS_{Na} plotted against PSS_{Cl} for all samples.

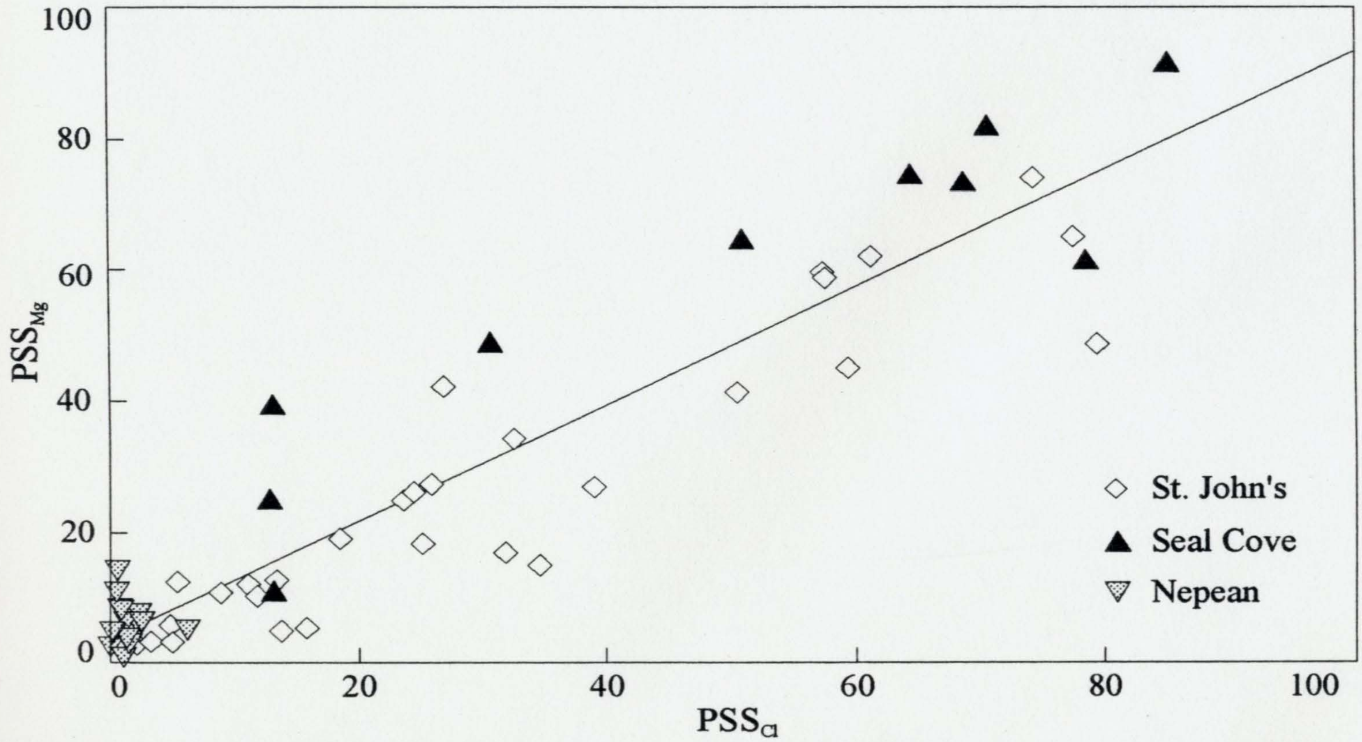

Figure 3.6 PSS_{Mg} plotted against PSS_{Cl} for all samples.

Table 3.4 Ion/Cl^- ratios for each site. Seawater values taken from Berner and Berner (1987).

Site	Ca^{2+}	K^+	Mg^{2+}	Na^+	SO_4^{2-}
Seawater	0.02	0.02	0.07	0.56	0.14
St. John's	0.13	0.02	0.07	0.59	0.71
Seal Cove	0.16	0.08	0.08	0.62	0.40
Nepean	3.80	0.31	0.38	1.46	20.2

have ratios which are quite close to seawater for Na^+ and Mg^{2+} while the ratios for Ca^{2+} and SO_4^{2-} are much higher than seawater. K^+ is close to its seawater ratio for St. John's as well, while Seal Cove is a bit high. Nepean has high ratios for all of the ions especially for SO_4^{2-}/Cl^- which is almost 150x greater than seawater.

3.1.3 Trace Metals

Concentrations were measured for forty-five elements and a complete table of these results is given in Appendix II. A number of the elements were below detection for all or most of the samples and these have been omitted from the summary tables in this section. Table 3.5 summarizes VWM metal concentrations for each site as well as the range of values at each site. When looking at these averages it is important to realize that often many samples have values below the detection limits and the mean can be influenced by only one or two samples with high concentrations. For samples below detection, values of half the detection limit have been used in the calculation of VWMs in order to avoid bias. The percentage of samples above the detection limit has been included in the table.

In order to see how the data compare with that of other areas, it can be compared to median values for metals in rain at urban, rural and remote locations compiled by Galloway *et al.* (1982). The St. John's site generally has the highest mean trace metal concentrations of the three sites and they are comparable with urban values from other studies. While a few elements such as Cr, Ni, and Zn are above the median, they are nevertheless well within the range for urban values (Table 1.11). The elements Mn, Co,

Table 3.5 VWM and Ranges for metal concentrations at each site *.

	Al	V	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Rb
St. John's											
VWM	9.17	66.77	33.73	159.83	4.10	0.94	70.56	3.43	186.65	<0.18	0.08
Range	<3.8 - 24.6	<0.81 - 531.8	<0.21 - 531.	<9 - 1607	<0.13 - 29.32	<0.01 - 10.06	<0.18 - 814.79	<0.46 - 26.9	<0.37 - 560.28	<0.18 - 0.44	<0.20 - 0.19
% samples †	35	58	35	29	97	94	87	74	97	3	48
Seal Cove											
VWM	6.11	1.89	<0.24	<9	4.80	0.04	0.59	0.48	146.35	0.12	0.10
Range	<3.8 - 11.5	<0.81 - 11.5	-	-	0.51 - 39.98	<0.01 - 0.11	<0.18 - 4.74	<0.46 - 3.39	2.15 - 426.85	<0.18 - 0.26	<0.20 - 0.68
% samples †	17	33	0	0	100	83	92	58	100	8	58
Nepean											
VWM	7.20	0.95	0.14	7.07	1.87	0.05	0.19	0.54	83.84	0.14	0.07
Range	<3.8 - 29.8	<0.81 - 2.64	<0.24 - 1.05	<9 - 30	0.46 - 8.29	<0.02 - 0.18	<0.18 - 1.84	<0.29 - 2.21	4.22 - 398.32	<0.17 - 0.41	<0.20 - 0.15
% samples †	31	6	6	12	100	94	31	50	100	31	56

*All concentrations in ppb

† % samples above detection limit

Table 3.5 (cont.) VWM and Ranges for metal concentrations at each site *

	Sr	Mo	Cd	Sn	Sb	I	Ba	La	Ce	Pb	Bi
St. John's											
VWM	1.26	4.45	0.05	0.10	0.03	0.44	0.81	0.03	0.01	0.48	<0.01
Range	<0.02 - 3.53	<0.03 - 48.5	<0.02 - 0.14	<0.05 - 0.49	<0.01 - 0.10	<0.16 - 2.21	0.03 - 2.94	<0.00 - 0.39	<0.00 - 0.05	<0.03 - 2.14	-
% samples †	98	75	65	45	97	74	100	97	87	94	3
Seal Cove											
VWM	0.93	0.16	0.03	0.07	0.03	0.36	0.59	0.04	0.00	0.13	0.01
Range	0.17 - 1.70	<0.03 - 0.86	<0.02 - 0.11	<0.05 - 0.33	<0.01 - 0.05	<0.16 - 2.46	0.21 - 2.16	0.00 - 0.41	<0.00 - 0.01	<0.09 - 0.34	<0.01 - 0.08
%samples †	100	92	58	58	92	58	100	100	92	83	17
Nepean											
VWM	1.11	0.04	0.04	0.09	0.06	0.20	0.90	0.01	0.01	0.77	0.00
Range	0.14 - 4.59	<0.01 - 0.41	<0.02 - 0.18	<0.05 - 0.30	0.01 - 0.20	<0.16 - 1.00	0.50 - 3.15	<0.00 - 0.06	<0.00 - 0.08	0.10 - 3.37	<0.01 - 0.02
% samples †	100	56	75	87	100	50	100	87	94	100	25

All concentrations in ppb

† % samples above detection limit

Cu, Cd and Pb were below the median rural values although ranges found in rural and urban areas tend to overlap. Overall there is great variation in the metal concentrations from sample to sample. A number of samples far exceed the urban values while others have very low concentrations for all metals.

The only metals which were found to be highest at the other sites were Mn (highest at Seal Cove) and Sb and Pb (highest at Nepean). Seal Cove has the lowest mean values for Co, Cu, Cd, Pb and Sb while Nepean has the lowest mean values for V, Mn, Ni, Zn, and Mo. Seal Cove and Nepean concentrations are both generally below the urban and rural averages except in the case of Zn which is high at all three sites. These sites show much less variation in metal concentrations from sample to sample than does the St. John's site.

Seasonal volume weighted means were also calculated for the metals and these are given in Table 3.6. Generally, concentrations for most of the metals are highest during the winter months although there are differences between the sites. The only metal at the St. John's site to exhibit a summer maximum is Ba while at Seal Cove, Pb is the only metal to reach a summer maximum. At Nepean, however, Mn, Sr, Ba, and Pb all have summer maximums. Cu, Rb, Cd, Sn, Sb, La, and Ce seem to show little or no variation at any of the sites while additionally Co and Ba do not vary significantly at Seal Cove, and Co, Mo, and I show no seasonal variation at Nepean.

Table 3.6 Seasonal VWM metal concentrations for each site *.

	Al	**V**	**Cr**	**Fe**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Rb**
St. John's										
Summer	6.39	23.50	4.23	25.48	1.86	0.17	12.54	1.56	145.84	0.06
Winter	11.67	105.88	60.40	281.24	6.12	1.82	136.85	5.70	248.33	0.11
SealCove										
Summer	3.03	1.04	-	-	4.04	0.03	0.26	0.47	141.29	0.09
Winter	9.29	2.78	-	-	5.59	0.04	0.93	0.50	151.58	0.11
Nepean										
Summer	6.05	0.98	0.12	6.30	2.10	0.04	0.11	0.57	43.90	0.06
Winter	9.33	0.88	0.19	8.52	1.44	0.07	0.32	0.49	158.46	0.08

*All concentrations in ppb.

Table 3.6 (Cont.) Seasonal VWM metal concentrations for each site *.

	Sr	Mo	Cd	Sn	Sb	I	Ba	La	Ce	Pb	As
St. John's											
Summer	0.68	0.68	0.03	0.10	0.02	0.24	0.98	0.01	0.01	0.28	-
Winter	1.99	8.75	0.07	0.11	0.04	0.69	0.72	0.05	0.01	0.74	-
SealCove											
Summer	0.58	0.06	0.03	0.09	0.02	0.28	0.61	0.01	-	0.18	0.10
Winter	1.30	0.26	0.03	0.05	0.03	0.45	0.56	0.06	-	0.08	0.14
Nepean											
Summer	1.24	0.03	0.05	0.10	0.06	0.18	0.98	0.01	0.01	0.86	0.12
Winter	0.87	0.06	0.04	0.09	0.06	0.22	0.76	0.02	0.01	0.59	0.16

*All concentrations in ppb.

3.2 Isotopic Composition

Tables II.16 to II.18 list the results of the sulphur, and oxygen (sulphate and water) isotope analyses for each of the samples at the three sites while Tables 3.7 and 3.8 summarize the volume weighted means and ranges for each site.

3.2.1 Sulphur Isotopes

The differences between the marine sites and the continental site, which have been noted for the chemical components, are also seen in their sulphur isotopic compositions. The average $\delta^{34}S$ value for the Nepean site is 4.4‰, while the marine sites, St. John's and Seal Cove, have values of 7.1‰ and 10.0‰ respectively. The range for the Nepean site is quite restricted, varying only between 3.0 and 5.9‰. The ranges for the Newfoundland sites are much larger. The St. John's samples $\delta^{34}S$ values range between 2.2 and 18.6‰ while those of Seal Cove range between 5.5 and 16.3‰.

The isotopic composition of the NSS fraction can be calculated from the PSS and $\delta^{34}S_{TOT}$ data using the equation:

$$\delta^{34}S_{TOT} = PSS * \delta^{34}S_{SS} + (100 - PSS) * \delta^{34}S_{NSS}$$

The subscripts TOT, SS, and NSS stand for total, seaspray, and non-seaspray respectively. A value of +21‰ has been assumed for $\delta^{34}S_{SS}$. These values have been calculated for the St. John's and Seal Cove sites, and are reported in Appendix II with a summary in Table 3.7. The PSS values for Nepean are extremely small and therefore NSS values were not calculated. The average $\delta^{34}S_{NSS}$ values for St. John's and Seal Cove are +4.7‰ and +3.0‰

Table 3.7 Summary of sulphur isotopic results for each site.

	St. John's	Seal Cove	Nepean
$\delta^{34}S$	7.3	10	4.4
Range	2.2 - 18.6	5.5 - 16.3	3.0 - 5.9
Summer	9.4	8.2	4.4
Winter	6.5	11.8	5.1
$\delta^{34}S_{NSS}$	4.7	3	-
Range	-10 - 14.8	-10.8 - 9.5	-
Summer	7.9	5.2	-
Winter	3.6	0.9	-

All values in ‰ with respect to CDT

Table 3.8 Summary of oxygen isotopic results for each site.

	St. John's	Seal Cove	Nepean
$\delta^{18}O_{SO4}$	29	12.8	14.7
Range	9.8 - 41.7	10.2 - 16.2	8.5 - 20.5
Summer	21.6	-	15.1
Winter	31.7	-	13.4
$\delta^{18}O_{NSS}$	30.8	14.5	-
Range	9.8 - 42	11.9 - 29.0	-
Summer	22.5	-	-
Winter	33.9	-	-
$\delta^{18}O_{H2O}$	-8.9	-7.6	-9.8
Range	(-14.8) - (-3.7)	(-12.8) - (-1.3)	(-21.4) - (-4.1)
Summer	-7.6	-	-8.4
Winter	-9.9	-	-13.2

All values in ‰ with respect to VSMOW.

respectively. The ranges observed at these sites are quite large. For St. John's the range is -10‰ to +14.8‰ while the range for Seal Cove is -10.8‰ to +9.5‰. The extremely low values were snow samples at both sites while a few rain samples had $\delta^{34}S_{NSS}$ values just below 0‰.

Typically, $\delta^{34}S_{SO4}$ is plotted against PSS and often reveals trends in the data. In this study it also highlights differences between the sites. Both the St. John's and Seal Cove sites exhibit linear trends suggestive of two-source mixing (Figures 3.7 and 3.8). The St. John's data are described by the equation:

$$\delta^{34}S = 0.126(\pm 0.05)*PSS + 6.30(\pm 1.66)$$

with an intercept of 18.9‰ at 100 PSS and +6.3‰ at 0 PSS. The correlation coefficient is 0..720 although some scatter can be seen, especially at lower PSS values which may indicate a third source. The Seal Cove data exhibit a much better fit with a correlation coefficient of 0.894 and are described by the equation:

$$\delta^{34}S = 0.124(\pm 0.05)*PSS + 5.82(\pm 2.50)$$

and the intercept at 100 PSS is +18.1‰ and +5.8‰ at 0 PSS. These regressions have been plotted along with the 95% confidence interval associated with them. In both cases the $\delta^{34}S$ at 100 PSS is not significantly different from bulk seawater dissolved sulphate. Using PSS_{Na} instead of PSS_{Cl} makes no real difference in these values. For example, at St. John's, the correlation coefficient is still 0.720 and the intercept at 100 PSS is 18.1‰ while at Seal Cove R becomes 0.892 with an intercept of 17.5‰ at 100 PSS. The fact that the

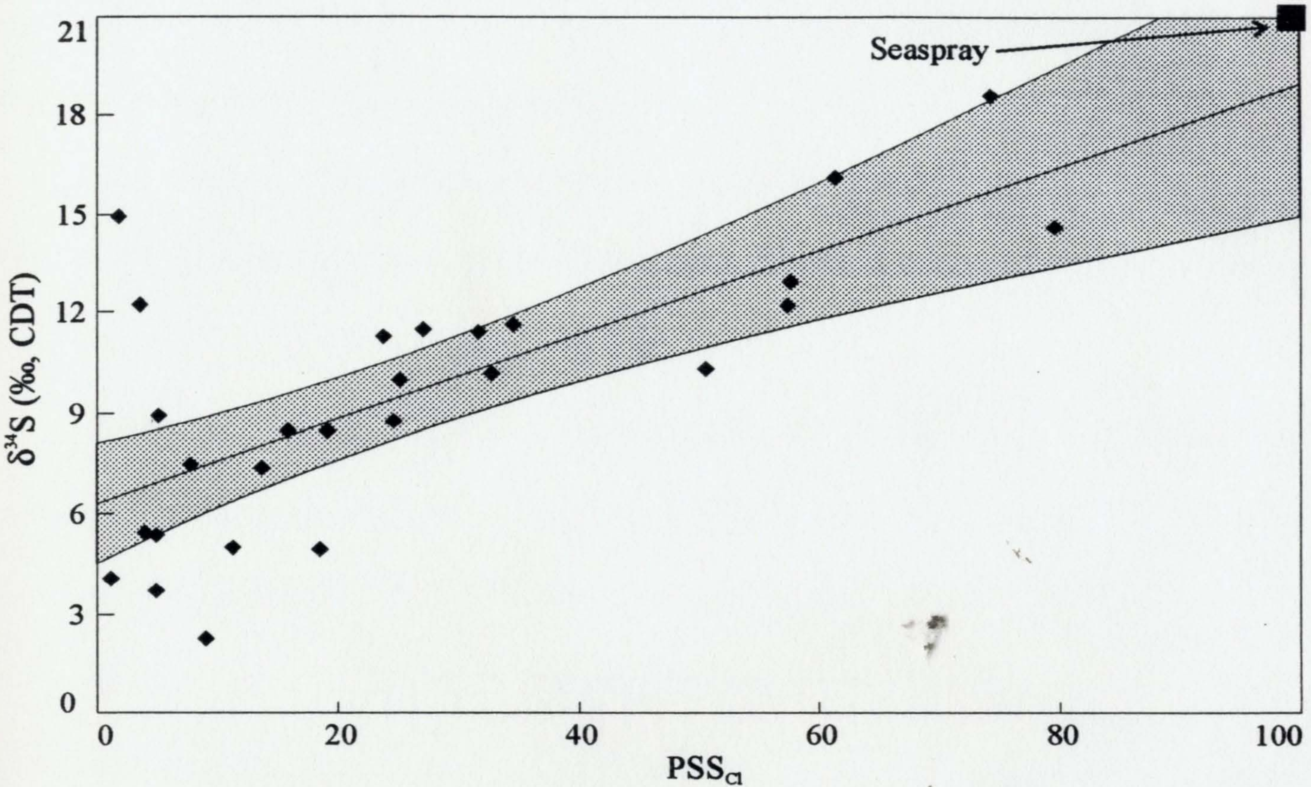

Figure 3.7 $\delta^{34}S$ plotted against PSS_{Cl} for St. John's. The line represents the regression and the shaded area represents the 95% confidence level.

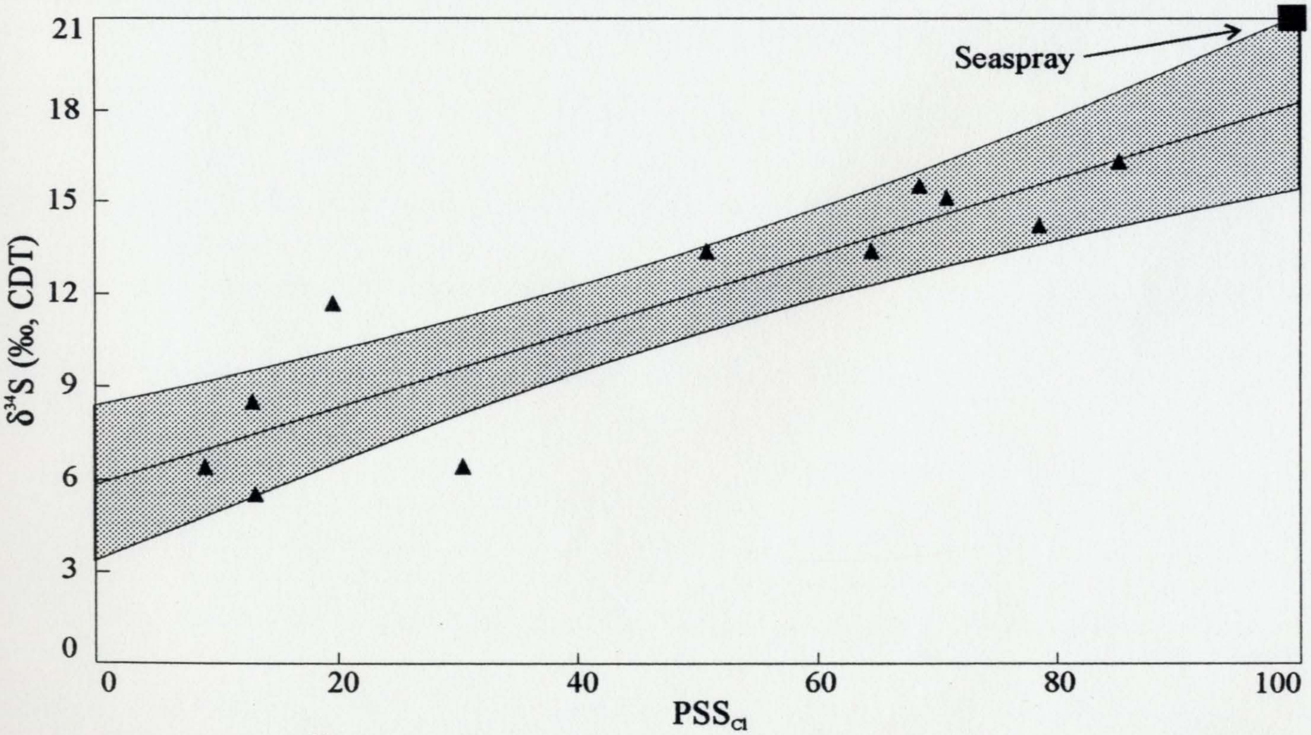

Figure 3.8 $\delta^{34}S$ plotted against PSS_{Cl} for Seal Cove. The line is the linear regression and the shaded area represents the 95% confidence level.

intercepts are further from the bulk seawater values when PSS_{Na} is used would seem to further confirm the validity of using PSS_{Cl}.

The Nepean data clearly contrasts with the St. John's and Seal Cove data. No linear trend (R of 0.533) can be found in this data set, and it clusters rather well with small ranges in both PSS and $\delta^{34}S$ (Figure 3.9).

When the data for all three sites is combined, a linear trend is observed with a correlation coefficient of 0.850, an intercept of 18.9‰ at 100 PSS and an intercept of +5.3‰ at 0 PSS (Figure 3.10). This trend is described by the equation:

$$\delta^{34}S = 0.136(\pm 0.02)*PSS + 5.29(\pm 0.78)$$

Summer (April to September) and winter (October to March) volume weighted means have been calculated for the sulphur data (Table 3.7), and seasonal variation can be seen at the three sites. St. John's has a summer enrichment of 2.9‰ while Seal Cove has a winter enrichment of 3.6‰. The Nepean site on the other hand exhibits a small enrichment of +0.7‰ in winter. Seasonal differences also appear in the $\delta^{34}S_{NSS}$ values. St. John's is again enriched in the summer by 4.3‰ while Seal Cove shows the opposite trend from its $\delta^{34}S$ values and is enriched in the summer by 4.3‰.

3.2.2 Oxygen Isotopes

The oxygen isotopic data also highlights interesting distinctions between the localities. The average $\delta^{18}O_{SO4}$ values are 30.0‰, 12.8‰, and 14.7‰ for St. John's, Seal Cove, and Nepean respectively. Seal Cove has the smallest range of 10.2‰ to 16.2‰,

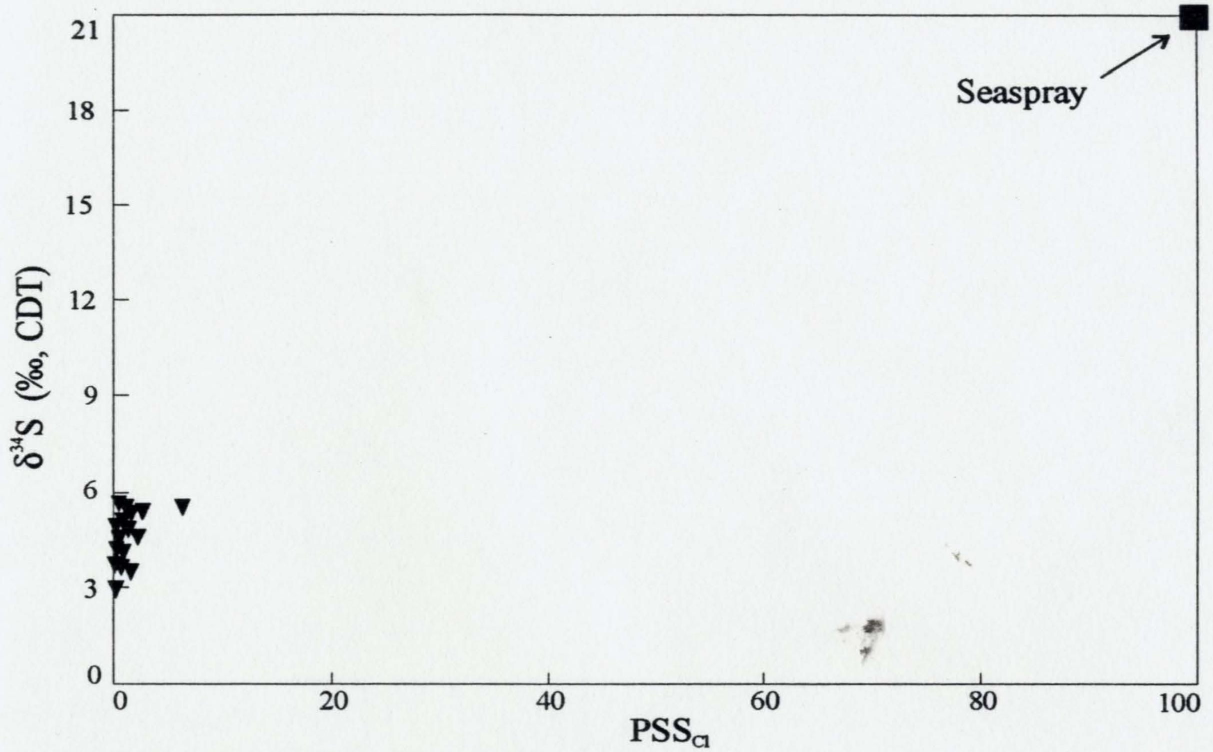

Figure 3.9 $\delta^{34}S$ plotted against PSS_{Cl} for Nepean.

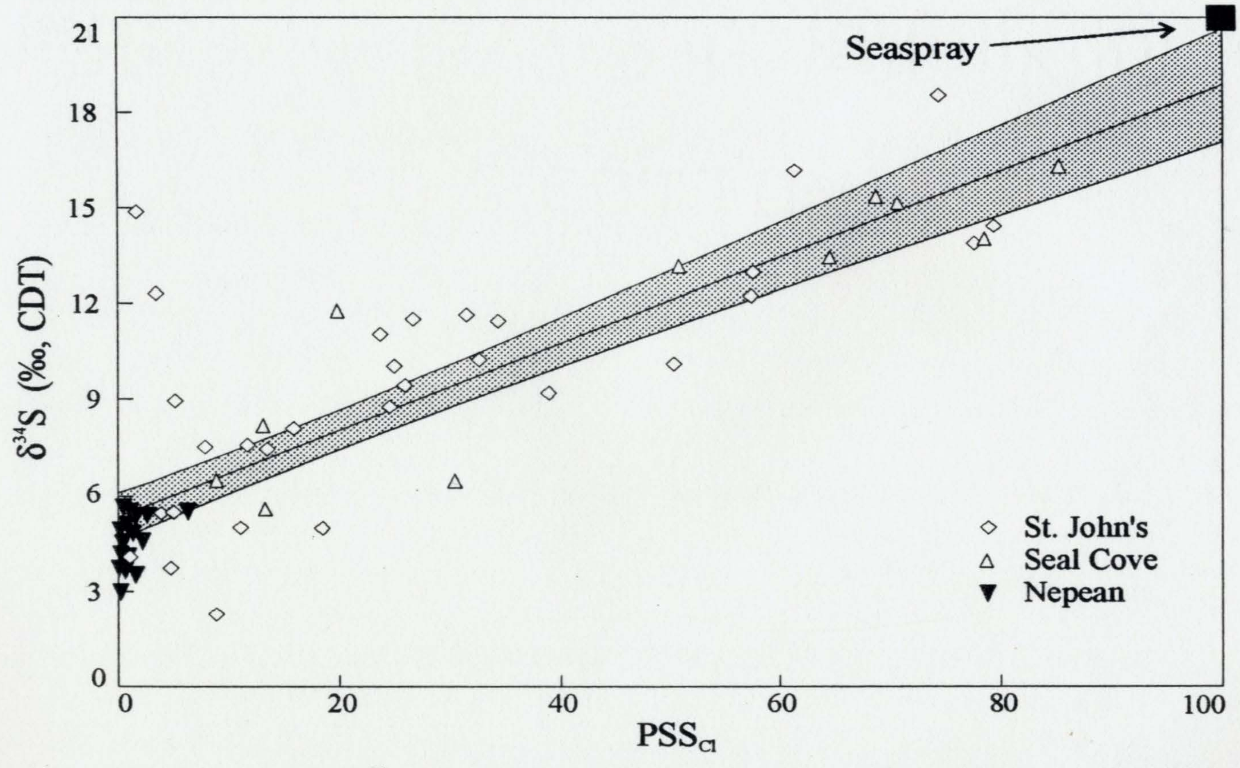

Figure 3.10 $\delta^{34}S$ plotted against PSS_{Cl} for all samples. The line represents the linear regression while the shaded area represents the 95% confidence interval of the regression.

although only six of the fourteen samples at this site could be analyzed for oxygen isotopic composition. The Nepean site has a larger range of 8.5‰ to 20.5‰, while the St. John's site displays an extremely large range of 9.8‰ to 41.7‰.

As with the sulphur data, non-seaspray values were calculated for the oxygen isotopic data. St. John's has a mean $\delta^{18}O_{NSS}$ of 31.7‰ while Seal Cove has a mean of only 14.5‰. St. John's experiences a large range of $\delta^{18}O_{NSS}$ (+9.8 - +42.0‰) which is 10‰ greater than the range for Seal Cove (+11.9 - +29‰).

The $\delta^{18}O_{SO4}$ data was also plotted versus PSS (Figures 3.11 to 3.13) to examine the relationship with seaspray. The Nepean site seems to exhibit no trends with respect to PSS. The St. John's data however, defines a triangular envelope widening at low PSS values to a range of 10‰ to 41.7‰, and narrowing in on a $\delta^{18}O_{SO4}$ value of +9.5‰ at 100 PSS. The Seal Cove data also seems to converge on the seawater sulphate $\delta^{18}O$ value of +9.5‰ at 100 PSS although the number of samples is small.

To examine the data further for local oxidation processes, $\delta^{18}O_{NSS}$ can be plotted against $\delta^{18}O_{H2O}$. No strong correlations are revealed by these plots. However, if the monthly volume weighted means are compared month to month, the Seal Cove location appears to exhibit some correlation (Figure 3.14). The St. John's data also seems to show a correlation, but it is an inverse trend, not what would be expected (Figure 3.15).

Seasonal variation may be seen in the VWM $\delta^{18}O_{SO4}$ values for summer and winter for St. John's and Nepean. Unfortunately there was not enough data for Seal Cove to

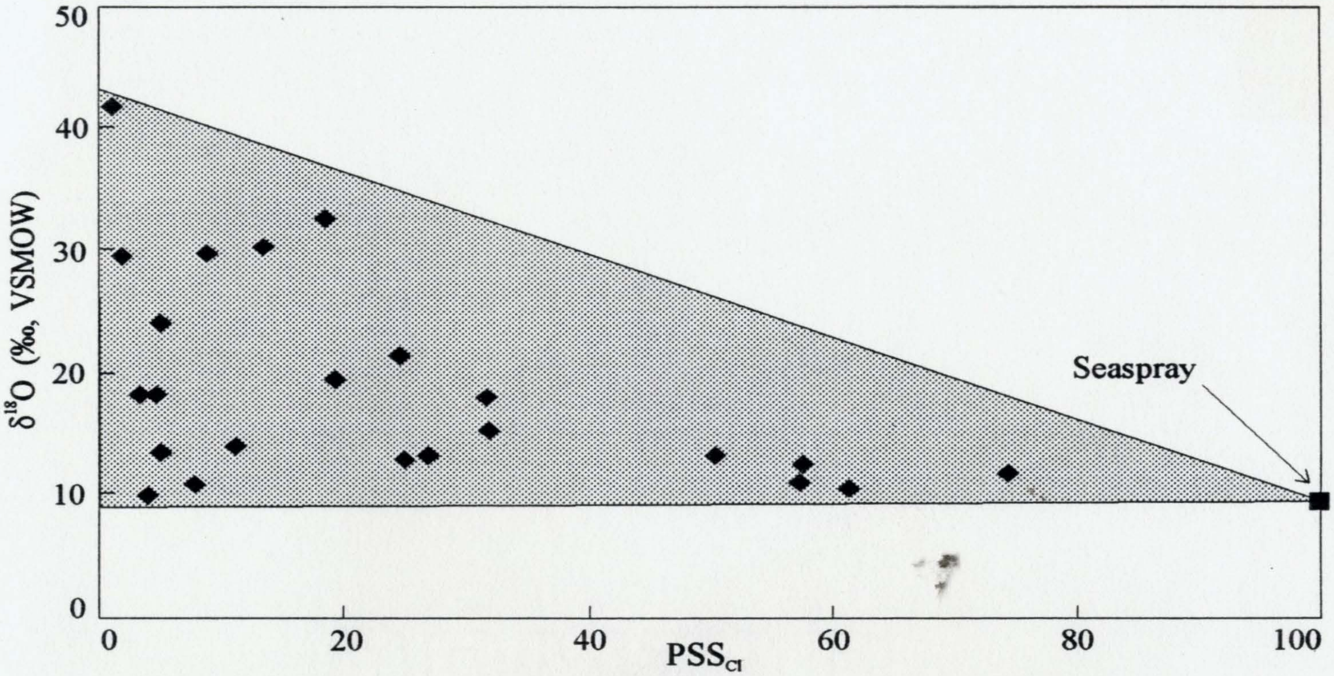

Figure 3.11 $\delta^{18}O_{SO4}$ plotted against PSS_{Cl} for St. John's. The shaded area represents the apparent three component mixing trend.

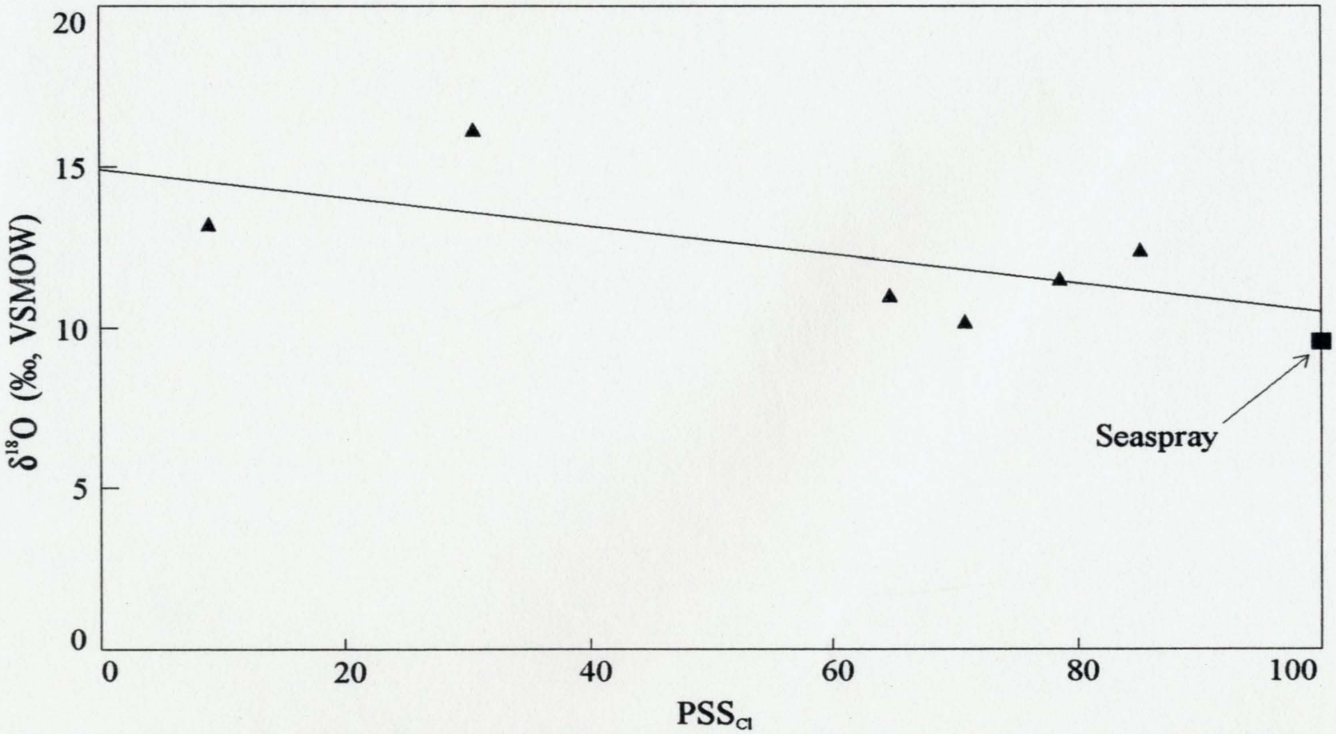

Figure 3.12 $\delta^{18}O_{SO4}$ plotted against PSS for Seal Cove. The line represents the linear regression.

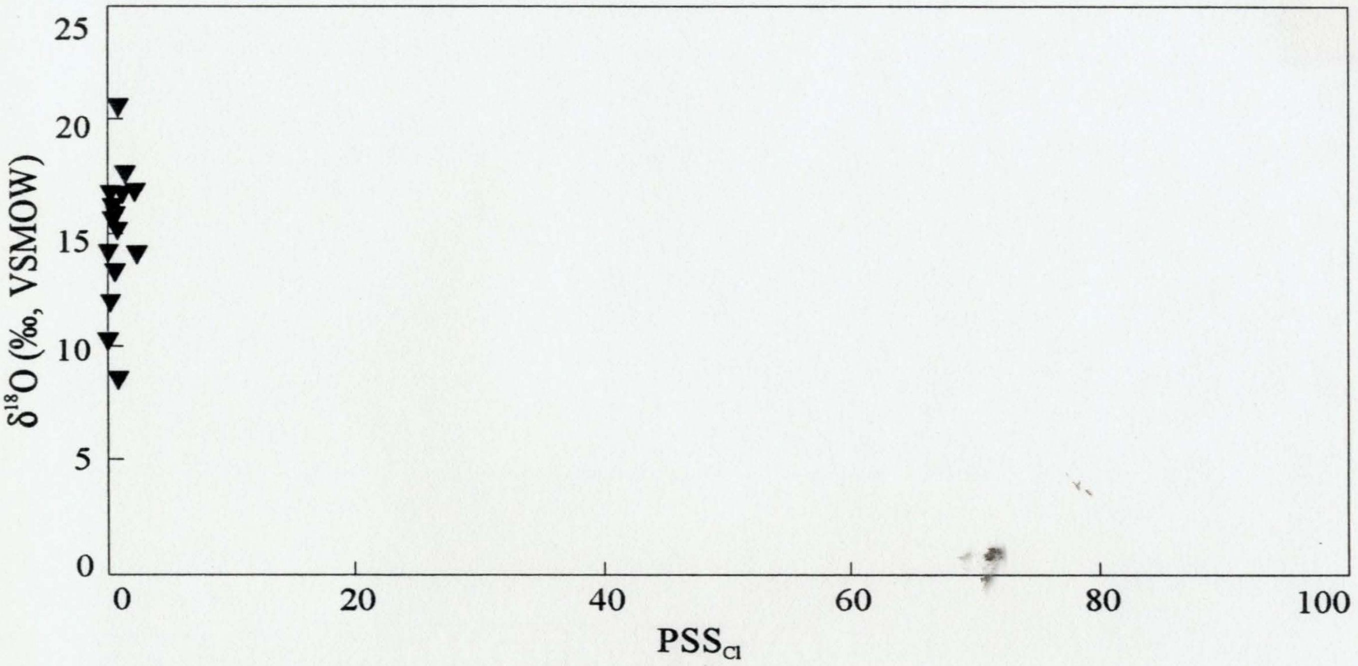

Figure 3.13 $\delta^{18}O_{SO4}$ plotted against PSS_{Cl} for Nepean.

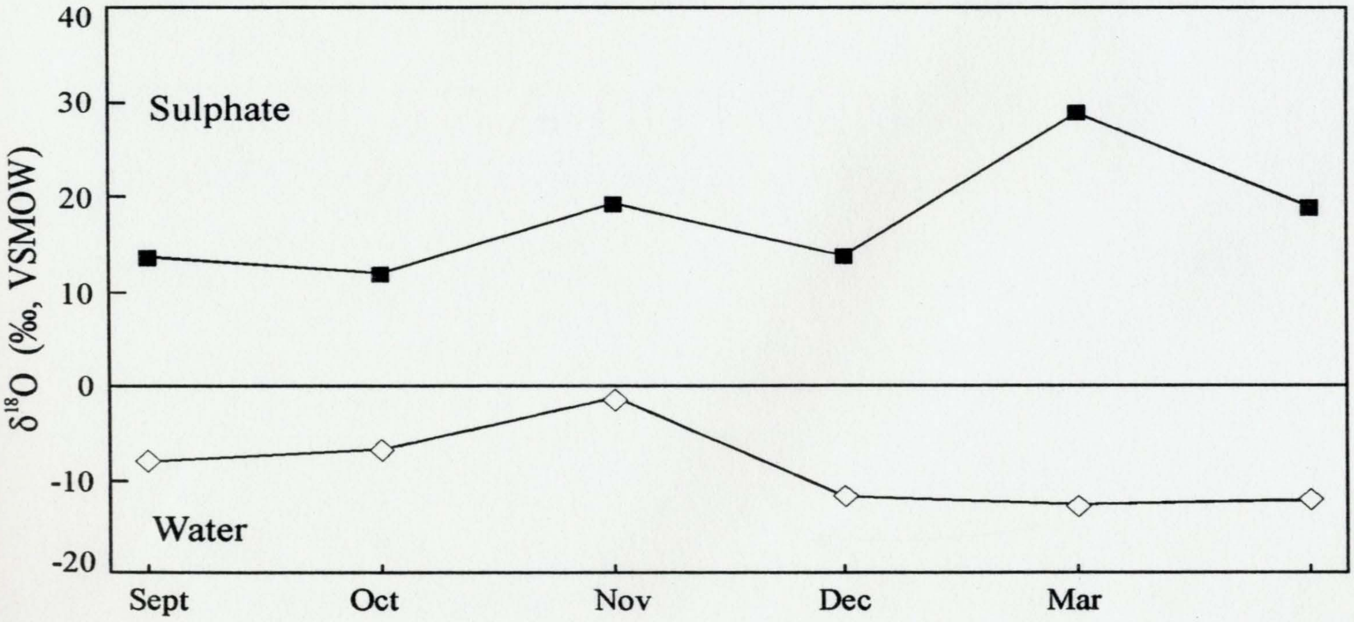

Figure 3.14 VWM $\delta^{18}O_{NSS}$ and $\delta^{18}O_{H2O}$ for Seal Cove.

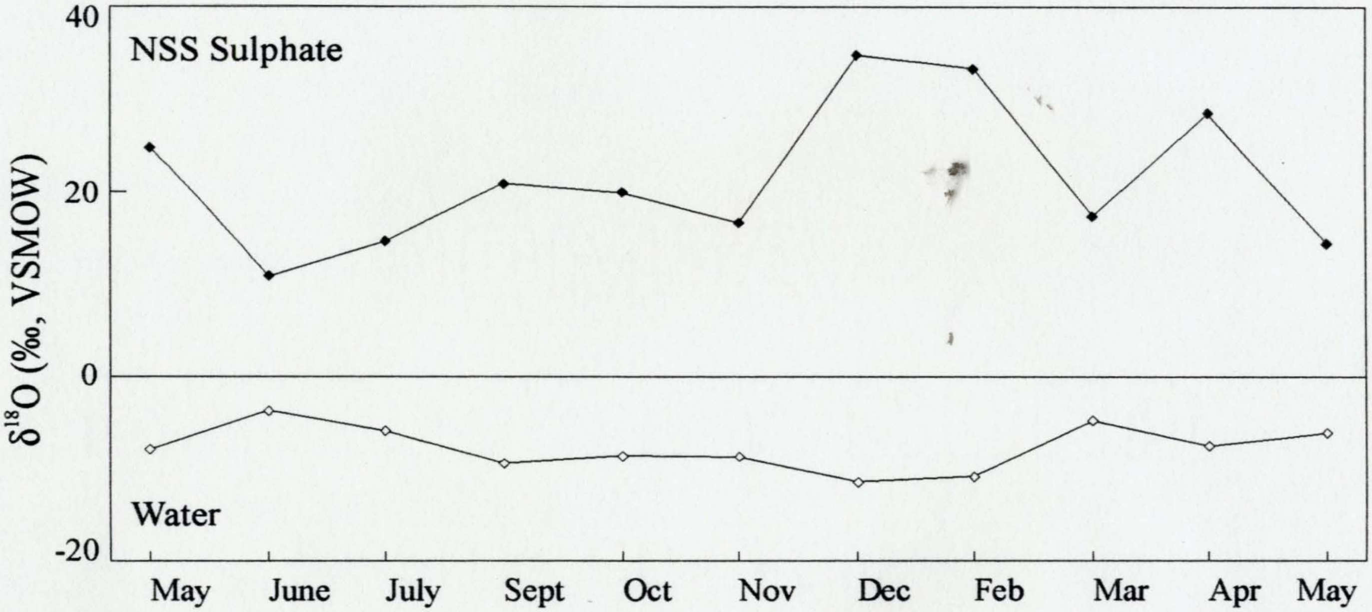

Figure 3.15 VWM $\delta^{18}O_{NSS}$ and $\delta^{18}O_{H2O}$ for St. John's

calculate summer and winter values. The St. John's and Nepean values are given in Table 3.8. St. John's has large winter enrichments for both $\delta^{18}O_{SC}$, and $\delta^{18}O_{NSS}$ of 9.4‰ and 10.8‰ respectively. Nepean on the other hand has a summer enrichment of only 1.7‰ for $\delta^{18}O_{SO4}$.

The $\delta^{18}O_{H2O}$ values also exhibit seasonal trends which would be expected from temperature effects (Dansgaard, 1964). Both St. John's and Nepean show enrichment in the winter months. St. John's has an enrichment of only 2.5‰ , while Nepean has a much larger enrichment of 4.8‰. This difference would probably be expected as the temperature variations in Ontario are much greater than those in Newfoundland.

3.3 Air Mass Back Trajectories

A six month time delay in processing prevented obtaining air mass trajectories for samples after December 1994. There are trajectories for the first nineteen St. John's samples, the first eight Seal Cove samples, and the first eleven Nepean samples.

For the St. John's site, the trajectories varied, representing different source regions. Some came from out over the Atlantic Ocean, not having interacted with any land masses before reaching the site. A number of the air masses originated in the Arctic, Yukon or the prairies, passing over Labrador and Quebec on route to the collection site. Others traveled a more southerly route crossing over Ontario and the northeastern United States. A couple of the air masses traveled along the eastern seaboard of the United States before reaching St. John's. All of these air masses would have to pass over the ocean at some point of course to reach Newfoundland. The air trajectories for Seal Cove are similar to those for St. John's. A few are purely marine, while a number originated in northern Canada and still a few others passed over the northeastern United States.

Most of the air masses which reached the Nepean site originated in the central or southern United States generally taking a northeasterly route up through Michigan to reach Ontario. These trajectories seem to show less variation in direction than the Newfoundland sites. A couple of the trajectories originated in British Columbia traveling through the northern States to Nepean. One unusual sample originated over the Atlantic, passing in a circular path back through the southeastern states and up around to Nepean.

The trajectories have not provided any clear-cut trends for variation with chemical parameters or for seasonal variation. These types of trends may become clearer with the addition of the trajectories for the remaining samples, and other pressure levels.

CHAPTER 4

SOURCE INTERPRETATION

4.1 Factor Analysis

In order to assist in understanding the possible sources affecting the composition of the rain at each site, factor analysis was carried out. This statistical technique tries to explain variations in the data in terms of uncorrelated factors consisting of variables which behave similarly. An attempt is made to find the least number of variables which will explain the greatest amount of the variance. These factors may then be interpreted to represent various sources; for example marine and continental factors might be observed.

A principle components factor analysis was carried out with a Varimax rotation using the Systat statistics program. Consideration of eigenvalues greater than 1 resulted in explanation of 75% of the variance for St. John's and 87% for Nepean. Logarithmic transformations were applied to variables that were not normally distributed to conform to the mathematical assumptions of the technique. This included all concentration data but not isotopic values or PSS. For other elements, if the concentration of a sample was below detection, a value of half the limit of detection was inserted. However, elements were not included if too many samples were below detection. The number of variables also had to be limited in order to maintain a sample to variable ratio of 2 or 3 to 1. The number of samples at Seal Cove was too small to allow a factor analysis to be carried out.

Tables 4.1 and 4.2 contain the results for the factor analysis for St. John's and Nepean as well as interpretations for the factors, which will be explained in the text.

4.2 St. John's

St. John's is a coastal city and the importance of this marine influence can be seen in both the chemical and isotopic data. PSS values show that there is a mean seaspray influence of 23.4%, with a range of 1 to 80%. The concentrations of Na^+, Cl^-, and Mg^{2+} correlate strongly (Figure 3.2) and the ion/Cl^- values for these three ions indicate a seaspray origin. Ion/Cl^- ratios also suggest that K^+ has a seaspray origin, however the concentrations for K^+ were very low, and below detection for a number of samples, which may hinder interpretation. Factor analysis reveals that Sr loads with PSS, Cl^-, and Mg^{2+} on Factor 2 which can be interpreted as the marine factor. Sr/Cl^- ratios indicate that Sr is indeed most likely a marine contribution with only slight enrichments in some samples. Pb also loads on Factor 2, and since it has been removed from gasoline, it would be expected to come from mainly natural sources.

The $\delta^{34}S$ values exhibit the linear trend of increasing $\delta^{34}S$ with increasing PSS that is typical of results found in other coastal areas (e.g. Mizutani and Rafter, 1969; Wakshal and Nielsen, 1982; Herut *et al.*, 1995; Wadleigh *et al.*, 1996; McArdle and Liss, 1995). This represents mixing between a seaspray source with a $\delta^{34}S$ value close to +21‰ and a low $\delta^{34}S$ source (or combination of sources) with a $\delta^{34}S$ value of approximately +5‰. Results from these other studies are compared with this study in Figure 4.1. The St. John's

Table 4.1 Factor Analysis results for St. John's.

	1	2	3
Log SO_4	**0.903**	0.201	0.135
$\delta^{18}O_{SO4}$	**0.891**	-0.211	-0.315
Log Mn	**0.825**	0.144	0.233
Log Ni	**0.799**	0.159	-0.308
Log Cl	0.161	**0.905**	-0.137
log Mg	0.171	**0.779**	0.228
Log Sr	**0.444**	**0.756**	0.142
Log Pb	**0.44**	**0.744**	0.117
PSS	**-0.493**	**0.744**	**-0.403**
$\delta^{34}S$	**-0.442**	**0.607**	-0.113
Log NO_3	-0.201	0.148	**0.862**
$\delta^{18}O_{H2O}$	-0.065	-0.081	**0.776**
Log Ca	0.184	0.047	**0.754**
% Variance	28.5	28	18.9
Interpretation	Pollution	Marine	Dust/Cont.

Table 4.2 Factor analysis results for Nepean.

	1	**2**	**3**
Log SO_4	**0.957**	-0.092	-0.111
Log Mg	**0.939**	0.115	0.297
Log NO_3	**0.908**	0.201	0.016
Log Ca	**0.844**	0.303	0.252
$\delta^{18}O_{H2O}$	**0.711**	0.254	**0.434**
PSS	**-0.593**	**0.61**	**0.418**
$\delta^{34}S$	-0.101	**0.893**	-0.207
Log Na	0.011	**0.866**	0.192
Log Cl	**0.472**	**0.781**	0.284
$\delta^{18}O_{SO4}$	0.166	0.145	**0.889**
% Variance	44.5	27.7	14.8
Interpretation	Continental	Seaspray	$\delta^{18}O_{SO4}$

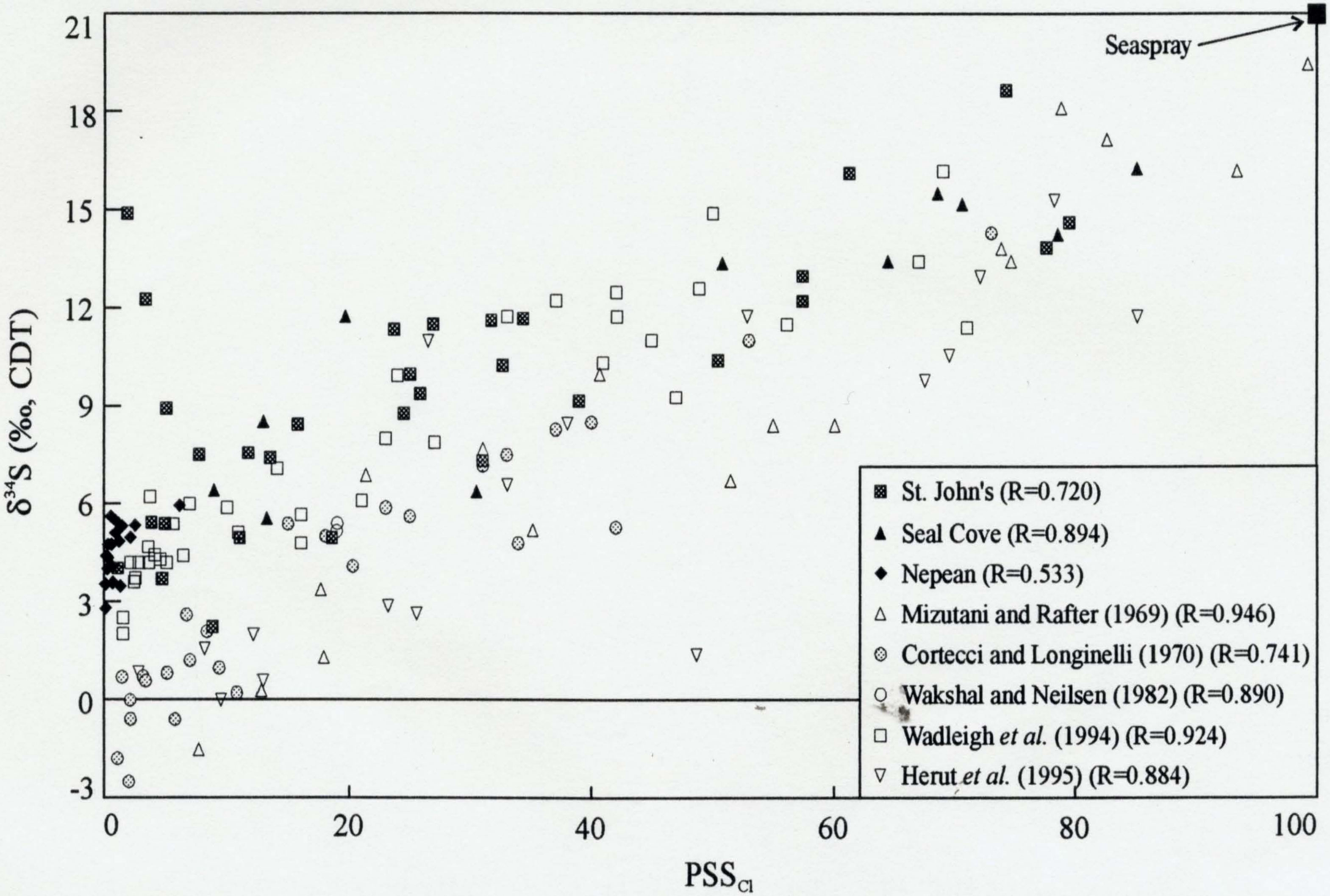

Figure 4.1 Comparison of $\delta^{34}S$ data for precipitation sulphate from a number of studies in coastal areas.

values fit well within the observed range, which is approximately -2.5 to +22‰. Varying 0 PSS intercepts have been found in these other areas, but the range is quite small, with $\delta^{34}S$ values falling between -1.1 and +3.8‰. Another study on the east coast of Canada, at Shelburne, Nova Scotia, by Wadleigh *et al.* (1996) found rainwater sulphate with a $\delta^{34}S$ intercept of +3.8‰ which is lower than the St. John's intercept of +6.3‰. Correlations between 0.741 and 0.946 have been observed in other areas which are similar to the St. John's correlation of 0.720.

There seems to be no obvious correlation between the air mass trajectories and the seaspray influence; completely marine trajectories still have low PSS values. This is probably a result of a number of factors. Weather conditions can affect the amount of seaspray which is injected into the atmosphere. These results are also consistent with other studies in the marine environment which have found that excess sulphate is always present, even over the open ocean (Gravenhorst, 1978; Ludwig, 1976). This must represent either transported continental/anthropogenic sulphate or marine biogenic sulphate. Gravenhorst (1978) measured the $\delta^{34}S$ values of marine aerosols over the Atlantic and found a range of values from +2 to +15‰ which he explained in terms of transported continental sulphate. Ludwig (1976) found that the $\delta^{34}S$ of marine aerosols off California tended to be lower than nearby urban areas. He attributed these low values to a marine biogenic input with a depleted $\delta^{34}S$ composition.

Another explanation for the lack of correlation between PSS and the air mass trajectories is that the seaspray sulphate deposited at St. John's may have been transported in the lower levels of the air mass. This was found by Wakshal and Nielsen (1982) for a study in Israel. Their data indicated that seaspray sulphate was being transported in lower air levels and being deposited close to the coast while biogenic sulphate was transported in higher levels and was brought further inland. The trajectories obtained for this study were for the 850 mb level which represents upper levels of the air mass.

Factor analysis shows that $\delta^{34}S$ loads on the marine factor which argues that seaspray is the principal control of the sulphur isotopic variation. The weighted mean $\delta^{34}S$ for St. John's, however, is only +7.3‰ which is 13.7‰ depleted in ^{34}S relative to the bulk seawater sulphate value. Only 6 of the thirty-one samples collected are dominated by seaspray (>50 PSS). These facts suggest that other sources of sulphate are significant in this area.

The seaspray component is easily identified in the $\delta^{34}S$ - PSS diagram, but a source must be found to account for the low $\delta^{34}S$ values. The $\delta^{34}S$ intercept (+6.3‰) for St. John's is consistent with values observed for continental sulphates. A number of studies have measured the $\delta^{34}S$ of continental sulphate and have found remarkably constant values of +4 to +5‰ with a range of approximately +2 to +10‰ (Nriagu and Coker, 1978a and 1978b; Holt *et al.*, 1972; Caron *et al.*, 1986; Nriagu *et al.*, 1987). This sulphate is thought to represent a mixture of continental and anthropogenic sources. It is possible that this continental/anthropogenic end-member is transported from the mainland and eventually deposited at St. John's.

The chemical composition of the rain at St. John's is typical of marine rains with high concentrations of Na^+ and Cl^-, but some ions in this environment are most likely the result of continental/crustal sources. For instance, it seems that the Ca^{2+} at St. John's is from a crustal source and Ca^{2+}/Cl^- ratios indicate that this element is quite enriched from seawater values Calcium in the atmosphere is often from soil dust while anthropogenic sources include cement manufacture and coal burning. The burning of coal is rare in Newfoundland and therefore the Ca^{2+} observed at this site is most likely a crustal input. The geology of the west coast of Newfoundland includes large amounts of carbonate rock and this may provide a potential source for this Ca^{2+}, but it may also be a result of long-range transport of continental material from mainland North America. Ca^{2+} loads along with NO_3^-, $\delta^{18}O_{H2O}$, and PSS on Factor 3. The loading for PSS is negative which is consistent with a decreasing seaspray influence. NO_3^{2-} tends to be a pollution indicator, mainly resulting from the combustion of fossil fuels in automobiles. Concentrations of these species vary between samples, but seasonally Ca^{2+} and NO_3^- show no variation indicating that there is a fairly constant background in the atmosphere and that perhaps they are part of a continental signal. If Factor 3 is the continental factor it would seem that $\delta^{18}O_{H2O}$ should decrease with increasing continental influence since marine rain is generally heavier than continental rain. This can be seen in the weighted mean $\delta^{18}O_{H2O}$ values for the three sites. Despite this inconsistency, a crustal source is certainly indicated for this area, and this would support the speculation of a continental/anthropogenic end-member.

In order to better assess the non-seaspray component of the sulphate at the St. John's site, the seaspray component has been extracted (as discussed in Section 3.2.1) using the calculated PSS values and assuming a $\delta^{34}S$ value of +21‰ for seaspray. The $\delta^{34}S_{NSS}$ values range from -10 to +14.8‰ with a weighted mean value of +4.7‰. The value of +4.7‰ is similar to continental values, but the large range of $\delta^{34}S_{NSS}$ values would seem to indicate that either the source is exhibiting large variations in $\delta^{34}S$ or that more than one source is represented in this area.

Examining the oxygen isotopic data shows that St. John's is not a simple two end-member system. This data clearly reveal that there is an active pollution influence at this site. Oxygen isotopic values delineate a triangular envelope with respect to PSS (Figure 3.11). By definition, the intercept at 100 PSS is 9.5‰, and the triangular shape widens at low PSS values, confirming that the sulphate seen at this site is not simply the result of mixing between a seaspray end-member and some other continental/anthropogenic end-member. Rain samples collected by Mizutani and Rafter (1969) at Gracefield, New Zealand, exhibited a similar trend, although the St. John's data is a more extreme example as the data is skewed towards much higher $\delta^{18}O_{SO4}$ values by the primary sulphate input.

The weighted mean $\delta^{18}O_{SO4}$ reported for St. John's is +29‰ which is much higher than those reported in other studies (see Table 1.4). Figure 4.2 compares the oxygen data for a number of these studies. Clearly the St. John's data is skewed upwards compared to the other sites. A number of samples have $\delta^{18}O_{SO4}$ values on the order of +30 to +40‰.

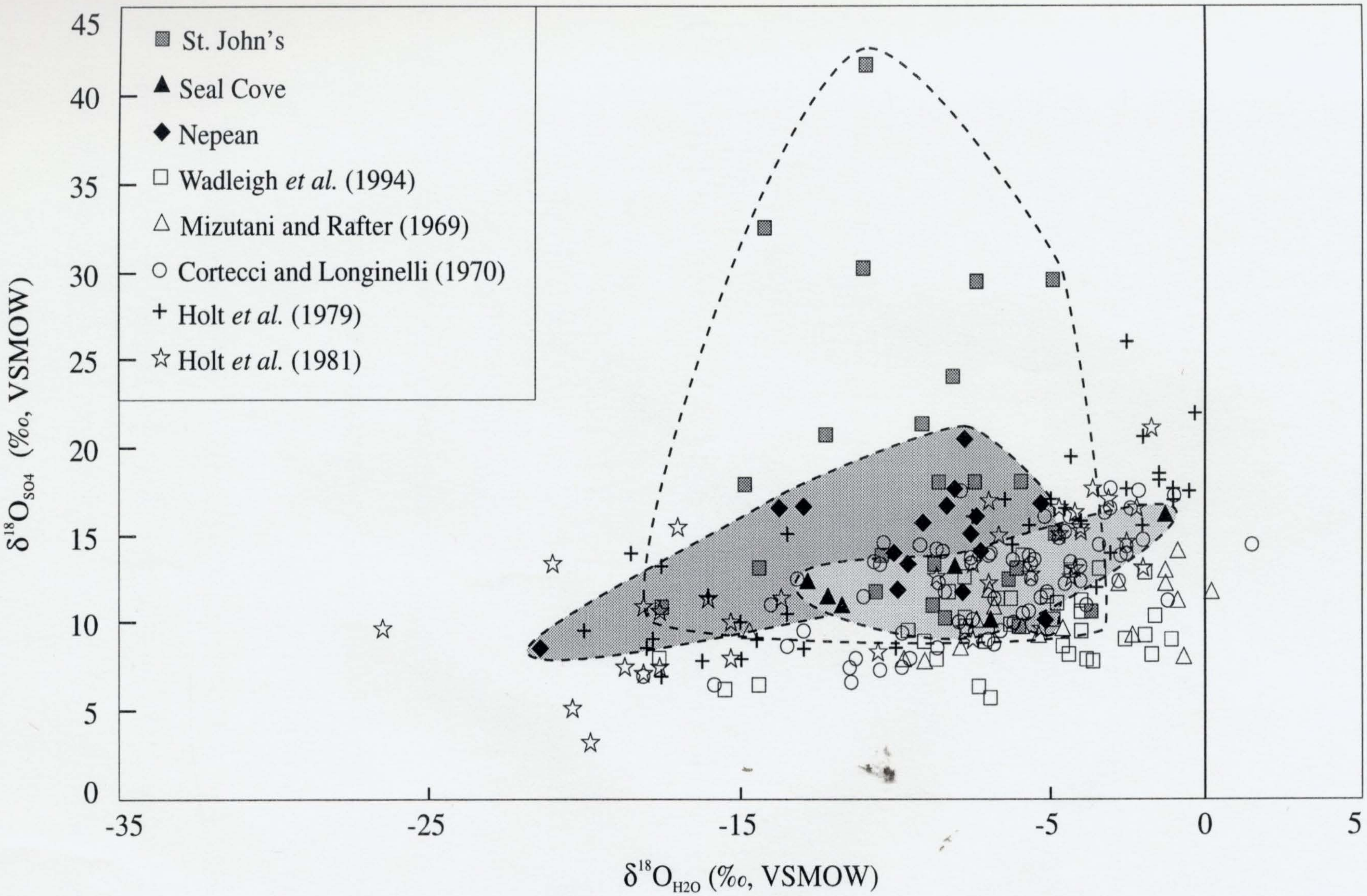

Figure 4.2 Comparison of $\delta^{18}O$ data from a number of studies of precipitation sulphate. The outlined areas represent the range of values for each of the sites from this study.

Values this high have not been measured elsewhere in natural samples and they appear to correspond with the composition predicted by Holt *et al.* (1984) for primary or combustion related sulphates. Interestingly, these high $\delta^{18}O_{SO4}$ samples also have elevated concentrations of both sulphate and metals, including V which is a tracer for oil combustion sources. Metal concentrations exhibit quite a large variation between samples from below detection to high urban type values. Concentrations of metals such as Ni, V, and Cu, which would be enriched by an oil burning source (Table 1.9), vary sympathetically indicating that they do indeed come from the same source. Factor 1 includes $\delta^{18}O_{SO4}$ as well as SO_4, Mn and Ni concentrations which clearly mark this as the pollution source. There is also a strong positive correlation between $\delta^{18}O_{NSS}$ and SO_4^{2-} concentration ($R = 0.865$) which reflects the strength of this source. The power plant next to the collection site is the most logical source of this pollution.

When the data is plotted relative to the curves constructed by Holt *et al.* (1981b), Holt *et al.* (1983), and Holt and Kumar (1984), it can be seen that some of the samples do approach expected primary oxidation values (Figure 4.3). Holt *et al.* (1982) presented a formula for calculating the proportion of primary sulphates in a sample (Section 1.3.1), and the percent of primary sulphate at this site has been calculated to vary between 5 and 100%. These calculations are based on simple two end-member mixing, and if more than two sources are operating at this site, these values will be overestimated. They do however, give an indication of the importance of primary pollution at this site.

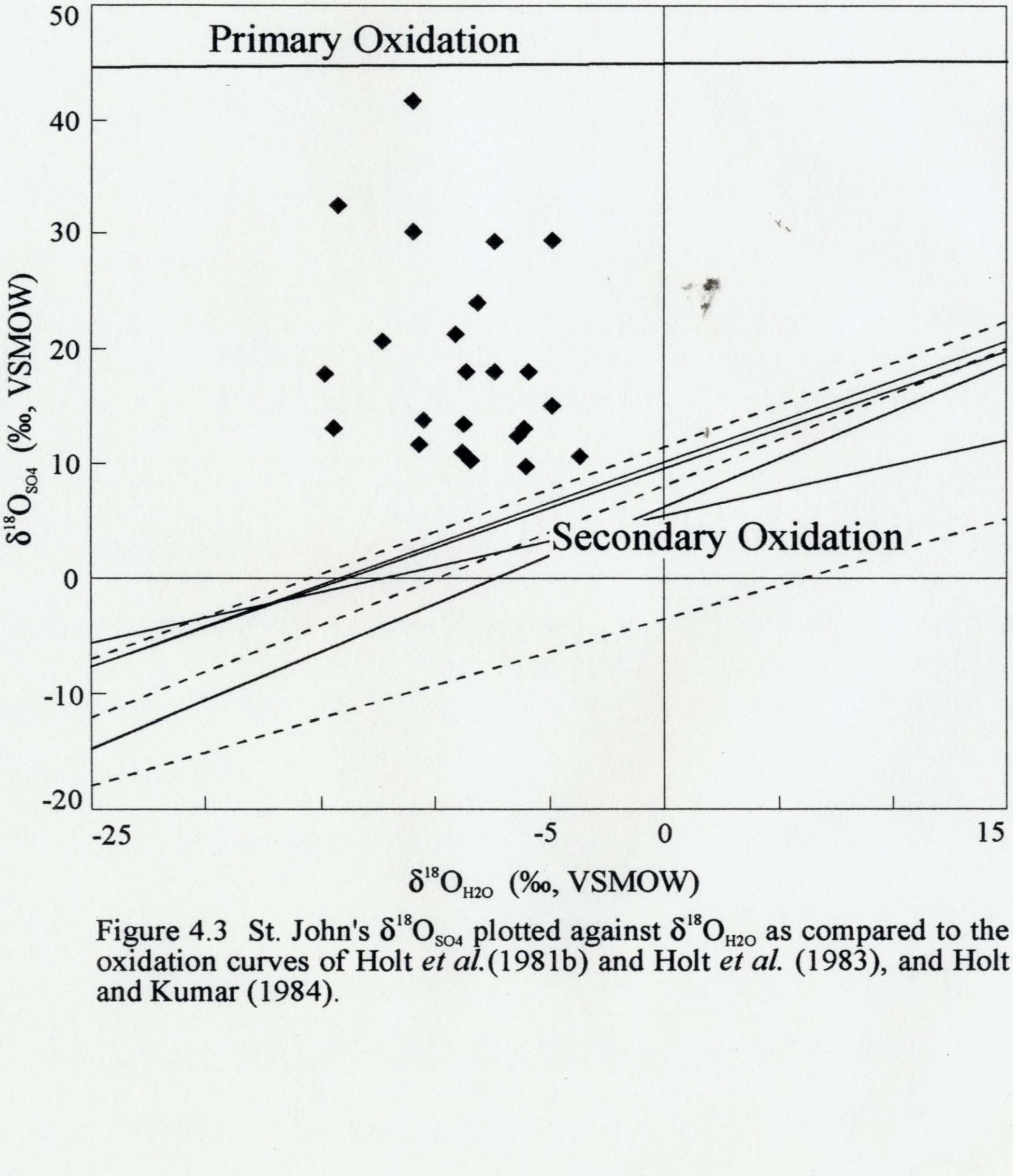

Figure 4.3 St. John's $\delta^{18}O_{SO4}$ plotted against $\delta^{18}O_{H2O}$ as compared to the oxidation curves of Holt *et al.*(1981b) and Holt *et al.* (1983), and Holt and Kumar (1984).

The oxygen isotopic data clearly reveals a pollution source, but on the other hand, it is also clear that some samples have a very small primary sulphate input. Some samples contain very low levels of metals, and V is only seen in a small number of samples. These samples must therefore reflect other inputs of sulphate which may be natural or transported pollutant sulphate.

The scatter in $\delta^{34}S$ values at low PSS in Figure 3.7 seems mainly attributable to two samples (MUN-28 and MUN-29). If these samples are removed from the plot, the fit of the data to the seaspray mixing curve is improved, increasing the correlation coefficient to 0.879 from 0.720. This brings the 100 PSS intercept to +20.4‰ and the 0 PSS intercept to +5.0‰. Potential sources of sulphate which might be used to explain these anomalous values would include biogenic inputs from the ocean or from the land, and perhaps anthropogenic inputs. Marine DMS is thought to have a $\delta^{34}S$ value of approximately +15‰ and this may provide a source for the sulphate of these high $\delta^{34}S$, low PSS samples. The fact that these samples were obtained during the spring would strengthen this hypothesis.

To assess the possibility of a DMS input, a number of mixing curves have been constructed representing mixing between seaspray, a continental/anthropogenic end-member and DMS. This type of three-way mixing would define a triangular area as shown in Figure 4.4. Samples MUN-28 and MUN-29 do indeed lie within this mixing area and therefore it would seem reasonable to speculate that there is a DMS source represented in these samples.

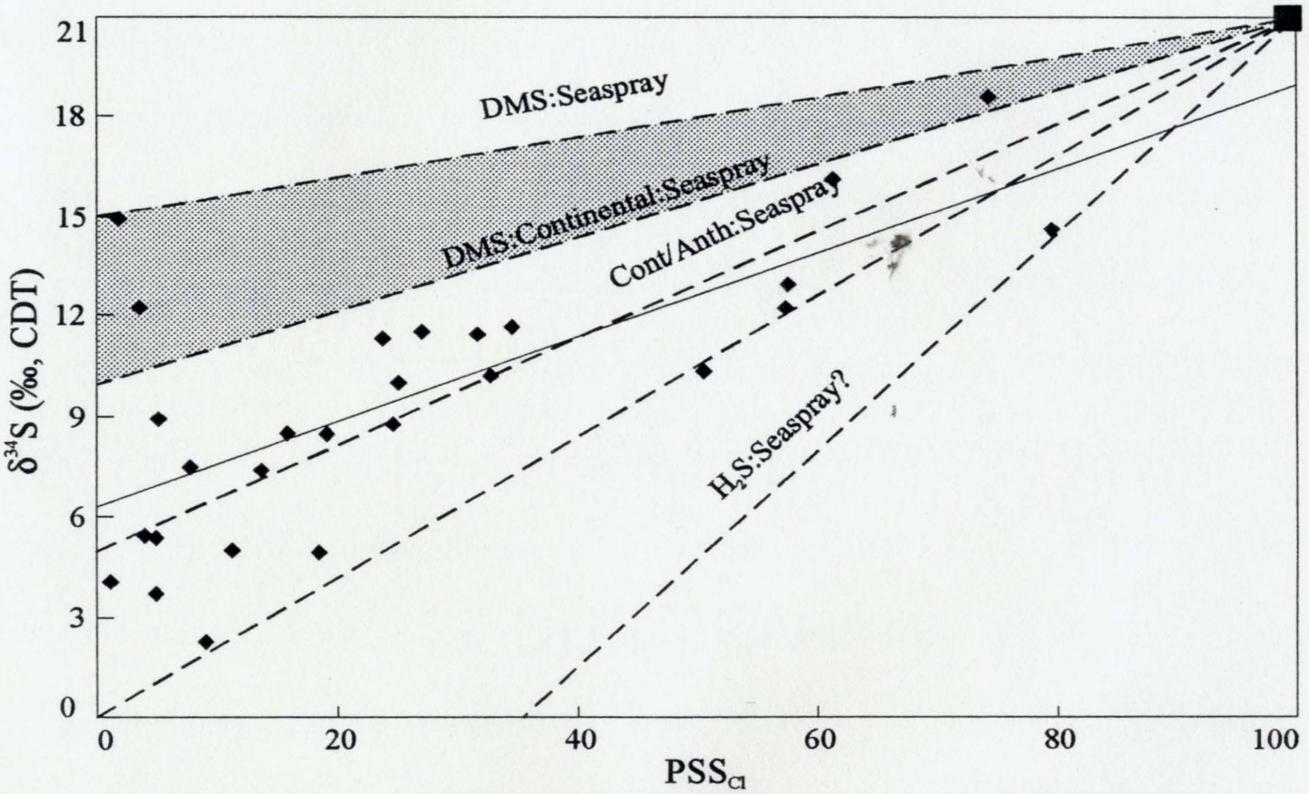

Figure 4.4 δ^{34}S plotted against PSS for St. John's with mixing curves. The solid line represents the actual linear regression and the dashed lines represent theoretical mixing lines.

The only coastal study which seems to have found a large contribution from DMS is a study by McArdle and Liss (1995). This study measured $\delta^{34}S$ for atmospheric sulphate aerosols in Ireland and Spitsbergen, Norway. Their data clearly reflected a DMS input with a signature of approximately +22‰. This DMS input was calculated to vary between 15 and 30% with the highest inputs in the summer. The St. John's data do not clearly reflect a DMS input as the McArdle and Liss (1995) study did.

Other problems emerge with the potential DMS samples at St. John's when the oxygen isotopic composition and metal concentrations of these samples are examined. MUN-28 has an extremely high $\delta^{18}O_{SO4}$ value (+29.0‰) which would seem to indicate that the sulphate is of primary origin. An estimate of the sulphur isotopic composition of the smokestack sulphate can be made by examining the $\delta^{34}S$ values of those samples which have high $\delta^{18}O_{SO4}$ values and high metal concentrations. The weighted mean $\delta^{34}S$ value for this sulphate is +5.8‰, and, excluding MUN-28, the values range from +2.2 to +7.4‰ (a 5.2‰ range). Although the composition of oil can vary, $\delta^{34}S$ values usually fall between 0 and +5‰ (see Figure 1.3) (Nielson, 1974). Power plants will often burn fuels from a number of sources and therefore a larger variation may be plausible. MUN-28 also has elevated metal concentrations and an elevated SO_4^{2-} concentration which further implies a pollution source.

Sample MUN-29 is a bit more problematic. The oxygen value still lies within the normal range (+18‰), the metal concentrations are not high and its SO_4^{2-} concentration is average. Although MUN-28 may be an unlikely candidate for DMS mixing, MUN-29 still remains as a potential example of a DMS source in the area.

Another feature of this data is that a couple of samples display $\delta^{34}S_{NSS}$ values very much lower than the other samples (-0.4 and -10‰), and these samples lie below the seaspray mixing curve. Sample MUN-20S has a $\delta^{34}S_{NSS}$ of -10‰, but unfortunately no $\delta^{18}O_{SO4}$ data could be obtained for this sample. These low $\delta^{34}S$ values are consistent with some type of biogenic input, however these samples were collected during the winter and therefore it may be more likely that they have been influenced by a relatively depleted anthropogenic input. This may indicate that there is an extremely large variation in the smokestack emissions.

Seasonal differences in $\delta^{34}S$ can indicate a number of possible scenarios for their origin: a change in source or source strength between seasons, a change in oxidation process or rate, or a change in deposition patterns (Nriagu *et al.*, 1987). $\delta^{34}S$ is enriched by 2.9‰ in the summer. Generally, a winter enrichment would be expected because of increased seasalt contributions, and an increased marine input has already been recognized in the chemical data. There is also an enrichment in $\delta^{34}S_{NSS}$ of 4.4‰ during the summer which is contrary to the results of a number of other studies including Nriagu and Coker (1978a and 1978b), Caron *et al.* (1986), and Nriagu *et al.* (1987). Caron *et al.* (1986) explained the seasonality they found in precipitation sulphate from Quebec by the effect of temperature change on fractionation. A decrease in temperature, however, should cause a winter enrichment, and therefore cannot be used to explain the results in this study. The summer enrichment of $\delta^{34}S_{NSS}$ is similar, however, to that observed by Wadleigh *et al.* (1996) in Shelburne, Nova Scotia. In this case, the enrichment was explained by a change of source between seasons.

The seasonal changes might have been explained by a change in the area being sampled by the traveling air masses between different seasons, but this is not indicated by the air mass trajectories. This means that a fluctuation in source importance is the most likely explanation, although it has already been shown that the increased seaspray input cannot explain the summer enrichment. A more probable explanation is an increase in the influence of the power plant emissions. The $\delta^{18}O_{SO4}$ and metal data show that there was an increase in the number of samples highly affected by the smokestack during the winter months. The increase in this low $\delta^{34}S$ source would result in a winter depletion. This is also reflected in SO_4^{2-} concentrations which are much higher in the winter.

It may be possible to gain further information by examining the oxygen isotopic data in more detail. The extreme $\delta^{18}O_{SO4}$ values may obscure any other oxidation processes occurring in this area, but if oxidation is occurring locally, some correlation between $\delta^{18}O_{NSS}$ and $\delta^{18}O_{H2O}$ may be seen. Otherwise, if the sulphate is transported from elsewhere, there will be no correlation as the sulphate will represent a mixture from a number of sources oxidized at different times. When $\delta^{18}O_{NSS}$ is plotted against $\delta^{18}O_{H2O}$ there is a trend noticeable with a correlation coefficient of 0.767. An interesting feature of this data, however, is the fact that this is a negative trend of increasing $\delta^{18}O_{NSS}$ with decreasing $\delta^{18}O_{H2O}$. This trend is highlighted in a plot of the monthly VWM $\delta^{18}O_{NSS}$ and $\delta^{18}O_{H2O}$ (Figure 3.15). Whenever $\delta^{18}O_{H2O}$ increases, $\delta^{18}O_{NSS}$decreases. This is opposite to the expected trend found by workers such as Holt *et al.* (1979), Holt *et al.* (1981), and Cortecci and Longinelli (1970) in which the $\delta^{18}O_{NSS}$ varies in sympathy with the $\delta^{18}O_{H2O}$. This may be a consequence of increased number of high $\delta^{18}O_{SO4}$ (pollution) episodes during the winter months. $\delta^{18}O_{H2O}$ decreases in the winter due to the colder temperatures and therefore these winter, high $\delta^{18}O_{NSS}$ samples will be associated with water of lower $\delta^{18}O$ composition.

If the seasonal variations in $\delta^{18}O$ are examined, $\delta^{18}O_{SO4}$ is in fact enriched in the winter by 2.9‰. A winter depletion in $\delta^{18}O_{SO4}$ might have been expected due to the decreased temperature, if oxidation alone was involved, but this in not observed. The $\delta^{18}O_{NSS}$ is enriched to an even greater extent (+5.4‰). This supports the hypothesis that the influence of the power plant increases during the winter. Large amounts of soot were often seen during the winter, in the area of the collector, and it appears that although it was operating year round, more of this material was being deposited in the local area. One particular event, MUN-24S, contained large amounts of soot and also exhibits the highest $\delta^{18}O_{SO4}$ values (+41‰) which is the expected value for a completely primary sulphate. Metal values also seem to reflect this increased pollution input because many of them were found to be more concentrated in the winter. The winter pollution may also be affected by the increased use of heating.

Three additional snow samples were taken in St. John's (NH-1 to NH-3), approximately three-quarters of a kilometer from the main sampling site in a relatively quiet, wooded area (see Figure 2.3). The data for these samples have been included in the tables for St. John's data in Appendix II. These samples had relatively high PSS values of 39%, 78%, and 59% which may indicate less of a pollution influence. Metal concentrations are also low for these samples compared to the MUN samples.

The $\delta^{34}S$ values are +9.2 and +13.9‰ for samples NH-1 and NH-2 respectively. When plotted with the other data for St. John's, these samples fit well with the overall trend. The $\delta^{34}S_{NSS}$ values, however, are interesting. NH-2 has a $\delta^{34}S_{NSS}$ value of -10.7‰ which is similar to sample MUN-20S. MUN-20 was collected in January while NH-2 was collected in February. Only NH-2 could be analyzed for $\delta^{18}O_{SO4}$ which is +10.9‰ while its $\delta^{18}O_{NSS}$ value is +15.7‰. The fact that this sample was taken in an area away from the direct influence of the smokestack and the fact that $\delta^{18}O_{SO4}$ is similar to that expected from secondary oxidation processes seems to indicate that a natural source may be responsible for these low $\delta^{34}S$ values. However, it may also indicate that the snow is having some influence on the isotopic composition. It is interesting that these very low $\delta^{34}S$ values have only been observed in snow samples. No mention of this type of effect has been found in other studies.

Three main influences can clearly be seen at St. John's with the combination of isotopic, chemical data, and factor analysis. Strong seaspray, continental and pollution sources can be identified. Oxygen values do not seem to support the presence of locally oxidized secondary sulphates, however this may be obscured by the pollution oxygen values. There is not enough evidence, at this time, to support the influence of a biogenic source.

4.3 Seal Cove

The Seal Cove data initially resemble the St. John's data because it clearly shows the same marine influence. Seaspray has a greater influence at this site however. The mean PSS is higher at 42.6%, and half of the fourteen samples have PSS values greater than 50%. The same linear trend is evident in the $\delta^{34}S$ data, representing the mixing of a seaspray component with some other low $\delta^{34}S$ component. The correlation is much stronger than St. John's, with a correlation coefficient of 0.894 (Figure 3.8). This site may allow a better investigation of the nature of sulphate sources in this region, unhindered by a direct pollution source. It must be remembered however, that there were less than half the number of samples at this site than at St. John's. This prevented the use of factor analysis for this site.

At 100 PSS the intercept gives a $\delta^{34}S$ value of +18.1‰, although the seaspray value of +21‰ is within the error of the regression. The intercept at 0 PSS is 5.8‰. This +5.8‰ value is comparable with St. John's (+6.3‰), and also with the background continental/anthropogenic values which were discussed earlier. Overall, the data fit within the observed range of values in other areas, and from Figure 4.1, it also fits well with the linear trends seen in other coastal studies.

Marine rain should be enriched in ions such as Na^+, Cl^-, and Mg^{2+}, and indeed the concentrations of these elements show strong correlations (Figure 3.3). Their concentrations are also within the expected ranges found for marine rains (Table 1.5). Although not as clear, the behaviour of K^+ concentration also bears some resemblance to the other marine ions, but ion/Cl^- ratios seem to indicate some enrichment. The concentrations of Ca^{2+} also seem to be enriched above the expected seawater contribution. This element is usually expected to be a crustal input and these enrichments would be consistent with this origin, however the concentration behaviour is again somewhat consistent with the other ions. The small sample number may be a problem for these types of observations because a month may be represented by only one sample. The concentrations of Ca^{2+}, Na^+, Cl^-, Mg^{2+}, and K^+ are all enriched in the winter which would seem to indicate that they are from the same source. A dust contribution would be expected to decrease in the winter and thus Ca^{2+} concentrations would decrease as well. This Ca^{2+} may therefore be influenced by a seaspray input. Concentrations of Pb, which must now be considered as a natural input, increase in the summer which may be an indication of the crustal/dust input. The winter enrichment of these ions, along with PSS, indicates that there is a stronger marine influence in the winter.

Seaspray is clearly not the only sulphate source at this site. PSS values vary quite widely (9 to 85.1%), and the weighted mean $\delta^{34}S$ is only 10‰ which indicates that other, low $\delta^{34}S$, sources are quite important. As seen at St. John's, some samples with marine air mass trajectories display quite low PSS values, indicating the presence of sulphate from sources other than seaspray which may be transported continental/anthropogenic sulphate or marine biogenic sulphate.

There are a number of potential sources for the low $\delta^{34}S$ end-member. Examining the non-seaspray component of the sulphate shows that it has a weighted mean $\delta^{34}S_{NSS}$ of 3.0‰ and a range of -10.8 to +9.5‰. The low values initially suggest a depleted biogenic source, but these values are seen in snow samples collected in March, similar to the low $\delta^{34}S_{NSS}$ samples at St. John's. The large range in values seems to indicate that more than one source is active. Mixing of sources, however, is not obvious from the $\delta^{34}S$ versus PSS diagram. There is no indication of a DMS input in the $\delta^{34}S$ data. The small number of samples however, may hinder interpretation.

Seasonal changes in $\delta^{34}S$ may help to determine whether there is only one source or a combination of sources for NSS sulphate. Contrary to the results at St. John's, $\delta^{34}S$ values increase from +8.2‰ in summer to +11.8‰ in winter (+3.6‰). This winter enrichment can be explained by the increased seaspray influence during the winter. Values for $\delta^{34}S_{NSS}$ have the opposite trend, decreasing from +5.2‰ in the summer to +0.9‰ in the winter (-4.3‰). This summer enrichment is more difficult to explain.

A summer enrichment was also seen at St. John's, and it was thought to result from the increased input of pollutant sulphate. Indeed the Seal Cove site is proximal to the Holyrood Generating Station, an oil burning power plant, which is only operational during the winter months. One of the winter samples (SC-11S) has a $\delta^{18}O_{NSS}$ of +29.0‰ which would indicate a significant primary sulphate component of 70%. The $\delta^{34}S_{NSS}$ value for this sample is -10.8‰ however, which would seem more indicative of a biogenic source. This type of very depleted value is again in a snow sample, as seen at St. John's, which may further suggest that this effect has something to do with the type of sample. There is no V associated with this sample, and the other metal concentrations do not seem to be high. There is no seasonal change in SO_4^{2-} concentration which would probably be associated with a seasonal change of source. It therefore does not seem likely that this power station is having a direct affect on the samples.

There is quite a variety in the histories of the air masses associated with this site, and this indicates that there are a number of source areas affecting this site which may account for some of the variation. Wind direction has often been seen to influence rain chemistry in other studies.

In order to gain further insight into the potential sulphate sources it is necessary to closely examine the oxygen isotopic data. The $\delta^{18}O_{SO4}$ data has a weighted mean of +12.8‰ and ranges between +10.2 and +16.2‰. A pollution source is not obvious for this site as it was for St. John's. The oxygen values at this site are much more in line with those of secondary sulphates from other studies (Figure 4.2), and they are all quite close to the secondary oxidation field of Holt *et al.* (1981b) and Holt *et al.* (1983) (Figure 4.5). There seems to be some primary sulphate associated with them, although it is still not obvious whether this sulphate is locally oxidized or transported. There are only six oxygen values for this site, but there would appear to be a trend towards more positive $\delta^{18}O_{SO4}$

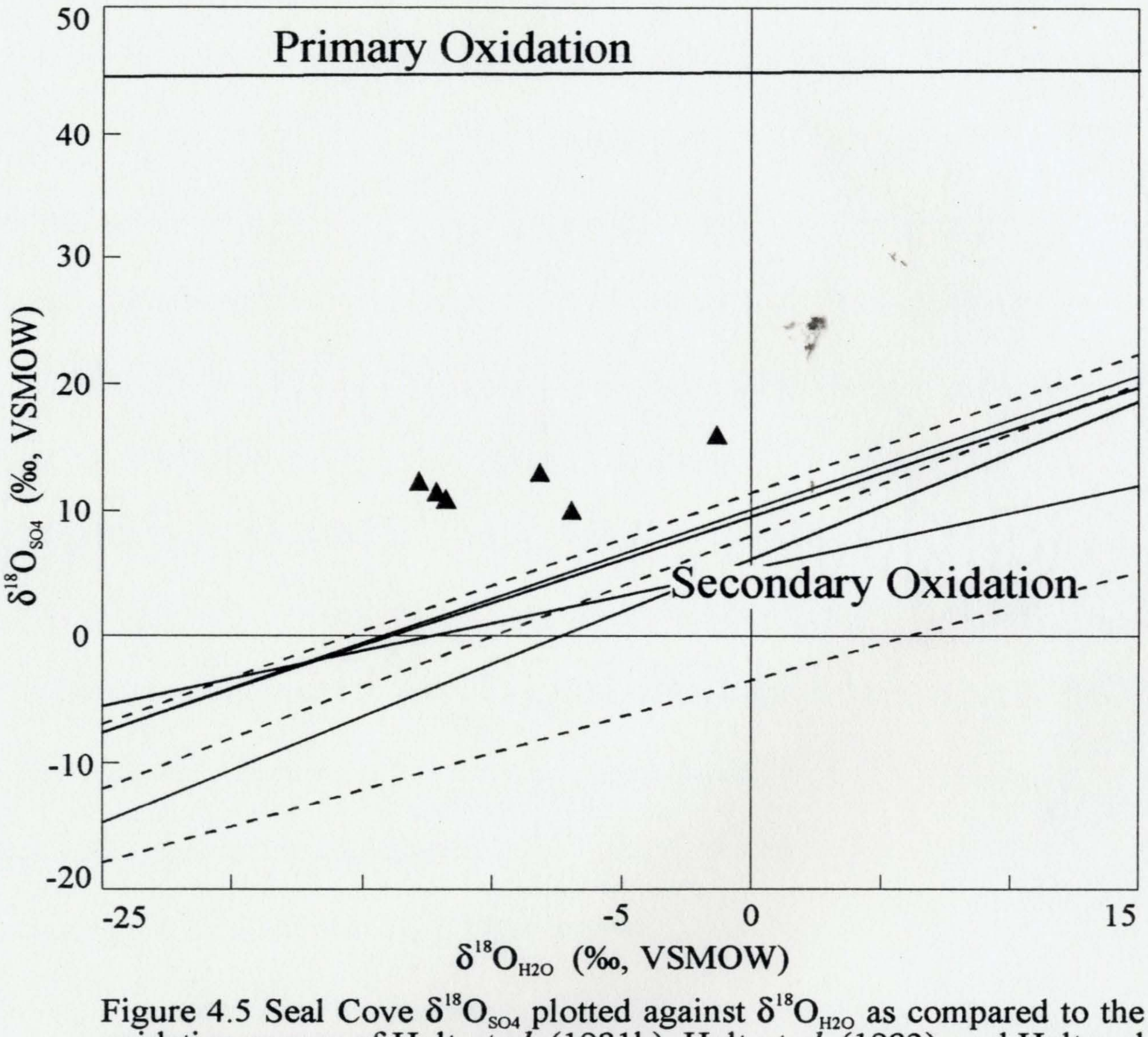

Figure 4.5 Seal Cove $\delta^{18}O_{SO4}$ plotted against $\delta^{18}O_{H2O}$ as compared to the oxidation curves of Holt *et al.* (1981b), Holt *et al.* (1983), and Holt and Kumar,(1984).

with decreasing PSS (Figure 3.12) with a correlation coefficient of 0.623. The data appear to converge on the expected seaspray value of +9.5‰ at 100 PSS.

Plotting $\delta^{18}O_{NSS}$ versus $\delta^{18}O_{H2O}$ should reveal whether the sulphate has been oxidized locally or has been transported from other areas. This plot can be seen in Figure 3.14 and it was found to have a correlation coefficient of 0.686. This is not a strong correlation, but looking at Figure 3.14, visually a correlation does seem to exist. This would imply that at least some of the sulphate is being oxidized locally and that $\delta^{18}O_{SO4}$ bears some relation to the ambient water. Unfortunately, it was not possible to calculate seasonal oxygen values because of the small number of oxygen analyses and therefore any variation in oxidation mechanisms between seasons could not be assessed. These variations may have elucidated temperature effects resulting from heterogeneous oxidation as seen in other studies (Holt *et al.*, 1979; Holt *et al.*, 1981a; Caron *et al.*, 1986).

The Come-by-Chance Oil Refinery, a potential source of pollution, was only in operation from late October 1994, and was closed during May 1995. Since the Holyrood Generating Station only operates during the winter, samples before October 1994 should have experienced no influence from these sources Any sign of pollutant sulphate would therefore likely have been transported from elsewhere.

Metal concentrations are found to be generally in the range of rural values (Table 1.11). Only a couple of samples seem to have concentrations which are relatively high (SC-1 and SC-8). These samples have V associated with them and this element was only found in four of the samples from Seal Cove. It also appears that Ni is enriched relative to the other Seal Cove samples for SC-1 and that Cu is high in SC-8. These are only high relative to the other samples though, and are still within the range expected for rural sites. It may therefore represent a remnant signal of transported pollution.

Unfortunately, isotopic analysis could not be performed on SC-1 as this was a very small sample, but SC-8 does have a fairly low $\delta^{34}S$ value (+6.4‰) and its oxygen isotopic value (+16.2‰) is relatively high compared with other samples from Seal Cove. The $\delta^{18}O_{NSS}$ is also slightly elevated at 19.0‰. In Figure 4.5 the oxygen composition does not stand out from the others and a calculation of the primary input gives a value of 26%. The trajectories show that SC-1 did indeed pass over the eastern seaboard of the United States, and the air mass for sample SC-8 passed in a more northerly route through Ontario, Quebec, and across New Brunswick. SC-1 has not been affected by local power plants as neither Holyrood nor Come-by-Chance were in operation during July 1994. This sample therefore, must contain transported pollutants. Sample SC-8 however, may have picked up local sulphates from either Holyrood or Come-by-Chance since both were operating during November 1994. The low metal concentrations however, would appear to support a transported origin. Metal concentrations seem to be higher in the winter which may result from increased pollution from heating sources.

Seal Cove is clearly influenced by a marine source. It appears that the continental/anthropogenic end-member observed at St. John's is also represented in the low PSS end-member at this site. Thre trend is more clearly demonstrated here than at St. John's because there is no direct pollution input present. The site does not, however, reveal a clear biogenic influence. Local oxidation may be indicated by the oxygen isotopic data, but this signal is not strong in the present data set. Transported sulphate is more likely to be an influence at this site. It appears that the local power plant has not had any real influence on this site. In order to more clearly delineate the effects of this local generating station it might be useful to have collectors placed in a number of sites immediately around the plant which would be more likely to pick up its influence.

In an attempt to try and define the influence of the Holyrood Generating Station, two snow samples were collected from different areas for the same snow event. One sample was taken at the normal sampling site (SC-11S) while the other was taken closer to the power plant in an area which seemed to fall directly under the smoke plume from the plant (SC-12S) (Figure 2.4). The results of this experiment were inconclusive. SC-12S did not exhibit any particular sign of contamination and, in fact, SC-11S seemed to be more concentrated for a number of elements. As discussed earlier, SC-11S also had a high value for $\delta^{18}O_{NSS}$ of +29‰, but no V is associated with this sample, and metal concentrations are not high. Both of these snow samples exhibit the same depleted $\delta^{34}S_{NSS}$ values observed in other snow samples and, as discussed, this would seem to further support some type of problem with snow samples. It is probable that wind direction and deposition processes will have a large impact on the observed compositions, and more samples would have to be collected in order to observe the effect of the power plant.

4.4 Nepean

There are distinct differences in the character of the Nepean site compared with St. John's and Seal Cove. The continental nature of this site is evident in both the chemical and isotopic data and is consistent with other studies in continental areas.

As expected, the PSS values are very low with a range of 0.1 to 6.2% and an average of 1.2%. Generally, concentrations of ions such as Ca^{2+} and Mg^{2+} are expected to be higher in a continental environment, while Na^{+} and Cl^{-} should be depleted relative to the marine environment. The measured values for ions at Nepean seem consistent with typical continental concentrations (see Table 1.5). Ion/Cl^{-} ratios show that all the ions at this site are quite enriched compared to seawater, and it is most likely that much of this enrichment is due to the continental input. The concentrations of Ca^{2+} and Mg^{2+} have also been found to vary sympathetically (Figure 3.4). Nepean and the surrounding area are underlain by sandstones and limestones, and presumably dust from this region should be rich in Ca^{2+} and Mg^{2+}. Concentrations for Ca^{2+}, SO_4^{2-}, and NO_3^{-} are higher in the summer months (April - September), although Mg^{2+} seems to show very little variation. Inputs from continental sources, such as dust, would be expected to increase in the summer when the snow cover is removed.

Factor analysis reveals three main sources for the isotopic and chemical variation at this site. Factor 1, which explains 44% of the variance, is the continental factor. This factor includes high loadings for SO_4^{2-}, Mg^{2+}, NO_3^{-}, Ca^{2+}, and $\delta^{18}O_{H2O}$ along with a moderately negative loading for PSS. The ions could all be expected to result from continental sources and a negative loading for PSS would also be expected. The fact that $\delta^{18}O_{H2O}$ loads on this factor is unusual, as it was for St. John's, because the opposite trend would be expected with $\delta^{18}O_{H2O}$ becoming depleted in the continental environment. As pointed out earlier, the expected trend is observed in the average $\delta^{18}O_{H2O}$ values for each site. Continental inputs seem to be the most important influence at this site and Factor 1 demonstrates this importance.

Although marine input to this area is very small, as shown by the small PSS values, it is still detectable. Na^+ and Cl^- concentrations still parallel somewhat in their behaviour (Figure 3.4), although Na^+ is enriched in most samples, as ion/Cl^- ratios illustrate. The winter increase found at both St. John's and Seal Cove is still displayed in the Na^+ and Cl^- concentrations at this site, although to a lesser degree. The fact that Cl^-, Na^+, and PSS all load on Factor 2 corroborates the evidence for a detectable marine input. Interestingly, $\delta^{34}S$ loads on factor 2 as well, hinting that there is an underlying link between this marine input and the small variation seen in the sulphur isotopic composition.

The $\delta^{34}S$ values are very restricted with a range of only +3 to 5.9‰, and a weighted mean of +4.4‰, similar to studies from other continental areas. The linear trend of increasing $\delta^{34}S$ with increasing PSS, which was so obvious at the Newfoundland sites, is absent here. A number of studies have examined sulphate in continental rainwater. Nriagu and Coker (1978b) found an average $\delta^{34}S$ of +4.7‰ near Sudbury, Ontario while a study in the Great Lakes region by Nriagu and Coker (1978b) found an average value of +4‰.

A $\delta^{34}S$ of +5‰ was observed by Caron *et al.* (1986) in a study carried out in rural Quebec. The Chicago area was studied by Holt *et al.* (1972) and they also found an average of +5‰. Figure 4.6 compares these studies by plotting $\delta^{34}S$ versus SO_4^{2-} concentration. The Nepean data fit quite well within the range of observed continental $\delta^{34}S$ values. The constant nature of the isotopic composition at Nepean could indicate that either one source is dominant or that the sulphate is a mixture from a number of sources.

The seasonal variation in $\delta^{34}S$ is very small (0.7‰), however there is enrichment in the winter which is consistent with the results of other studies in this region (Nriagu and Coker, 1978a; Caron *et al.*, 1986; Nriagu *et al.*, 1987). This difference could be explained by a fluctuation of the source composition or strength, a change in oxidation mechanism, or a change in source area. Variation in the air mass trajectories does not seem to be related in any way to season. This makes the idea of changing source areas seem unlikely.

Nriagu *et al.* (1987) found that biogenic inputs could account for up to 30% of the atmospheric sulphate in northern Ontario. From measurements of DMS concentrations along with $\delta^{34}S_{SO4}$ and SO_4^{2-} concentrations in bulk precipitation samples in remote wetlands of northern Ontario, Nriagu *et al.* (1987) concluded that biogenic inputs were very important at their remote northern Ontario site. They observed seasonal variations in both $\delta^{34}S$ (~2.4‰) and SO_4^{2-} concentration with $\delta^{34}S$ peaking in the winter and SO_4^{2-} concentrations highest in the summer. An increase in biogenic sulphate during the summer would deplete the $\delta^{34}S$ values.

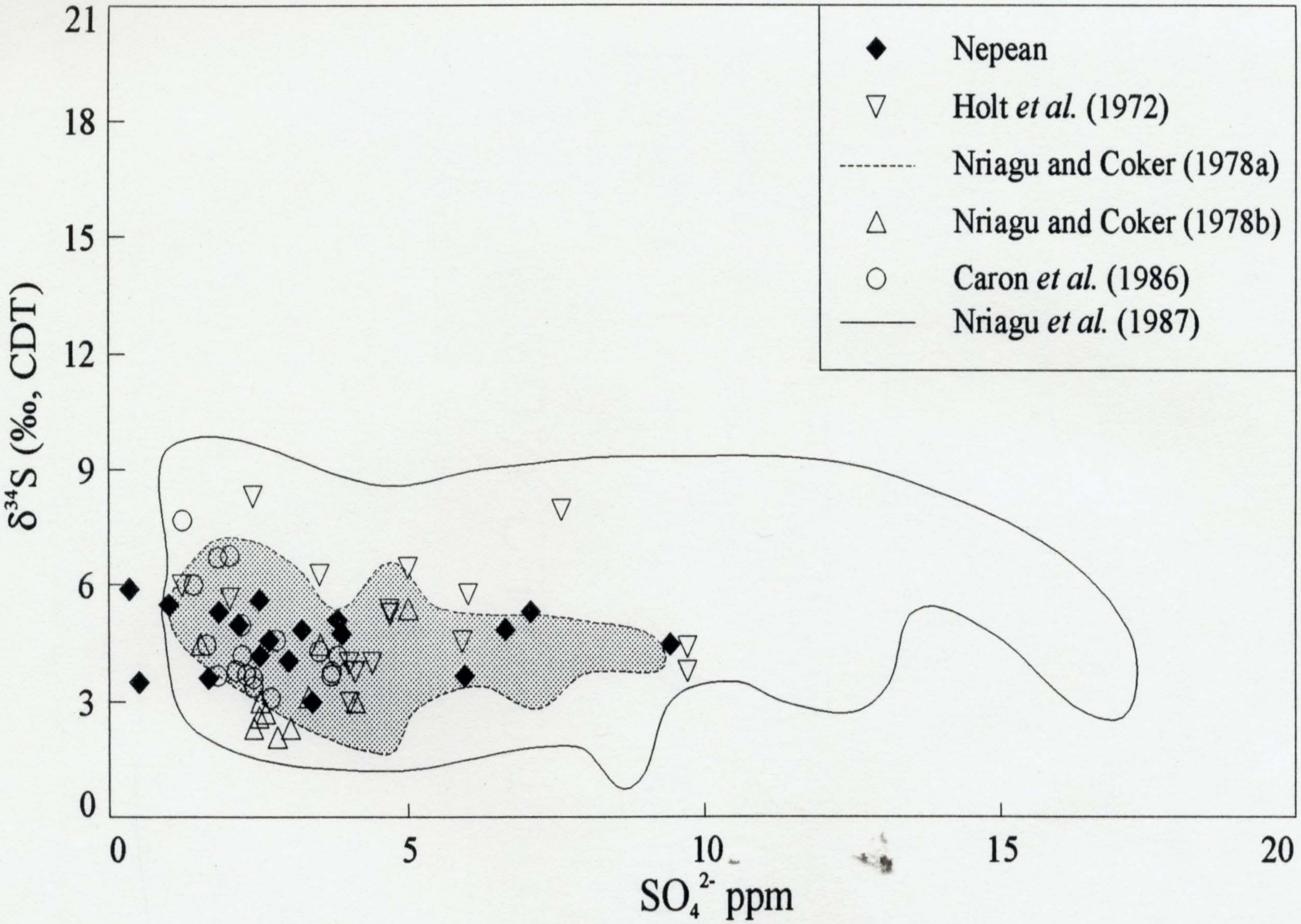

Figure 4.6 Comparison of $\delta^{34}S$ values from a number of studies of continental precipitation sulphates. The shaded area represents the range of values from 51 samples from Nriagu and Coker (1978a), and the outlined area represents the range of values from 189 samples from Nriagu *et al.* (1987).

The same trends in $\delta^{34}S$ and SO_4^{2-} concentration have been noted at Nepean. While these trends may indeed indicate the strengthening of a biogenic source during the summer, Saltzman *et al.* (1983a) also observed increased SO_4 aerosol concentrations during summer at Hubbard Brook, New Hampshire, but they observed a concurrent decrease in $SO_{2\,(g)}$ concentrations, and they attributed this to an increase in SO_2 oxidation during the warmer summer months.

Oxygen isotopes are more useful for revealing changes in oxidation mechanisms than sulphur isotopes since much larger differences in isotopic values should be observed. The mean $\delta^{18}O_{SO4}$ at Nepean is +14.7‰ with a range of +8.5 to +20.5‰, which fits well with data from other studies (Figure 4.2). It is similar to continental data of Holt *et al.* (1979) and Holt *et al.* (1981a) for a site at Argonne, Illinois (+7.0 to +26‰) as well as that of Caron *et al.* (1986) for rural Quebec (+8.3 to +13.5‰).

Plotting $\delta^{18}O_{SO4}$ against $\delta^{18}O_{H2O}$ gives a correlation coefficient of 0.360 which indicates that no significant relationship is present between these variables (Figure 4.7). A relationship would indicate that local oxidation was occurring in this area. The studies at Argonne, Illinois, carried out by Holt *et al.* (1979) and Holt *et al.* (1981), found a linear relation between $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$ with a slope of 0.7. They believed that was a result of the heterogeneous oxidation of $SO_{2\,(g)}$ to SO_4^{2-} (as explained in Section 1.3.1). Factor analysis results show that $\delta^{18}O_{SO4}$ loads high on Factor 3 with only a minor loading for $\delta^{18}O_{H2O}$. An underlying relationship between the sulphate oxygen and the rainwater oxygen may be indicated by this, however it is probably weak. It is likely that the sulphate

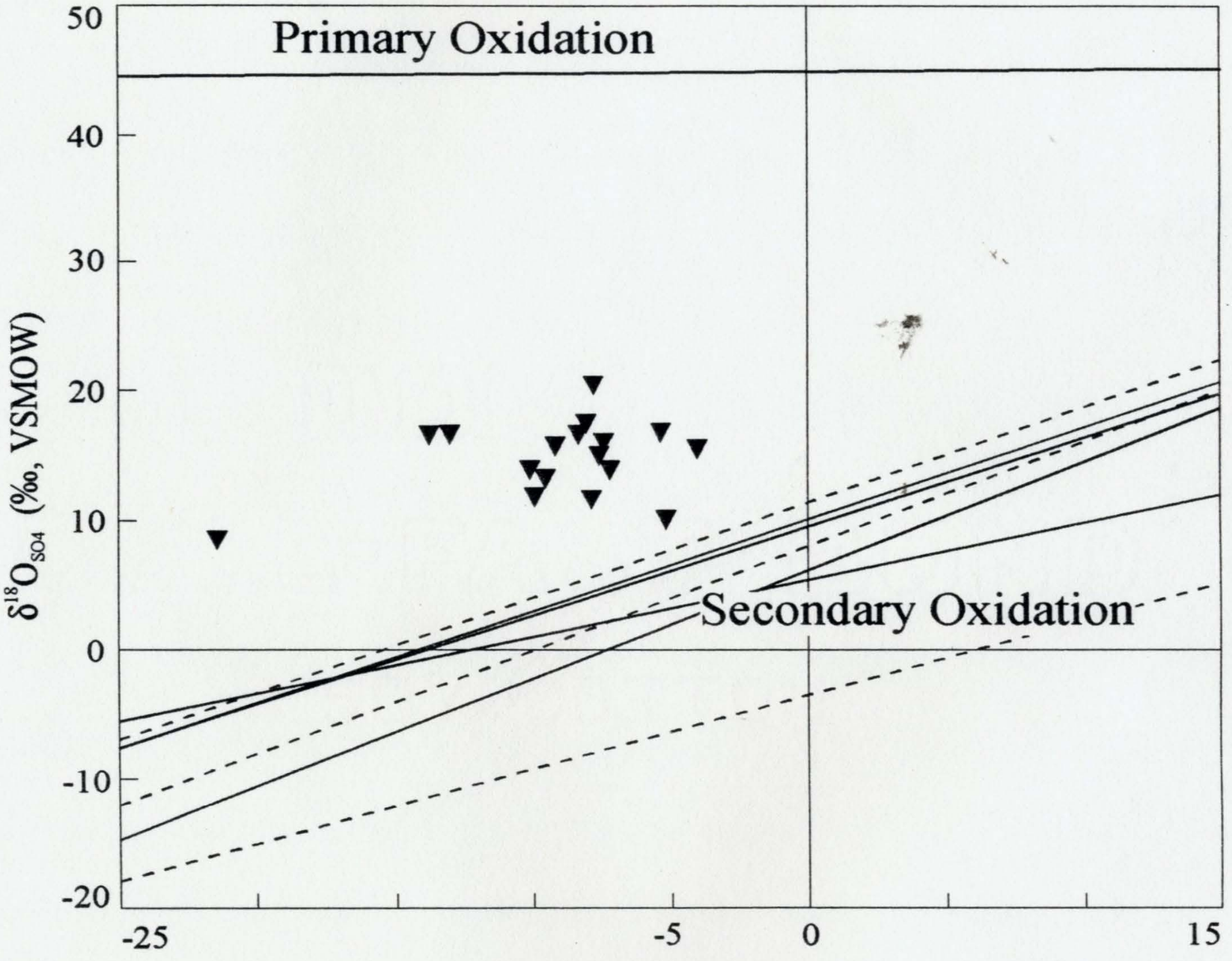

Figure 4.7 Nepean $\delta^{18}O_{SO4}$ plotted against $\delta^{18}O_{H2O}$ as compared to the oxidation curves of Holt *et al.* (1981b), Holt *et al.* (1983), and Holt and Kumar (1984).

in this area has been transported from other areas. There is also a minor loading for PSS on Factor 3 which would be consistent with the enrichment of $\delta^{18}O_{SO4}$ with the input of heavy marine rain.

A piece of evidence which may point to local oxidation is the seasonal variation in $\delta^{18}O_{SO4}$. There is an average decrease in $\delta^{18}O_{SO4}$ of 1.7‰ in winter which may suggest that heterogeneous oxidation is indeed having some affect. $\delta^{18}O_{H2O}$ varies with temperature, and was found to decrease by 4.8‰ at Nepean during the winter. Sulphate oxidized by this water may reflect this temperature dependence with decreasing $\delta^{18}O_{SO4}$ values. Caron *et al.* (1986) found a 3.8‰ depletion in $\delta^{18}O_{SO4}$ in Quebec during the winter, but they were not convinced of the temperature dependence of this change. They did not, however, measure $\delta^{18}O_{H2O}$ to further examine this relationship. The fact that a number of studies have found similar seasonal variations in different continental areas may reflect the importance of heterogeneous oxidation on a larger scale. If heterogeneous oxidation is important on a continental scale, there could be an overall depletion in $\delta^{18}O_{SO4}$ values even though the sulphates have been mixed and no longer directly reflect the ambient water.

The Nepean site does not have a direct primary sulphate influence. The values do not reach the same enrichments seen at St. John's, but they are similar to those of Seal Cove (Figure 4.2). Although there is no direct pollution influence, all of the samples lie above the secondary oxidation curves of Holt, indicating that some primary sulphates must be present (Figure 4.7). While this collection site can be considered to be in a rural area, there are industrialized and urban areas in the surrounding region, including parts of

Ontario, Quebec, and the northeastern United States. It is reasonable to expect that this site would experience input of pollutant sulphate from these areas. Air mass trajectories indicate that many of the air masses reaching Nepean have passed through the Great Lakes region where a great deal of the pollution originates.

Metals are present in very low concentrations at Nepean, and seem most consistent with typical rural or remote values. This further confirms that there is no local pollution affecting this site. Metals such as V and Ni which would be expected from oil burning sources such as power plants are below detection for the majority of samples. Enrichment factors are of little use in this instance because most of the samples had reference element concentrations which were below detection. It seems most likely that these metals are a mixture of the surrounding natural sources and pollution transported from the more industrialized areas of Ontario, Quebec, and the northern United States. The homogeneity of the sulphate $\delta^{34}S$ values suggests that these sources have become well mixed by the time they reach Nepean. Most of the metals show little, if any, seasonal variation.

$\delta^{18}O$ evidence suggests that the sulphate is a product of mixing between a number of sources, and therefore changes in oxidation are not important with respect to the variation in $\delta^{34}S$ data. The seasonality of $\delta^{34}S$ and the increase in SO_4^{2-} concentration during the summer imply that a biogenic source is responsible, consistent with the results of Nriagu *et al.* (1987). This influence however, is probably not as strong as the 30% indicated by their results because the change in $\delta^{34}S$ is very small.

The Nepean site is clearly different from the coastal Newfoundland sites. The continental nature of this site seems to impart a uniform character to the elemental concentrations and isotopic values. This is explained by two factors: the sources areas sampled by air masses traveling to this site are generally less variable than the marine influenced sites and the sulphates from different areas are becoming well mixed before their deposition at this site. The oxygen isotopic data is particularly useful in illustrating this process. The relationship between $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$ is not strong which implies that the sulphate has been oxidized in a number of air masses which have eventually mixed giving the measured sulphate an oxygen signature which bears no resemblance to the $\delta^{18}O$ of the ambient water. This mixing also results in fairly uniform sulphur isotopic values. The seasonal change in $\delta^{18}O_{SO4}$ however may indicate a pervasive influence by heterogeneous oxidation processes throughout North America.

CHAPTER 5

CONCLUSIONS

5.1 Overview

This study set out to examine the characteristics of atmospheric sulphate at three sites in eastern Canada, representing both marine and continental environments. It is unique because it has incorporated metal concentration and meteorological data to augment the isotopic data allowing greater confidence to be placed in the interpretations.

The St. John's and Seal Cove coastal sites have chemical and isotopic trends typical of marine areas. $\delta^{34}S$ data from both sites clearly reflect the mixing between a seaspray end-member (+21‰) and continental/anthropogenic end-member (~+5‰). The continental/anthropogenic end-member is a mixture of transported of sulphate from both natural and anthropogenic sources. The marine influence is stronger for Seal Cove than for St. John's which is probably a reflection of increased pollution at the urban St. John's site. Although these sites are clearly similar, there are differences which become clear when the data is examined in detail.

While St. John's is predominantly influenced by this marine-continental interaction, there is also a clear local pollution source at the this site which has been defined by extremely high $\delta^{18}O_{SO_4}$ values and increased metal concentrations. This input is clearly from a local power plant and it may be responsible for some of the scatter in $\delta^{34}S$ values (-10‰ to +14‰) of the low PSS samples. Some of the scatter may reflect a biological input, however there is not enough data to say this unequivocally. The strong pollution signal may overwhelm any sign of locally oxidized secondary sulphates as these are not apparent in the oxygen data. The data show however, that not all of the samples have experienced contamination.

There is no indication of a strong pollution influence at the Seal Cove site. Oxygen isotopes point to a relatively high pollution input in one sample (SC-11S), and it is plausible that the local power generating station has had some influence on this sample. Metal concentrations, however, are not consistent with this interpretation. The site does not appear to be pristine either. Primary sulphate must be present in order to explain the discrepancy between measured $\delta^{18}O_{SO4}$ values and the expected secondary oxidation values. Some locally oxidized sulphate may be present, as shown by the apparent correlation of $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$, however this is not a strong influence. Air mass trajectories show that some of the air masses have passed over the industrialized areas of eastern North America and therefore transported sulphate inputs from these areas are plausible. These factors point to transported sulphate as a large source of sulphates, and they are therefore linked to the continental/anthropogenic end-member.

As a continental site, Nepean has a completely different character from the coastal sites. The sulphur isotopic signature at this site is very constant and oxygen isotopic values indicate that oxidation is not local. The sulphate at this site therefore represents transported sulphate which has likely been mixed to give a homogeneous signal. Oxygen isotopic values and metal concentrations indicate that there is no direct input of pollution at this site, and the chemistry of the samples is consistent with a rural site. As with Seal Cove, the presence of primary sulphate is indicated in the $\delta^{18}O_{SO4}$ values. This primary sulphate is probably transported and air mass trajectories indicate that the industrialized areas of eastern North America are the likely source. It is interesting to note that not only is a continental influence observed at the coastal sites, but there is a small marine influence felt at the Nepean site, far from the ocean. This illustrates how well the different parts of the atmosphere interact, resulting in the transport of materials far from their places of origin.

The lack of correlation between $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$ at Nepean indicates that local oxidation is unimportant. The summer enrichment in $\delta^{18}O_{SO4}$ observed at this site has been seen at other continental sites and this leads to the hypothesis that perhaps this seasonal variation in $\delta^{18}O_{SO4}$ simply represents the importance of heterogeneous oxidation on a continental scale, rather than in the local area. There is a general enrichment of $\delta^{18}O_{H2O}$ in all areas during the summer and therefore $\delta^{18}O_{SO4}$ will reflect this enrichment independent of where it is oxidized.

5.2 Linking the Sites

Figure 5.1 is a composite $\delta^{34}S$ - PSS diagram which includes the data from all three sites. Here it is clear that the St. John's and Seal Cove data are comparable; both with 0 PSS intercepts of approximately +5‰. The Nepean data cluster quite nicely at this

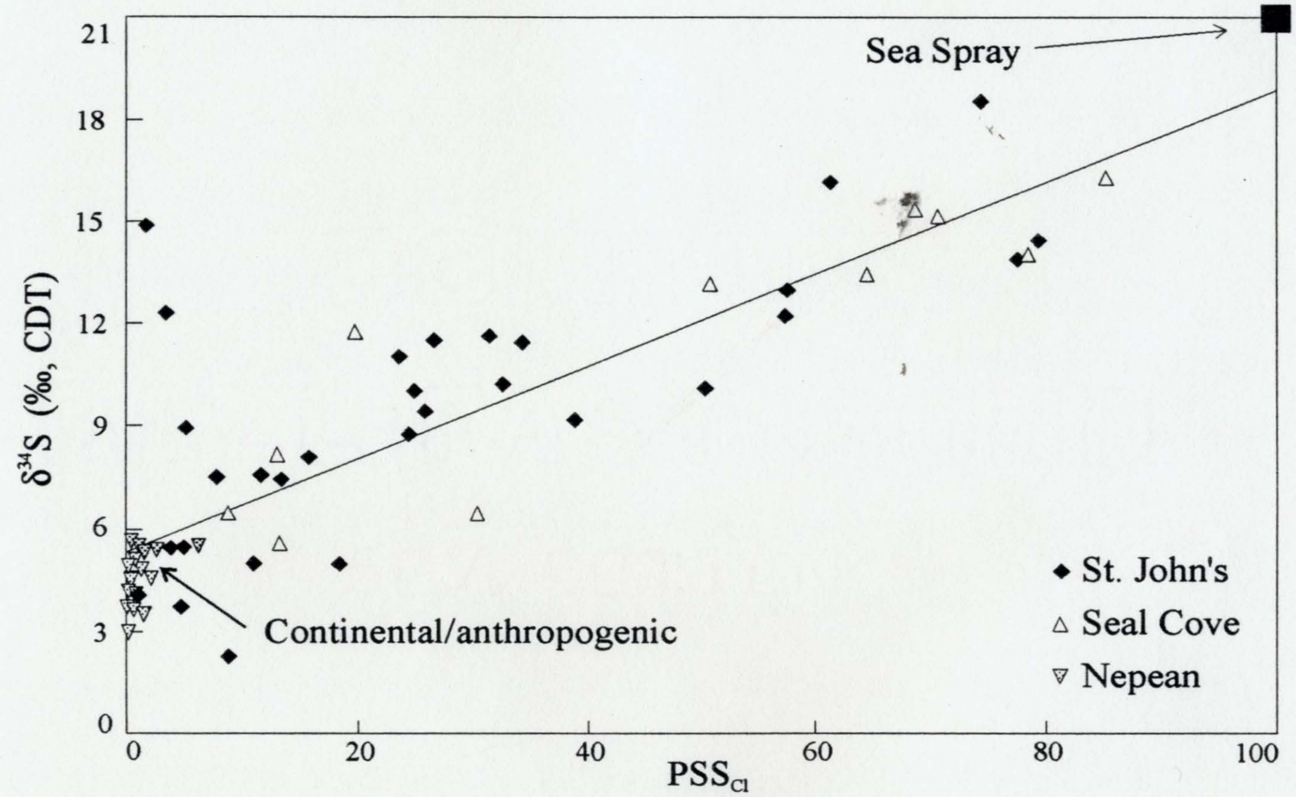

Figure 5.1 $\delta^{34}S$ plotted against PSS_{Cl} for all samples. The line represents the linear regression.

intercept with an average $\delta^{34}S$ value of +4.4‰ which is also similar to the $\delta^{34}S_{NSS}$ values for St. John's (+4.7‰) and Seal Cove (+3.0‰). A relationship can be found in the oxygen isotopic data as well. A composite $\delta^{18}O_{SO4}$ - PSS diagram is presented in Figure 5.2, and again, the St. John's and Seal Cove data indicate some relationship with PSS, but the Nepean data cluster around a $\delta^{18}O_{SO4}$ value of +14.7‰.

The patterns seen in the total data set seem to confirm the existence of the relationship between the continental and marine environments. Factor analysis was performed on the total data set and the results are presented in Table 5.1. Four factors were found which explained 80% of the variance in the data. There may be some bias in the results because there were more samples for the St. John's site. There is, however, confirmation of the importance of the marine-continental interaction. The first two factors, which together explain 47% of the variance in the data set, are the seaspray and continental factors. The third factor seems to represent the influence of pollution with high loadings for metals, SO_4^{2-}, and $\delta^{18}O_{SO4}$. The analysis indicates that $\delta^{18}O_{H2O}$ is independent of $\delta^{18}O_{SO4}$ and seems to confirm that secondary oxidation was not important at the three sites. Factor 4 includes $\delta^{18}O_{H2O}$, K^+, and Mn and may represent seasonality in the data. It is known that $\delta^{18}O_{H2O}$ varies with temperature and K^+ is often associated with biological inputs and therefore these would vary in sympathy.

The findings of this study confirm what has been observed before in other studies of long-range transport. Coastal sites exist at the boundary between the continental and marine environments and thus atmospheric sulphate should represent a mixture between

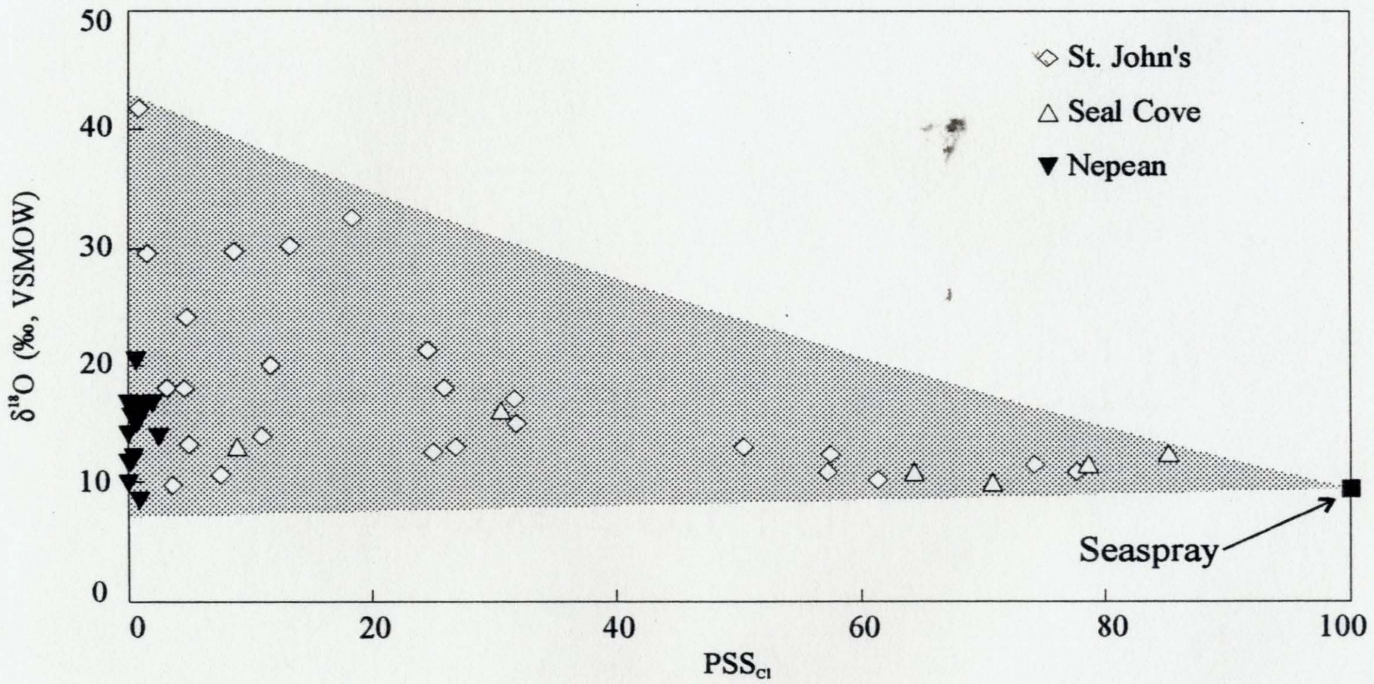

Figure 5.2 $\delta^{18}O_{SO4}$ plotted against PSS_{Cl} for all samples. The shaded area represents the apparent three component mixing trend.

Table 5.1 Factor Analysis results for total data set.

	1	**2**	**3**	**4**
Log Cl	**0.887**	0.008	0.317	0.128
PSS	**0.882**	-0.302	-0.195	-0.092
Log Na	**0.861**	0.035	0.303	0.029
$\delta^{34}S$	**0.851**	-0.266	-0.111	0.002
Log Mg	**0.603**	**0.431**	0.126	0.394
Log Pb	0.009	**0.846**	-0.037	-0.121
Log NO_3	-0.391	**0.797**	-0.324	0.104
Log SO_4	-0.236	**0.791**	**0.449**	0.127
Log Sr	0.416	**0.692**	0.228	0.298
Log Ca	-0.183	**0.682**	0.018	0.348
$\delta^{18}O_{SO4}$	-0.199	-0.03	**0.914**	0.001
Log Ni	0.218	0.018	**0.894**	0.014
Log Mo	0.278	0.106	**0.894**	-0.03
$\delta^{18}O_{H2O}$	-0.136	0.091	-0.031	**0.779**
Log K	0.345	-0.003	-0.156	**0.721**
Log Mn	0.061	0.389	**0.429**	**0.674**
% Variance	25.7	21.5	20.4	12.6
Interpretation	Seaspray	Continental	Pollution	Seasonal

these two sources. The continental signature becomes modified by interaction with the marine environment. The Nepean site represents a typical continental signature with a consistent $\delta^{34}S$ signature representing a mixture of sulphates oxidized in different areas. Air masses travel from the North American continent over the ocean to Newfoundland carrying this mixture of both natural and anthropogenic sulphates. Interaction with marine sources results in the typical linear mixing pattern which is seen at both the St. John's and Seal Cove sites. Local influences, however, such as pollution and climate, are also important to form the complete character of sulphate at a particular site.

5.3 Other Findings

A number of other important points have been demonstrated by this study. Most significantly, the $\delta^{18}O_{SO4}$ values measured at the St. John's have validated the experimental work of Holt *et al.* (1984) with regard to primary sulphate in natural rain samples. Although Holt *et al.* (1984) had predicted that very high $\delta^{18}O_{SO4}$ values would be observed near power plants, and had measured these in stack sulphates, these values had never actually been reported in natural rain samples. This type of information is important for confirmation of the presence of primary sulphates in precipitation samples. Secondary oxidation mechanisms cannot account for the high values measured in atmospheric sulphates; some proportion of primary sulphates must be included. Holt *et al.* (1984) had predicted values of approximately +40‰ for these primary sulphates, but we have found that $\delta^{18}O_{NSS}$ was as high as +42‰.

This study has also demonstrated the utility of combining isotopic, chemical and meteorological data to better interpret sulphur sources to the atmosphere. In past studies, these techniques were generally applied separately. Isotopic studies have often included major ion chemistry, but have not encompassed trace metal chemistry. At times, these different types of data can reinforce one another, or present alternative, perhaps better explanations, for particular features of the data. This study has shown this to be a useful approach and it will likely provide a very useful tool for other studies in this field.

The processes governing the formation, transport and deposition of sulphate in the environment are very complicated. Studies such as this seek to unravel these processes in an attempt to provide information which can be used to assess the impacts of anthropogenic sulphate on the environment. A thorough understanding of natural processes is required before the full impact of anthropogenic pollutants can be understood. This study has highlighted not only differences between particular sites, but the large scale interaction between regions which can only result in the widespread impact of anthropogenic emissions. Regions do not exist in isolation, and long range atmospheric transport can bring these pollutants to areas far from their place of origin.

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APPENDIX I

ANALYTICAL METHODS

I.1 Sulphate Extraction

In order to carry out stable isotopic measurements on sulphate it is necessary to precipitate this sulphate in the form of $BaSO_4$. When working with large volumes of water, it is desirable to use the techniques of ion exchange to concentrate the sulphate into a smaller volume of water. This procedure was carried out using Bio-Rad AG1-X8 resin and following a procedure after van Stempvoort (1989).

Initially the sample must be filtered to remove any particulates. This was carried out using a nitrogen pressured high volume filter system, utilizing 0.45 µm membrane filters.

The resin is cleaned before use by soaking in a solution of 0.5 M NaCl and washing with deionized water. Self-zeroing burets were used as columns in this study and proved very convenient, providing an opening where a tube from the sample container could be easily attached. Approximately 15 cm of resin was used and glass wool was placed in the bottom of the column to prevent the resin from escaping.

The sample is passed through the column at approximately 2-3 ml/min. Faster rates have been attempted, but experimentation has found that, for low concentration samples, faster rates may lead to lower yields.

Once the sample has passed through the column, the column is washed with 100 ml of deionized water. The waste water may be discarded, but it may be wise to retain it until the yield is known.

The sulphate on the column is eluted into a clean beaker using 0.5 M NaCl. 100 ml of the NaCl solution is passed through the column, again at 2-3 ml/min. Thorough elution can be checked by taking a few drops of the eluent in a small beaker, acidifying with HCl, and adding about 0.5 ml $BaCl_2$. If a white precipitate appears, continue to pass NaCl through the column. Once elution is complete, pass 100 ml of deionized water through the column into the same beaker.

The beaker of eluent is now heated until it begins to boil. HCl is used to acidify it to a pH of approximately 4, but not below. A few drops of $KMnO_4$ are also added to oxidize any organics present. It is then left to sit for 1/2 to 1 hour. If a brown precipitate appears, the sample is filtered using 0.45 µm nitrate cellulose membrane filters.

The sample is again heated to boiling, and approximately 5 ml of warm 10% $BaCl_2$ is added dropwise to the boiling mixture. A fine white precipitate should form. The heat is reduced and the sample is allowed to digest for 1 to 2 hours.

Once the sample has digested, it can be filtered using the 0.45 µm filters. The precipitate should be washed with deionized water several times until the washing are free of chloride when tested with $AgNO_3$. The precipitate can now be placed in the oven overnight at not greater than 80°C.

The precipitate is scraped from the filter membrane and stored for future analysis. Care must be taken when removing the precipitate as it tends to stick to the membrane due to static electricity. The membranes are also prone to tearing.

Some samples proved to be too small (<10 mg) to recover using the nitrate membrane filters. In these cases the precipitate was collected with Whatman #42 quantitative ashless filter paper. The filter paper was then gently heated in a vitrosil crucible over a bunsen burner. The filter paper will char and eventually disappear, leaving the precipitate. The filter paper should not be allowed to ignite as this may affect the oxygen isotopic composition.

A number of tests were carried out to determine the affect that various steps in the procedure might have on the isotopic composition of the sulphate. Some concern has been expressed by some workers (Rafter, 1967) that igniting a sample over a gas flame may cause the $BaSO_4$ to exchange with air oxygen and thus change the $\delta^{18}O$ composition of the sample. We have attempted both oven drying and igniting but have failed to find any real difference in the isotopic results. We have opted to follow the oven drying procedure where possible as it proved to be the easiest, but we feel that the ignition method could have been used without fear of changing the isotopic composition of the sample as long as care is taken not to ignite the filter paper.

APPENDIX II

Table II 1 Descriptions of St. John's samples.

Sample	Date Opened	Time	Date Closed	Time	Volume (l)
MUN-1	May 13/94	12:45 PM	May 13/94	11:05 PM	10
MUN-2	May 25/94	11:30 PM	May 26/94	12:30 PM	2.025
MUN-3	June 22/94	11:15 AM	June 23/94	9:15 AM	5.5
MUN-4	June 28/94	9:45 AM	June 29/94	2:15 PM	20
MUN-5	July 11/94	9:45 AM	July 11/94	5:45 PM	3.8
MUN-6	July 16/94	12:55 PM	July 17/94	11:35 AM	18
MUN-7	July 25/94	11:30 AM	July 26/94	11:30 AM	16.2
MUN-8	Aug. 23/94	10:15 AM	Aug. 24/94	9:40 AM	4.5
MUN-9	Sept. 1/94	11:45 PM	Sept. 2/94	4:40 PM	9
MUN-10	Sept. 5/94	6:15 PM	Sept. 7/94	8:50 AM	36.3
MUN-11	Sept. 11/94	9:45 AM	Sept. 12/94	2:45 PM	20
MUN-12	Oct. 11/94	3:30 PM	Oct. 12/94	9:40 AM	19.6
MUN-13	Oct. 23/94	3:50 PM	Oct. 24/94	11:00 AM	3.5
MUN-14	Oct. 25/94	11:15 AM	Oct. 26/94	2:00 PM	0.75
MUN-15	Oct. 26/94	10:00 PM	Oct. 28/94	8:00 PM	10.3
MUN-16	Nov. 7/94	10:00 AM	Nov. 10/94	10:00 AM	15.5
MUN-17	Nov. 29/94	12:30 AM	Nov. 29/94	5:30 PM	6.4
MUN-18	Dec.6/94	10:30 AM	Dec.7/94	6:30 PM	19.4
MUN-19	Dec.17/94	10:15 PM	Dec.19/94	2:00 PM	17.5
MUN-20S	Jan. 13/95	9:30 AM	Jan. 13/95	7:00 PM	11.6
MUN-21S	Jan. 22/95	11:45 PM	-	-	0.33
MUN-22S	Feb. 17/95	2:00 PM	-	-	12.3
MUN-23	Feb. 21/95	1:00 PM	Feb. 22/95	10:30 AM	14.6
MUN-24S	Feb. 22/95	11:30 AM	-	-	24.6
MUN-25	Mar. 14/95	4:40 PM	Mar. 15/95	8:30 PM	8
MUN-26	Mar. 21/95	10:00 PM	Mar. 24/95	4:00 PM	18
MUN-27	Mar. 24/95	11:00 PM	Mar. 26/95	12:30 PM	3.2
MUN-28	April 15/95	12:55 PM	April 17/95	3:00 PM	12.5
MUN-29	April 22/95	1:00 PM	April 23/95	2:00 PM	3
MUN-30	April 25/95	10:00 PM	April 26/95	11:55 PM	13.2
MUN-31	May 19/95	1:00 PM	May 19/95	11:00 PM	6.7
NH-1S	Jan. 28/95	10:00 AM	-	-	8
NH-2S	Feb. 18/95	3:00 PM	-	-	20.2
NH-3S	Feb. 22/95	12:30 PM	-	-	18

S" denotes a snow sample

Table II.2 Descriptions of Seal Cove samples.

Sample	Date Opened	Time	Date Closed	Time	Volume (l)
SC-1	July 6/94	3:35 PM	July 6/94	6:30 PM	1.275
SC-2	August 4/94	8:20 AM	August 4/94	12:05 PM	8
SC-3	August 7/94	9:30 PM	August 8/94	7:30 PM	2.7
SC-4	Sept 2/94	7:15 AM	Sept. 2/94	3:20 PM	9.5
SC-5	Sept. 11/94	9:10 AM	Sept. 12/94	7:20 AM	10
SC-6	Sept. 30/94	9:15 PM	Oct. 1/94	10:55 AM	4
SC-7	Oct. 18/94	7:50 AM	Oct. 19/94	7:25 PM	11
SC-8	Nov. 1/94	7:20 PM	Nov. 2/94	10:25 PM	4.7
SC-9	Dec. 25/94	9:20 AM	Dec. 26/94	8:05 AM	9
SC-10	Jan. 7/95	4:15 PM	Jan. 8/95	5:10 PM	10.5
SC-11S	Mar. 20/95	2:30 PM	-	-	19.6
SC-12S	Mar. 20/95	4:00 PM	-	-	16.2
SC-13	May 24/95	7:50 PM	May 25/95	7:12 AM	1.4
SC-14	July 2/95	8:50 PM	July 3/95	7:25 PM	10

S" denotes a snow sample

Table II.3 Descriptions of Nepean samples.

Sample	Date Opened	Time	Date Closed	Time	Volume (l)
LM-1	July 15/94	7:00 PM	July 16/94	8:30 AM	4
LM-2	July 22/94	11:00 AM	July 22/94	8:00 PM	3
LM-3	July 23/94	5:00 AM	July 23/94	11:00 AM	19.5
LM-4	July 30/94	8:30 AM	July 30/94	3:30 PM	20
LM-5	August 4/94	9:00 AM	August 4/94	3:00 PM	19
LM-6	August 25/94	6:00 PM	August 26/94	5:00 AM	7.3
LM-7	Sept. 13/94	7:30 AM	Sept. 14/94	5:00 AM	7
LM-8	Oct. 19/94	7:30 AM	Oct. 20/94	7:00 AM	4.2
LM-9	Oct. 31/94	8:30 PM	Nov. 1/94	11:30 AM	18.1
LM-10	Nov. 28/94	5:30 AM	Nov. 28/94	3:00 PM	6.3
LM-11	Dec. 5/94	8:00 AM	Dec. 5/94	9:30 PM	13
LM-12	Jan. 20/95	9:00 AM	Jan. 20/95	9:00 PM	10.1
LM-13	Mar. 7/95	6:00 AM	Mar. 8/95	7:00 AM	4.5
LM-14	April 3/95	10:00 AM	April 4/95	1:00 PM	6.2
LM-15	April 12/95	8:51 AM	April 13/95	6:00 AM	12.2
LM-16	April 27/95	12:00 PM	April 28/95	6:00 AM	6.8
LM-17	May 10/95	6:00 AM	May 11/95	8:30 PM	20
LM-18	May 17/95	6:00 AM	May 17/95	7:00 PM	12

Table II.4 pH and conductivity for St. John's samples.

Sample	**pH**	**Conductivity (uS/cm)**
MUN-1	4.22	36.7
MUN-2	5	22.4
MUN-3	4.77	22.5
MUN-4	4.98	26.6
MUN-5	4.77	11.9
MUN-6	4.91	10.8
MUN-7	5.19	5.9
MUN-8	5.54	12.2
MUN-9	5.09	15.4
MUN-10	5.05	13.4
MUN-11	4.96	20.8
MUN-12	5.38	19.5
MUN-13	4.34	38.2
MUN-14	6.26	30.2
MUN-15	5.06	14
MUN-16	6.32	44.3
MUN-17	5.64	16.6
MUN-18	4.1	66
MUN-19	5.82	18.2
MUN-20S	5.43	17
MUN-21S	5.27	22.2
MUN-22S	4.96	66.2
MUN-23	4.82	35.2
MUN-24S	4.13	48.6
MUN-25	5.32	8.9
MUN-26	5.38	28.4
MUN-27	4.78	22.6
MUN-28	4.41	30.2
MUN-29	5.16	13.9
MUN-30	5.66	5.6
MUN-31	6.01	37.3
NH-1S	5.17	8.3
NH-2S	5.33	31.7
NH-3S	5.48	7

"S" denotes a snow sample.

Table II.5 pH and conductivity for Seal Cove samples.

Sample	pH	Conducitivity (uS/cm)
SC-1	5.12	22.4
SC-2	5.49	11.7
SC-3	5.76	9.3
SC-4	4.91	17
SC-5	5.47	7.6
SC-6	5.69	19.2
SC-7	5.8	20.9
SC-8	5.27	22
SC-9	5.97	19.6
SC-10	6.07	11.8
SC-11S	5.5	17.2
SC-12S	5.59	8.2
SC-13	5.86	28.6
SC-14	5.75	9

"S" denotes a snow sample.

Table II.6 pH and conductivity for Nepean samples.

Sample	pH	Conducitivity (uS/cm)
LM-1	4.08	50.9
LM-2	3.97	72.7
LM-3	4.32	158.6
LM-4	4.31	29.6
LM-5	4.24	32.7
LM-6	4.59	24.7
LM-7	4.67	32.1
LM-8	4.37	42.3
LM-9	6.39	15.3
LM-10	5.8	116.3
LM-11	5.05	10.9
LM-12	5.07	8
LM-13	4.01	69.4
LM-14	5.9	24.1
LM-15	4.87	17.1
LM-16	4.93	27.3
LM-17	5.45	11.6
LM-18	4.35	35

Table II.7 Anion concentrations for St. John's samples.

Sample	Cl^- (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)
MUN-1	1.41	4.04	0.11
MUN-2	1.09	1.11	0.42
MUN-3	2.28	1.27	0.55
MUN-4	0.31	0.55	0.42
MUN-5	0.31	1.13	0.76
MUN-6	0.18	0.67	0.55
MUN-7	0.17	0.52	0.12
MUN-8	0.30	0.59	0.28
MUN-9	0.39	1.07	0.50
MUN-10	1.19	0.87	0.14
MUN-11	2.04	1.17	0.23
MUN-12	2.54	0.58	0.15
MUN-13	2.32	3.65	0.42
MUN-14	0.80	2.02	0.88
MUN-15	0.75	0.94	0.48
MUN-16	7.36	1.79	0.40
MUN-17	2.55	0.71	0.21
MUN-18	7.10	5.35	0.28
MUN-19	3.13	0.76	0.13
MUN-20S	2.55	0.45	0.25
MUN-21S	3.59	0.68	0.19
MUN-22S	6.41	2.83	0.36
MUN-23	3.26	3.39	0.12
MUN-24S	0.75	10.36	0.06
MUN-25	0.97	0.40	0.08
MUN-26	4.24	1.82	0.48
MUN-27	2.39	1.41	0.72
MUN-28	0.55	4.25	0.29
MUN-29	0.48	2.00	0.25
MUN-30	0.22	0.20	0.15
MUN-31	3.49	1.82	0.60
NH-1	0.73	0.26	0.15
NH-2	6.22	1.12	0.26
NH-3	0.56	0.13	0.05

"S" denotes a snow sample.

Table II.8 Anion concentrations for Seal Cove samples.

Sample	Cl^- (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)
SC-1	2.36	2.51	-
SC-2	0.07	0.15	0.07
SC-3	0.78	0.55	0.25
SC-4	0.75	1.18	0.58
SC-5	0.68	0.13	0.30
SC-6	3.42	0.70	0.21
SC-7	3.36	0.67	-
SC-8	3.33	1.53	0.12
SC-9	3.24	0.70	0.24
SC-10	0.96	0.27	0.08
SC-11S	3.22	0.53	0.08
SC-12S	1.18	0.21	0.10
SC-13	2.69	2.90	1.75
SC-14	0.32	0.34	0.21

"-" indicates that the concentration was below detection
"S" denotes a snow sample.

Table II.9 Anion Concentrations for Nepean samples.

Sample	Cl^- (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)
LM-1	0.10	6.63	3.02
LM-2	0.29	9.41	5.09
LM-3	0.04	2.48	1.08
LM-4	0.05	2.66	1.46
LM-5	0.03	3.39	1.21
LM-6	0.09	2.49	1.97
LM-7	0.07	5.94	1.42
LM-8	0.24	3.79	5.73
LM-9	0.05	0.47	0.52
LM-10	0.33	1.79	1.22
LM-11	0.07	0.96	0.91
LM-12	0.14	0.31	0.30
LM-13	0.78	7.07	6.38
LM-14	0.27	3.20	3.21
LM-15	0.33	2.13	1.39
LM-16	0.19	3.88	4.00
LM-17	0.08	1.64	1.19
LM-18	0.17	3.00	3.05

Table II.10 Cation concentrations for St. John's samples.

Sample	**Ca^{2+} (ppm)**	**Mg^{2+} (ppm)**	**Na^{+} (ppm)**	**K^{+} (ppm)**
MUN-1	0.17	0.06	0.82	-
MUN-2	0.23	0.03	0.66	-
MUN-3	0.36	0.11	1.34	0.09
MUN-4	0.17	-	0.19	-
MUN-5	0.43	-	0.27	0.05
MUN-6	0.23	-	0.12	-
MUN-7	0.30	-	0.14	-
MUN-8	0.43	-	0.28	-
MUN-9	0.27	0.03	0.25	0.05
MUN-10	0.16	0.08	0.69	0.02
MUN-11	0.12	0.14	1.21	0.04
MUN-12	0.17	0.17	1.52	0.12
MUN-13	0.36	0.18	1.39	0.07
MUN-14	1.61	0.12	0.52	0.09
MUN-15	0.17	0.05	0.43	0.02
MUN-16	0.34	0.50	3.86	0.18
MUN-17	0.17	0.14	1.52	0.04
MUN-18	0.27	0.48	3.92	0.13
MUN-19	0.19	0.22	1.95	0.10
MUN-20S	0.03	0.11	1.62	0.05
MUN-21S	0.09	0.24	2.18	0.04
MUN-22S	0.78	0.23	6.98	0.06
MUN-23	0.39	0.21	1.95	0.01
MUN-24S	0.06	0.08	0.57	-
MUN-25	0.13	0.03	0.70	-
MUN-26	0.55	0.30	2.73	0.07
MUN-27	0.32	0.17	1.50	0.02
MUN-28	0.62	0.05	0.38	-
MUN-29	0.89	0.03	0.30	-
MUN-30	0.23	0.01	0.25	-
MUN-31	1.06	0.37	2.72	0.10
NH-1	0.06	0.03	0.48	-
NH-2	0.22	0.35	3.60	0.10
NH-3	0.06	0.03	0.37	-

"-" indicates that the concentration was below detection
"S" denotes a snow sample.

Table II.11 Cation concentrations for Seal Cove samples.

Sample	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^{+} (ppm)	K^{+} (ppm)
SC-1	0.23	0.13	1.26	0.69
SC-2	-	-	0.07	-
SC-3	0.17	-	0.45	0.09
SC-4	0.04	-	0.52	-
SC-5	0.04	-	0.37	-
SC-6	0.19	0.24	1.93	0.16
SC-7	0.21	0.26	2.04	0.36
SC-8	0.34	0.36	2.12	0.17
SC-9	0.26	0.25	2.09	0.13
SC-10	0.69	0.08	0.66	0.06
SC-11S	0.11	0.23	1.96	0.06
SC-12S	0.06	0.06	0.76	0.03
SC-13	1.43	0.35	2.01	0.27
SC-14	0.40	0.06	0.07	0.17

"-" indicates that the concentration was below detection
"S" denotes a snow sample.

Table II.12 Cation concentrations for Nepean samples.

Sample	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^{+} (ppm)	K^{+} (ppm)
LM-1	0.81	0.08	0.10	-
LM-2	1.71	0.18	0.10	0.12
LM-3	0.17	-	0.25	-
LM-4	0.17	-	0.08	-
LM-5	0.30	-	0.04	-
LM-6	0.38	0.04	0.04	0.11
LM-7	0.85	0.13	0.02	0.02
LM-8	0.74	0.14	0.45	0.06
LM-9	0.05	0.01	0.06	0.02
LM-10	0.62	0.05	1.01	0.05
LM-11	0.07	0.00	0.13	0.04
LM-12	0.26	0.01	0.38	0.19
LM-13	1.48	0.09	0.86	-
LM-14	1.16	0.09	0.25	0.06
LM-15	0.80	0.07	0.34	0.05
LM-16	1.64	0.20	0.16	0.02
LM-17	0.63	0.11	0.04	0.03
LM-18	0.69	0.12	0.08	0.07

"-" indicates that the concentration was below detection

Table II.13 Percent Sea Spray values for St. John's samples.

Sample	PSS_{Cl}	PSS_{Na}	PSS_{Mg}
MUN-1	4.9	5.1	3.1
MUN-2	13.7	14.8	4.8
MUN-3	25.1	26.3	18.1
MUN-4	7.7	8.8	-
MUN-5	3.8	6.0	-
MUN-6	3.9	4.4	-
MUN-7	4.7	6.9	-
MUN-8	7.2	12.1	-
MUN-9	5.1	5.8	5.7
MUN-10	19.2	19.9	19.2
MUN-11	24.5	26.1	25.9
MUN-12	61.3	65.5	61.9
MUN-13	8.9	9.5	10.5
MUN-14	5.5	6.5	12.5
MUN-15	11.1	11.5	12.1
MUN-16	57.5	53.8	58.7
MUN-17	50.4	53.5	41.2
MUN-18	18.6	18.3	18.8
MUN-19	57.4	64.0	59.6
MUN-20S	79.4	90.2	48.9
MUN-21S	74.3	80.6	74.1
MUN-22S	31.7	61.7	16.9
MUN-23	13.5	14.4	12.8
MUN-24S	1.0	1.4	1.7
MUN-25	34.4	44.2	15.0
MUN-26	32.6	37.4	34.2
MUN-27	23.7	26.6	24.9
MUN-28	1.8	2.2	2.5
MUN-29	3.4	3.8	3.2
MUN-30	15.8	31.0	5.5
MUN-31	26.9	37.4	42.3
NH-1	39.0	45.9	26.7
NH-2	77.6	80.2	65.2
NH-3	59.3	69.8	45.0

"S" denotes a snow sample.

Table II.14 Percent Sea Spray values for Seal Cove samples.

Sample	PSS_{Cl}	PSS_{Na}	PSS_{Mg}
SC-1	13.1	12.5	11.3
SC-2	6.2	10.6	-
SC-3	19.7	20.4	-
SC-4	9.0	11.0	-
SC-5	73.6	71.9	-
SC-6	68.6	69.1	73.6
SC-7	70.7	76.8	82.2
SC-8	30.5	34.5	49.2
SC-9	64.5	74.3	75.1
SC-10	50.8	62.7	64.8
SC-11S	85.1	92.6	92.1
SC-12S	78.5	90.1	61.7
SC-13	13.0	17.3	25.1
SC-14	13.2	4.9	39.8

"S" denotes a snow sample.

Table II.15 Percent Sea Spray values for Nepean samples.

Sample	PSS_{Cl}	PSS_{Na}	PSS_{Mg}
LM-1	0.2	0.4	2.4
LM-2	0.4	0.3	3.9
LM-3	0.2	2.5	-
LM-4	0.3	0.7	-
LM-5	0.1	0.3	-
LM-6	0.5	0.4	3.6
LM-7	0.2	0.1	4.7
LM-8	0.9	2.9	7.7
LM-9	1.4	3.0	3.8
LM-10	2.6	14.2	6.1
LM-11	1.0	3.4	0.9
LM-12	6.2	30.7	4.8
LM-13	1.5	3.0	2.7
LM-14	1.2	2.0	6.1
LM-15	2.2	4.0	7.3
LM-16	0.7	1.0	10.7
LM-17	0.7	0.7	13.9
LM-18	0.8	0.7	8.1

Table II.16 Isotope data for St. John's samples.

Sample	$\delta^{34}S$ (‰)	$\delta^{18}O_{SO4}$ (‰)	$\delta^{18}O_{H2O}$ (‰)	$\delta^{34}S_{NSS}$ (‰)	$\delta^{18}O_{NSS}$ (‰)
MUN-1	5.4[α]	24.0	-8.1	4.6	24.7
MUN-2	-	-	-7.3	-	-
MUN-3	10.0[α]	-	-3.3	6.3	-
MUN-4	7.5[α]	10.7	-3.7	6.4	10.8
MUN-5	-	-	-2.7	-	-
MUN-6	5.4	9.8	-6.0	4.8	9.8
MUN-7	3.7	18.0	-5.9	2.8	18.4
MUN-8	-	-	-6.3	-	-
MUN-9	9.0	13.4	-8.8	8.3	13.6
MUN-10	8.5	19.3	-10.1	5.5	19.8
MUN-11	8.8	21.4	-9.1	4.8	25.3
MUN-12	16.1	10.3	-8.4	8.4	11.6
MUN-13	2.2	29.6	-4.9	0.4	31.6
MUN-14	-	-	-4.6	-	-
MUN-15	5.0	13.9	-10.5	3.0	14.4
MUN-16	13.0	12.5	-6.3	2.1	16.6
MUN-17	10.4[W]	13.1	-14.4	-0.4	16.8
MUN-18	4.9	32.5	-14.2	1.3	37.7
MUN-19	12.2	11.0	-8.8	0.4	13.0
MUN-20S	14.6[W]	-	-12.4	-10.0	-
MUN-21S	18.6[W]	11.7	-10.6	11.8	18.1
MUN-22S	11.5	17.9	-14.8	7.0	21.8
MUN-23	7.4	30.2	-11.0	5.3	33.4
MUN-24S	4.1	41.7	-10.9	3.9	42.0
MUN-25	11.7[W]	-	-9.1	6.8	-
MUN-26	10.2	15.1	-4.9	5.0	17.8
MUN-27	11.3[W]	12.7	-	8.3	13.8
MUN-28	14.9	29.4	-7.4	14.8	29.8
MUN-29	12.3	18.0	-8.6	12.0	18.3
MUN-30	8.5[W]	-	-13.2	6.1	-
MUN-31	11.5	13.1	-6.1	8.0	14.4
NH-1S	9.2	-	-11.3	1.6	-
NH-2S	14.1[W]	10.9	-17.5	-10.7	15.7
NH-3S	-	-	-11.5	-	-

"-" indicates that the sample was too small to be analyzed. [W] Sample analyzed at Univ. of Waterloo

"S" indicates a snow sample. [α] Sample analyzed at Univ. of Ottawa

Table II.17 Isotope data for Seal Cove samples.

Sample	**$\delta^{34}S$ (‰)**	**$\delta^{18}O_{SO4}$ (‰)**	**$\delta^{18}O_{H2O}$ (‰)**	**$\delta^{34}S_{NSS}$ (‰)**	**$\delta^{18}O_{NSS}$ (‰)**
SC-1	-	-	-1.5^{W}	-	-
SC-2	-	-	-9.7^{W}	-	-
SC-3	11.7	-	-2.3^{W}	9.5	-
SC-4	6.4	13.2	-8.1^{W}	5.0	13.6
SC-5	-	-	-10.4^{W}	-	-
SC-6	15.5^{W}	-	-6.4^{W}	3.5	-
SC-7	15.1	10.2	-6.9^{W}	1.0	11.9
SC-8	6.4	16.2	-1.3^{W}	0.0	19.1
SC-9	13.4	11.0	-11.8^{W}	-0.4	13.7
SC-10	13.4^{W}	-	-7.6^{W}	5.5	-
SC-11S	16.3	12.4	-12.8	-10.8	29.0
SC-12S	14.2^{W}	11.5	-12.2	-10.5	18.8
SC-13	8.5^{W}	-	-7.7	6.7	-
SC-14	5.5	-	-	3.2	-

"-" indicates that the sample was too small to be analyzed. ^{W} Sample analyzed at Univ. of Waterloo
"S" indicates a snow sample.

Table II.18 Isotope data for Nepean samples.

Sample	$\delta^{34}S$ (‰)	$\delta^{18}O_{SO4}$ (‰)	$\delta^{18}O_{H2O}$ (‰)
LM-1	4.9	11.8	-7.8
LM-2	4.5[Ot]	15.6	-4.1
LM-3	4.2[Ot]	16.7	-8.3
LM-4	4.6[Ot]	11.9	-9.9
LM-5	3.0[Ot]	14.1	-7.3
LM-6	5.6[Ot]	16.1	-7.4
LM-7	3.7	10.2	-5.2
LM-8	5.1	15.1	-7.6
LM-9	3.5	16.6	-13.7
LM-10	5.4	14.0	-10.1
LM-11	5.5	8.5	-21.4
LM-12	5.9[W]	-	-13.7
LM-13	5.3	16.3	-8.1
LM-14	4.9	16.7	-13.0
LM-15	5.0[W]	16.8	-5.3
LM-16	4.8[W]	15.7	-9.1
LM-17	3.6	12.4	-9.6
LM-18	4.1	20.5	-7.8

NSS calculations were not done for Nepean because PSS values low.

"-" indicates that the sample was too small to be analyzed.

[W] Sample analyzed at Univ. of Waterloo

[Ot] Sample analyzed at Univ. of Ottawa

Table II.19 ICP-MS data for St. John's sampling site.*

Sample	Li 6	Li 7	Be	B	C (cps)	N (cps)	Mg	Al	Si	P	S	Cl	Ca 42	Ca 43	Ti	V
MUN-1	<8.91	<4.02	<0.42	<9.46	6636	14017	99.7	5.1	<66	<132	<4062	6471	<864	<1006	<1.24	74.58
MUN-1	<6.11	<0.43	0.19	<12.96	1932	13049	98.0	<25.6	<23	<84	<2355	5046	<483	<2306	<1.32	77.81
MUN-2	<8.91	<4.02	<0.42	<9.46	5817	17202	90.5	9.2	<66	<132	<4062	5196	<864	<1006	<1.24	4.48
MUN-3	<8.91	<4.02	<0.42	<9.46	5668	16750	165.8	13.6	<66	<132	<4062	5907	<864	<1006	<1.24	<2.32
MUN-4	<8.91	<4.02	<0.42	<9.46	5572	16775	34.8	6.5	<66	<132	<4062	3638	<864	<1006	<1.24	<2.32
MUN-5	<8.91	<4.02	<0.42	<9.46	5655	16873	43.7	23.6	<66	<132	<4062	3551	<864	<1006	<1.24	<2.32
MUN-6	<8.91	<4.02	<0.42	<9.46	5804	16947	17.2	4.7	<66	<132	<4062	3603	<864	<1006	<1.24	<2.32
MUN-7	<8.91	<4.02	<0.42	<9.46	5697	16710	14.4	<3.8	<66	<132	<4062	3364	<864	<1006	<1.24	<2.32
MUN-7	<8.91	<4.02	<0.42	<9.46	5381	15615	11.6	<3.8	<66	<132	<4062	2465	<864	<1006	<1.24	<2.32
MUN-8	<8.91	<4.02	<0.42	<9.46	5929	16342	36.4	6.0	<66	<132	<4062	2550	<864	<1006	<1.24	<2.32
MUN-9	<8.91	<4.02	<0.42	<9.46	6250	17435	36.3	8.9	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32
MUN-10A	<8.91	<4.02	<0.42	<9.46	5677	16652	<6.5	<3.8	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32

Sample	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Cu	Zn	As	Br	Se	Rb	Sr	Mo
MUN-1	14.96	16.43	35	2.37	87	76	0.30	31.59	4.85	20.04	<0.18	<12.44	9.23	0.04	0.81	2.87
MUN-1	15.80	15.79	75	2.34	80	77	0.30	32.67	8.09	20.71	<0.32	<10.59	<0.53	<0.20	0.79	3.03
MUN-2	<0.24	<10.29	<9	1.59	<31	<17	0.09	5.29	17.67	28.60	<0.18	<12.44	<6.10	0.05	0.82	0.09
MUN-3	<0.24	<10.29	<9	3.35	<31	<18	0.06	0.63	2.52	88.86	<0.18	<12.44	<6.14	0.12	1.20	0.04
MUN-4	<0.24	<10.29	<9	3.60	<31	<18	0.08	0.23	<0.46	18.89	<0.18	<12.44	<6.11	0.06	0.90	<0.03
MUN-5	<0.24	<10.29	<9	5.21	<32	<18	0.07	0.36	0.82	81.71	<0.18	<12.44	<6.11	0.15	0.69	<0.03
MUN-6	<0.24	<10.29	<9	0.99	<31	<17	0.03	<0.18	<0.46	141.13	<0.18	<12.44	<6.10	0.05	0.22	<0.03
MUN-7	<0.24	<10.29	<9	0.73	<31	<17	0.02	0.28	<0.46	99.47	<0.18	<12.44	<6.09	0.04	0.16	<0.03
MUN-7	<0.24	<10.29	<9	0.72	<31	<16	0.03	0.28	<0.46	91.64	<0.18	<12.44	<6.11	0.02	0.18	<0.03
MUN-8	<0.24	<10.29	<9	3.53	<31	<18	0.05	0.31	<0.46	514.72	<0.18	<12.44	<6.11	0.10	0.60	<0.03
MUN-9	<0.24	<10.29	<9	1.58	<31	<17	0.05	0.26	0.70	463.11	<0.18	<12.44	<6.09	0.08	0.45	<0.03
MUN-10A	<0.24	<10.29	<9	<0.13	<31	<16	<0.02	<0.18	<0.46	<0.37	<0.17	<12.44	<6.08	<0.02	<0.02	<0.03

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.19 (Cont.) ICP-MS data for St. John's sampling site.*

Sample	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U
MUN-1	<0.12	0.04	<0.05	0.02	0.59	<0.01	0.78	0.04	0.02	<0.06	<0.01	0.90	<0.01	<0.01
MUN-1	<0.01	0.05	0.15	0.02	0.32	<0.00	0.87	0.04	0.02	<0.31	<0.03	1.14	<0.01	<0.02
MUN-2	<0.12	0.03	0.09	0.02	<0.16	<0.01	2.84	0.02	0.02	<0.06	<0.01	0.77	<0.01	<0.01
MUN-3	<0.12	0.02	<0.05	0.03	0.37	<0.01	1.48	0.02	0.02	<0.06	<0.01	0.63	<0.01	<0.01
MUN-4	<0.12	<0.02	<0.05	0.01	0.20	<0.01	1.92	0.01	0.01	<0.06	<0.01	0.05	0.01	<0.01
MUN-5	<0.12	0.05	<0.05	0.04	0.21	<0.01	2.94	0.02	0.05	<0.06	<0.01	0.49	<0.01	<0.01
MUN-6	<0.12	0.03	0.13	0.01	<0.16	<0.01	0.76	0.01	0.01	<0.06	<0.01	0.15	<0.01	<0.01
MUN-7	<0.12	0.03	0.06	<0.01	<0.16	<0.01	0.62	0.00	0.00	<0.06	<0.01	0.07	<0.01	<0.01
MUN-7	<0.12	<0.02	<0.05	0.01	0.29	<0.01	0.62	<0.00	0.00	<0.06	<0.01	0.10	<0.01	<0.01
MUN-8	<0.12	0.05	0.13	0.03	0.50	<0.01	1.88	0.01	0.01	<0.06	<0.01	0.20	<0.01	<0.01
MUN-9	<0.12	0.05	0.11	0.04	0.28	<0.01	1.49	0.01	0.01	<0.06	<0.01	0.60	<0.01	<0.01
MUN-10A	<0.12	<0.02	<0.05	0.01	<0.16	<0.01	0.03	<0.00	<0.00	<0.06	<0.01	<0.03	<0.01	<0.01

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.19 (Cont.) ICP-MS data for St. John's sampling site.*

Sample	Li 6	Li 7	Be	B	C (cps)	N (cps)	Mg	Al	Si	P	S	Cl	Ca 42	Ca 43	Ti	V
MUN-10B	<8.91	<4.02	<0.42	<9.46	6056	17079	147.4	<3.8	<66	<132	<4062	2293	<864	<1006	<1.24	19.91
MUN-11	<8.91	<4.02	<0.42	<9.46	6179	17554	176.7	<3.8	<66	<132	<4062	3025	<864	<1006	<1.24	<2.32
MUN-12	<8.91	<4.02	<0.42	<9.46	6530	16898	171.2	8.9	<66	<132	<4062	2456	<864	<1006	<1.24	100.22
MUN-13	<8.91	<4.02	<0.42	<9.46	6706	16847	120.3	4.7	301	<132	<4062	<1279	1549	1510	<1.24	2.43
MUN-14	<8.91	<4.02	<0.42	<9.46	6247	16765	56.6	24.6	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32
MUN-15	<8.91	<4.02	<0.42	<9.46	6163	16826	41.2	<3.8	<66	<132	<4062	<1279	<864	<1006	<1.24	15.87
MUN-16	<6.11	<0.43	<0.16	<12.96	1338	9637	502.6	<25.6	<23	<84	<2355	8579	621	<2306	<1.32	1.95
MUN-17	<6.11	<0.43	<0.16	<12.96	1551	10770	136.7	<25.6	<23	<84	<2355	3378	<483	<2306	<1.32	<0.81
MUN-18	<6.11	<0.43	<0.16	<12.96	1527	9611	464.7	<25.6	<23	<84	<2355	7947	<483	<2306	<1.32	183.84
MUN-19	<6.11	<0.43	<0.16	<12.96	1355	10899	209.9	<25.6	<23	<84	<2355	4029	<483	<2306	<1.32	<0.81
MUN-20S	<6.11	<0.43	<0.16	<12.96	1295	10516	107.6	<25.6	<23	<84	<2355	3373	<483	<2306	<1.32	1.64
MUN-21S	<6.11	<0.43	<0.16	<12.96	1413	11055	229.8	<25.6	<23	<84	<2355	4526	<483	<2306	<1.32	1.18

Sample	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Cu	Zn	As	Br	Se	Rb	Sr	Mo
MUN-10B	12.05	12.44	55	1.93	56	61	0.33	22.42	1.30	157.48	<0.18	<12.44	<6.15	0.04	0.90	1.82
MUN-11	<0.24	<10.29	<9	0.50	<31	<18	0.02	<0.18	<0.46	202.97	<0.18	<12.44	<6.15	0.05	1.07	<0.03
MUN-12	20.63	20.15	55	2.81	64	73	0.22	36.12	2.43	532.98	<0.18	<12.44	<6.17	0.10	1.36	3.25
MUN-13	<0.24	<10.29	<9	5.01	<32	<22	0.11	1.99	1.76	560.28	<0.18	<12.44	<6.15	0.19	2.30	0.48
MUN-14	<0.24	<10.29	<9	0.86	<31	<17	0.03	0.29	<0.46	265.58	<0.18	<12.44	<6.10	0.05	0.51	0.04
MUN-15	1.65	<10.29	<9	0.72	<31	21	0.07	5.45	<0.46	410.59	<0.18	<12.44	<6.11	0.06	0.41	1.26
MUN-16	<0.21	<3.23	<18	0.95	<35	<15	0.04	0.58	1.64	211.78	<0.33	<10.59	<0.55	<0.20	3.03	0.05
MUN-17	<0.21	<3.23	<18	0.56	<35	<14	0.01	<0.21	0.66	230.66	<0.32	<10.59	<0.54	<0.20	0.95	0.05
MUN-18	38.95	38.72	271	4.50	286	281	0.65	53.90	3.70	173.46	<0.33	<10.59	<0.55	<0.20	2.87	4.32
MUN-19	<0.21	<3.23	<18	0.99	<35	<14	0.01	1.01	0.60	189.12	<0.32	<10.59	<0.54	<0.20	1.43	0.05
MUN-20S	<0.21	<3.23	<18	0.57	<35	<13	<0.01	0.32	0.99	47.55	<0.32	<11	<0.53	<0.20	0.78	0.07
MUN-21S	<0.21	<3.23	<18	0.36	<35	<14	0.01	0.64	0.81	36.53	<0.32	<10.59	<0.54	<0.20	1.41	0.07

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.19 (Cont.) ICP-MS data for St. John's sampling site.*

Sample	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U
MUN-10B	<0.12	<0.02	0.49	0.02	<0.16	<0.01	0.40	0.00	0.00	<0.06	<0.01	0.16	<0.01	<0.01
MUN-11	<0.12	<0.02	<0.05	0.01	0.23	<0.01	0.53	0.01	0.00	<0.06	<0.01	0.26	<0.01	<0.01
MUN-12	<0.12	0.03	<0.05	0.05	2.21	<0.01	1.01	0.01	0.01	<0.06	<0.01	0.53	<0.01	<0.01
MUN-13	<0.12	0.08	0.10	0.09	1.17	<0.01	2.40	0.01	0.01	<0.06	0.01	0.29	<0.01	<0.01
MUN-14	<0.12	<0.02	<0.05	0.03	0.51	<0.01	0.83	0.01	0.01	<0.06	<0.01	0.41	<0.01	<0.01
MUN-15	<0.12	<0.02	<0.05	0.01	0.21	<0.01	0.36	0.01	0.00	<0.06	<0.01	0.11	<0.01	<0.01
MUN-16	<0.01	<0.03	<0.10	0.04	1.13	<0.00	0.53	0.39	0.00	<0.31	0.05	0.40	<0.01	<0.02
MUN-17	<0.01	<0.03	<0.10	0.01	0.47	<0.00	0.44	0.02	<0.00	<0.31	<0.03	2.14	<0.01	<0.02
MUN-18	<0.01	0.11	0.17	0.02	0.32	<0.00	0.65	0.02	0.01	<0.31	<0.03	1.52	<0.01	<0.02
MUN-19	0.02	<0.03	<0.10	0.01	0.36	<0.00	0.24	0.01	<0.00	<0.31	<0.03	0.63	<0.01	<0.02
MUN-20S	<0.01	0.06	<0.10	0.02	<0.24	<0.00	0.62	0.02	0.00	<0.31	<0.03	1.42	<0.01	<0.02
MUN-21S	<0.01	<0.03	<0.10	<0.01	0.38	<0.00	0.54	0.01	<0.00	<0.31	<0.03	0.51	<0.01	<0.02

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.19 (Cont.) ICP-MS data for St. John's sampling site.*

Sample	Li 6	Li 7	Be	B	C (cps)	N (cps)	Mg	Al	Si	P	S	Cl	Ca 42	Ca 43	Ti	V
MUN-22S	<6.11	<0.43	<0.16	<12.96	1523	9503	219.4	<25.6	<23	<84	<2355	14860	624	<2306	<1.32	33.15
MUN-23	<6.11	<0.43	<0.16	<12.96	1513	8753	224.6	<25.6	<23	<84	<2355	3736	717	<2306	<1.32	50.17
MUN-24S	<6.11	<0.43	0.23	<12.96	1446	8316	99.1	<25.6	<23	<84	2744	1040	<483	<2306	<1.32	531.81
MUN-25	<6.11	<0.43	<0.16	<12.96	1918	16695	41.8	<25.6	<23	<84	<2355	1347	<483	<2306	<1.32	3.32
MUN-26	<6.11	<0.43	<0.16	<12.96	2068	14234	302.2	<25.6	<23	<84	<2355	4672	721	<2306	<1.32	1.49
MUN-27	<6.11	<0.43	<0.16	<12.96	1940	13538	171.4	<25.6	<23	<84	<2355	2452	<483	<2306	<1.32	<0.81
MUN-28	<6.11	<0.43	<0.16	<12.96	2051	13883	56.6	<25.6	<23	<84	<2355	424	600	<2306	<1.32	209.75
MUN-29	<6.11	<0.43	<0.16	<12.96	3147	22044	40.2	<25.6	<23	<84	<2355	446	968	<2306	<1.32	14.23
MUN-30	<6.11	<0.43	<0.16	<12.96	2918	23204	17.5	<25.6	<23	<84	<2355	<379	<483	<2306	<1.32	1.15
NH-1S	<6.11	<0.43	<0.16	<12.96	1428	10027	41.1	<25.6	<23	<84	<2355	1320	<483	<2306	<1.32	1.02
NH-2S	<6.11	<0.43	<0.16	<12.96	1547	12403	343.8	<25.6	<23	<84	<2355	7048	<483	<2306	<1.32	1.08
NH-3S	<6.11	<0.43	<0.16	<12.96	1525	11989	37.0	<25.6	<23	<84	<2355	1464	<483	<2306	<1.32	<0.81

Sample	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Cu	Zn	As	Br	Se	Rb	Sr	Mo
MUN-22S	10.56	10.57	84	3.40	88	91	0.38	22.04	2.01	48.80	<0.33	<10.59	<0.54	<0.20	3.53	1.61
MUN-23	43.34	44.61	385	8.81	401	394	1.62	87.28	4.44	266.85	<0.32	<10.59	<0.54	<0.20	1.80	7.64
MUN-24S	388.59	390.94	1607	29.32	1622	1642	10.06	814.79	26.92	12.54	0.44	<10.59	<0.53	<0.20	1.23	48.57
MUN-25	0.60	<3.23	24	0.43	<35	<13	0.02	1.71	0.64	62.25	<0.32	<10.59	<0.53	<0.20	0.49	0.25
MUN-26	<0.21	<3.23	<18	2.59	<35	<15	0.84	1.00	1.72	359.24	<0.32	<10.59	<0.54	<0.20	2.24	0.19
MUN-27	<0.21	<3.23	<18	1.43	<35	<14	0.37	0.43	1.17	199.49	<0.32	<10.59	<0.54	<0.20	1.38	0.12
MUN-28	26.88	27.20	172	4.32	>5278	200	1.07	104.32	5.62	266.42	<0.32	<10.59	<0.53	<0.20	1.45	3.96
MUN-29	0.45	<3.23	<18	1.76	<35	<16	0.21	16.47	3.49	450.51	<0.32	<10.59	<0.53	<0.20	1.40	0.35
MUN-30	<0.21	<3.23	<18	0.50	<35	<14	0.06	0.73	0.89	153.01	<0.32	<10.59	<0.53	<0.20	0.36	0.10
NH-1S	<0.21	<3.23	<18	<0.27	<35	<12	<0.01	0.28	0.38	2.78	<0.32	<10.59	<0.53	<0.20	0.27	<0.01
NH-2S	<0.21	<3.23	<18	3.64	<35	<13	<0.01	0.29	2.71	5.14	<0.32	<10.59	<0.54	<0.20	2.18	0.04
NH-3S	<0.21	<3.23	<18	<0.27	<35	<13	<0.01	<0.21	<0.29	2.55	<0.32	<10.59	<0.53	<0.20	0.24	0.03

All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.19 (Cont.) ICP-MS data for St. John's sampling site.*

Sample	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U
MUN-22S	<0.01	<0.03	<0.10	0.03	<0.24	<0.00	1.33	0.01	0.01	<0.31	0.13	0.98	<0.01	<0.02
MUN-23	<0.01	0.10	0.16	0.03	0.25	<0.00	0.36	0.01	0.00	<0.31	<0.03	0.33	<0.01	<0.02
MUN-24S	<0.01	0.12	0.17	0.10	<0.24	<0.00	0.56	0.01	0.01	<0.31	<0.03	<0.09	<0.01	<0.02
MUN-25	<0.01	0.03	0.19	0.01	0.70	<0.00	0.18	0.01	0.00	<0.31	<0.03	0.20	<0.01	<0.02
MUN-26	<0.01	0.14	0.12	0.03	0.77	0.00	0.71	0.01	0.01	<0.31	<0.03	0.65	<0.01	<0.02
MUN-27	<0.01	0.10	<0.10	0.03	0.63	<0.00	0.74	0.01	0.01	<0.31	<0.03	0.64	<0.01	<0.02
MUN-28	<0.01	0.04	<0.10	0.04	0.65	0.00	1.84	0.02	0.02	<0.31	<0.03	0.60	<0.01	<0.02
MUN-29	<0.01	0.05	<0.10	0.05	0.65	<0.00	1.39	0.01	0.01	<0.31	<0.03	0.34	<0.01	<0.02
MUN-30	<0.01	0.11	0.11	0.02	<0.24	<0.00	0.53	0.00	0.00	<0.31	<0.03	0.19	<0.01	<0.02
NH-1S	<0.01	<0.03	<0.10	0.01	0.24	<0.00	0.19	0.00	<0.00	<0.31	<0.03	0.09	<0.01	<0.02
NH-2S	<0.01	<0.03	0.11	0.02	<0.24	<0.00	0.50	0.01	0.01	<0.31	<0.03	0.33	<0.01	<0.02
NH-3S	<0.01	<0.03	0.16	<0.01	<0.24	<0.00	0.21	0.01	<0.00	<0.31	<0.03	<0.09	<0.01	<0.02

All concentrations are in ppb unless otherwise indicated < indicates that the concentration was below the limits of detection.

Table II.20 ICP-MS data for Nepean site.*

Sample	Li 6	Li 7	Be	B	C (cps)	N (cps)	Mg	Al	Si	P	S	Cl	Ca 42	Ca 43	Ti	V
LM-1	<8.91	<4.02	<0.42	<9.46	5618	15961	122.4	8.8	<66	<132	<4062	2084	<864	<1006	<1.24	<2.32
LM-2	<8.91	<4.02	<0.42	13.86	6054	17094	236.5	29.8	<66	<132	<4062	3259	2288	1671	<1.24	<2.32
LM-3	<8.91	<4.02	<0.42	<9.46	5969	17553	12.0	<3.8	<66	<132	<4062	2846	<864	<1006	<1.24	<2.32
LM-3	<8.91	<4.02	<0.42	<9.46	5547	16263	8.3	<3.8	<66	<132	<4062	2534	<864	<1006	<1.24	<2.32
LM-4	<8.91	<4.02	<0.42	<9.46	5787	16390	15.2	<3.8	<65	<132	<4062	1908	<864	<1006	<1.24	<2.32
LM-5	<8.91	<4.02	<0.42	<9.46	5636	16447	22.7	<3.8	<66	<132	<4062	2028	<864	<1006	<1.24	<2.32
LM-6	<8.91	<4.02	<0.42	<9.46	5742	16185	49.0	4.5	<66	<132	<4062	1607	<864	<1006	<1.24	<2.32
LM-7	<8.91	<4.02	<0.42	<9.46	6598	18195	67.0	6.3	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32
LM-8	<8.91	<4.02	<0.42	<9.46	6516	17180	140.8	13.4	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32

Sample	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Cu	Zn	As	Br	Se	Rb	Sr	Mo
LM-1	<0.24	<10.29	<9	3.15	<32	21	0.04	0.25	0.48	15.43	0.20	<12.44	<6.11	0.07	1.66	<0.03
LM-2	<0.24	<10.29	30	8.29	46	44	0.09	0.47	1.34	34.09	0.28	<12.44	<6.14	0.15	4.59	0.04
LM-3	<0.24	<10.29	<9	0.48	<31	<17	0.02	<0.18	<0.46	4.27	<0.18	<12.44	<6.10	0.02	0.14	<0.03
LM-3	<0.24	<10.29	<9	0.44	<31	<16	0.03	<0.18	<0.46	4.17	<0.18	<12.44	<6.07	0.02	0.15	<0.03
LM-4	<0.24	<10.29	<9	0.84	<31	<16	0.02	<0.18	<0.46	7.93	<0.18	<12.44	<6.10	0.03	0.39	<0.03
LM-5	<0.24	<10.29	<9	0.75	<31	<16	<0.02	<0.18	1.31	25.91	<0.18	<12.44	<6.09	0.03	0.32	<0.03
LM-6	<0.24	<10.29	<9	2.42	<31	<17	0.04	<0.18	<0.46	72.95	<0.18	<12	<6.08	0.06	1.12	<0.03
LM-7	<0.24	<10.29	<9	2.90	<32	<19	0.03	<0.19	<0.46	110.84	0.19	<12.44	<6.11	0.09	2.25	0.03
LM-8	<0.24	<10.29	<9	3.84	<32	<19	0.18	<0.18	<0.46	386.23	0.19	<12.44	<6.12	0.14	1.48	0.07

Sample	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U
LM-1	<0.12	0.18	0.06	0.08	<0.16	<0.01	1.30	0.03	0.05	<0.06	<0.01	1.77	0.01	<0.01
LM-2	<0.12	0.11	0.07	0.09	0.25	<0.01	3.15	0.04	0.08	<0.06	<0.01	2.00	<0.01	<0.01
LM-3	<0.12	0.02	0.06	0.04	<0.16	<0.01	0.32	<0.00	0.00	<0.06	<0.01	0.60	<0.01	<0.01
LM-3	<0.12	0.03	<0.05	0.03	<0.16	<0.01	0.34	0.00	0.01	<0.06	<0.01	0.53	<0.01	<0.01
LM-4	<0.12	<0.02	0.06	0.06	<0.16	<0.01	0.50	<0.00	0.01	<0.06	<0.01	0.87	<0.01	<0.01
LM-5	<0.12	0.03	0.13	0.05	<0.16	<0.01	0.37	0.00	0.01	<0.06	0.01	1.07	<0.01	<0.01
LM-6	<0.12	0.02	0.11	0.04	<0.16	<0.01	1.31	0.00	0.01	<0.06	<0.01	0.50	<0.01	<0.01
LM-7	<0.12	0.10	0.16	0.11	0.17	<0.01	1.53	0.01	0.02	<0.06	<0.01	1.27	0.01	<0.01
LM-8	<0.12	0.12	0.08	0.20	0.37	<0.01	2.14	0.01	0.01	<0.06	<0.01	1.98	0.01	<0.01

*All concentrations are in ppb unless otherwise indicated < indicates that the concentration was below the limits of detection.

Table II.20 (Cont.) ICP-MS data for Nepean site.*

Sample	Li 6	Li 7	Be	B	C (cps)	N (cps)	Mg	Al	Si	P	S	Cl	Ca 42	Ca 43	Ti	V
LM-9	<8.91	<4.02	<0.42	<9.46	6445	18406	21.8	<3.8	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32
LM-10	<6.11	<0.43	<0.16	<12.96	1420	10119	59.1	<25.6	<23	<84	<2355	869	<483	<2306	<1.32	<0.81
LM-11	<6.11	<0.43	<0.16	<12.96	1331	10255	16.3	<25.6	<23	<84	<2355	655	<483	<2306	<1.32	<0.81
LM-12	<6.11	<0.43	<0.16	<12.96	1476	11618	14.2	<25.6	<23	<84	<2355	631	<483	<2306	<1.32	<0.81
LM-13	<6.11	<0.43	<0.16	<12.96	1969	13233	100.2	<25.6	<23	<84	<2355	1185	1553	<2306	<1.32	2.79
LM-13	<6.11	<0.43	<0.16	<12.96	2917	20880	102.5	<25.6	<23	<84	<2355	1007	1569	<2306	<1.32	2.49
LM-14	<6.11	<0.43	<0.16	<12.96	2694	21070	98.8	<25.6	<23	<84	<2355	<379	998	<2306	<1.32	<0.81
LM-15	<6.11	<0.43	<0.16	<12.96	2787	22333	63.5	<25.6	<23	<84	<2355	429	851	<2306	<1.32	<0.81
LM-16	<6.11	<0.43	<0.16	<12.96	3224	24991	193.7	<25.6	<23	<84	<2355	<379	1715	<2306	<1.32	<0.81

Sample	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Cu	Zn	As	Br	Se	Rb	Sr	Mo
LM-9	<0.24	<10.29	<9	0.79	<31	<17	0.02	<0.18	<0.46	70.27	<0.17	<12.44	<6.10	0.04	0.37	<0.03
LM-10	<0.21	<3.23	<18	2.00	<35	<14	0.16	0.33	<0.29	216.45	<0.32	<10.59	<0.53	<0.20	2.34	0.07
LM-11	<0.21	<3.23	<18	0.63	<35	<12	0.02	0.36	0.76	123.07	<0.32	<10.59	<0.53	<0.20	0.50	0.03
LM-12	<0.21	<3.23	<18	0.68	<35	<13	0.07	<0.20	<0.29	124.32	<0.32	<10.59	<0.53	<0.20	0.28	<0.01
LM-13	1.09	<3.23	26	5.10	40	46	0.18	1.84	2.28	400.78	0.42	<10.59	<0.53	<0.20	2.67	0.44
LM-13	1.01	<3.23	24	4.95	42	30	0.19	1.84	2.13	395.85	0.39	<10.59	0.74	<0.20	2.71	0.38
LM-14	<0.21	<3.23	<18	4.35	<35	<16	0.10	<0.23	0.76	123.75	<0.32	<10.59	<0.53	<0.20	2.74	0.11
LM-15	<0.21	<3.23	<18	3.13	<35	<16	0.05	<0.23	0.43	75.94	<0.32	<10.59	<0.53	<0.20	1.87	0.03
LM-16	<0.21	<3.23	<18	5.93	<35	<19	0.08	<0.25	0.94	104.46	<0.32	<10.59	<0.53	<0.20	4.30	0.08

Sample	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U
LM-9	<0.12	<0.02	<0.05	0.01	<0.16	<0.01	0.35	<0.00	0.00	<0.06	<0.01	0.10	<0.01	<0.01
LM-10	<0.01	<0.03	0.14	0.04	0.33	<0.00	1.02	0.01	0.02	<0.31	<0.03	0.11	<0.01	<0.02
LM-11	<0.01	0.05	0.12	0.08	<0.24	<0.00	0.60	0.06	0.01	<0.31	<0.03	0.42	<0.01	<0.02
LM-12	<0.01	<0.03	<0.10	0.02	<0.24	0.08	0.34	0.00	<0.00	<0.31	0.05	0.16	<0.01	<0.02
LM-13	<0.01	0.18	0.29	0.17	0.97	0.01	2.09	0.04	0.05	<0.31	<0.03	3.54	0.02	<0.02
LM-13	<0.01	0.14	0.31	0.19	1.03	0.01	2.19	0.03	0.05	<0.31	<0.03	3.20	0.02	<0.02
LM-14	<0.01	0.07	0.14	0.12	0.32	0.01	1.85	0.01	0.02	<0.31	<0.03	0.48	<0.01	<0.02
LM-15	<0.01	0.04	0.14	0.05	0.58	0.00	1.25	0.01	0.01	<0.31	<0.03	0.51	<0.01	<0.02
LM-16	<0.01	0.10	0.14	0.10	0.40	0.00	2.59	0.01	0.02	<0.31	<0.03	1.02	<0.01	<0.02

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.21 ICP-MS data from Seal Cove samples.*

Sample	Li 6	Li 7	Be	B	C (cps)	N (cps)	Mg	Al	Si	P	S	Cl	Ca 42	Ca 43	Ti	V
SC-1	<8.91	<4.02	<0.42	9.77	5627	15944	203.3	11.5	<66	<132	<4062	3624	<864	<1006	<1.24	2.72
SC-2	<8.91	<4.02	<0.42	<9.46	5896	17113	9.3	<3.8	<66	<132	<4062	2176	<864	<1006	<1.24	<2.32
SC-2	<6.11	<0.43	<0.16	<12.96	1874	13131	7.6	<25.6	<23	<84	<2355	2796	<483	<2306	<1.32	<0.81
SC-3	<8.91	<4.02	<0.42	<9.46	6480	17451	61.4	<3.8	<66	<132	<4062	2416	<864	<1006	<1.24	<2.32
SC-4	<8.91	<4.02	<0.42	<9.46	6213	17426	57.3	4.9	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32
SC-5	<8.91	<4.02	<0.42	<9.46	5915	16993	49.4	<3.8	<66	<132	<4062	<1279	<864	<1006	<1.24	<2.32
SC-6	<8.91	<4.02	<0.42	<9.46	6398	17789	246.1	<3.8	<66	<132	<4062	3897	<864	<1006	<1.24	<2.32
SC-7	<8.91	<4.02	<0.42	<9.46	6094	16808	259.8	<3.8	<66	<132	<4062	3485	<864	<1006	<1.24	<2.32
SC-8	<6.11	<0.43	<0.16	<12.96	1613	11596	348.2	<25.6	<23	<84	<2355	4564	<483	<2306	<1.32	11.53
SC-9	<6.11	<0.43	<0.16	<12.96	1433	10902	243.6	<25.6	<23	<84	<2355	4093	<483	<2306	<1.32	1.20
SC-10	<6.11	<0.43	<0.16	<12.96	1463	10802	85.7	<25.6	<23	<84	<2355	1769	<483	<2306	<1.32	1.76
SC-11	<6.11	<0.43	<0.16	<12.96	1958	15318	233.2	<25.6	<23	<84	<2355	3427	<483	<2306	<1.32	<0.81
SC-12	<6.11	<0.43	<0.16	<12.96	2189	18694	74.7	<25.6	<23	<84	<2355	1133	<483	<2306	<1.32	<0.81

Sample	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Cu	Zn	As	Br	Se	Rb	Sr	Mo
SC-1	<0.24	<10.29	<9	39.98	<31	<17	0.11	0.84	3.39	52.88	0.26	<12.44	<6.15	0.68	1.61	0.04
SC-2	<0.24	<10.29	<9	1.08	<31	<16	0.03	0.22	<0.46	28.76	<0.18	<12.44	<6.07	0.02	0.15	<0.03
SC-2	<0.21	<3.23	<18	1.33	<35	<13	0.03	0.34	1.43	30.70	<0.32	<10.59	<0.53	<0.20	0.18	<0.01
SC-3	<0.24	<10.29	<9	5.00	<32	<18	0.05	0.59	<0.46	426.85	<0.18	<12.44	<6.11	0.16	0.63	0.08
SC-4	<0.24	<10.29	<9	2.20	<31	<17	0.04	<0.18	<0.46	191.29	<0.18	<12.44	<6.12	0.06	0.48	0.05
SC-5	<0.24	<10.29	<9	3.33	<31	<15	0.02	0.28	<0.46	103.34	<0.18	<12.44	<6.10	0.05	0.41	0.06
SC-6	<0.24	<10.29	<9	4.41	<31	<17	0.03	0.22	<0.46	174.29	<0.18	<12.44	<6.16	0.10	1.70	0.13
SC-7	<0.24	<10.29	<9	10.74	<31	<16	0.02	0.26	<0.46	176.39	<0.18	<12.44	<6.19	0.12	1.55	0.04
SC-8	<0.21	<3.23	<18	6.75	<35	<14	0.09	4.74	0.51	111.09	<0.32	<10.59	<0.54	<0.20	1.62	0.86
SC-9	<0.21	<3.23	<18	3.03	<35	<13	0.06	0.47	0.87	143.82	<0.32	<10.59	<0.54	<0.20	1.60	0.15
SC-10	<0.21	<3.23	<18	1.62	<35	<14	0.02	0.28	0.49	149.63	<0.32	<10.59	<0.53	<0.20	0.68	0.30
SC-11	<0.21	<3.23	<18	2.15	<35	<13	<0.01	0.48	0.55	2.15	<0.32	<10.59	<0.54	<0.20	1.38	0.08
SC-12	<0.21	<3.23	<18	0.51	<35	<12	<0.01	0.44	0.64	3.62	<0.32	<10.59	<0.53	<0.20	0.50	0.09

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.

Table II.21 (Cont.) ICP-MS data from Seal Cove samples.*

Sample	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U
SC-1	<0.12	0.11	0.06	0.05	2.46	<0.01	2.16	0.07	0.01	<0.06	<0.01	0.51	<0.01	<0.01
SC-2	<0.12	<0.02	0.08	0.01	<0.16	<0.01	0.31	0.00	<0.00	<0.06	<0.01	0.07	<0.01	<0.01
SC-2	<0.01	<0.03	0.12	0.01	<0.24	<0.00	1.37	0.03	0.00	<0.31	<0.03	0.14	<0.01	<0.02
SC-3	<0.12	0.02	0.07	0.03	0.45	<0.01	0.41	0.00	0.00	<0.06	<0.01	0.12	<0.01	<0.01
SC-4	<0.12	0.07	<0.05	0.03	0.34	<0.01	0.40	0.00	0.01	<0.06	<0.01	0.34	<0.01	<0.01
SC-5	<0.12	<0.02	0.06	0.01	<0.16	<0.01	0.44	0.01	0.00	<0.06	<0.01	0.12	<0.01	<0.01
SC-6	<0.12	0.02	0.33	0.02	0.24	<0.01	0.77	0.01	0.01	<0.06	<0.01	0.08	<0.01	<0.01
SC-7	<0.12	<0.02	<0.05	0.02	0.28	<0.01	0.56	0.00	0.00	<0.06	<0.01	0.08	<0.01	<0.01
SC-8	<0.01	<0.03	<0.10	0.05	1.82	<0.00	0.62	0.41	0.01	<0.31	<0.03	0.21	0.08	<0.02
SC-9	<0.01	0.04	0.10	0.05	<0.24	<0.00	0.60	0.01	0.00	<0.31	<0.03	<0.09	<0.01	<0.02
SC-10	<0.01	0.04	<0.10	0.02	0.27	<0.00	0.50	0.01	0.00	<0.31	<0.03	<0.09	0.02	<0.02
SC-11	<0.01	<0.03	0.11	<0.01	<0.24	<0.00	0.63	0.01	0.01	<0.31	<0.03	0.11	<0.01	<0.02
SC-12	<0.01	0.04	<0.10	0.01	<0.24	<0.00	0.21	0.01	<0.00	<0.31	<0.03	0.14	<0.01	<0.02

*All concentrations are in ppb unless otherwise indicated   < indicates that the concentration was below the limits of detection.