Investigating Sources of Stream Chloride near Kejimkujik National Park, Southwestern Nova Scotia: A Chlorine Stable Isotope Approach

by

Timothy P. Bachiu

Submitted in partial fulfilment of the requirements
for the degree of Master of Science

at

Dalhousie University
Halifax, Nova Scotia
September 2010

DALHOUSIE UNIVERSITY

DEPARTMENT OF EARTH SCIENCES

The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "Investigating sources of stream chloride near Kejimkujik National Park, southwestern Nova Scotia: A chlorine stable isotope approach." by Timothy P. Bachiu in partial fulfilment of the requirements for the degree of Master of Science.

Dated: September 8, 2010

Supervisors: ______________________________

____

Readers: ______________________________

____

____

____

DALHOUSIE UNIVERSITY

DATE: September 8, 2010

AUTHOR: Timothy P. Bachiu

TITLE: Investigating Sources of Stream Chloride near Kejimkujik National Park, Southwestern Nova Scotia: A Chlorine Stable Isotope Approach

DEPARTMENT OR SCHOOL: Department of Earth Sciences

DEGREE: MSc. CONVOCATION: October YEAR: 2010

Permission is herewith granted to Dalhousie University to circulate and to have copied for non-commercial purposes, at its discretion, the above title upon the request of individuals or institutions.

Signature of Author

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

The author attests that permission has been obtained for the use of any copyrighted material appearing in the thesis (other than the brief excerpts requiring only proper acknowledgement in scholarly writing), and that all such use is clearly acknowledged.

Table of Contents

List of Tables:

List of Figures

Abstract

Chlorine stable isotope analysis ($\delta^{37}Cl$) means of stream water (- 0.95 ‰, n = 22), rainwater (- 1.51 ‰, n = 12), fog water (- 1.08 ‰, n = 7) and silicate mineral bound chloride (+ 0.13 ‰, n = 3) are used in an isotope mass balance approach to estimate sources of stream chloride. During summer-baseflow conditions, the chloride budget of two catchments in southwestern Nova Scotia is approximately 39 % from rainfall, 37 % from fog water and 24 % from rock/water interactions. The results of a significant source of geological chloride suggest the use of chloride as a proxy for marine derived sulphate may not be valid. This conclusion implies that anthropogenic sources of sulphate to acid sensitive ecosystems of southwestern Nova Scotia have been underestimated when chloride is assumed to be a conservative ion in the hydrological cycle.

Glossary

ALET- Atlantic Laboratory for Environmental Testing.

Atmospheric deposition- In this study it refers to the combined deposition of all forms including wet deposition, dry deposition, cloud water and fog.

Catchment- the area of land where rainfall or snowmelts deposition drains downhill into a water body or stream. In this study, the catchment boundaries have been defined using a LiDAR derived digital elevation model and ArcHydro.

CNEF- Cosmogenic Nuclide Exposure Dating Facility at Dalhousie University. Location of AgCl precipitation for preparation of chlorine stable isotope analysis. Host of dedicated chlorine laboratory, typically used for chlorine extraction of sample for ^{36}Cl analysis.

Dry deposition- The component of atmospheric deposition from impaction or sedimentation of aerosols and suspended particulate.

EC- Environment Canada

Flux- Transport unit of measurement. In this study, it refers to mass/area/time, typically kg/ha/yr. Flux comparisons are useful for comparing the output of catchments of different sizes.

Fog- The fog referred to in this study is marine advective fog, although other types of fog exist.

Fog water- Refers to the solution collected during fog sampling.

HF decomposition- Treatment of silicate samples to dissolve mineral structure using hydrofluoric acid to release mineral bound chloride.

KNP- Kejimkujik National Park

Occult deposition- The component of atmospheric deposition that includes dry deposition, cloud water and fog.

Mineral bound chloride- Chlorine (assumed to be chloride) hosted by silicate minerals either within the lattice framework or fluid inclusions. Chloride released by HF decomposition is assumed to be mineral bound chloride.

Relative error- Measure of uncertainty calculated by dividing the error by the mean value.

Standard deviation of the mean- Measure of uncertainty calculated by dividing the standard deviation by the square root of the number of samples used to calculate the standard deviation.

SMOC- Standard Mean Ocean Chloride. Referring to the use of seawater as the standard for chlorine stable isotopes analysis as a result of a homogenized isotopic composition in the oceans (Godon et al. 2004a)

Wet deposition- The portion of atmospheric deposition contributed by rainfall and snowfall.

Acknowledgements

This work was made possible through the assistance and support of many individuals. Funding for the project was provided through the Environment Canada Acid Rain Project. Many thanks to Dr. Thomas Clair for providing the opportunity to work on the project and for providing an excellent combination of reassuring guidance and focused direction. The assistance and support provided by Dr. Anne Marie Ryan was essential to keeping the ideas flowing, keeping on budget and keeping focused. I am privileged to have had a supervisor as patient, dedicated and open-minded as Dr. Ryan. The enthusiasm and good humour provided by Dr. John Gosse was contagious and his encouragement provided motivation and confidence. Access to laboratory facilities and expertise provide by Dr. Gosse were essential both for the completion of the project and increasing what was learned through the study. The patience and kindness shown by Guang Yang allowed room for substantial learning and is greatly appreciated. Access to lab facilities, training and answers to a multitude of questions provided by Dr. Len Wassenaar was essential to completion of the project as well as facilitating a great deal of learning. The staff at the Atlantic Laboratory for Environmental Testing, specifically Mark Thibodeau, were kind to answer many questions and provide excellent analytical work. Assistance provided by Nova Scotia Department of Natural Resources Mineral Branch scientists such as Dr. Chris White, Dan Utting and Gavin Kennedy was helpful and informative. Ideas and suggestions provided by Dr. Steve Beauchamp of Environment Canada were very useful for designing the fog collector and developing an understanding of atmospheric processes. Lodging and communication facilities provided by the Mersey Tobeatic Research Institute while conducting field work were wonderful and fun. Thank you to Randy Naugler for the access to his blueberry field which provided an ideal location for fog sampling. The science staff at Kejimkujik National Park were very helpful and accommodating during the field season of the project. Thanks to Sumaya and Oscar for being awesome.

Chapter 1 : Introduction

1.1 Problem and Objectives

Chloride is a mobile ion in the hydrological cycle as a result of high solubility in natural waters. The mobility of chloride facilitates its use as a conservative tracer ion which can be used in the quantification of marine influence on streams (Watt 1979, Vet 1986, Wadleigh et al. 1994) and hydrological modeling (Kirchner et al. 2000, Neal and Kirchner 2000, Page et al. 2007, Soulsby and Tetzlaff 2008, Hrachowitz 2009).

Primary cycling of chloride occurs as sea spray is emitted into the boundary layer of the atmosphere by breaking waves (Erickson and Duce 1988) and atmospheric processes transport the chloride from the oceans to terrestrial realms, into fresh water courses and back to the ocean. A segment of this primary cycling can be quantified at the watershed scale where chloride input fluxes are approximated by direct measurement of volumes and concentrations of wet precipitation and output fluxes by flow monitoring and concentrations of stream water. However, examination of chloride fluxes at numerous watersheds has revealed localized imbalance between chloride inputs and outputs which are commonly rectified by unmeasured atmospheric deposition (Reynolds et al. 1997, Yanni 2000, Neal and Kirchner 2000, Godsey et al 2010). Primary cycling of chloride may be augmented by processes such as: weathering of earth materials (Peters 1991), groundwater storage (Hrachowitz 2009), biological cycling (Lovett et al. 2005, Bastviken et al. 2006) or anion adsorption (Chen et al. 2002). In turn, studies within the past ten years (Viers et al. 2001, Öberg 2002, Lovett et al. 2005, Bastviken et al. 2006) have called into question the use of chloride as a tracer ion.

This thesis project was initiated to address the imbalance between chloride output of stream water and chloride input from wet deposition where an excess of chloride is consistently observed in stream fluxes (Fig. 1.1). The precipitation and stream monitoring that provided data for these observations of chloride imbalance originate from Environment Canada’s (EC) long term Acid Rain Program which includes regular sampling in and near Kejimkujik National Park (KNP) of southwestern Nova Scotia (Fig. 1.2). However, stream water chloride fluxes in excess of measured atmospheric deposition are not exclusive to this region as a similar imbalance has been observed elsewhere (Reynolds and Pomeroy 1988, Neal and Kirchner 2000, Chen et al. 2002, Lovett et al. 2005, Godsey et al. 2010).

To address the problem of catchment chloride flux imbalance, the primary question addressed in this study is:

> Q1: What are the sources of the excess chloride in two catchments of southwestern Nova Scotia during summer, baseflow conditions?

The working hypothesis is that unmeasured atmospheric deposition is the overwhelming source of the excess chloride.

An alternative hypothesis is that in addition to unmeasured atmospheric deposition, the excess chloride has a terrestrial source such as chloride released during rock/water interactions.

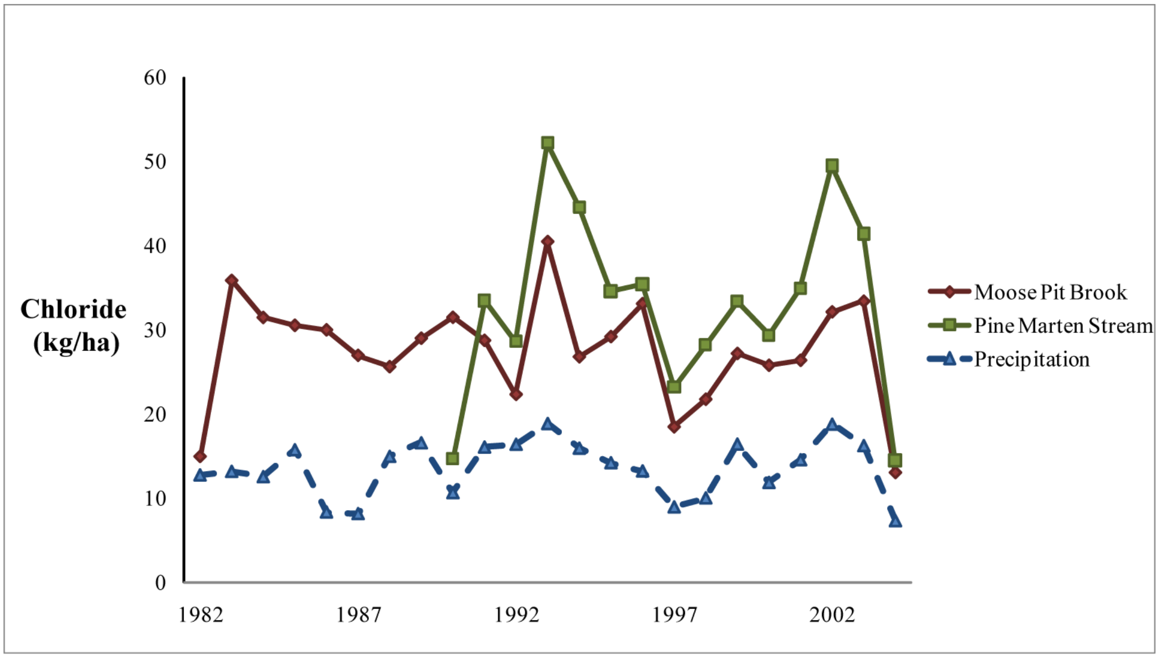


Figure 1.1: Yearly chloride stream fluxes are consistently greater than the input of precipitation. Data from Environment Canada Acid Rain Program.

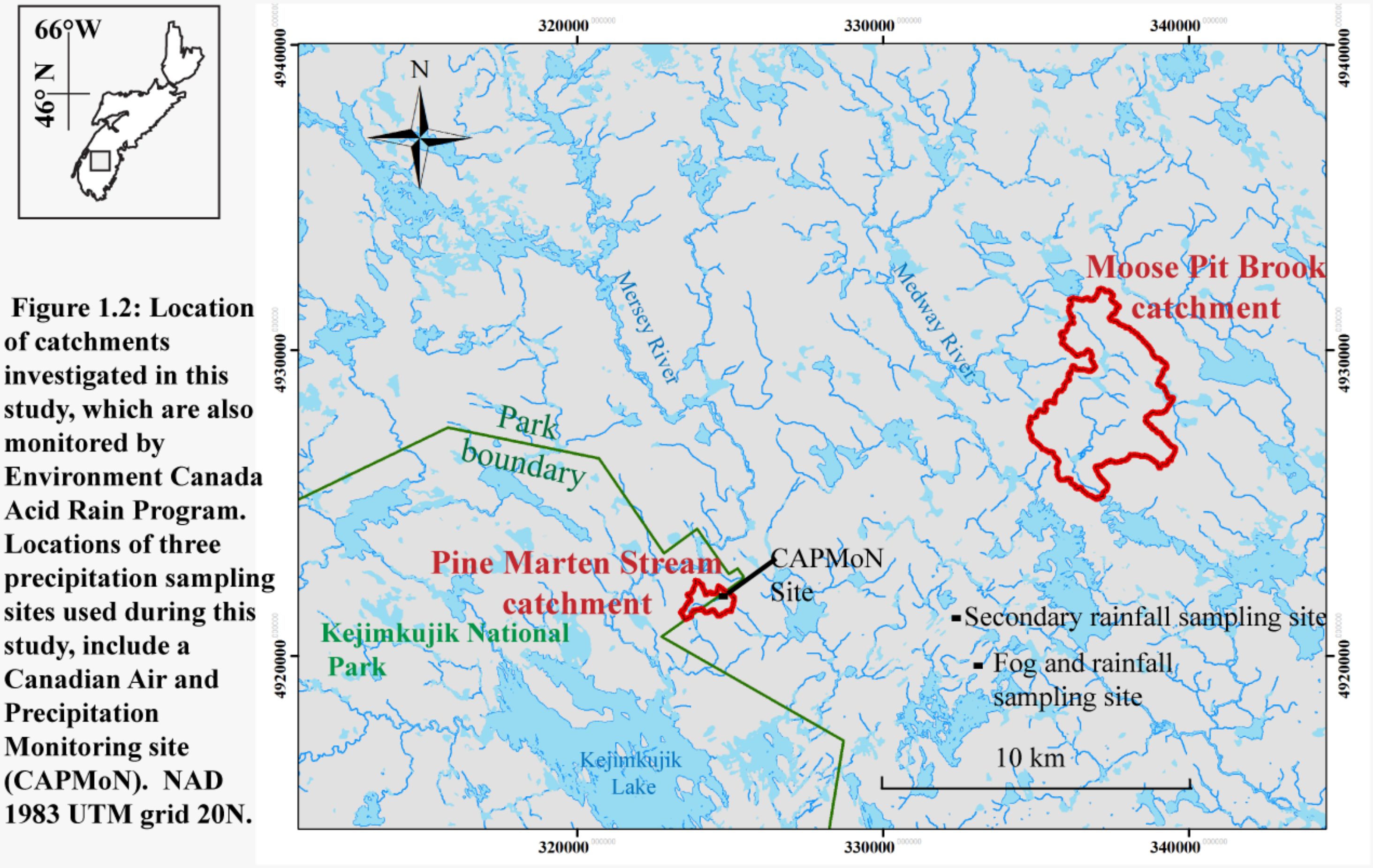


Figure 1.2: Location of catchments investigated in this study, which are also monitored by Environment Canada Acid Rain Program. Locations of three precipitation sampling sites used during this study, include a Canadian Air and Precipitation Monitoring site (CAPMoN). NAD 1983 UTM grid 20N.

The rationale for the thesis stems from a necessity to quantify marine and anthropogenic sources of stream sulphate in acid sensitive freshwater systems of southwestern Nova Scotia. Chloride in stream water is used as a proxy for marine sulphate by applying an assumption that all stream water chloride is sourced from oceans and deposited by atmospheric deposition (Watt et al. 1979, Vet 1986, Clair et al. 2002). Therefore distinguishing between terrestrial and atmospheric sources of stream chloride relates to the validity of the application of chloride as a proxy for marine sulphate. The implications being if atmospheric deposition is verified as the overwhelming contributor to stream chloride, then the use of chloride as proxy for marine sulphate is valid. However, if a terrestrial source of chloride is identified, then the proportion of stream sulphate assumed to have marine origins is overestimated.

> The primary objective of this thesis is to identify and quantify sources of stream chloride for two catchments in southwestern Nova Scotia.

The objective is addressed using a combination of methods including analysis of EC's long term monitoring data set, detailed investigation of geological features of the catchments, as well as ionic and stable isotope analyses of chloride in stream water, rainfall, fog water, soil solutions and bedrock. Through the use of these methods a second set of questions are addressed to achieve the primary objective. These questions include:

> Q2: Are there trends in the long term monitoring data set that indicate sources of stream chloride?
>
> Q3: Can geological features of the catchments be used to explain chloride concentrations and fluxes of stream water?
>
> Q4: Do marine advection fog events deposit chloride to catchments 60 km inland from the ocean?
>
> Q5: Do chlorine stable isotopes provide an effective method for distinguishing among sources of chloride?
>
> Q6: Can chlorine stable isotopes be used to quantify sources of chloride in stream water?

This thesis contributes to the evaluation of chloride cycling for two catchments in the KNP area by providing an investigation of the earth materials and providing a survey of chlorine stable isotopes in streams, fog water, rainfall, soils and bedrock. The direct sampling of fog water and bedrock have implications for Environment Canada's Acid Rain Program and are new contributions to the wealth of ecological and hydrological observations collected near KNP over the past half century.

1.2 Chloride Cycling

1.2.1 Marine and Atmospheric Chloride

Atmospheric deposition of chloride is a major input to chloride catchment budgets, but is variable both temporally and spatially. Atmospheric deposition occurs in several forms; wet deposition, fog, cloud water and dry deposition. Wet deposition is considered to be the component of atmospheric deposition that is measured in typical collectors and is primarily in the form of rainfall and snowfall. Wet deposition is commonly sampled to quantify contributions to watersheds, but dry deposition and fog contributions to watersheds are sampled and quantified in fewer instances than wet deposition (Reynolds et al. 1997, Yanni et al. 2000, Lovett et al. 2005). Dry deposition is the component of atmospheric deposition which is composed of suspended particulates and aerosols that are removed from the lower atmosphere by gravity or impaction on foliage or other objects. The type of fog which is likely to contribute to chloride catchment budgets is marine advection fog which is generated as warm air masses pass over cooler ocean waters creating lower troposphere conditions that initiate condensation. As condensation occurs over the ocean, wave generated aerosols are incorporated into the fog which increases the chloride content of the fog water. Difficulties in quantifying each of the different forms of atmospheric deposition arise from technical challenges as well as a high degree of variability in spatial, temporal and chemical patterns.

One challenge in quantifying atmospheric chloride deposition is the collection of samples. The method of sampling wet deposition used by EC meteorological monitoring is by automated device which excludes collection of dry deposition in between precipitation events (Environment Canada 2010). Atmospheric deposition other than wet deposition is referred to as occult deposition which includes fog, cloud water and dry deposition. Occult deposition is rarely measured directly, but is approximated by several methods. One method is sampling of bulk deposition, which includes wet deposition and a portion of dry deposition. In some cases, it is sampled by a funnel collector that is left open between precipitation events, allowing for the collection of a portion of aerosol sedimentation (Chan et al. 1983). The difference between the wet deposition and bulk deposition is a portion of dry deposition and is used to estimate the minimum occult deposition. Occult deposition also can be estimated by sampling the water that drips from the forest canopy (throughfall) and water dripping down the trunk of trees (stemflow). The difference between wet deposition and either throughfall or stemflow can be used to estimate dry deposition (Farrell 1995, Lovett et al. 1996). Fog water can be sampled by passively or actively allowing fog water to impact a surface that facilitates dripping into a collection container (Demoz et al. 1996). Aerosols can be sampled by drawing air through a filter allowing for the sampling of aerosols of various diameters. Because atmospheric deposition occurs in a series of forms, requiring numerous instruments and methods to provide an accurate account of total atmospheric deposition, inputs to stream catchments are rarely directly quantified.

Chloride concentrations in atmospheric deposition are highly variable which add a measure of uncertainty to the quantification of deposition rates sampled over short time periods (Reynolds et al. 1997). The spatial distribution of chloride deposition, at a regional scale, can be approximated as a systematic decrease with distance from the ocean (Underwood et al. 1988, Yin and Arp 1994, Clair et al. 2007) (Fig. 1.3). Chloride concentrations in atmospheric deposition are also highly variable when comparing depositional events. Kirchner et al. (2000) examined temporal patterns of wet deposition chloride in catchments of Mid-Wales and highlighted the high degree of variability in wet deposition compared to lesser variability in stream water. In the same catchments, Reynolds et al. (1997) reported a higher degree of variability in occult deposition than in wet precipitation alone. Nevertheless, a seasonal pattern of chloride deposition is clear from many studies in temperate climates (e.g.Yanni 1995, Reynolds et al.1997, Lovett et al. 2005) where chloride deposition is higher in winter months and lower in summer months. The variability of chloride quantities in atmospheric deposition necessitates long term and intensive sampling programs to characterize deposition patterns.

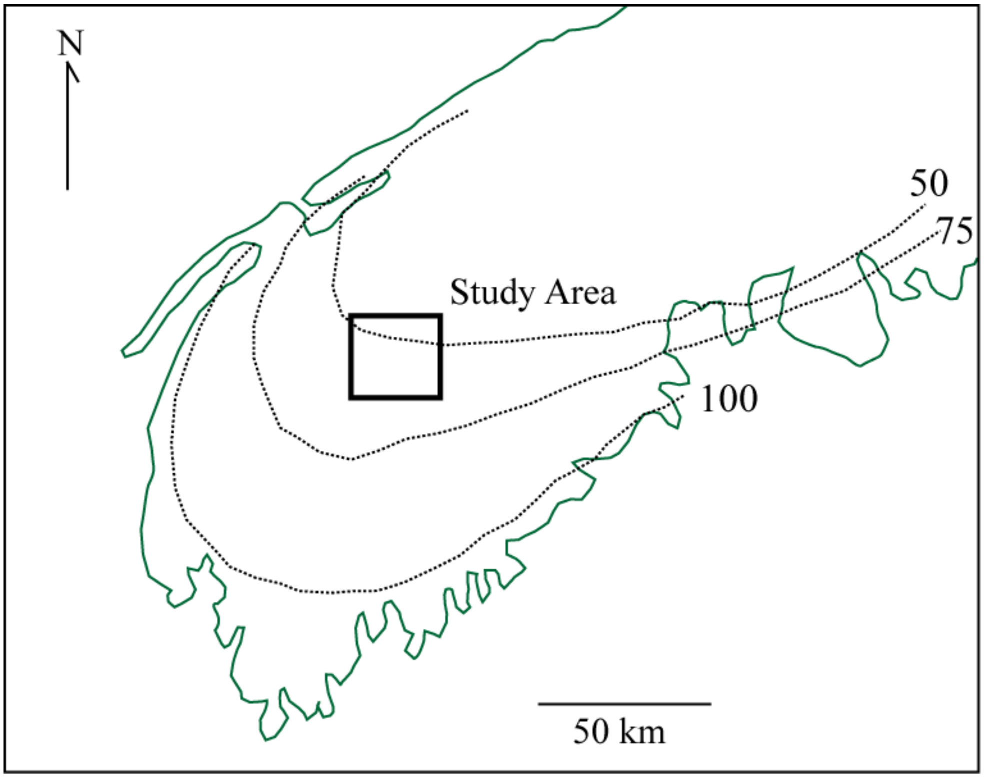


Figure 1.3: Annual chloride deposition (meq/m) rainfall and snowfall. Isopleths in dotted lines represent systematic decrease in chloride deposition with distance from the Atlantic coastline. After Underwood et al. 1988.

1.2.2 Geological Sources of Chloride

Chloride is a volatile ion concentrated in evaporites and only minor quantities are incorporated into the framework of silicate minerals. When it is bound in silicate minerals, chlorine is often located in the hydroxyl sites of amphiboles and micas. It may also be within the lattice framework of feldspathoid minerals such as sodalite and phosphates such as apatite. Chloride may also be a significant ion in fluid inclusions of feldspars and quartz (Kuroda and Sandell 1953). The chloride content of rocks increases from mafic to felsic composition and chloride content typically increases from sandstone to shales/clays (Johns and Huang 1967). In granitic rocks of Great Britain, one third to two thirds of chloride is water soluble, a result of chloride rich fluid inclusions (Fuge 1979). Examination of deep cores from the Stripa mines of Sweden indicates an enrichment of chloride in groundwater resulting from rock/water interactions at depth (Nordstrom et al. 1989). Despite the general knowledge of the mineral assemblages that host chloride, total chloride content in rocks is rarely measured or reported.

Generally the concentration of mineral bound chloride is low (< 500 ppm) with identifiable exceptions such as evaporites. In chloride budgets of catchments underlain by silicate bedrock, the chloride flux from weathering is generally considered to be negligible (eg. Watmough et al. 1994, Yanni 1995, Godsey et al. 2010). In some instances, approximations of chloride contributions from silicate bedrock have been made through the use of weathering rates and characterization of chloride content in the bedrock (Lovett et al. 2005). Challenges associated with these approximations are the difficulties in establishing accurate weathering rates (White 2008) and the lack of total chlorine measurements in silicate rocks, but they provide a first order approximation of chloride contributions from geological sources. In a comparison of two catchments, Peters (1991) attributes a greater chloride flux from one catchment to a higher proportion of amphiboles in the till. Chloride contributions from geological sources are typically considered minimal, but careful evaluation of watershed scale variations in bedrock and tills is required before geological sources of chloride can be dismissed.

1.2.3 Biological Influences on the Chloride Cycle

Biological cycling of chloride can produce large fluxes, but directly identifying processes is challenging (Öberg 2002, Lovett et al. 2005, Bastviken et al. 2007). Watershed deforestation experiments in Hubbard Brook Experimental Watershed showed an initial reduction of chloride uptake following deforestation and an increase in chloride output attributed to mineralization of the plant material. This short period of higher chloride fluxes following deforestation is followed by a number of years of lower chloride outputs, compared to an undisturbed catchment, attributed to an increase of vegetative uptake as the primary succession occurs (Lovett et al. 2005). Using ^{36}Cl as a tracer and sequential leaching, soil column retention experiments show that microbial activity can retain up to 24% of chloride inputs and release it within a time period of months (Bastviken et al. 2007). These experiments display the effects biological processes can have on chloride cycling, but conclude that during constant net primary productivity (NPP), the biological effects on the chloride cycle do not significantly alter the primary cycling of chloride beyond the phenology of the biota. In this study it is assumed that the loss of chloride through the release of methyl chloride from flora is negligible compared to the inputs and outputs of the catchments. Biological cycling of chloride and the potential effects on stream chloride budgets are addressed in the discussion of this thesis, however no attempt at sampling and quantifying these effects was made during the study.

1.2.4 Relevance of the Chloride Cycle to Hydrological Modeling

When coupled with hydrographic flow data, chloride used as a tracer has contributed significantly to the understanding of hydrological processes. Long term studies examining catchment-scale chloride fluxes display chloride stream outputs greater than wet deposition inputs. This catchment-scale imbalance is coupled with observations of lower variability in stream chloride concentrations than chloride concentrations in wet deposition (Kirchner et al. 2000, Neal and Kirchner 2000, Chen et al. 2002, Page et al. 2007). The apparent dampening of the atmospheric chloride signal has implications which are two-fold; it shows a significant portion of stream flow is 'pre-event' groundwater, and that chloride is retained within watersheds much longer than previously inferred (Neal and Kirchner 2000). Significant 'pre-event' chloride in stream water requires a mechanism to produce this effect such as groundwater storage (Neal and Kirchner 2000), retention of chloride by the adsorption of soils (Chen et al. 2002) or significant biological retention (Bastviken et al. 2006) have been invoked, but are difficult to quantify. These studies highlight the complexities of groundwater movement and challenge the perception of chloride as a conservative element. Attempts to understand and quantify the reservoirs of chloride highlight the limitations of using ionic data alone in catchment budgets.

In summary, the process of chloride transport from the oceans, to the boundary layer, to streams and back to the oceans is the primary mechanism of short term chloride cycling. However, studies summarized above have examined potential disruptions of the chloride cycle and identified processes that call into question the assumed conservative nature of chloride. Processes that may alter chloride cycling can be inferred using ionic data, but quantifying the effects of these processes using ionic data alone is problematic.

1.3 Local Relevance of Chloride Use as a Tracer Ion

Geological, biological and hydrological processes drive secondary cycling of chloride which may produce variations that alter the primary cycling of chloride. While observations of secondary cycling have contributed to the understanding of hydrological processes and biological activity, these developments also question the use of chloride as a marine tracer ion. A specific application that assumes chloride is a conservative, non-reactive tracer ion is in the estimation of marine sulphate contributions to inland fresh water systems of southwestern Nova Scotia.

1.3.1 Acidification of Fresh Waters

The physical geography and geology of southwestern Nova Scotia creates a unique interaction of marine influence, acidic soils and high inputs of transported atmospheric pollutants, resulting in streams with low pH. This convergence of acidifying agents stresses ecosystems and limits biological productivity (Freedman and Ogden 1981). Despite decreased deposition of anthropogenic sulphate during the past decades, the pH of fresh water systems has not returned to background conditions (Clair et al. 2002). Understanding and quantifying the sources of acidifying agents is therefore an integral step in developing realistic mitigation and prevention plans.

1.3.2 Sulphate Contributions

Sulphate (SO_4^{2-}) is a major ion in most fresh water systems and is a major contributor to the acidification of fresh waters. In the water systems of this study (Fig. 1.2), local point sources of sulphate are minimal (Shaw 1979). Therefore the sources of sulphate in these streams are a combination of weathering of bedrock and soils, air pollution from burning of fossil fuels, and wave generated marine aerosols. Acid generating sulphide minerals such as pyrite and pyrrhotite contribute to the sulphate budget through oxidation reactions. The Meguma terrane bedrock of southern Nova Scotia contains sulphide minerals which can contribute to acid generation (Worgan 1987). However, the sulphide contributions from bedrock have been estimated to be minimal in areas where the bedrock remains undisturbed (Clair et al. 1989). Sulphate from the dissolution of evaporites, such as gypsum, may contribute to a sulphate budget but is not considered an acidifying agent because the dissolution releases buffering cations resulting in net neutral products.

The atmospheric contribution to fresh water sulphate budgets in near-coastal environments has two primary sources; marine generated aerosols and anthropogenic sources of smelting and fossil fuel burning. Marine derived sulphate is generally considered to be present as neutral salts and is important to distinguish from anthropogenic sulphates (Farrell 1995). Burning of fossil fuels and smelting releases sulphur dioxide to the troposphere and reduces the pH of precipitation. Gases and particulates released during combustion are transported by prevailing weather patterns and deposited downwind from production. The pollution component of sulphate in precipitation can be quantified using stable sulphur isotopes (Wadleigh et al. 1994), but is commonly deduced by subtracting the marine derived sulphate from the total sulphate in precipitation. Marine derived sulphate is commonly quantified indirectly as well, through the use of chloride as a proxy for marine contributions (Watt 1979, Vet 1986, Wadleigh et al. 1994, Farrell 1995).

1.3.3 Chloride as a Proxy for Marine Sulphate

In EC's freshwater monitoring programs, chloride concentrations in fresh water are used as a proxy for marine-derived sulphate. This proxy is based on the consistent mass ratio of SO_4^{2-} to Cl^- in ocean waters and chloride concentrations in stream water (Vet 1986, Wadleigh et al. 1994). The marine sulphate estimate in turn is used to estimate the sulphate contributions from anthropogenic sources. These estimates of sulphate contributions hinge on the assumption that the overwhelming majority of chloride in the stream is recently and directly derived from marine aerosols transported inland via atmospheric transport. If the chloride in the stream water has a significant secondary source of chloride such as geological materials, biological cycling, groundwater storage or soil retention, then the validity of chloride as a proxy for marine sulphate may be compromised.

The initiation of this study arises from the use of chloride in stream water to estimate marine sulphate in stream water, where accurate assessments of the sources of stream chloride are essential for accurate determinations of anthropogenic sources of acid deposition. In the assessment of sources of stream chloride, measured wet deposition only accounts for a portion of the chloride (Fig. 1.1) and the excess chloride is often assumed to be deposited by occult deposition. In contradiction to this assumption, recent studies have called into question the use of chloride as a conservative tracer suggesting secondary sources and sinks of chloride (Viers et al. 2001, Chen et al. 2002, Bastviken et al. 2007). At the root of this dilemma is the difficulty in distinguishing between atmospheric and terrestrial sources of chloride once they are integrated in stream water. In order to properly account for anthropogenic sources of acid deposition and assess the validity of the use of chloride as a conservative tracer ion, a new approach is needed that can distinguish and quantify sources of chloride in stream water.

1.4 Chlorine Stable Isotopes

The chlorine stable isotope composition of atmospheric deposition may be distinct from other sources of stream chloride which could provide a method to identify and potentially quantify sources of stream chloride (Fig. 1.4). Estimates of the isotopic composition of chloride sources in stream water can be constructed based on previous results from rainfall, geological sources and organic chlorinated molecules. However, the isotopic composition of occult deposition is by and large unknown, and because geological sources of chloride have variable isotopic compositions, the effects of geological and biological cycling on chlorine stable isotopes in solution can only be approximated. The limited scope of previous research of chlorine stable isotopes necessitates further investigation to quantify sources of stream chloride.

1.4.1 Stable Isotopes

The halogen element chlorine has an atomic mass of 35.453 g/mol (75.7% ^{35}Cl, 24.3% ^{37}Cl) (Shields et al.1961). The chloride ion is the dominant species in nature. Typical fractionation of stable isotopes involves a process that preferentially incorporates or excludes one of the stable isotopes. Chlorine stable isotopes are reported as δ^{37}Cl (‰), which represents the ratio (R) of ^{37}Cl to ^{35}Cl, defined by the equation:

$$\delta^{37}Cl = [R_{sample} - R_{standard} / R_{standard}] \times 1000$$

Refinements in the analytical precision of chlorine stable isotope measurements have facilitated investigations of specific problems and advancements in the understanding of fractionation mechanisms. Branches of research which use chlorine stable isotopes include investigations of geological cycling of chloride (Sharp et al. 2007, Bonifacie et al. 2008), hydrogeology (Desaulniers et al. 1986, Hendry et al. 2000, Sie and Frape 2002) and ore deposits (Eastoe and Guilbert 1992, Willimore et al 2002).

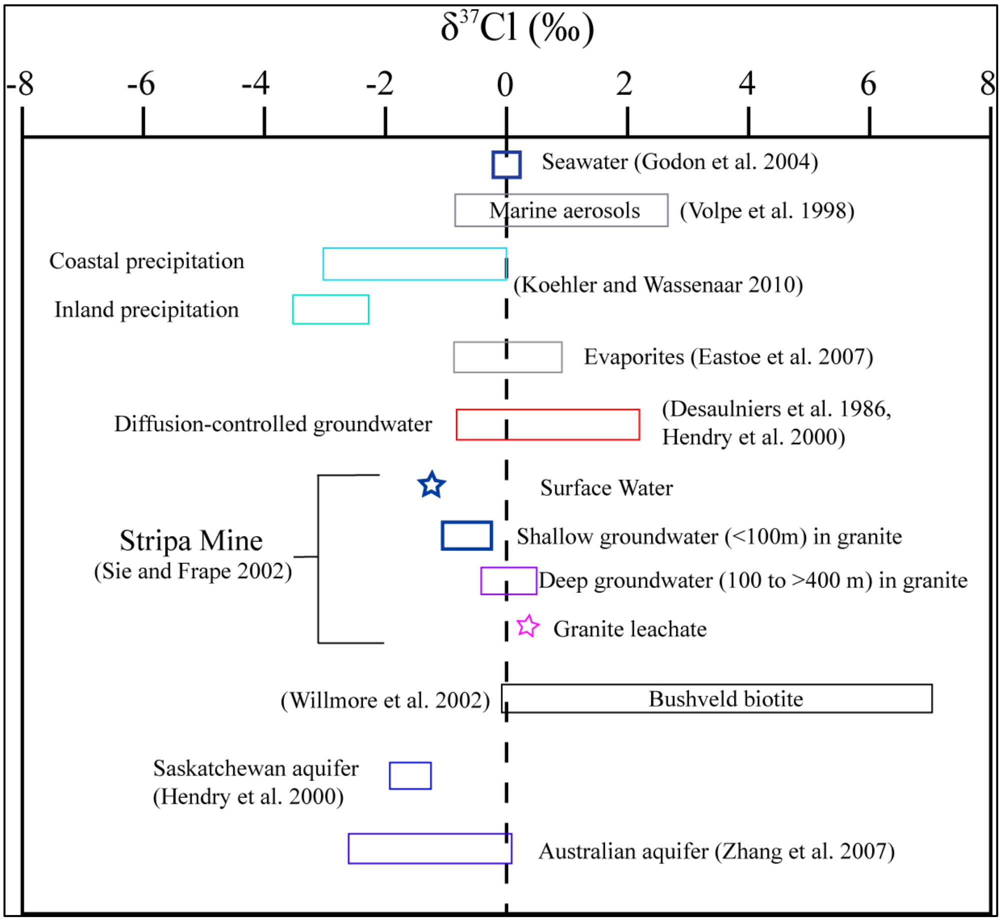


Figure 1.4: Range of chlorine stable isotopes values of references cited in text. Boxes represent ranges of δ^{37}Cl values; stars represent single measurement values.

1.4.2 History of Chlorine Stable Isotope Measurements

Urey (1947) provided the theoretical framework for chlorine stable isotope fractionation and calculated fractionation factors for hydrochloric acid and perchloric acid in equilibrium. Hoering and Parker (1961) examined the chlorine stable isotope composition of meteorites using a double-collector mass spectrometer and sample chloride isolated as HCl, but found no significant isotopic variation detectable with analytical precision ranging from ± 0.3 to 0.9 ‰. Kaufmann (1984) reported an analytical precision of ± 0.24 ‰ (1σ) in CH_3Cl using positive ion mass spectrometry and the improved precision facilitated the first observations of isotopic variations in natural materials. Implementing careful yield controls and optimizing the instrumentation of dual-inlet isotope ratio mass spectrometry (IRMS) resulted in routine precision of ± 0.09 ‰ or better on geological and aqueous samples (Long et al. 1993, Eggenkamp 1994). Wassenaar and Koehler (2004) augmented the input systems to continuous-flow IRMS resulting in a reduction of the quantity of chloride needed for analysis (0.2 μmol) while maintaining precision better than ± 0.08 ‰. Recently, the refinement of IRMS methods of chlorine stable isotope measurements have been developed to the degree where small variations of isotopic composition in low concentrations can be measured precisely.

1.4.3 Chlorine Stable Isotopes in Ocean Water

In chlorine stable isotope measurements the $\delta^{37}Cl$ of a sample is stated in reference to measurements of a standard isotopic ratio. The standard used for chlorine is standard mean ocean chloride (SMOC) and is set at a value of 0 ‰. In an investigation of 24 seawater samples from the Atlantic, Pacific and Indian Oceans at various depths, Godon et al. (2004) established the chlorine stable isotope composition in seawater is not variable within analytical precision. This permits the use of seawater chloride as a standard for isotopic measurements.

1.4.4 Fractionation Processes

Three processes are invoked to explain variations in chlorine stable isotopes; volatilization, ion filtration and diffusion. During the volatilization of HCl from marine aerosols by HNO_3 and H_2SO_4, the lighter ^{35}Cl is preferentially incorporated into HCl.

This has a twofold effect; the remaining aerosols are isotopically heavy and the light HCl is readily dissolved into precipitation resulting in isotopically light precipitation (Volpe and Spivack 1994, Koehler and Wassenaar 2010).

Under pressure gradients in clays with low permeability, fractionation is observed where ion filtration results in isotopically light chloride retained by the clay membrane and isotopically heavy chloride being released preferentially through the membrane (Campbell 1985). The factor controlling this is a difference in ion mobility of ^{35}Cl and ^{37}Cl (Phillips and Bentley 1987). The governing principle is described by Godon et al. (2004b) where the negatively charged clay surfaces repel the negative chloride, but ^{35}Cl is repelled more strongly than ^{37}Cl resulting in an increase of ^{37}Cl crossing the membrane. On the other hand, diffusive systems facilitate the mobility of the lighter isotopes (Eggenkamp and Coleman 2009). In diffusion controlled, clay-rich aquitards, the lighter ^{35}Cl is able to travel at a faster rate than the heavier ^{37}Cl isotope resulting in progressively isotopically light chloride migrating further from the source of the chloride (Desaulniers et al. 1986).

1.4.5 Chlorine Stable Isotopes in Atmospheric Deposition

Atmospheric chloride has two major natural sources. One is the ephemeral input from volcanic gases and the second is the mobilization of seawater into aerosols. Over time scales of millions of years, eruption and degassing of volcanoes has provided a mechanism of chloride transfer from the large mantle reservoir to the surface. Examination of the chlorine isotope composition of volcanic fumarole gases displays a large δ^{37}Cl range from -2 ‰ to 12 ‰ with ranges of values distinct for different sample locations (Eggenkamp and Schuiling 1995, Godon et al. 2004b, Sharp et al. 2010).

On shorter time scales, chloride cycling is dominated by atmospheric transport of marine aerosols. In marine aerosol samples collected near Bermuda and in the Pacific (Volpe and Spivack 1994, Volpe et al. 1998), the δ^{37}Cl of aerosol particles indicates an enrichment of heavy isotopes with decreasing size of particles. The increase in the proportion of heavy isotopes also corresponds with increasing chloride depletion as a result of volatilization. The mechanism proposed to explain the enrichment of heavy isotopes in small aerosols is the volatilization of isotopically light HCl, which is validated by volatilization experiments (Volpe and Spivack 1994, Eggenkamp 1994). An examination of δ^{37}Cl in archived precipitation samples from coastal (Bay D'Espoir, Newfoundland) and inland (Bonner Lake, Ontario) Canadian Air and Precipitation Monitoring Network (CAPMoN) sites provides insight to atmospheric chloride processes (Koehler and Wassenaar 2010). The coastal precipitation samples are isotopically light with an average δ^{37}Cl of -1.3 ‰ and a range of -3.1 ‰ to 0.0 ‰. Inland precipitation samples are even lighter with a mean δ^{37}Cl of -2.3 ‰ and a range of -3.5 ‰ to – 1.2 ‰. These values are interpreted to be the result of kinetically controlled acidification of marine aerosols related to the amounts of HNO_3 and H_2SO_4 in the atmosphere and support the theory of isotopically light HCl being volatilized from marine aerosols as a mechanism of fractionation.

1.4.6 Chlorine Stable Isotopes in Geological Materials

Chlorine stable isotope compositions in geological materials offer a wide scope of applications for geological investigations. A comprehensive summary of chlorine stable isotope compositions in geological materials was provided by Stewart and Spivack (2004). Summarized below are selected studies relevant to this project and developments in the literature since Stewart and Spivack (2004).

Halite and other evaporites are major sinks of chloride into geological material. As no isotopic variation can be detected in modern seawater, isotopic variation in evaporites would require a fractionation process to produce the effect. Evaporite precipitation experiments conducted by Eggenkamp (1995) show minor but detectable fractionation of chlorine stable isotopes in the chloride-bearing evaporites, NaCl, KCl and $MgCl_2 \cdot 6H_2O$. The physical fractionation experiments indicate that the isotopically heavy chloride will be incorporated into the solid phase preferentially, leaving the brine and subsequent precipitates progressively isotopically lighter. Rayleigh fractionation theory was invoked to explain the process, but corroboration in the form of highly depleted phases was not found. Experimental evidence was supported by analysis of evaporite cores that had higher δ^{37}Cl values (+0.24 ‰) with increasing proportion of halite and lower δ^{37}Cl values (-0.56 ‰) with increasing proportion of bischofite ($MgCl_2 \cdot 6H_2O$) and carnallite ($KMgCl_3 \cdot 6H_2O$). In a survey of δ^{37}Cl in Phanerazoic evaporites, Eastoe et al. (2007) conclude that δ^{37}Cl in bedded halite range from -0.9 ‰ to +0.9 ‰ with most of the values between -0.5 ‰ and +0.5 ‰. In summary, minor variations of chlorine stable isotopes in evaporites occurs, but in a general sense the composition is similar to seawater, at 0 ‰ (Fig. 1.4).

Much of the current research using chlorine stable isotopes to investigate geological material revolves around crustal cycling of chloride and evaluating whether chloride reservoirs at the surface are in a steady state exchange with the mantle reservoir (Bonifacie et al. 2005, Sharp et al. 2007, Bonifacie et al. 2008, Barnes et al. 2008). Values of δ^{37}Cl reported in these studies are typically negative with a range from – 8 ‰ to + 0.51 ‰, with most values clustering around – 1 ‰.

During investigations for suitable sites for long term nuclear waste storage in the Stripa mine, Sweden, observations of increasing chloride concentrations with depth in the granitic body were observed (Nordstrom et al. 1989). In an attempt to understand groundwater movement through the granite, Sie and Frape (2002) examined the chlorine stable isotope composition of groundwater at various depths (~100 m to > 400 m) and of one granite leachate (Fig. 1.4). Results of the Sie and Frape (2002) study display an increase in δ^{37}Cl values with depth; surface water (-1.32 ‰) and shallow ground water (-1.30 ‰ to -0.34 ‰), deep (> 400 m) mine water (-0.50 ‰ to +0.69 ‰) and granite leachate (+0.43 ‰) are explained as the mixing of isotopically light meteoric waters and isotopically heavy, fluid inclusion influenced groundwater (Fig. 1.1).

Chloride is a common ion in hydrothermal fluids. Investigations of numerous ore deposits by Eastoe and Guilbert (1992) include δ^{37}Cl values for biotite ranging from 0.0 to + 1.7 ‰. Willmore et al (2002) examined the anomalously chlorine rich Bushveld Complex using chlorine stable isotopes to characterize the mineralization model of the deposit type and found δ^{37}Cl values of 0 to + 7 ‰ (Fig. 1.4).

Debate still exists regarding the chlorine stable isotope composition of the mantle, but consensus appears to be building that it is either enriched in light isotopes or it is close to SMOC (Bonifacie et al. 2005, Sharp et al. 2007, Bonifacie et al. 2008, Barnes et al. 2008). Some reported results of the chlorine stable isotope values of geological materials have been called into question (Wei et al. 2008, Sharp and Barnes 2008) because of questionable analytical methods, but chlorine stable isotope compositions in rocks and minerals may range from - 4 to + 7 ‰ (Fig. 1.4).

1.4.7 Chlorine Stable Isotopes in Groundwater

Chlorine stable isotopes are a useful tool to identify sources of groundwater and to characterize the mechanisms of groundwater transport. In low permeability Quaternary glacial deposits of southwestern Ontario, chlorine stable isotopes were used to determine if increases in chloride concentrations with depth in the till are the result of upward diffusion from shallow bedrock (Desaulniers et al. 1986). Observations of increasing enrichment in light isotopes with increasing distance from the bedrock established the bedrock as the source of chloride enrichment and diffusion as a process that fractionates chlorine stable isotopes. Hendry et al. (2000) used ^{36}Cl and Br^{-} in conjunction with chlorine stable isotopes to define five end members mixing in a clay-rich aquitard. To explain an increase in chloride concentrations of the groundwater of the Great Artesian Basin, Australia, Zhang et al. (2007) used chlorine stable isotopes to identify mixing of low chloride concentration meteoric waters with higher chloride concentration shale pore waters. As with the Desaulniers et al. (1986) study, physical fractionation during diffusion is the process used to explain the isotopically light (-2.0 ‰) shale leachate and affected groundwaters of the Australian study.

1.4.8 Chlorine Stable Isotopes in Contaminants and Organic Molecules

Research investigating chlorine stable isotope composition in anthropogenic and organic substances has been used to track and evaluate the degradation of chlorinated compounds in groundwater (Sturchio et al. 2007, Hunkeler et al. 2009). While the isotopic composition of organic molecules is variable, mineralization of Cl^{-} following Rayleigh equation releases chloride ~ 8 ‰ more negative than the parent (Hunkeler et al. 2009). In fractionation theory estimates, Schauble et al. (2003) predicted that organic molecules should be enriched in heavy isotopes (+ 5.8 to + 8.3 ‰) compared to SMOC. The effects of these biological and physical fractionation processes during primary cycling of chloride remain untested, but they are potentially significant. Biological fractionation during vegetative growth leads to the preferential uptake of ^{37}Cl resulting in isotopically light residual chloride and during mineralization physical fractionation would release progressively heavier chloride. While biological cycling is typically considered to be minimal compared to the primary cycling, research indicates biological processes in ‘soil act as a sink or source of chloride that cannot be considered negligible in relation to the transport of chloride soil through soil’ (Öberg 2002). If biological cycling is significant, then fractionation processes that occur during formation and mineralization of organic matter may be significant as well. While these processes may influence the isotopic composition of chloride in stream water, identifying biological effects on the chloride cycle is not within the scope of this project but merits detailed investigation.

1.5 Summary

Questions regarding the conservative nature and the use of chloride as a tracer ion arise from examinations of secondary cycling of chloride. The questions of which cycles contribute to stream chloride budgets, how much do they contribute and on what time scales are they relevant, remain partly unresolved because of an inability to quantify the inputs and outputs of the cycles. Refinements in analytical methods used to detect chlorine stable isotope variations have opened the doors to investigations of global chloride cycling, groundwater movement and fractionation processes. Chlorine stable isotopes thus offer an opportunity to characterize the inputs and outputs of chloride cycling, which may be useful in quantifying the fluxes of the primary and secondary cycling.

Chapter 2 : Physical Setting

Identification of sources of chloride in stream water requires sampling of a variety of possible sources of chloride, but it also requires a thorough knowledge of what and where the potential sources may be. This chapter provides a summary of information relevant to potential sources of chloride for the geographic region of the catchments investigated in this study.

2.1 Atmospheric Deposition

Atmospheric deposition patterns in Nova Scotia are influenced by Atlantic Ocean weather systems and systems that pass over North America. The marine influence on precipitation is dominant at the coast and decreases exponentially away from the coast (Fig. 1.3) (Underwood et al. 1988). Occult deposition (fog and aerosols) plays a large role in atmospheric deposition of near-coastal environments (Soulsby 1995, Yin and Arp 1994, Farrell 1995), but the role of occult deposition on inland catchments is unclear. Yanni et al. (2000) proposed the streams in this study, which are ~ 60 km from the ocean, could have up to 60% of the stream chloride budget derived from fog and dry deposition. However, this estimation was based on samples collected in near-coastal environments and fog deposition models. Doubtless, Nova Scotia atmospheric deposition is heavily influenced by marine systems, which in turn influence stream biogeochemistry. Yet direct quantification of occult deposition is lacking for these catchments near Kejimkujik National Park (Fig. 1.2).

2.2 Catchments

Pine Marten Stream and Moose Pit Brook catchments are located in southwestern Nova Scotia approximately 60 km from the Atlantic coast line. To the south, west and east the terrain gentle slopes from the < 200 m elevation of the catchments to the shoreline. To the north of the catchment lies a topographic high of the North Mountain before the Bay of Fundy. The catchments of this study are in a sparsely populated region of Nova Scotia. While they are within 10 km of a secondary highway, both of these catchments lack heavily travelled or paved roads. The roads that exist are KNP access roads in the case of Pine Marten Stream catchment and predominantly temporary, seasonal, logging roads in Moose Pit Brook which in both cases are not treated with road salts during the winter months. Both catchments lack residential housing and infrastructure other than roads. It is assumed in both catchments that the only direct human disturbances are related to deforestation.

2.2.1 Pine Marten Stream Catchment

Pine Marten Stream Catchment is 112 ha in area and is located on the northeastern boundary of Kejimkujik National Park (Figs. 1.2 and 2.1). The upper, headwater portion of the catchment is bound by drumlins comprising silty till and the lower portion is poorly drained with little relief. In a transition area from the upper to the lower portions of the catchment, the stream passes through a culvert underneath a small gravel road. In the lower portion of the catchment, the till is thin (less than 1 m) and a fen has formed as shown by the low relief area in Fig. 2.2. Stream water is sampled for the EC monitoring program from two locations; upstream of the culvert (upper Pine Marten) and as the stream exits the fen (lower Pine Marten) (Fig. 2.1). Stream flow was measured at the lower Pine Marten sampling site from 1990 to 1995 and the flow has been modeled by Dr. Paul Arp at the University of New Brunswick using ForHyMod from 1995 to 2004.

The forest cover of Pine Marten catchment comprises mostly spruce, fir, pine, maple and birch, which is typical for the Park area as a whole (Yanni 1995). While a segment of the catchment (58%) is within the park boundary, there are human disturbances within the catchment. The Park maintenance compound is located partly within the north western section of the watershed. According to the Nova Scotia Department of Natural Resources 2002 forest inventory (NSDNR 2010), approximately 26.5% of the catchment area has had trees harvested before 2002 and the rest of the forest has been intact for 50 years or longer. The CAPMoN site and a segment of the access road are also located with the catchment boundary (Fig. 2.1).

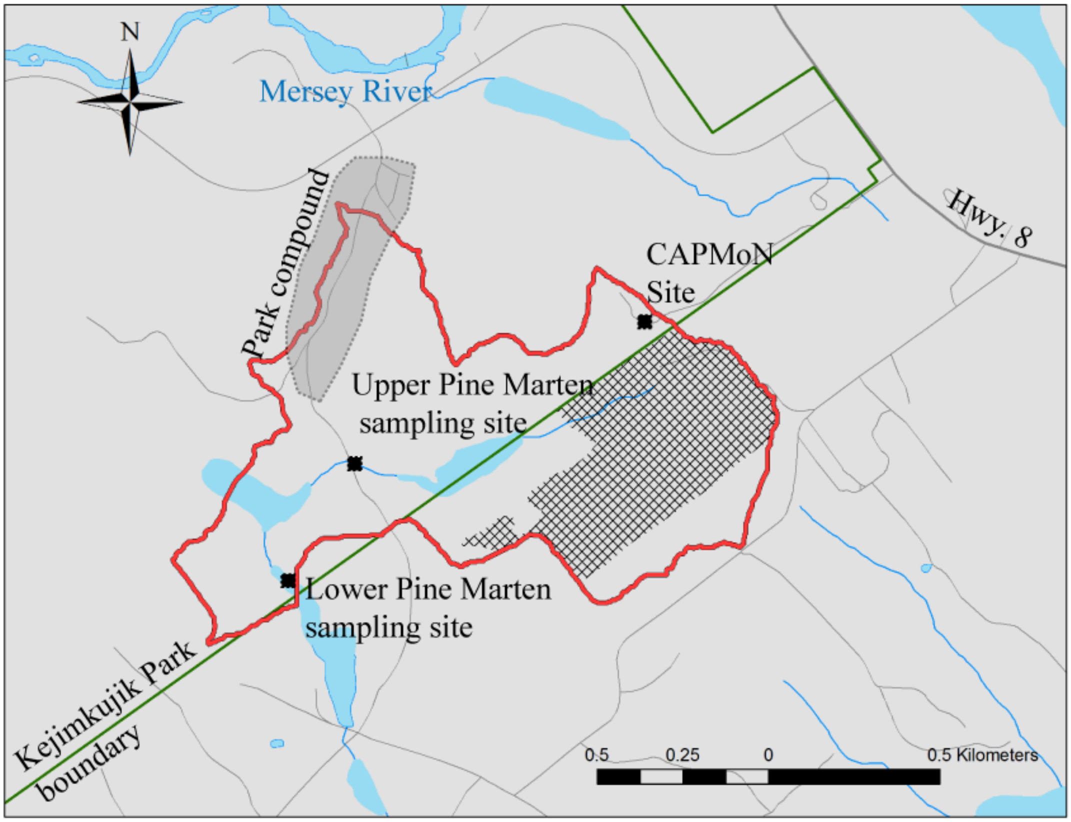


Figure 2.1: Pine Marten Stream catchment (red outline) was delineated from a LiDAR derived DEM using ArcHydro. Cross hatched area represents disturbed forest area. Grey lines represent the road network.

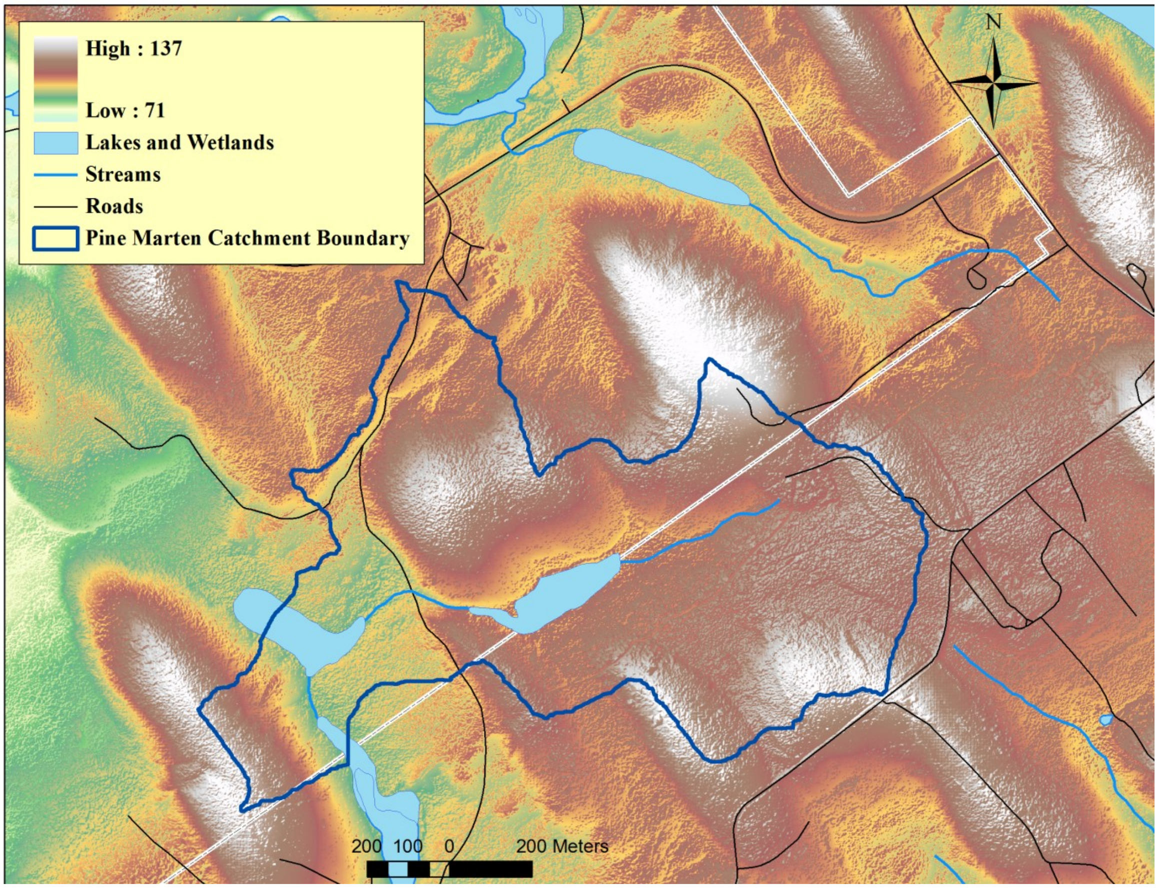


Figure 2.2: Hillshade display of digital elevation model of Pine Marten Stream catchment produced from LiDAR data courtesy of Dr. Chris Hopkinson of the College of Geographical Sciences, Bridgetown, NS.

2.2.2 Moose Pit Brook Catchment

The Moose Pit Brook catchment is outside the Park boundary and is about 11 km northeast of Pine Marten Stream catchment (Fig. 1.2). It covers 1738 ha and where it drains into Tupper Lake, stream flow has been monitored by EC since 1983 (Fig. 2.3). The higher elevation portions of the catchment are stony drumlins and thin till (likely less than 5 m thick) with near to surface bedrock (Figs. 2.4 and 2.9). The soils and tills in Moose Pit are typically sandy and well drained with the exception of low-lying bog areas (represented as lakes and wetlands in Fig. 2.4).

The forest cover of Moose Pit Brook catchment is similar to Pine Marten Stream catchment (spruce, fir, pine, maple, birch; Yanni 1995), but the age distribution of the forest is more varied in Moose Pit as a result of logging activities. The NSDNR forest inventory indicates approximately 31% of the catchment has been disturbed by forestry activities (clearcutting, plantation or treatment; Fig. 2.3). Field observations indicate more forest harvesting has occurred since 2002 and 31% is likely an underestimate. Therefore the NPP catchment is not constant, but is likely accumulating biomass as forest succession occurs, which is also the case for Pine Marten Stream catchment.

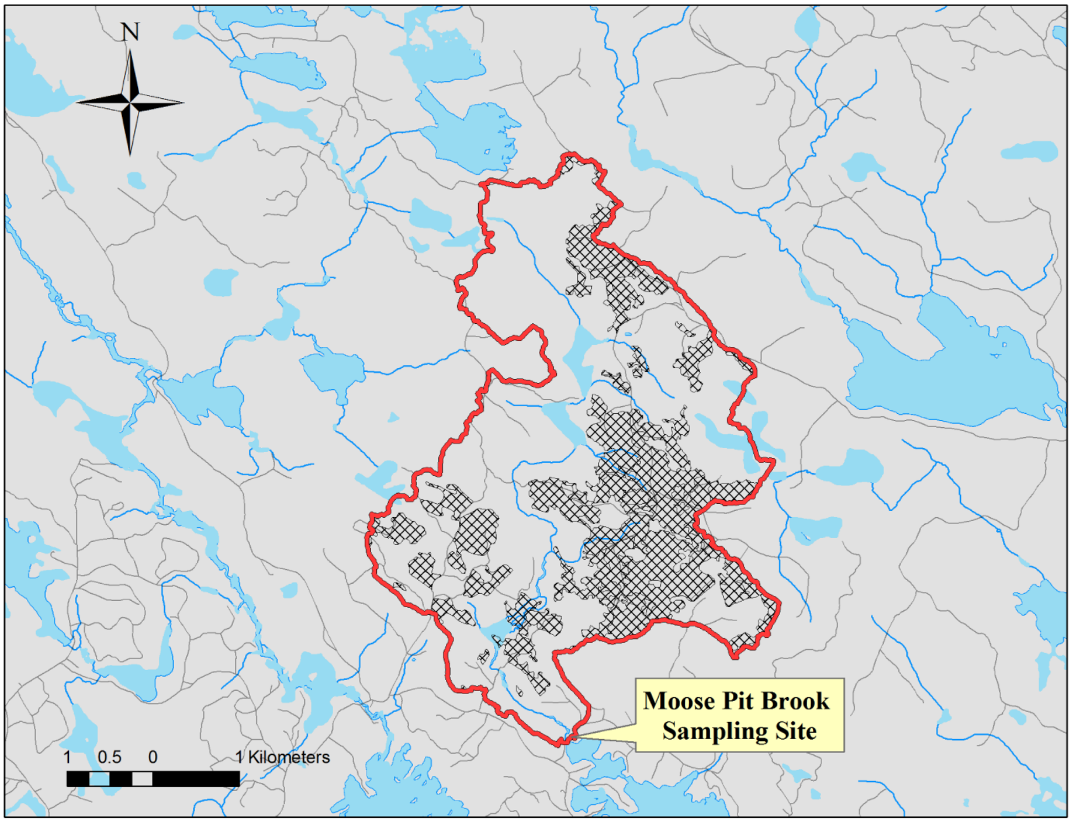


Figure 2.3: Moose Pit Brook catchment (red boundary) with area of disturbed forest (cross hatching). Grey lines represent road network.

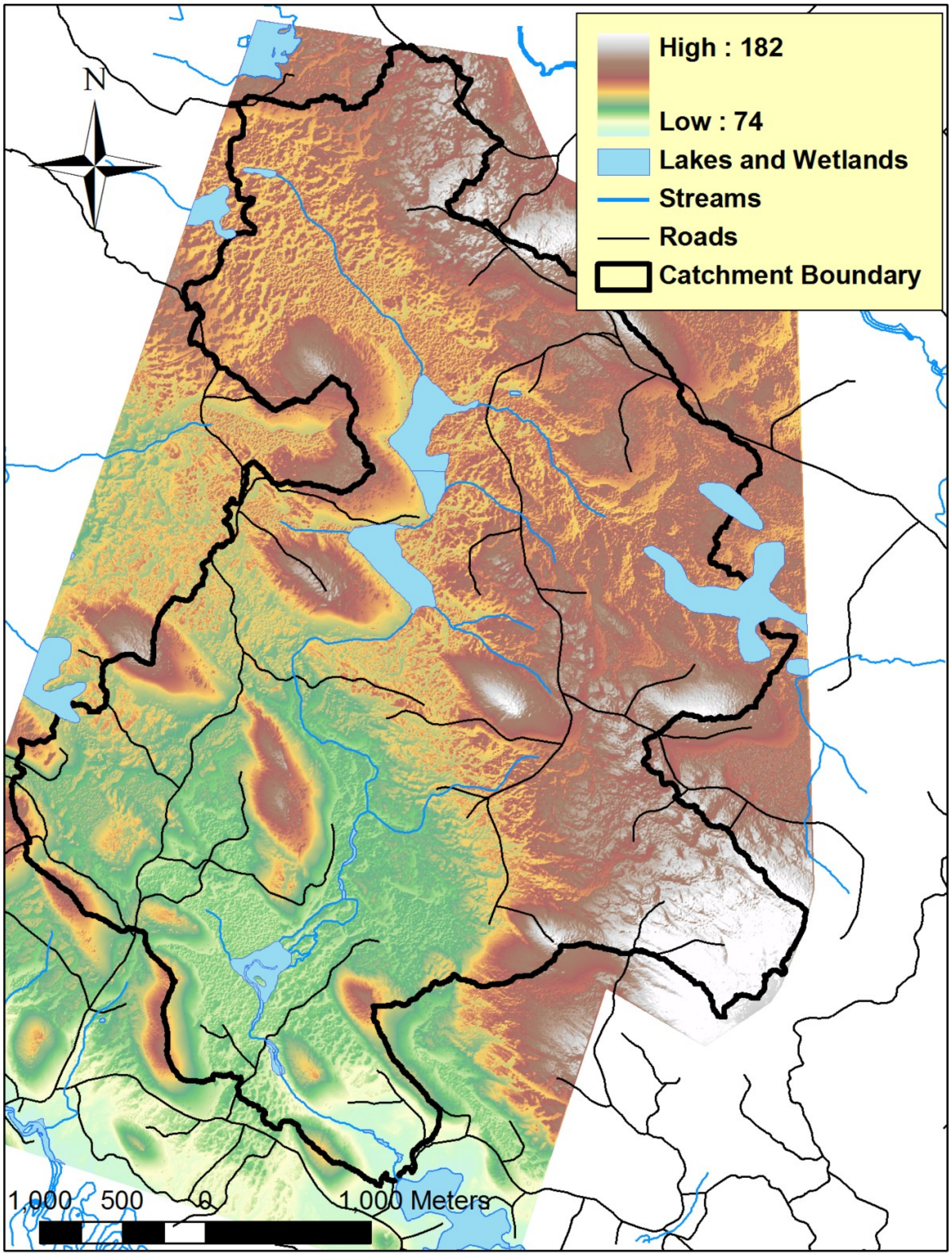


Figure 2.4: Hillshade display of digital elevation model of Moose Pit Brook catchment from LiDAR data, courtesy of Dr. Chris Hopkinson.

2.3 Physical Features

The two catchments of this study are 11 km apart from one another and can be described by regional characteristics. However, by examining differences between the catchments, subtle variations in physical features may provide insight into factors that may impact chloride outputs.

2.3.1 Bedrock Geology

Nova Scotia geology is comprised of five geological provinces; the Neoproterozoic Avalon terrane in the north, the Cambrian-Ordovician Meguma terrane in the south, the Devonian South Mountain Batholith in the south, Mesozoic basalts and sediments in the west and Carboniferous basins in central and northern Nova Scotia. The characterization of Nova Scotian geology (Fig. 2.5) for groundwater mapping (Kennedy and Drage 2008) is an appropriate simplification for the purpose of this study because the classifications provide a framework for controls on groundwater movement and illustrates potential sources of glacial sediment.

The bedrock geology of southern Nova Scotia is dominated by two groupings; Meguma terrane metasedimentary rocks and South Mountain Batholith granites. Meguma rocks are composed of metamorphosed fine grained sandstones (greywacke/quartzite) to mudstones (slate) that were deposited during the Cambrian to Ordovician on a continental passive margin (Schenk 1997). Variations in grain size and composition have been used to subdivide the Meguma rocks into Groups and Formations. These rocks were metamorphosed to greenschist facies and deformed into northeast to southwest trending folds during the Neoacadian Orogeny (Van Staal et al. 2007, White et al. 2007). The South Mountain Batholith is a large granitoid body that intruded the Meguma terrane ca 370 Ma (Clarke and Halliday 1980, Reynolds et al. 1981). Ham et al. (1990) used variations in texture, grain size and modal percentages of minerals to classify eight different lithological types within the batholith. Evidence for contact metamorphism includes andalusite, biotite and cordierite hornfels found within 2 km of the contact between the country rock and the intrusion (Jamieson et al. 2006).

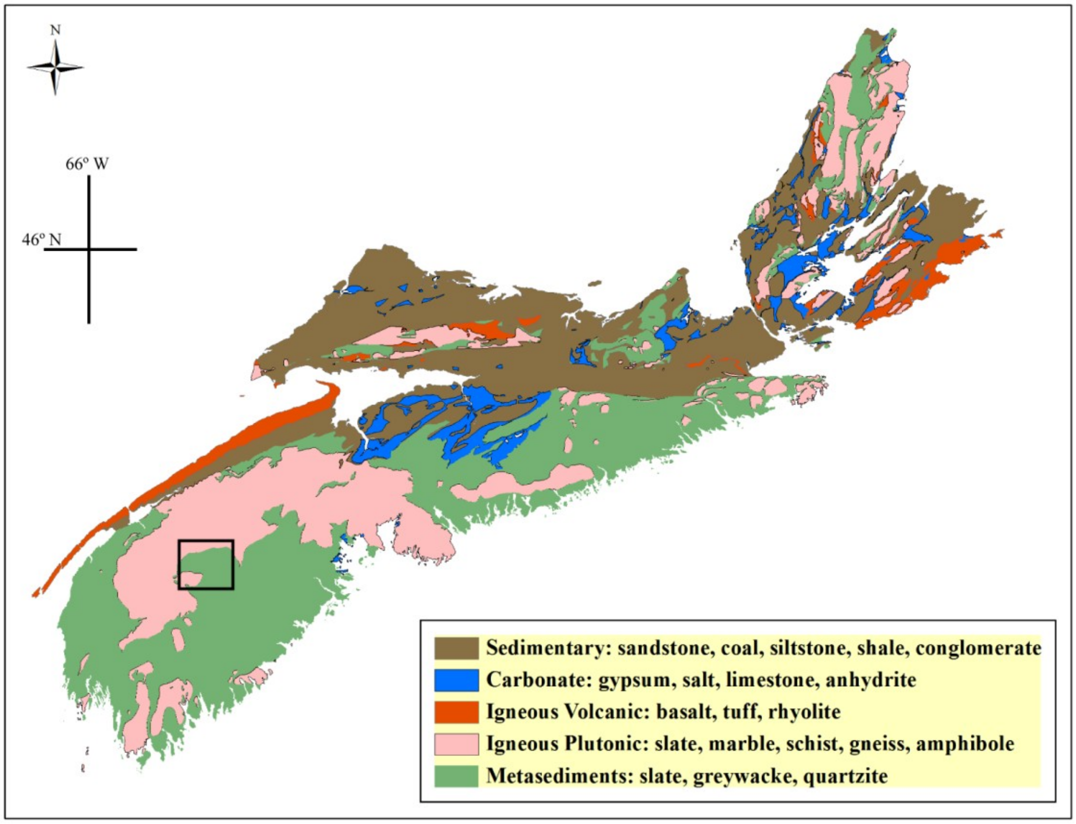


Figure 2.5: Generalized geology of Nova Scotia after hydrogeological map of Kennedy and Drage (2008). Black rectangle represents the study area for this project.

The larger catchment, Moose Pit Brook, is underlain by more diverse and more commonly exposed bedrock than Pine Marten Stream catchment. The country rock of Moose Pit Brook catchment is a composite of Meguma terrane rocks. The oldest Meguma rock in Moose Pit Brook is the Government Point formation of the Goldenville Group (Fig. 2.6). It is typically composed of grey, thinly to thickly bedded metasandstone, rhythmically laminated green to greyish-green metasiltstone, and black slate (White 2010 in press) and is found in the southernmost segment of the catchment (Fig. 2.6). Stratigraphically overlying the Government Point rocks is the Moshers Island formation which is a thin unit of well laminated metasiltstone to slate, interlayered with minor, fine-grained, 1 to 10 cm-thick metasandstone beds. This unit is distinguished from the Government Point formation by the steel blue manganiferous nodules and laminations.

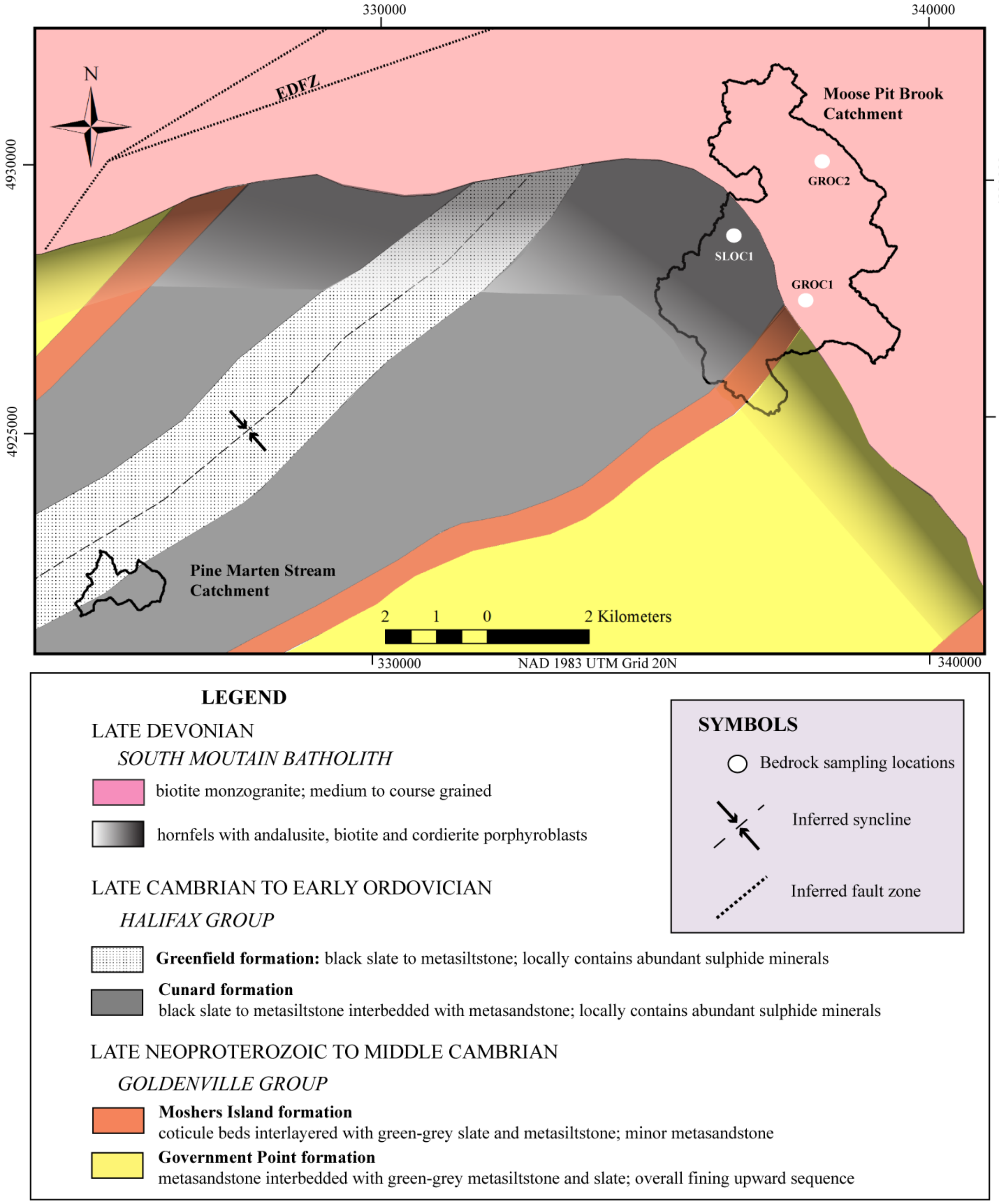


Figure 2.6: Bedrock geology of the study area from White (2007) and White 2010 personal communication. EDFZ – East Dalhousie Fault Zone from Horne et al. (1992).

Overlying the Moshers Island formation is the lowermost formation of the Halifax Group, the black to rust-brown slate with thin beds and lenses of minor black metasiltstone named the Cunard formation. Within the catchment, the best exposures of outcrop are of the hornfelsic Cunard formation in the vicinity of site SLOC1 of Fig. 2.6. The weathered surfaces appear rusty and in thin section opaques occupy up to 5% of the mineralogy (Fig. 2.7). Large quartz veins (up to 20 cm in width) are found in outcrop and road rubble.

The fissile Cunard formation typically displays axial planar cleavage, however, in the contact aureole the cleavage is mostly annealed with only minor remnants observed in thin section. The hornfels is composed of idioblastic chiastolite (up to 2 mm), biotite and cordierite with granoblastic quartz and minor feldspar (Fig. 2.7e and f). The contact metamorphism of the Cunard formation has resulted in more indurated bedrock producing coarse grained tills and soils and perhaps contributing to the higher topography near the contact (Figs. 2.4 and 2.6).

Bisecting the catchment in a northwest-southeast trend is a contact between the Meguma rocks and South Mountain Batholith biotite monzogranite. The biotite monzogranite is medium to coarse grained with localized concentrations of apatite up to 0.5 mm in length (Fig. 2.7a-d). Both field and petrographic observations indicate shallow surface weathering effects. Approximately 3 km northwest of the catchment is the inferred trace of the East Kemptville – East Dalhousie Fault Zone (Horne et al. 1992) (Fig. 2.6). Field and thin section observations did not yield any evidence of major deformation in the biotite monzogranite, but jointing was observed in numerous, small outcrop exposures.

The smaller, Pine Marten Stream catchment is underlain by Halifax Group rocks and includes the inferred transition from the Cunard formation to the overlying Feltzen formation. The Fetzen formation is composed of light grey to blue-grey slate, rhythmically interlayered with laminated to thinly bedded, fine-grained metasandstone. Bedrock exposure within Pine Marten Stream catchment is minimal and the only observation of bedrock was at the bottom of a soil sampling pit. From the small (1 m^2) outcrop observed, the fissile black slate appeared to fit the description of the Feltzen formation (White 2010 in press).

GROC 1: Biotite Monzogranite

Medium grained biotite monzogranite. Minor apatite. Biotite with chlorite alteration. Feldspar with clay alteration products.

GROC 2: Biotite Monzogranite

Medium to coarse grained biotite monzogranite. Apatite up to 1 %. Biotite with chlorite alteration.

SLOC 1: Andalusite, Biotite Hornfels

Fine grained, polymineral matrix (qtz>fdsp>bt>musc)

And. (up to 2mm), bt. (1mm), ± cord. porphyroblasts.

Figure 2.7: Field and petrographic photos (cross polarized light) of bedrock samples in Moose Pit Brook catchment. Q- quartz, Bi- biotite, Pl- plagioclase, Kp- potassium feldspar, Ap- apatite, And- andalusite.

Even though both catchments are in the same region, the variability of the composition and grain size of bedrock and the proximity to major structures of Moose Pit Brook catchment provide a distinct geological setting to the fine grained composition and lack of deformation in the bedrock of Pine Marten Stream catchment. Furthermore, the fine grained metasediment in Pine Marten Stream is unlikely to have total chloride contents higher than 100 ppm, whereas the biotite monzogranite in Moose Pit Brook is more likely to have total chlorine concentrations higher than 200 ppm (Johns and Huang 1967). The difference in the underlying geological units is likely to have a strong influence on the composition and texture of glacial sediments and the hydrology of the catchments. Therefore the differences in the geology of the two catchments may have a significant influence on the chloride fluxes of the catchment streams, if stream chloride has a geological source.

2.3.2 Glacial Deposits

During the late Cenozoic, the fluvial landscape of Nova Scotia was re-shaped by ice flow dynamics leaving behind a post-glacial terrain dominated by glacial deposits. The texture and composition of the glacial deposits is in part controlled by the bedrock underlying the ice flow path. Erosion and transport of sediments by glaciers can result in deposits with highly variable composition and a stratigraphy that reflects changing ice flow patterns. Stea et al. (1998) described dynamic ice centers that governed flow trajectories across Nova Scotia throughout the last glacial phase (Fig. 2.8). The first phase of flow documented with sufficient evidence in Nova Scotia, the Caledonia Phase ca 75-40 ka, was sourced by Appalachian ice and resulted in a southeast ice flow which passed over metamorphic terranes of eastern North America before reaching Nova Scotia (Fig. 2.8a). The deposits of this phase are found in the core of drumlins and are referred to as Hartlen Till in the central mainland of Nova Scotia. During the subsequent glaciation, evidence for the early Escuminac Phase (22-18 ka) suggests an in ice center over Prince Edward Island resulted in southwestern sediment transport (Fig. 2.8b). The glacial deposits of this phase compose the middle to upper stratigraphy of drumlins and are regionally referred to as Lawrencetown Till. As the ice sheets began to retreat (Scotian Phase 18-15 ka) and experience small advances, local ice centers governed ice dynamics

(Fig. 2.8c). The resulting glacial deposits are represented commonly by the uppermost till which is dominated by clasts of local bedrock and referred to as Beaver River Till.

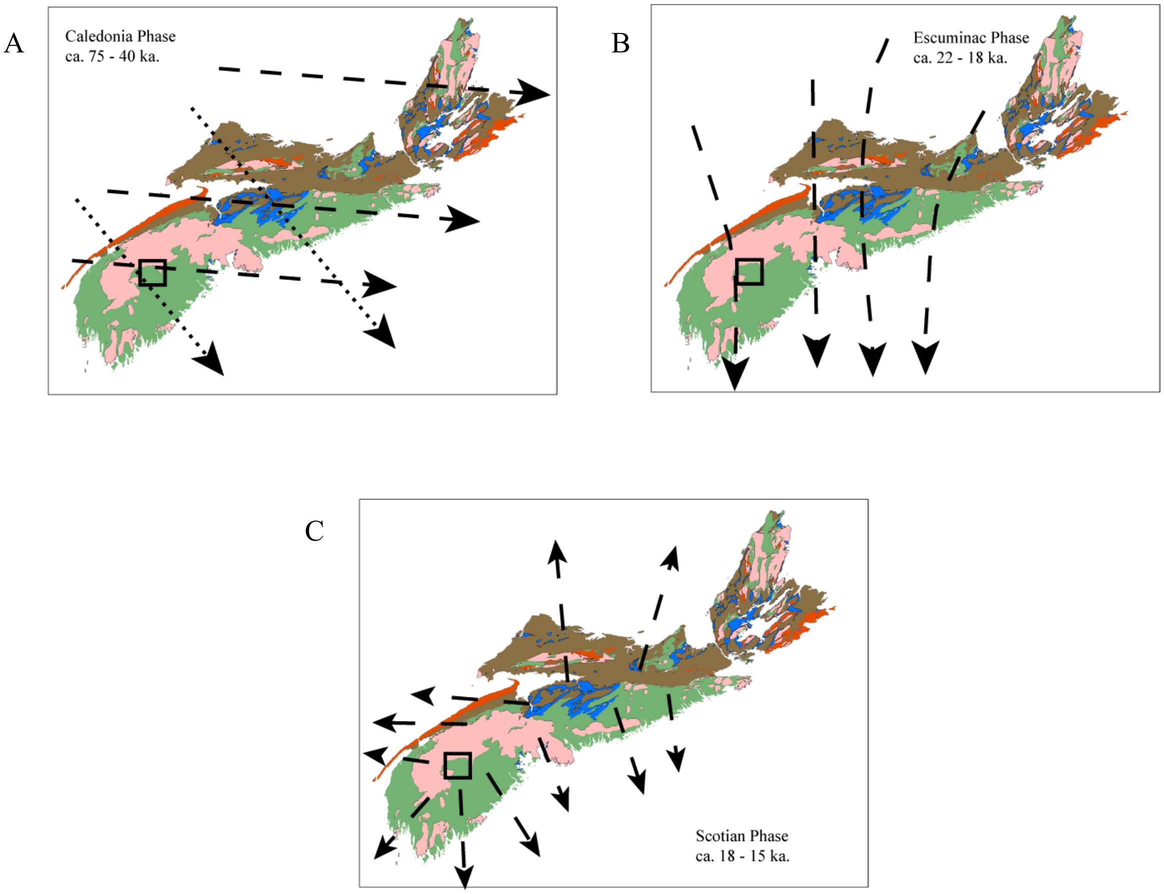


Figure 2.8: Depiction of the different phases of glacial flow during the last glaciation (after Stea et al.1998). Geological units correspond to the legend in Figure 2.5. Blue lithologies represent Carboniferous basins which host evaporite deposits. Black squares represent study area.

The stratigraphy of glacial deposits in the study area is therefore defined by the composition of clasts and can be observed in cross sections of drumlins. The core of many drumlins is composed of the older, Hartlen Till, covered by Lawrencetown Till and capped by locally derived Beaver River Till. Stea and Brown (1989) examined four groupings of drumlin fields in Nova Scotia and infer the direction of ice flow which deposited the drumlins based on axes orientations and striations. Regional scale mapping of glacial deposits (Finck and Stea 1995) identified variations in glacial deposits and distinguished between different tills based on grain size and composition.

The surficial materials of the field area for this study could generally be described as thin till cover dominated by clasts of local bedrock between thick drumlinized till with variable compositions. The drumlins in the field area represent the eastern edge of the Lunenburg drumlin field. Field observations indicate the upper portions of the drumlins are influenced by the composition of local bedrock lithologies. For instance, the drumlins in Moose Pit Brook catchment have been mapped as stony till drumlins and this reflects the sandy texture and clasts dominated by biotite monzogranite and hornfels. The drumlins in Pine Marten Stream catchment are mapped as silty drumlins and this is a reflection of the high clay content and high proportion of slate clasts.

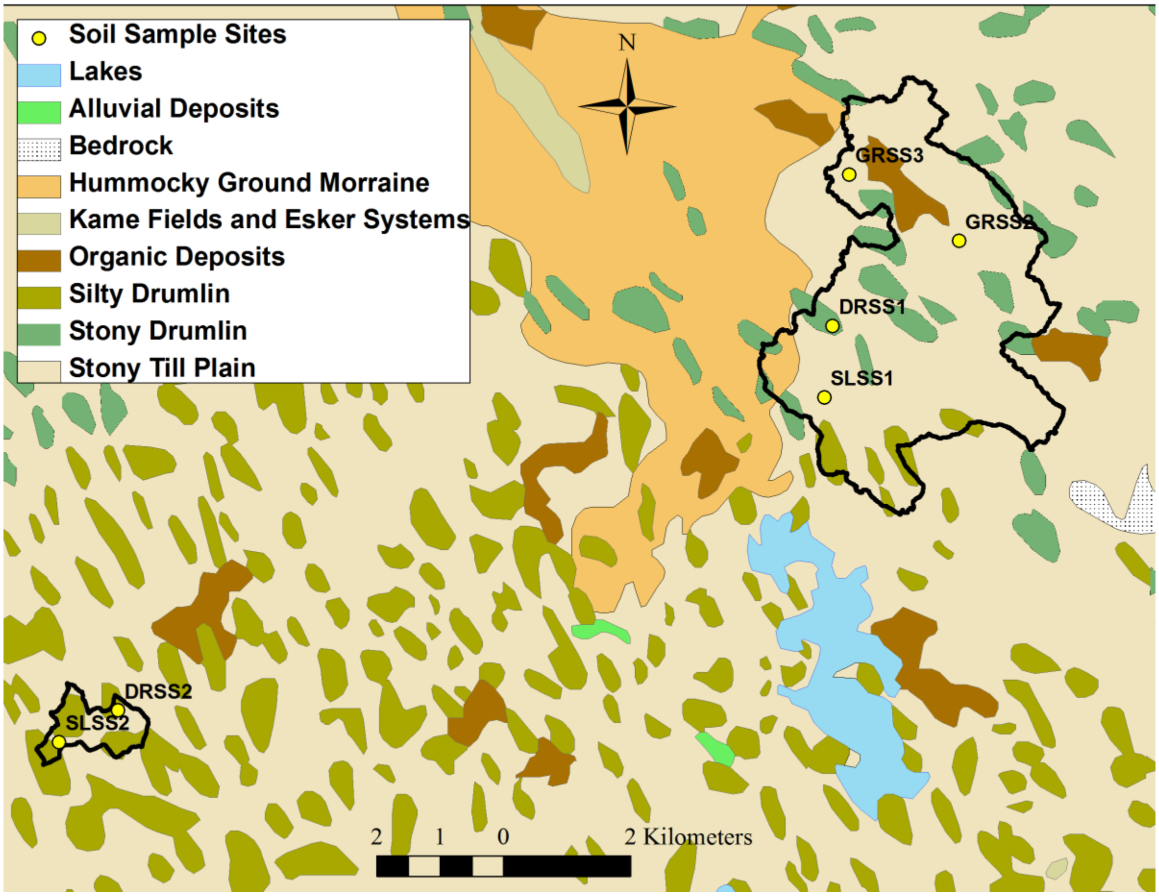


Figure 2.9: Surficial deposit types of the study area with locations of soil pits for sampling in this study. After Stea et al. 2006.

In Moose Pit Brook, the till is a sandy diamicton nearly exclusively with clasts of bedrock in the surrounding region up to a distance of a few kilometers. Specifically, the area underlain by Cunard rocks is sandy loam reflecting the coarse grained and indurated properties of the hornfels. In the Pine Marten Stream catchment, the till is thin (<50 cm), clay rich and dominated by slate clasts from the Cunard and Feltzen formations.

2.3.3 Soils

Soil characteristics are reflective of the parent material which is controlled by the underlying bedrock and overlying glacial deposits. Although some of the soils appear to be derived from bedrock regolith, despite the low relief and relatively wet climate, the majority of the soils are immature and poorly developed as a result of their ca. 15 ka age. A regional soil survey (MacDougall et al. 1969) indicates the catchments of this study are generally composed two soil types, with Moose Pit in the Gibraltar Series and Pine Marten in the Bridgewater Series. The Gibraltar Series is characterized by sandy loam soils and high permeability with many granite pebbles and cobbles. Field observations were consistent with the description of the Gibraltar Series. The Bridgewater Series is heavily influenced by steep sloped drumlins with shaly or sandy loam parent material and thin soils between the drumlins. In Pine Marten catchment the soils and tills are sandy clay loams with low permeability. Observations of planar oxidized zones within the C horizon indicated localized groundwater movement through the silt and clay rich glacial deposits. Soil characteristics, such as texture, composition and thickness, influence the hydrology and chemistry of the catchments.

2.3.4 Hydrology

Mechanisms of water transport influence the character of stream chemistry. These transport mechanisms are controlled by ground cover, soil porosity/hydraulic conductivity and slope. The physical characteristics that control transport of atmospheric deposition to stream water influence the duration of soil/rock and water interactions which have a major influence on stream water chemistry.

At the provincial scale, groundwater flow is characterized by shallow groundwater movement (in the upper 150 m) and generally controlled by the catchment boundaries (Kennedy et al. 2010). In Kejimkujik National Park, Ambler (1983) used a water balance method to estimate that less than 5% of precipitation is transported to groundwater storage. However, catchment specific examinations of groundwater movement suggest nearly one quarter of the stream flow could be water other than throughflow. An estimate of baseflow using gauged (Moose Pit Brook) and modeled (Pine Marten Stream) daily flow values and a Web based GIS Hydrograph Analysis Tool (Lim et al. 2005) with groundwater movement specified as 'Perennial stream with hard rock aquifer' produces Base Flow Index (BFI) values of 0.223 for Moose Pit Brook and 0.209 for Pine Marten Stream. The BFI values indicate the proportion of runoff that can be attributed to baseflow. Flow data and stream chloride concentrations have been used to estimate catchment mean transit times of 179 days for Pine Marten Stream and 223 days for Moose Pit Brook (Godsey et al. 2010). Discerning the influence of groundwater on stream chemistry is required to evaluate non-atmospheric sources of chloride and other ions, but groundwater is not included in the sampling design of this study and deserves further investigation. The baseflow contributions and transit time distributions derived from catchment scale data indicate a larger proportion of stream water has been in contact with tills and bedrock than the regional estimate of Ambler (1983).

In general, the flow of the streams in this study are similarly controlled by throughflow and interflow with contributions from baseflow. Yet, there are minor differences between the watersheds in baseflow and mean transit times.

2.4 Summary

The two catchments of this study share many similar general physical characteristics, but an examination of the differences may be useful for explanations of potential sources of chloride. The main difference between the catchments is the variation of bedrock, which in turn influences a difference in glacial deposits and soils, which cause differences in the hydrology of the catchments. The larger Moose Pit Brook catchment is underlain by coarse grained igneous rocks and fine to medium grained metasedimentary rocks with a major igneous contact bisecting the catchment. The glacial deposits and soils in part reflect the underlying bedrock and are well drained. Water transport in the catchment has a longer transit time and more baseflow than Pine Marten

Stream catchment. The smaller Pine Marten Stream catchment is underlain by very fine grained, fissile black slate. The glacial deposits and soils are silt and clay rich which limits permeability. The general lack of permeability is reflected in shorter resident time and lower baseflow.

Chapter 3 : Methods

This chapter summarizes the collection, preparation and analysis of samples collected for this study. All fog water, soil and bedrock samples were collected by the author, while some rainfall samples and most stream water samples were collected by an EC field technician, Deborah Veinot. All ionic analyses were shipped to the Atlantic Laboratory for Environmental Testing (ALET) and total chloride analyses of bedrock and soils were sent to SGS laboratory in Lakefield, ON. The author learned and applied methods of chlorine stable isotope measurement including sample preparation at Cosmogenic Nuclide Exposure Dating Facility (CNEF) at Dalhousie University and laboratory analysis using Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) at the National Water Research Institute in Saskatoon, SK. Detailed accounts of methods are provided for procedures the author played a major role in designing or implimenting

3.1 Field Methods

In order to identify and quantify sources of chloride in stream water, samples were collected between June and October, 2009. Unless otherwise stated, sample bottles used were certified clean, 250 mL high density poly ethylene (HDPE) provided by ALET. Deionized (DI) water used for rinsing and dilution in this study is re-circulated filtered reverse osmosis water deionized though single or double mixed bed resins used for cosmogenic ^{36}Cl exposure dating provided by the CNEF.

3.1.1 Atmospheric Deposition

A total of twelve fog water samples were collected between June 20 and August 3 on a per event basis to characterize chloride input to streams from marine advection fog using a passive fog collector design (Fig. 3.1). Sample volumes range from 40 mL to 250 mL.

The site used for fog water collection is in a blueberry field on a drumlin located less than 15 km from each of the two study watersheds (Fig. 1.2). The sampling location has typical physiography and elevation for the region, but the field on top of the hill is clear of trees allowing fog to be intercepted without direct interference from the forest canopy. The blueberry fields hosting the fog collector have not been sprayed with pesticides (Randy Naugler, personal communication 2009).

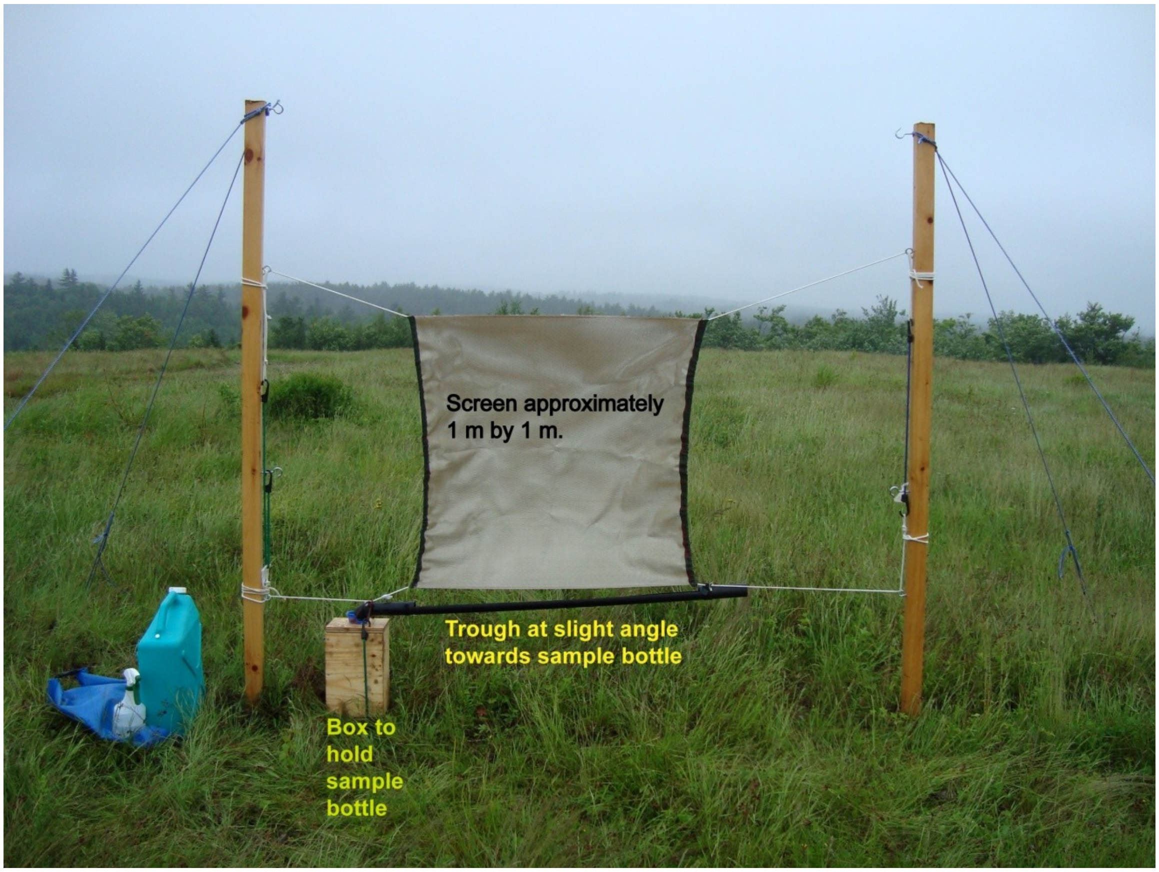


Figure 3.1: Annotated photo of fog interceptor without tarp.

The passive fog collector designed and constructed for this project intercepts fog on a screen and collects the accumulation in a trough directed to a sampling bottle following suggestions of Dr. Steve Beauchamp of EC (personal communication 2009). The fog interception screen is composed of an open weave nylon fabric with 1 to 2 mm gaps between the 0.5 mm thread. The screen is double layered to increase surface area for fog impaction. The layers are in close contact with one another to facilitate increased drip frequency. To collect fog water, the screen is suspended between two posts at an elevation of 30 to 50 cm above the ground. Underneath the screen a polyvinyl chloride (PVC) pipe, with 1 m section of it cut in half lengthwise to create a trough, is suspended beneath the screen to collect the dripping fog water. At the end of the pipe, an elbow joint with a hose connector that fits snuggly in the sample bottle is attached.

The intent of the fog collector was to sample atmospheric deposition that would not be collected by a rainfall collector. In order to prevent sampling of rainfall, a tarp was set up over-top of the screen during weather events that had rain mixed with fog. The tarp was suspended approximately 50 cm above the screen and did not prevent wind-blown fog from impacting the screen.

The passive design of the fog collector requires specific weather conditions to collect enough fog water for a sample to be analyzed (minimum 50 ml). A qualitative assessment of fog can be characterized by the distance of visibility during the event (Gates 1973) and it was observed that visibility less than 200 m was required for adequate volume collection. Other factors that contribute to the effectiveness of the apparatus were the speed of the wind and the duration of the fog event. Conditions which yielded a sample > 50 mL include visibility less than 200 m, wind speed greater than 10 km/hr and lasting three hours or more. A decrease in visibility, increase in wind speed and duration improved the yield of samples.

The fog collector was dismantled during clear conditions and erected when weather conditions indicated an inland fog event may occur. The screen was set up facing the prevailing wind to increase impaction. The screen and trough were rinsed with deionized water sprayed as a fine mist or poured. Following the rinse, more deionized water was sprayed on to the screen, passed over the PVC pipe and collected as a process blank to establish if the screen rinse was adequate or the materials used contribute to chloride concentrations in the analysis. The excess deionized water was shaken off and a new bottle put under the trough to collect the fog water. Once a sample was collected, the screen and trough were rinsed thoroughly before being dismantled. Between each sampling event, the screen was dried inside and stored in a waterproof container.

There may be an unquantified sampling error in all the ionic concentration values of samples collected using the fog collector resulting in an underestimation of concentration. The screen rinse water was not completely removed from the screen before sampling began and up to 100 mL may have remained on the screen following rinsing.

A total of thirteen precipitation samples were collected between June 20 and October 13 on a per event basis to characterize the chloride input of precipitation to stream water. Wet precipitation volumes were recorded at the CAPMoN site daily and provided by EC. Two sampling sites were used to collect bulk precipitation. The primary sampling site was the same location as the fog collection site (Fig. 1.2). At the second sampling site (Fig. 1.2) samples collected by the same EC field technician responsible for wet deposition and stream water sampling of the long term EC monitoring program.

Bulk precipitation was collected using a 20 cm mouthed, polyvinyl funnel attached to a sampling bottle. Prior to sample collection, the funnel was rinsed with deionized water. The bulk precipitation collector was set out just before or during a precipitation event and retrieved once a bottle was full (250 mL) or when the precipitation ceased. Weather patterns were recorded for each sampling event in the same method as described for fog collection.

Weather systems were monitored during the sampling season to predict when a fog or rainfall event was likely to occur and to characterize the origin and travel path of the systems from fog or rainfall sampling events. To predict a fog event occurring at the study location, EC weather updates were monitored for forecasts of ‘inland fog’. Also, coastal weather conditions were monitored in Halifax and Lunenburg to evaluate fog development. Characterization of a rainfall or fog event was completed following sample collection using Geostationary Operational Environmental Satellite (GEOS-12) infrared and visible light images (Environment Canada 2006). Images were downloaded at thirty minute intervals from twelve hours before the event and six hours following the event. These images were used to characterize the origin and trajectory of the weather system sampled. Weather patterns were categorized based on the trajectory path before reaching the study area. One category of weather systems follows a trajectory passing over the Atlantic Ocean from the south to the north and is herein termed Marine System (MS). A second category of weather system passes over continental North America, and is termed Continental system (Con). Categorization of atmospheric deposition events can be one or a combination of both types of weather systems. While these are very general categories and ignore other potential influencing factors of dynamic atmospheric systems, they are intended to provide a first order approximation of air mass source and influence of anthropogenic pollution, with Continental systems likely containing more industrial by-products.

3.1.2 Streams

Twelve stream water samples from each of Pine Marten Stream and Moose Pit Brook were collected between June 10 and October 25, 2009 at two week intervals to characterize the chloride output of these watersheds. The sampling site locations were the same locations used for the long term stream monitoring by EC (Figs. 2.1 and 2.3). Stream samples were collected every two weeks by an EC field technician as part of the long term monitoring program and an extra two 250 mL samples from each stream were collected for this study. The sampling locations were upstream of bridges and culverts. Samples were stored in cool, dark conditions in HDPE bottles up to one month prior to transport to Dalhousie University.

3.1.3 Soils and Bedrock

A total of thirty five soil samples at various depths were collected from six pits to characterize the water soluble chloride and the silicate mineral bound chloride in the soils. First order site selections were made consulting the surficial, bedrock and soils maps to select sites that are representative of the geological variations. Specific sites were located in undisturbed forests on relatively flat terrain that appeared representative of the area.

Pits up to 1.6 m deep, 3 m long and 2 m wide were dug using spades, pickaxes and pry bars. The sides of the pit were scraped clean to describe the soils, identify evidence of changes in soil forming processes and to facilitate sampling. Samples (0.5 to 2 kg) were collected in sequence from the bottom most to the topmost layers in the soil profile and were stored in labeled zip-lock bags. Sampling intervals were determined by evidence of changes in soil characteristics including evidence of illuviation of clay, oxidized zones, iron-oxide-cemented layers and interactions with the water table. The number of samples ranged from 1 to 6 samples per pit depending on the depth of the pit and distinguishable soil features. In soil layers greater than 50 cm in thickness, a sample was collected from the top of the layer and from the greatest depth in the pit. A sample from the deepest part of the pit was collected from each pit even if a change in soil features was not observed. An on-site pebble count of at least 50 clasts was completed to characterize the till parent material.

Biotite monzogranite, hornfels and slate bedrock samples were collected to characterize the silicate mineral bound chloride in the two watersheds. Samples were collected at outcrops or at the bottom of a soil pit. Samples were labeled and stored in zip-lock bags.

3.2 Pretreatment Methods

3.2.1 Samples without Pretreatment

Aqueous samples sent for ionic analysis such as stream water, fog water and precipitation were not filtered or acidified. Once at Dalhousie, the HDPE bottles were sealed with parafilm to prevent evaporation and kept at room temperature before shipment for analysis. The maximum duration a sample was kept in a bottle before analysis was 6 months, but typically not longer than 2 months.

3.2.2 Soil Solutions

Soil samples were treated to characterize water soluble chloride in soils (soil solution). Samples were dried at 70°C before being sieved to remove the greater than 2 mm fraction. Approximately 125.0 g of soil and 250.0 g of deionized water were placed in 1 LNalgene containers and agitated for 24 hours. The samples were allowed to settle before decanting the solution into beakers. The solutions were centrifuged at 5500 rpm for 10 minutes before being vacuum filtered using 0.45 μm Whatman filter paper. This method was effective at removing the suspended sediment from solution with samples that contained a high proportion of sand, but was not effective at removing colloids from solution. In order to remove the colloids from solution, either a longer centrifugation or filtering through a build-up of clay on the filter proved to be effective. Concern regarding potential fractionation of chlorine stable isotopes during a pressurized filtering led to a side experiment testing for fractionation effects (See Appendix C for details).

3.2.3 Samples for Total Chlorine

Bedrock and soil samples were treated to remove meteoric chloride before being analyzed for total chloride by XRF. The weathered surface of the bedrock samples was removed and the remaining sample was broken into pebble sized chunks. More than 500 g of fresh chunks were soaked in a mass of deionized water 4 times greater than the mass of the rock sample, scrubbed and rinsed ten times with deionized water before being shipped for analysis.

Soil samples were dried and sieved to remove the greater than 2 mm fraction. To remove meteoric chloride, the soils were immersed in 1 M HNO_3 and agitated for eight hours. The solution was drained off and the acid treatment was repeated twice, followed by five rinses with deionized water. The samples were dried at 70°C before being shipped for analysis.

3.2.4 Solid Samples for Chlorine Stable Isotopes

Bedrock and soil samples were decomposed at CNEF to extract silicate mineral bound chloride for stable isotope analysis. Following the procedure to remove meteoric chloride detailed above, samples were crushed and pulverized resulting in silt to sand sized particles. Samples were rinsed with deionized water to remove water soluble chloride. Samples were dried at 70°C, the mass recorded to 0.1 g and placed in Teflon coated bottles. To decompose the silicate samples, for every 10 g of soil sample, 12 ml of 2 M HNO_3 and 15 ml of concentrated HF were added. Samples were kept at 80°C for two weeks. More acids were added as needed until silicate grains were dissolved into a gel. The solution containing the sample chloride was centrifuged from the gel and the solution kept for chloride extraction.

3.3 Analytical Methods

3.3.1 Ionic Analysis

All aqueous samples of this study were measured for ionic concentrations, specific conductivity and pH at ALET. The anions Cl^-, SO_4^{2-}, NO_3^-, and Br^- in aqueous samples were measured using high pressure liquid chromatography (HPLC), Dionex DX

120. The detection limits are: Cl^- 0.1 mg/L, NO_3^- 0.02 mg/L, SO_4^{2-} 0.1 mg/L. For chloride analyses, the expanded precision is ± 0.09 mg/L using a coverage factor of 2 and a level of confidence of 95% (C. Losier, personal communication 2010). The cations Ca^{2+}, K^+, Mg^{2+}, and Na^+ in aqueous samples were measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP/-OES). The analysis was completed using Varian model 725-ES ICP with the following detection limits; Ca^{2+} 0.01 mg/L, Mg^{2+} 0.01 mg/L, Na^+ 0.01 mg/L and K^+ 0.02 mg/L.

3.3.2 Ionic QA/QC

Of the 83 samples submitted for ionic analysis by HPLC and ICP-OES, seven of the samples were duplicates (Table 3-1) and eight were process blanks (Table 3-2). The correlation of chloride concentrations in the duplicate analyses has an R^2 value of 0.999 (Fig. 3.2). The correlation of chloride between duplicates is consistent with other ions that were analyzed. The duplicates indicate the analytical error in ionic analyses is minimal.

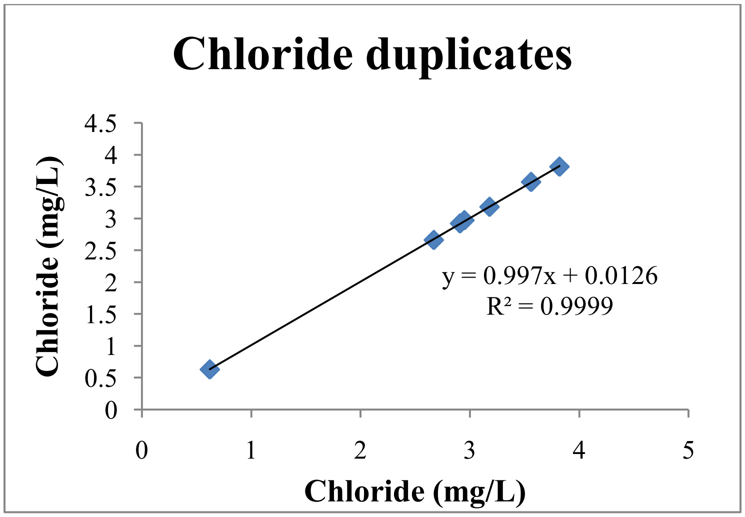


Figure 3.2: Correlation of chloride concentration in duplicate samples.

Table 3-1: Chemical analyses of duplicate samples.

Sample Identification	Chloride mg/L	Sulphate mg/L	Nitrate mg/L	Conductivity uS/cm	pH	Sodium mg/L	Potassium mg/L	Calcium mg/L	Magnesium mg/L	Bromide mg/L
PM10 Aug 24	3.82	2.65	<0.02	28.5	5.75	2.88	0.3	1.15	0.64	<0.10
PM10 Aug 24	3.81	2.64	<0.02	28.5	5.73	2.86	0.31	1.15	0.65	<0.10
PM11 Sept 7	2.91	0.75	<0.02	20	6.04	2.66	<0.10	0.66	0.41	<0.10
PM11 Sept 7	2.92	0.75	<0.02	19.9	6.05	2.62	<0.10	0.66	0.4	<0.10
PM12 Oct 6	3.57	1.35	<0.02	24.7	5.4	2.7	0.43	0.74	0.5	<0.10
PM12 Oct 6	3.56	1.36	<0.02	24.5	5.42	2.7	0.44	0.73	0.5	<0.10
PM7 july 27	2.67	0.38	<0.02	21	6.08	2.54	0.14	0.93	0.53	<0.10
PM7 july 27	2.66	0.39	<0.02	20.7	6.24	2.57	0.13	0.96	0.55	<0.10
PM9 Aug 9	3.18	0.37	<0.02	30.3	6.51	2.86	<0.10	2.16	1.11	<0.10
PM9 Aug 9	3.18	0.43	<0.02	30.2	6.47	2.83	<0.10	2.07	1.09	<0.10
TBA09-SLSS1C2	0.63	0.49	<0.02	5.6	5.7	0.41	0.18	0.12	0.06	<0.10
TBA09-SLSS1C2	0.62	0.47	<0.02	5.4	5.78	0.41	0.1	0.11	0.07	<0.10
MP7 july 27	2.95	0.38	<0.02	30.3	4.76	2.98	0.28	1.2	0.6	<0.10
MP8 july 27	2.97	0.39	<0.02	30.1	4.78	2.98	0.2	1.2	0.6	<0.10

Table 3-2: Chemical analyses of process blanks.

Sample Identification	Chloride mg/L	Sulphate mg/L	Nitrate mg/L	Conductivity uS/cm	pH	Sodium mg/L	Potassium mg/L	Calcium mg/L	Magnesium mg/L	Bromide mg/L
DI HDPE	<0.10	<0.10	<0.02	0.7	5.6	<0.02	<0.10	<0.01	<0.05	<0.10
DI ENCAN	<0.10	<0.10	<0.02	1.3	5.52	<0.02	<0.10	<0.01	<0.05	<0.10
DI ENCAN	<0.10	<0.10	<0.02	1	5.57	<0.02	<0.10	<0.01	<0.05	<0.10
DI CNEF	<0.10	<0.10	<0.02	<0.5	5.62	<0.02	<0.10	<0.01	<0.05	<0.10
DI CNEF	<0.10	<0.10	<0.02	0.7	5.6	<0.02	<0.10	<0.01	<0.05	<0.10
Soil	<0.10	<0.10	<0.02	3.2	5.15	<0.02	<0.10	<0.01	<0.05	<0.10
FC Blank	0.22	0.13	<0.02	2.4	5.91	0.18	0.18	0.07	<0.05	<0.10
FC Blank	0.28	0.16	<0.02	3	6.18	0.18	0.1	0.13	<0.05	<0.10

Many of the samples in this study deal with low ionic concentrations; therefore contamination from sampling materials has the potential to significantly impact the results. To address this issue, a series of process blank samples were submitted for ionic analysis to determine if the solutions and materials used to collect samples contribute to the reported results. The results of these samples are listed in Table 3-2 and include 2 samples collected as rinse water from the fog screen collector (FC Blank), 2 samples of deionized water from EC (DI ENCAN), 2 samples of deionized water from the CNEF (DI CNEF), one sample of DI CNEF water was kept in a high density polyethylene bottle for one month (DI HDPE) to evaluate the possibility of chloride leaching, and one sample of DI CNEF water run through the procedure of soil solution extraction (Soil).

All samples, with the exception of the fog collector blanks, were below detection limits of all the ions measured. The fog collection blank samples have ionic concentrations typically twice the detection limits. For chloride, the amount detected on the screen is approximately 10% of the chloride in typical stream water samples. In the case of sulphate, the amount detected on the screen can represent up to 50% of the sulphate in low concentration samples. The proportional concentrations of the major ions are similar to rainfall (Table 4-2), suggesting incomplete rinsing of fog water between sampling events.

3.3.3 X-Ray Florescence

Total chloride in rock and soil samples was measured to identify sources of silicate mineral bound chloride. The analysis was completed by SGS laboratory in Lakefield, Ontario using X-Ray Fluorescence pressed pellet (XRF). The limit of quantification is 10 ppm (Lab reference material and online resource: http://www.amptek.com/xrf.html).

3.3.4 Chlorine Stable Isotopes

Chlorine stable isotopes in aqueous and solid samples were analyzed to characterize chloride sources and quantify their relative contributions to stream water. The chloride of aqueous and silicate samples was precipitated as AgCl at CNEF and analyzed for the chlorine stable isotope composition using a Continuous Flow Isotope

Ratio Mass Spectrometer (CF-IRMS, GV Instruments) at the National Water Research Institute (NWRI) in Saskatoon.

3.3.4.1 AgCl Extraction from Aqueous Samples

The chloride of aqueous samples were concentrated and precipitated as AgCl following the procedures of Long et al. (1993), Kaufmann (1994) and Wassenaar and Koehler (2004) with modifications. Details of the procedure including modifications are detailed in Appendix A.

3.3.4.2 Conversion of AgCl to $CH_3Cl_{(g)}$

To analyze the chloride of the samples, $AgCl_{(s)}$ was converted to $CH_3Cl_{(g)}$ which was injected into the mass spectrometer. The $AgCl_{(s)}$ samples on filter paper were inserted into 10 mL serum bottles, capped with butyl blue stoppers and crimped with aluminum seals. The bottles were evacuated to 40 mtorr before excess CH_3I was added to convert the chloride to $CH_3Cl_{(g)}$. The bottles were placed in an oven at 80°C for 48 hours to ensure complete reaction of the methyl chloride production.

3.3.4.3 Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS)

The chlorine stable isotope composition was determined using CF-IRMS following the method described in Wassenaar and Koehler (2004). Values stated in this study are typically (54 of 60 samples) from a single analysis of the sample. In six cases, the reported result is the mean of multiple analyses (See Appendix B for details). The $\delta^{37}Cl$ values were measured by a multi-collector CF-IRMS using an Elementar Isoprime. The isotopic composition is a measure of the ratio of the area beneath the curves of CH_3Cl^{37} (atomic mass 52) and CH_3Cl^{35} (atomic mass 50). During the analysis, the ratio of an individual sample was compared to the ratio of an automated injection of a laboratory specific CH_3Cl gas. The global standard for chloride is Standard Mean Ocean Chloride (SMOC), where the daily SMOC was set to 0 and all samples were compared in relation to this origin. The daily SMOC was the mean value of repeated analyses of multiple seawater samples. The reported measure of analytical uncertainty for the duration of 5 days of analyses was provided by the standard deviation of all the seawater daily values.

In the results and isotope mass balance sections of this thesis, the uncertainty is represented at times by both an absolute value (‰) and a relative uncertainty (%). In the conversion of relative uncertainty to an absolute value, the raw $\delta^{37}Cl$ before normalization to SMOC is used. For example, if the raw value of an analysis is -6.47 ‰ and the SMOC of the day is -6.14 ± 0.22 ‰, the relative error is 4 % and the normalized sample value is -0.33 ‰. When the $\delta^{37}Cl$ value is stated as -0.33 ‰ ± 4 %, the relative error is kept in relation to the raw value, not the normalized $\delta^{37}Cl$ value stated.

At the beginning of each day and before any samples were analyzed, the instrument was tested for stability and for sample injection linearity. Stability was tested by running ten automated injections of a reference CH_3Cl gas. The standard deviation of these injections can be used to represent the internal precision of the instrument (range from 0.02 to 0.04 ‰). However, the samples being analyzed were injected manually, potentially introducing a measure of uncertainty as a result of variations in sample volume injection. In previous studies (Wassenaar and Koehler 2004, Shouakar-Stash 2008) the $\delta^{37}Cl$ was highly correlated ($R^2 > 0.95$) to the volume of gas injected and a linearity correction was made to account for variable manual injection volumes. However, during the analyses of samples in this study, the correlation was not as strong (R^2 ranged from 0.53 to 0.88). A comparison $\delta^{37}Cl$ values with linearity correction and without linearity correction shows that in repeat analyses of individual seawater samples, the standard deviation increases in 6 of the 8 samples when the linearity correction was made (Table 3-3). Therefore, the results of this study have not been corrected for variability in volume injection.

3.4 Isotopic Mass Balance

An isotopic mass balance approach is used in this study to attempt to quantify the proportional contributions of chloride from mineral/water interactions and from fog deposition to stream water. Two assumptions are required for the application of this approach; the isotopic composition of each of the components (streams, rainfall, fog water, silicate mineral bound chloride) is accurately characterized by a single value which can be used in the isotope mass balance equation, and the second assumption is all of the sources of chloride to the stream water are accounted for in the components of the mass balance. The validity of these assumptions is addressed in the discussion chapter.

Table 3-3: Comparison of seawater replicate analyses with linear correction and without correction.

Seawater Sample Number	Dates Analyzed	Linearity corrected Mean δ^{37}Cl (‰)	1σ Seawater (‰)	Un-corrected Mean δ^{37}Cl (‰)	1σ Seawater (‰)
9112	Dec 10, Dec 11	-5.94	0.19	-5.98	0.16
9113	11-Dec	-6.33	0.10	-6.01	0.07
9119	Dec 10, Dec 11	-6.34	0.39	-6.42	0.19
9114	16-Dec	-6.72	0.17	-6.24	0.09
9115	Dec 16, Dec 17	-6.72	0.27	-6.21	0.21
9116	17-Dec	-6.65	0.11	-6.10	0.12
9117	18-Dec	-6.51	0.03	-5.76	0.15
9118	18-Dec	-6.43	0.15	-5.80	0.09
	Mean	-6.46		-6.07	
	1σ	0.26		0.22	

Four steps are required to assess the mass balance: 1. Provide a best estimate of the mean isotopic composition of each component; 2. Estimate the proportional contribution of chloride from wet deposition to stream water; 3. Use an isotope mass balance equation to estimate the isotopic composition of the excess chloride; 4. Use an isotope mass balance equation to estimate the proportional contributions of mineral/water interaction and fog deposition. While estimates of analytical uncertainty in the measurements have not been fully evaluated, an attempt is made to represent uncertainty in the isotope mass balance. This is done using statistical measures of uncertainty for each of the components and the rules of uncertainty propagation (Taylor 1982).

The first step of estimating the isotopic composition of each component is provided by a mean value of the measurements of each component. Uncertainty related to the true value is represented by a 95 % confidence interval. However, as a result of the small sample size and large range of isotopic values of some components, a 95 % confidence interval can sometimes overwhelm the values in the isotope mass balance.

Therefore, in the isotope mass balance equations, the uncertainty is represented by the standard error of the mean.

An estimate of the proportion of chloride in stream water which can be accounted for by measured wet deposition is estimated using the long term data set from EC which is summarized as weekly, monthly and yearly fluxes of chloride in wet deposition and streams. An estimate of the proportion of chloride from precipitation in Table 3-4 is produced by dividing the monthly averages of precipitation fluxes by the monthly averages of stream fluxes for the sampling period of this study (June to October), and taking the mean of the monthly proportions. During the months of June to October, 39% of the chloride in stream water comes from measured wet deposition.

Table 3-4: Monthly averages of precipitation and stream chloride fluxes with total proportional estimate.

Month	Wet Deposition Chloride Flux (kg/ha)	Moose Pit Chloride Flux (kg/ha)	Proportion of Chloride in Moose Pit Brook from Wet Deposition	Pine Marten Stream Chloride Flux (kg/ha)	Proportion of Chloride in Pine Marten Stream from Wet Deposition
June	0.31	1.03	0.30	0.53	0.58
July	0.19	0.63	0.30	0.33	0.57
August	0.25	0.73	0.34	1.05	0.24
September	0.49	1.00	0.49	1.98	0.25
October	1.02	1.92	0.53	3.16	0.32
		Mean	0.39	Mean	0.39
		Std.err	0.05	Std.err	0.08

The third step requires the use of a simple mass balance equation:

$$\delta^{37}Cl_s = (X_p)\ \delta^{37}Cl_p + (X_{p-1})\ \delta^{37}Cl_e \qquad (1)$$

where X_p is the proportion of stream chloride from precipitation (Table 3-4) and X_{p-1} is the proportion of stream chloride in excess of precipitation chloride; and

$$X_p + X_{p-1} = 1$$

As well, $\delta^{37}Cl_s$ is the isotopic composition of the stream water, $\delta^{37}Cl_p$ is the isotopic composition of precipitation, $\delta^{37}Cl_e$ is the isotopic composition of the excess chloride. Solving equation 1 for $\delta^{37}Cl_e$ provides an estimate of the isotopic composition of the excess chloride.

Assuming the excess chloride comes from fog deposition and mineral/water interactions, an estimate of the proportional contributions of each can be made using the equations:

$$\delta^{37}Cl_e = (X_f)\,\delta^{37}Cl_f + (X_w)\,\delta^{37}Cl_w \qquad (2a)$$

where X_f is the proportional contribution of fog to the excess chloride, X_w is the proportional contribution of mineral/water interactions to the excess chloride and

$$X_f + X_w = 1 \qquad (2b)$$

As well, $\delta^{37}Cl_f$ is the mean isotopic composition of fog water and $\delta^{37}Cl_w$ is the estimate of the isotopic composition of silicate mineral bound chloride. Equation two can be solved for the proportional contributions of fog and mineral/water interactions,

$$X_f = (\delta^{37}Cl_e - \delta^{37}Cl_w) / (\delta^{37}Cl_f - \delta^{37}Cl_w) \qquad (3)$$

The majority of soil and bedrock samples in this study were collected for Moose Pit Brook, therefore a complete isotope mass balance is produced for this catchment alone. However for Pine Marten Stream catchment, an isotopic mass balance approach is used to estimate the chlorine stable isotope composition of the terrestrial source of excess chloride.

Chapter 4 : Ionic and δ^{37}Cl Results

The results of this study consist of 83 ionic chemistry analysis, 11 XRF total chlorine analyses and 60 chlorine stable isotope analyses of fog water, rainfall, stream water, soil water solution, soils and bedrock samples. The sampling and analysis of fog water provides an opportunity to quantify a component of chloride stream budgets that is often estimated. The application of chlorine stable isotopes analyses from fog water, precipitation, stream water, soils and bedrock to identify sources of chloride is a new application of chlorine stable isotope results. The ionic and isotopic results of this study begin to clarify sources of chloride to stream water in KNP.

4.1 Ionic Results

Samples of stream water (22), rainwater (12), fog water (8), soils and bedrock were collected between May and October 2009. Aliquots of aqueous samples were submitted to ALET for ionic analysis of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-} and Br^{-}, pH and specific conductivity. These data are compared to the long term data set of stream and precipitation monitoring made available through the EC Acid Rain Program (EC, Environdat Database). Monthly means and standard deviations of wet deposition and stream concentrations and fluxes are calculated from sampling durations of 13 years for Pine Marten Stream, 22 years for Moose Pit Brook and 22 years for wet deposition.

4.1.1 Chloride in Fog Water

Eight fog water samples greater than 50 mL were collected during this study, of which seven were collected during a wet and foggy period from June 21 to July 1, 2009 and one sample was collected later in the summer on August 3. The weather systems creating and transporting the fog were typically Atlantic systems originating in the south Atlantic and travelling northward, while other systems tracked over parts of the eastern United States or Canada (Table 4-1).

Table 4-1: Summary of fog water sample ionic estimates. Measured chloride concentrations from HPLC analysis. Concentration estimate is from the yield of AgCl during the preparation of samples for isotopic analysis.

Sampling Date	Concentration Estimate from AgCl Extraction (µeq/L)	Measured Concentration (µeq/L)	Weather Transport Summary
22-Jun	169		Marine System
23-Jun	1128	929.7	Marine System
26-Jun	564		Continental System passed over New York State
28-Jun	226	94.5	Mostly Marine
29-Jun	113	32.4	Mostly Marine
1-Jul	874		Convergence of Marine and Continental systems
3-Aug	254		Mostly Marine

The volume of fog water samples collected ranged from 50 mL to 225 mL. Because of unknown and potentially variable ionic concentrations in the fog water, a minimum sample size of 50 mL was designated for each of ionic and isotopic analysis. In situations where the sample volume was less than 100 mL, the sample was kept for chlorine stable isotope analysis. The rationale for this is related to the unknown dilution effect of the fog sampler (see Methods), which would affect the concentration results, but not the isotopic results. The application of this reasoning resulted in only three samples being submitted for ionic analysis. However, an estimate of concentration is made using the mass yield of AgCl from the sample preparation for chlorine stable isotope analysis. In so doing, the number of moles of chloride is calculated from the mass of AgCl precipitated and then the mass of chloride in the initial volume of sample solution is used to provide a concentration estimate. The estimated concentrations from AgCl yield are higher than measured and may be a result of incomplete drying of the AgCl sample or impurities in the precipitate.

Despite the unknown dilution factor, chloride concentrations in the fog water samples have a greater range than stream water or precipitation (Table 4-2) which is consistent with occult deposition sampling in near coastal environments of Wales (Reynolds et al. 1997).

4.1.2 Chloride in Rainfall

During the months of May to October, 2009, twelve rainfall samples were collected which had adequate volume and lacked any obvious contamination such as pollen or debris. During the study period, rainfall volumes followed the general pattern of seasonal precipitation, but were at the extremes of monthly averages (Fig. 4.1A). The months of June, July, August and October were months of high rainfall and September was a drier month than normal. Rainfall chloride concentrations were within two standard deviations of monthly averages, with the exception of two samples (Fig. 4.1B). These two anomalous samples are likely not true outliers because of the high variability of chloride concentrations in precipitation (Neal and Kirchner 2000).

4.1.3 Stream Water Chloride

Twelve individual samples from each stream were collected between June 1 and October 25, 2009. Flow data were not available at the time of the thesis compilation. Moose Pit Brook samples display chloride concentrations less than the monthly mean concentrations, but typically within two standard deviations (Fig. 4.1C). Water samples of Pine Marten Stream display higher concentrations and a larger range of chloride concentrations compared to Moose Pit Brook. The chloride concentrations from Pine Marten Stream samples are less than monthly means and commonly less than two standard deviations of the average (Fig. 4.1D).

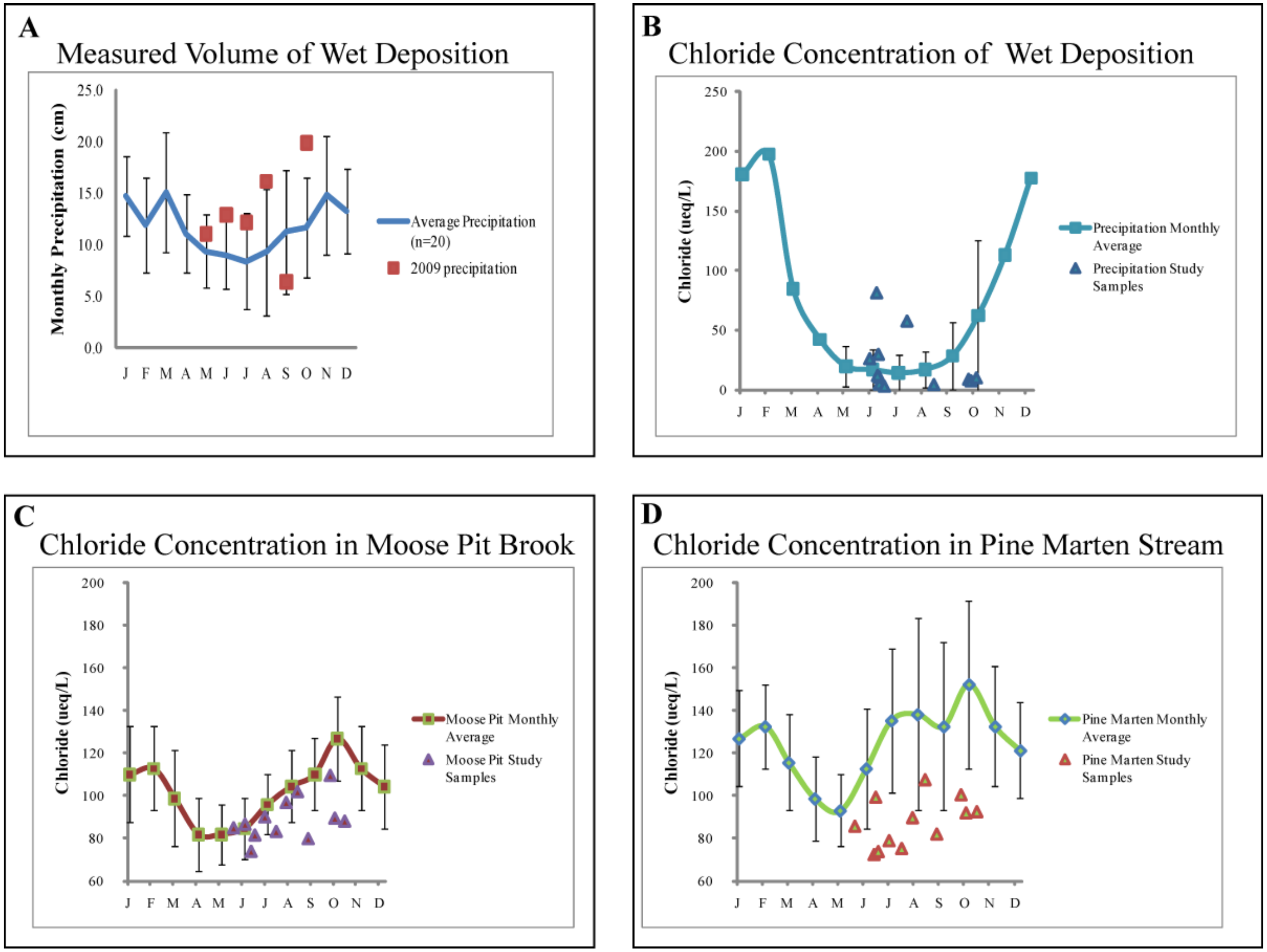


Figure 4.1: Comparison of samples of this study to trends in long term deposition and stream output. Squares (4.1A) and triangles (4.1B,C,D) represent individual samples collected during this study. Bars represent monthly standard deviations of long term monitoring.

4.1.4 Cations and Anions in Atmospheric Deposition and Streams

Precipitation, fog water and stream samples collected during this study were analyzed using HPLC and ICP-OES for concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-} and Br^-, pH and specific conductivity and are summarized in Table 4-2. Measured atmospheric deposition accounts for a large proportion of sodium, chloride, nitrate and sulphate in stream water, but contributes much less to calcium, magnesium and potassium in stream water (Figs. 4.2 and 4.3).

The input of calcium from precipitation to streams is minimal as shown by the large differences between precipitation and stream values in Figs. 4.2A and B. The streams have similar calcium outputs to one another. Exceptions include lower Pine Marten concentrations in September and a Pine Marten sample on August 9 with much higher calcium concentrations.

The concentration of magnesium in precipitation ranges from below detection limits to 18.11 μeq/L. In stream water, concentrations of magnesium closely follow the trends of calcium.

The concentrations of potassium in precipitation are low and commonly below detection limits (<2.5 – 8.18 μeq/L). In Moose Pit Brook, the levels of potassium are consistently above detection limits (5.12 - 13.56 μeq/L). In Pine Marten Stream, potassium concentrations range from below detection limits to 11.25 μeq/L.

Sodium in precipitation is variable (Fig. 4.3A), but is a significant contributor to the stream budget (Fig. 4.3B). The concentration of sodium was higher in Moose Pit Brook during this study, but the long term flux shows higher outputs of sodium per hectare in Pine Marten Stream.

Table 4-2: Ionic results of rainfall, fog and stream samples collected during this study.

Sample	Date	Conductivity (uS/cm)	pH	Na (ueq/L)	Ca (ueq/L)	Mg (ueq/L)	K (ueq/L)	Cl (ueq/L)	SO4 (ueq/L)	NO3 (ueq/L)	Br (ueq/L)
Fog Water	23-Jun	162.40	4.67	896.91	50.40	195.06	40.92	929.68	193.00	21.13	<1.25
Fog Water	28-Jun	42.00	5.89	100.04	55.39	17.28	46.04	94.49	83.07	14.03	<1.25
Fog Water	29-Jun	14.70	4.91	32.19	5.49	6.58	5.12	32.44	27.27	3.55	<1.25
Rainfall	12-Jun	12.70	6.72	27.84	14.97	4.12	<2.5	26.23	16.45	1.45	<1.25
Rainfall	20-Jun	16.50	6.32	80.90	13.97	18.11	3.32	81.52	22.90	0.32	<1.25
Rainfall	21-Jun	7.20	6.15	12.61	4.49	<2.05	<2.5	12.13	13.32	1.94	<1.25
Rainfall	22-Jun	17.90	4.59	26.97	3.99	5.76	<2.5	29.90	25.61	3.87	<1.25
Rainfall	23-Jun	2.20	5.92	9.57	3.49	<2.05	2.56	5.08	4.16	0.32	<1.25
Rainfall	23-Jun	4.10	5.95	12.18	2.50	<2.05	<2.5	11.00	14.57	0.48	<1.25
Rainfall	29-Jun	1.60	6.02	3.48	2.50	<2.05	<2.5	3.10	2.29	<0.32	<1.25
Rainfall	25-Jul	13.90	6.18	56.11	12.48	13.17	<2.5	57.82	20.61	1.94	<1.25
Rainfall	25-Aug	2.90	5.76	6.96	4.99	<2.05	9.21	4.51	2.29	<0.32	<1.25
Rainfall	4-Oct	3.10	5.79	10.00	5.49	<2.05	<2.5	9.03	5.20	0.32	<1.25
Rainfall	7-Oct	3.90	5.61	7.39	4.99	<2.05	3.07	7.62	4.37	<0.32	<1.25
Rainfall	13-Oct	4.30	5.70	8.26	6.49	<2.05	8.18	10.15	6.04	0.65	<1.25

Sample	Date	Conductivity (uS/cm)	pH	Na (ueq/L)	Ca (ueq/L)	Mg (ueq/L)	K (ueq/L)	Cl (ueq/L)	SO4 (ueq/L)	NO3 (ueq/L)	Br (ueq/L)
Moose Pit Brook	1-Jun	23.90	4.97	117.44	32.44	28.80	5.12	84.90	15.82	<0.32	<1.25
Moose Pit Brook	16-Jun	25.00	4.97	125.27	35.43	32.09	2.56	86.59	13.95	<0.32	<1.25
Moose Pit Brook	24-Jun	29.30	4.73	122.66	49.90	41.97	5.12	73.90	12.91	<0.32	<1.25
Moose Pit Brook	29-Jun	30.60	4.70	129.62	52.90	44.44	5.12	81.52	7.91	<0.32	<1.25
Moose Pit Brook	12-Jul	28.20	4.87	136.58	46.91	40.32	5.12	89.98	10.62	<0.32	<1.25
Moose Pit Brook	27-Jul	30.10	4.78	129.62	59.88	49.37	5.12	83.77	8.12	<0.32	<1.25
Moose Pit Brook	9-Aug	30.30	4.91	141.37	53.40	46.90	7.42	96.75	10.20	<0.32	<1.25
Moose Pit Brook	24-Aug	37.30	4.66	142.67	65.37	59.25	10.23	101.82	42.47	<0.32	<1.25
Moose Pit Brook	7-Sep	32.80	4.58	122.66	55.39	47.73	4.60	79.82	10.62	<0.32	<1.25
Moose Pit Brook	6-Oct	40.30	4.44	118.31	63.88	57.60	13.56	109.44	17.49	<0.32	<1.25
Moose Pit Brook	12-Oct	33.60	4.52	109.61	48.41	43.61	8.95	89.41	18.95	<0.32	<1.25
Moose Pit Brook	25-Oct	30.90	4.59	107.44	42.42	38.68	5.12	88.00	24.78	<0.32	<1.25
Pine Marten Stream	1-Jun	19.60	6.23	117.44	33.93	34.56	<2.5	85.75	10.83	<0.32	<1.25
Pine Marten Stream	24-Jun	19.90	5.82	110.48	37.93	37.03	<2.5	72.49	14.57	<0.32	<1.25
Pine Marten Stream	26-Jun	22.40	6.37	120.49	44.41	47.73	<2.5	99.29	9.37	<0.32	<1.25
Pine Marten Stream	29-Jun	20.10	5.90	112.22	38.43	37.03	<2.5	73.90	11.03	<0.32	<1.25
Pine Marten Stream	12-Jul	23.30	6.17	122.23	55.89	54.31	<2.5	78.98	8.54	<0.32	<1.25
Pine Marten Stream	27-Jul	21.00	6.08	110.48	46.41	43.61	3.58	75.31	7.91	<0.32	<1.25
Pine Marten Stream	9-Aug	30.20	6.47	123.10	103.30	89.69	<2.5	89.70	8.95	<0.32	<1.25
Pine Marten Stream	24-Aug	28.50	5.73	124.40	57.39	53.49	7.93	107.47	54.96	<0.32	<1.25
Pine Marten Stream	7-Sep	19.90	6.05	113.96	32.94	32.92	<2.5	82.36	15.61	<0.32	<1.25
Pine Marten Stream	6-Oct	24.70	5.40	117.44	36.43	41.14	11.25	100.70	28.11	<0.32	<1.25
Pine Marten Stream	12-Oct	22.30	5.52	113.96	29.94	35.38	5.12	91.95	30.40	<0.32	<1.25
Pine Marten Stream	25-Oct	23.00	5.42	108.31	30.44	36.21	9.46	92.52	34.98	<0.32	<1.25

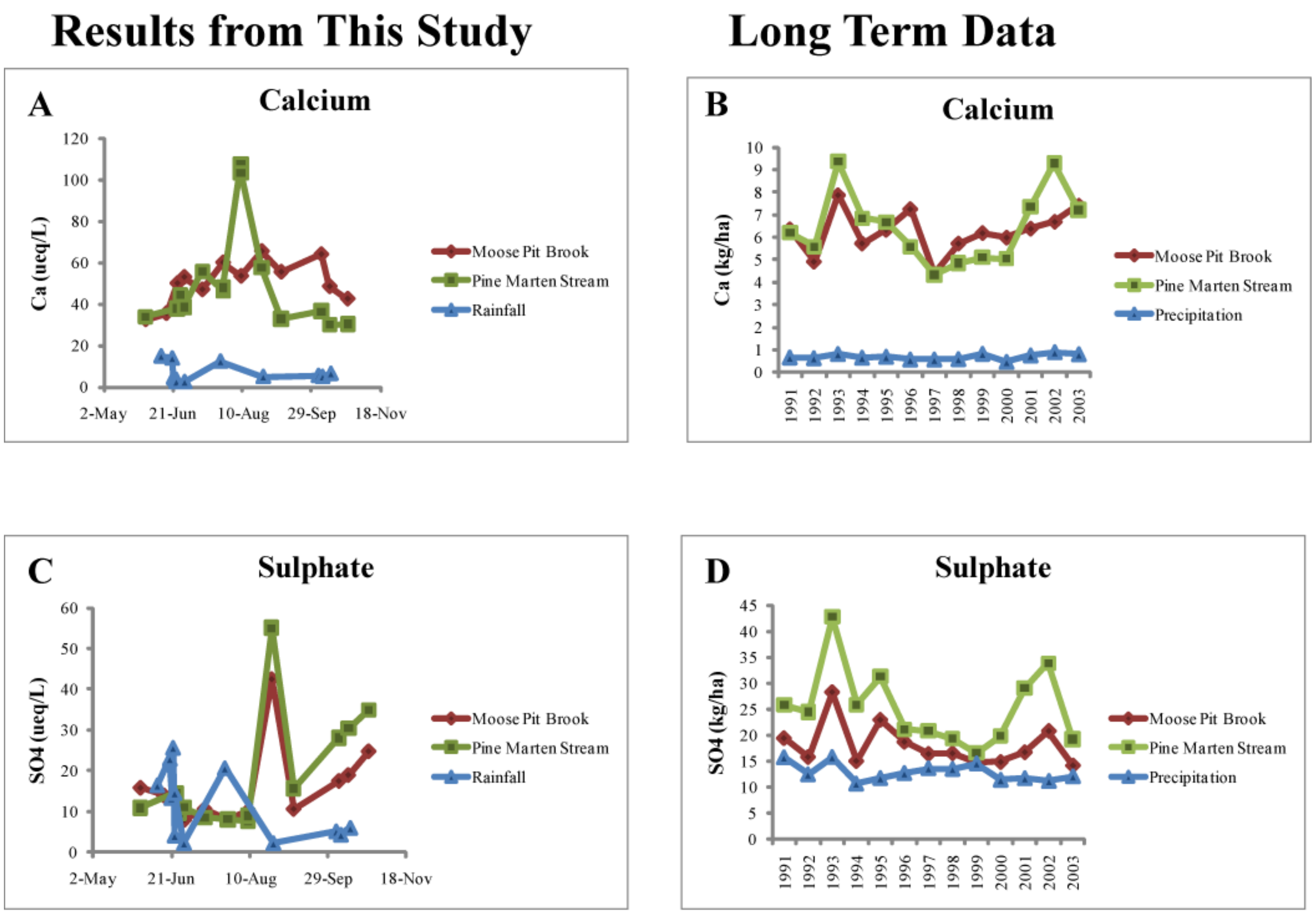


Figure 4.2: Calcium and sulphate concentrations from stream and rainfall samples of this study compared to yearly averages of ionic fluxes provided by EC.

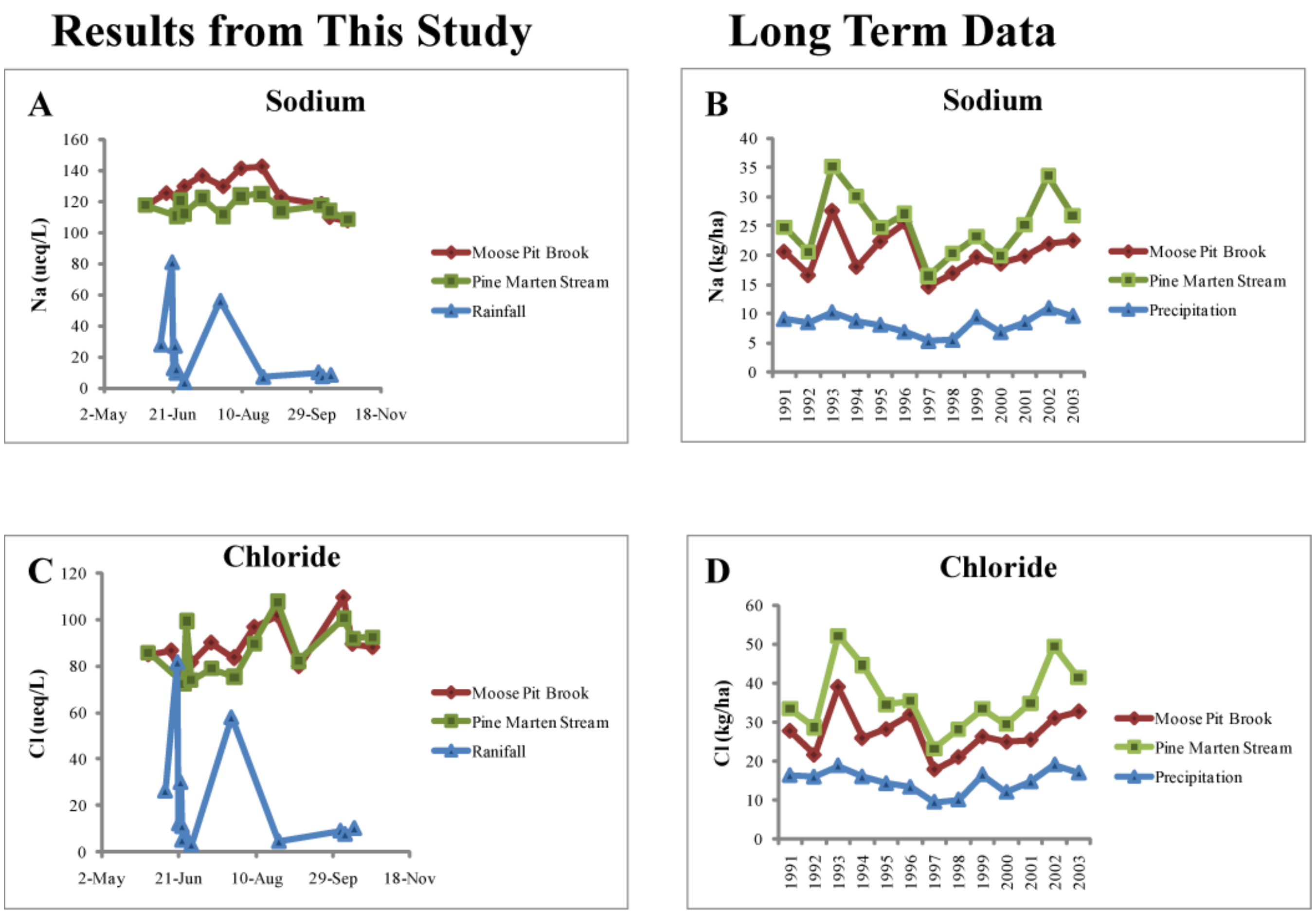


Figure 4.3: Sodium and chloride concentrations of rainfall and stream samples from this study compared to yearlyfluxes.

Atmospheric deposition has sulphate concentration and fluxes comparable to stream water (Figs. 4.2C and D). Sulphate in stream water appears to be lower in the months of June and July with a sharp increase in August followed by a steady increase in the fall. Correlation between calcium and sulphate is stronger ($R^2 = 0.71$) in Pine Marten Stream yearly fluxes than Moose Pit Brook ($R^2 = 0.32$), but the correlation is insignificant ($R^2 < 0.05$) in data of this study (Fig. 4.4). The slope and intercept of the calcium and sulphate yearly flux trendline is 3.9 and 0.5 for Pine Marten Stream and 2.7 and 2.0 for Moose Pit Brook.

Chloride concentrations in precipitation are more variable than in stream water (Fig. 4.3B) which is consistent with previous studies examining chloride in precipitation and streams (eg. Neal and Kirchner 2000). Concentration of chloride in precipitation approached that of stream water during the heavy rainfall periods of June, while the chloride concentration of fog water greatly exceeded that of stream water and rainfall on June 23 (Table 4-2) which is consistent with previous studies (Reynolds et al 1997).

The flux of chloride from Pine Marten Stream is greater than from Moose Pit and similar to sodium flux patterns (Figs. 4.3B and D). The correlation between chloride and sodium in Pine Marten Stream is stronger than Moose Pit Brook in data from this study and in yearly fluxes. (Figs. 4.3C and D). The intercept of the chloride and sodium trendline is higher in Moose Pit Brook, but the slopes are similar (Fig. 4.4D). The monthly average sodium to chloride ratios in Pine Marten Stream catchment and Moose Pit Brook catchment diverge during summer months (Fig. 4.5).

Nitrate in precipitation ranged from below detection limits (<0.32 μeq/L) to 3.87 μeq/L. The concentration of nitrate in both streams is consistently below detection limits. The concentration of bromide in all stream and precipitation samples is below detection limits (<1.25 μeq/L).

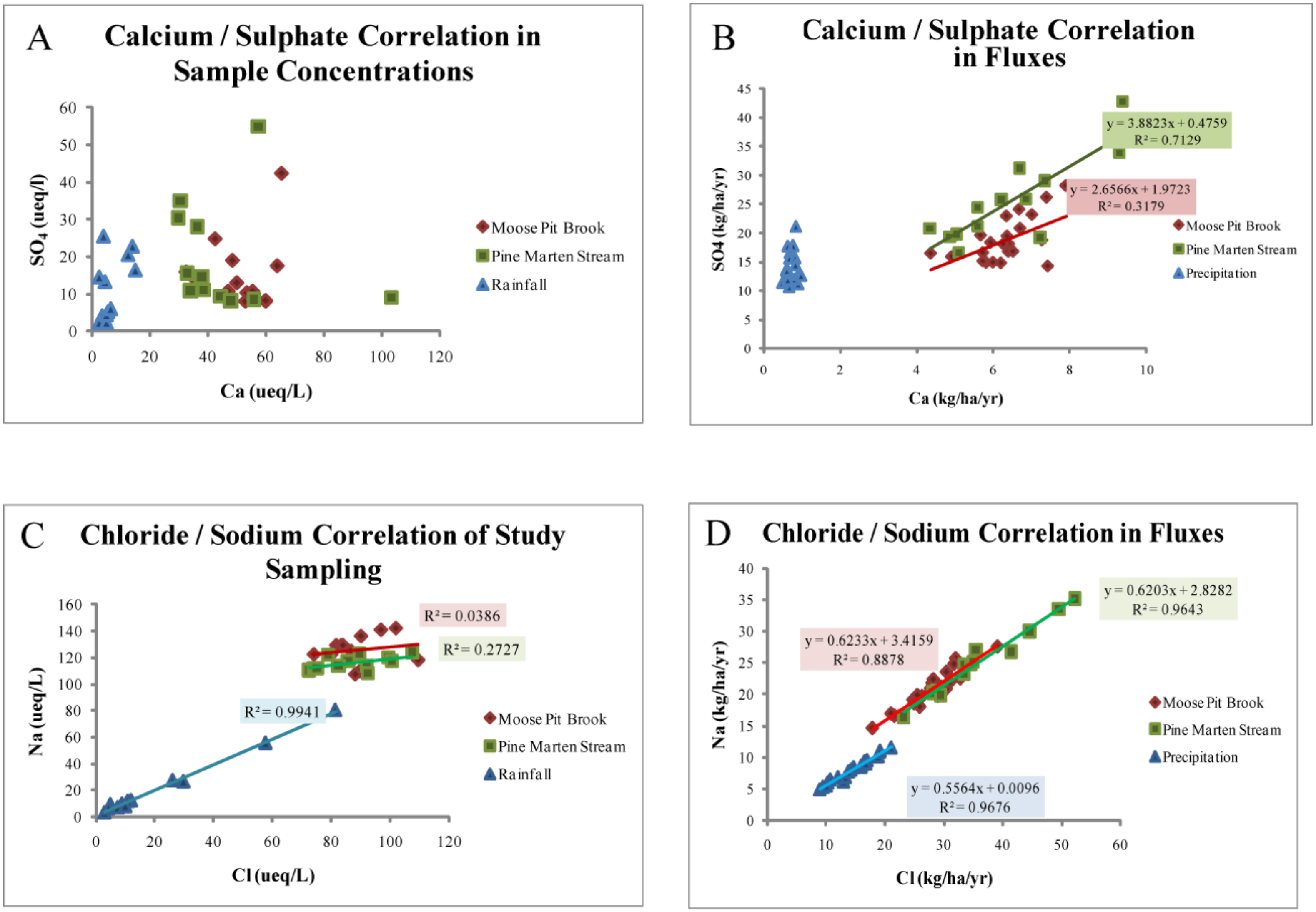


Figure 4.4: Correlations of ions in study samples and in yearly fluxes.

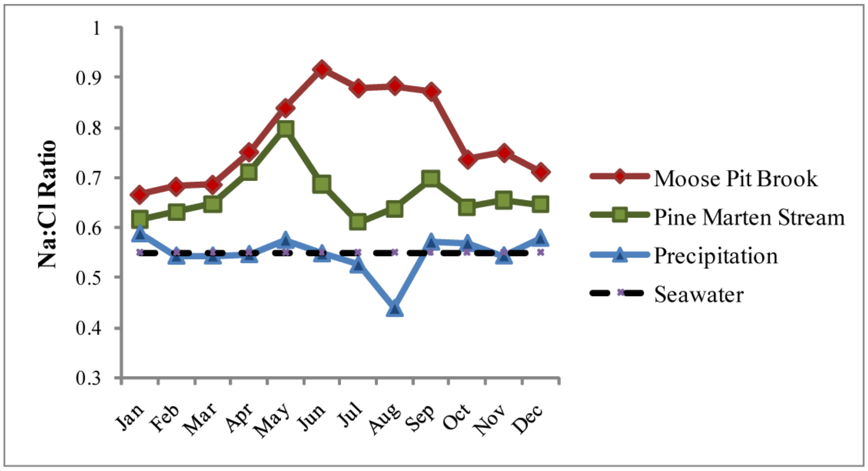


Figure 4.5: Monthly average sodium to chloride mass ratios in stream and rainfall compared to seawater. Data are from EC long term monitoring.

The ionic concentrations and fluxes of precipitation are distinct from those of the streams. The differences between deposition and stream output are likely a result of processes occurring within the catchments. Identification of differences in ionic concentrations and fluxes between catchments suggests contrasting geochemical compositions and processes influencing fluxes. The differences in ionic fluxes between catchments and the implications are addressed in the discussion.

4.1.5 Soil Solutions

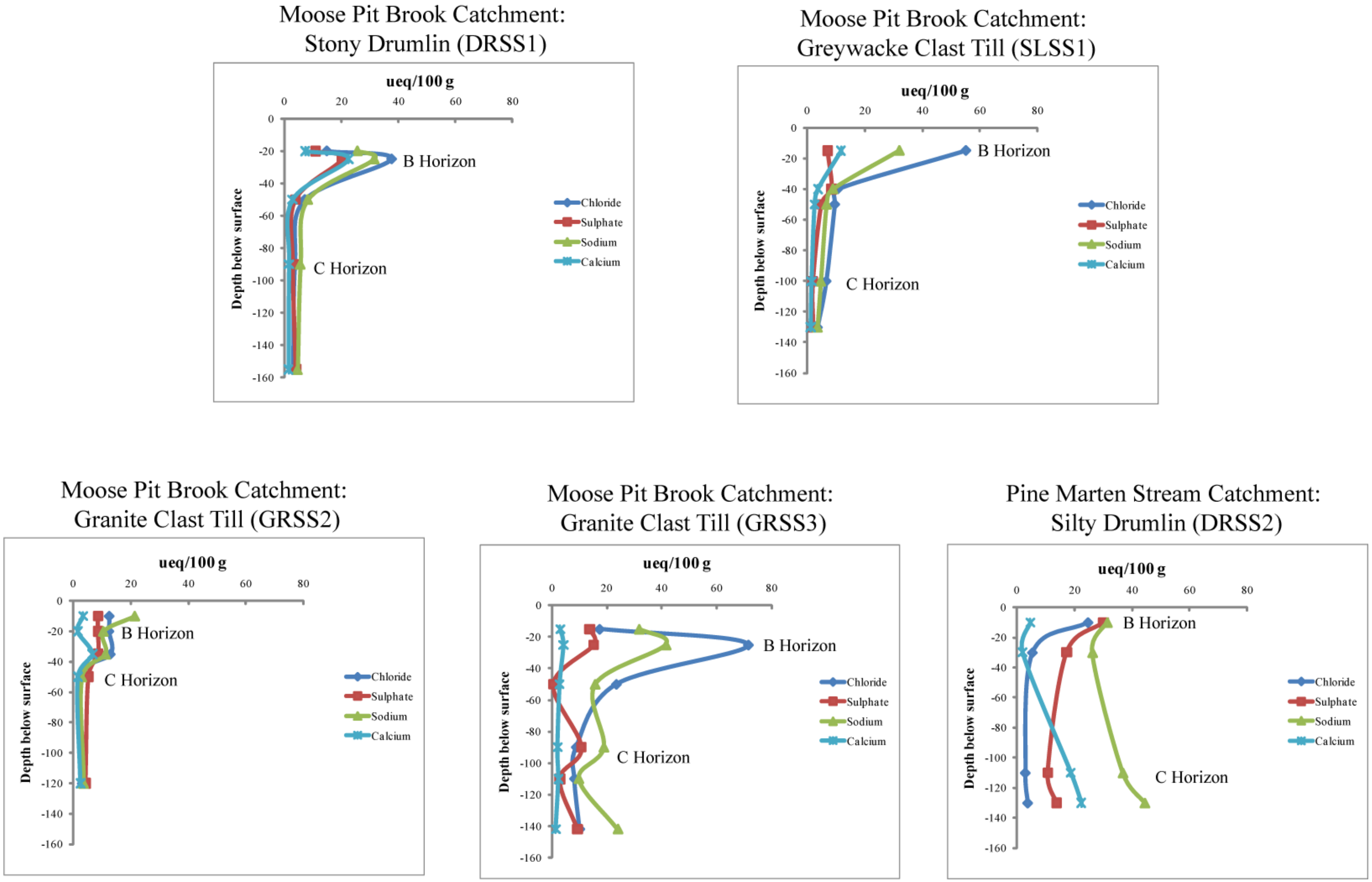
Six soil pits were dug (locations in Fig. 2.9) to examine soil characteristics and collect samples for chemical analysis. The pits are representative of the different till types in the two catchments. The pit labeled DRSS1 was located on a stony till drumlin in Moose Pit catchment and represents the coarse grained drumlins in that catchment. The pits labeled GRSS2 and GRSS3 were pits dug in the Beaver River Till of Moose Pit Brook and represent till common in the catchment which is dominated by clasts of biotite monzogranite (> 95 %). The pit labeled SLSS1 was a pit dug in Beaver River Till of Moose Pit Brook with greater than 90 % clasts of hornfels. Two pits were dug in Pine Marten Stream catchment. The pit labeled SLSS2 was in a thin, clay rich till representative of the Beaver River Till in that catchment. The pit labeled DRSS2 was located on a silty drumlin representative of the drumlins in Pine Marten Stream catchment. Ionic depth profiles (Fig. 4.6) are generally consistent with previous investigations of soil solution features in these catchments (Yanni 1995). The concentrations of ions changing with depth follow a pattern of low abundances in the leached (Ae) layer, sharp increases to maximum abundances in the B layer followed by decreasing abundances to the underlying C horizon. Field observations of evidence of soil forming processes correspond to the fluctuations of ionic abundances. For instance, the upper Ae layers were pale grey and laterally continuous and discontinuous depending on the pit, and the B horizons were identified by increased red and brown colorations.

The soils of Moose Pit Brook can be characterized as sandy and well drained with a high proportion of clasts from local bedrock lithologies. The two granite clast tills are similar in general soil descriptions, but the water soluble profiles are different (Fig.4.6). The ionic concentrations of all measured ions from pit GRSS2 are low with little variation from top to the bottom of the profile. Pit GRSS3 has higher chloride and sodium concentrations in the B horizon and increase again near the bottom of the pit. Calcium concentrations in GRSS3 are low and display little variation from top to bottom.

The hornfels clast till (SLSS1) has high sodium and chloride concentrations near the surface with a sharp drop off below the B horizon. Calcium follows a similar pattern, but is not as pronounced. Sulphate concentrations peak in the BCc, but are generally low throughout the profile.

The stony drumlin (DRSS1) ionic concentrations profile displays a consistent pattern for each of the ions measured. The concentrations are lowest in the leached soil, highest in the B horizon with a steep decrease to the C horizon where concentrations maintain consistently low values to a depth of 155 cm.

The soils in the Pine Marten Stream catchment have higher clay and silt content than the soils in Moose Pit. The water soluble ions in the soil from a silty drumlin (DRSS2) in Pine Marten catchment display a pattern of higher concentrations near the surface followed by a decrease with depth and an increase in the lower C-horizon. Chloride and sulphate maxima are near the surface, while sodium and calcium have highest values at depth. Potassium and magnesium concentrations are highest at depth, following a similar pattern to calcium.



Moose Pit Brook Catchment: Stony Drumlin (DRSS1)

Moose Pit Brook Catchment: Greywacke Clast Till (SLSS1)

Moose Pit Brook Catchment: Granite Clast Till (GRSS2)

Moose Pit Brook Catchment: Granite Clast Till (GRSS3)

Pine Marten Stream Catchment: Silty Drumlin (DRSS2)

Figure 4. 6: Soil solution depth profiles from five sampling sites.

Table 4-3: Characteristics and soil water soluble concentrations of soil samples.

Sample Identification	Soil Horizon	Soil Texture	Date Sampled	Sampling Depth	Chloride ueq/100g	Sulphate ueq/100g	Nitrate ueq/100g	Conductivity uS/cm	pH	Sodium ueq/100g	Potassium ueq/100g	Calcium ueq/100g	Magnesium ueq/100g	Bromide ueq/100g
TBA09-DRSS1E	Ae	Sandy Loam	10-Jul	-20	14.80	10.97	0.06	51.0	6.42	25.69	9.08	7.27	7.06	<0.22
TBA09-DRSS1B	Bm	Sandy Loam	10-Jul	-25	37.43	20.08	1.81	64.2	6.55	31.57	6.72	22.41	14.52	1.10
TBA09-DRSS1B/C	BC	Sandy Loam	10-Jul	-50	7.12	3.92	0.16	11.5	6.26	8.28	1.84	2.80	2.14	<0.22
TBA09-DRSS1C1	C	Sandy Loam	10-Jul	-90	3.60	3.03	0.06	6.1	5.77	5.64	0.97	1.59	0.33	<0.22
TBA09-DRSS1C21	C	Sandy Loam	10-Jul	-155	3.01	4.09	<0.064	5.9	5.71	4.65	0.50	1.45	0.32	0.22
TBA09-SLSS2B	Bm	Clay Loam	4-Aug	-20	45.67	8.93	0.32	63.9	4.46	15.52	2.92	3.10	12.04	2.63
TBA09-GRSS3E	Ae	Sandy Loam	6-Aug	-15	17.25	13.73	<0.064	74.5	4.01	31.64	8.23	3.09	7.89	<0.22
TBA09-GRSS3B	Bm	Sandy Loam	6-Aug	-25	71.31	15.24	0.61	100.8	6.68	41.41	12.48	4.19	11.03	10.76
TBA09-GRSS3B/C	BC	Sandy Loam	6-Aug	-50	23.35	0.62	0.13	19.6	5.76	15.65	3.22	2.89	2.63	0.45
TBA09-GRSS3C1	C	Sandy Loam	6-Aug	-90	8.75	10.75	0.23	14.7	5.88	18.82	1.36	2.14	0.34	<0.22
TBA09-GRSS3CR	C	Sandy Loam	6-Aug	-110	8.13	2.92	0.13	9.9	5.84	9.75	1.07	2.40	1.15	0.50
TBA09-GRSS3CW	C	Sandy Loam	6-Aug	-142	10.04	9.33	0.55	16.2	6.20	23.96	1.44	1.50	0.33	<0.22
TBA09-SLSS1B	Bm	Sandy Loam	29-Jul	-15	55.08	7.05	0.33	69.5	6.79	31.93	8.51	11.74	15.35	1.93
TBA09-SLSS1B/C	BC	Sandy Loam	29-Jul	-40	10.64	8.44	0.16	18.6	6.23	8.94	1.74	3.69	3.45	0.40
slss1ind	BCc	Sandy Loam	29-Jul	-50	9.58	4.91	0.26	14.3	6.62	6.72	1.25	2.54	1.67	<0.22
TBA09-SLSS1C1	C	Sandy Loam	29-Jul	-100	6.57	1.96	0.13	7.4	6.19	4.72	0.67	1.50	0.83	<0.22
TBA09-SLSS1C2	C	Sandy Loam	29-Jul	-130	3.55	2.04	<0.064	5.6	5.70	3.57	0.92	1.20	0.99	<0.22
TBA09-DRSS2B	Bm	Sandy Loam	7-Aug	-10	24.78	30.10	1.56	59.8	5.83	31.36	7.44	4.64	4.65	0.66
TBA09-DRSS2B/C	BC	Clay Loam	7-Aug	-30	5.42	17.30	0.45	18.6	6.16	26.22	2.05	1.90	3.62	<0.22
TBA09-DRSS2CG	C	Clay Loam	7-Aug	-110	2.95	10.76	0.16	19.6	6.68	36.82	48.28	18.66	96.78	<0.22
TBA09-DRSS2C2	C	Clay Loam	7-Aug	-130	3.78	13.86	0.39	22.7	6.70	44.44	60.95	22.35	114.01	<0.22
TBA09-GRSS2E	Ae	Sandy Loam	9-Jul	-10	12.49	8.55	<0.064	26.9	4.81	21.27	5.79	3.40	3.30	<0.22
TBA09-GRSS2B	Bm	Sandy Loam	9-Jul	-20	12.38	8.60	0.19	25.1	6.21	10.50	7.70	1.69	6.56	1.05
TBA09-GRSS2FER	Bc	Sandy Loam	9-Jul	-35	12.85	8.57	2.32	25.4	5.55	11.21	3.37	6.68	3.45	0.85
TBA09-GRSS2C1	BC	Sandy Loam	9-Jul	-50	2.65	5.24	0.10	7.3	5.29	3.04	0.92	1.70	0.33	<0.22
TBA09-GRSS2C2A	C	Sandy Loam	9-Jul	-120	3.16	4.26	<0.064	6.2	5.84	3.68	2.51	2.55	0.32	<0.22

Concentrations of bromide are above detection limits in the B horizons of many samples, but below detection limits in most other samples of this study. Nitrate concentrations are above detection limits in many of the soil horizons and display highest values in the B horizons.

The ionic concentrations shown in the profiles of Fig. 4.6 are similar to previous studies and differences between sample locations may be useful for explaining effects of soil type variations.

4.1.6 Silicate Mineral Bound Chloride in Soils and Bedrock

Soil samples from the C horizon of six pits and four bedrock samples were analyzed for total chloride content by XRF (Table 4-4) and are consistent with the range of chloride content of similar lithologies (Johns and Huang 1967). The highest total chloride occurs in biotite monzogranites, but there is a considerable variation between the two samples. The Cunard Member slate has chloride levels below detection limits. The hornfelsic greywacke also has low chloride concentration values. The C horizon chloride abundances of all the soil samples are greater than that of metasedimentary rocks, but lower than the igneous rocks.

Table 4-4: Total chloride in soil and bedrock samples.

Sample	Total Chloride (ppm)
Slate (Cunard Member)	< 10
Greywacke (Hornfelsic Government Point Member)	40
Biotite Monzogranite 1	160
Biotite Monzogranite 2	320
Granite Clast Till 2 (GRSS2C1)	100
Granite Clast Till 3 (GRSS3C1)	110
Greywacke Till (SLSS1C2)	100
Slate Till (SLSS2B)	60
Silty Drumlin (DRSS2C2)	100
Stony Drumlin (DRSS1C1)	130

4.2 Chlorine Stable Isotopes

In total, 60 chlorine stable isotope samples were analyzed with the objective of characterizing the composition of fog water, precipitation, streams, soil solution chloride and silicate mineral bound chloride. Results show significant ($\alpha = 0.05$) difference between the mean δ^{37}Cl value of rainfall (-1.51 ± 0.23 ‰) and stream water (-0.95 ± 0.13 ‰) while results from fog water (-1.08 ± 0.46 ‰) and silicate mineral bound chloride (0.04 ± 0.72 ‰) are less distinctive and show a wide range of isotopic compositions.

4.2.1 Streams

Chlorine stable isotope analysis of eleven samples from each stream have δ^{37}Cl values with a greater enrichment of light isotopes relative to seawater, (the enrichment of light isotopes is henceforth referred to as 'lighter' and enrichment of heavy isotopes referred to as 'heavier'). Moose Pit Brook samples have a range from -0.29 ‰ to -1.36 ‰ (Table 4-5) with a mean of -0.93 ± 0.20 ‰ ($\alpha = 0.05$) (Fig. 4.7). The range of Pine Marten Stream values (-0.40 ‰ to -1.41 ‰) is smaller than Moose Pit Brook (Table 4-5) and the mean is slightly lower at -0.97 ± 0.19 ‰ ($\alpha = 0.05$) (Fig. 4.7). The means and spread of chlorine stable isotope values of the two streams are the same within the precision of this study.

4.2.2 Atmospheric Deposition

The chlorine stable isotope composition of seven fog water samples have relatively large range of δ^{37}Cl values from -1.73 ‰ to -0.23 ‰ (Table 4-6). The mean with a 95 % confidence interval ($\alpha = 0.05$) of fog water analyses is -1.08 ± 0.46‰ (Fig. 4.8).

The δ^{37}Cl values of nine rainfall samples are lighter and have a narrower range (-0.79 ‰ to -2.07 ‰) than the fog water samples (Fig. 4.8). The mean δ^{37}Cl of rainfall samples in this study is -1.51 ± 0.23 ‰ ($\alpha = 0.05$). The large range of δ^{37}Cl values in rainfall is similar to the large range in chloride concentrations of rainfall.

Table 4-5: Chloride concentrations and δ^{37}Cl of stream samples. Values in bold are SMOC corrected values.

Sample type	Cl measured (μeq/L)	Raw δ^{37}Cl (‰)	Daily SMOC (‰)	**δ^{37}Cl (‰)**	Analytical uncertainty (‰)	Relative uncertainty (%)
Moose Pit Brook	84.9	-6.52	-6.05	**-0.47**	0.22	4
Moose Pit Brook	86.6	-7.41	-6.14	**-1.27**	0.22	4
Moose Pit Brook	73.9	-6.43	-6.14	**-0.29**	0.22	4
Moose Pit Brook	81.5	-7.00	-6.05	**-0.95**	0.22	4
Moose Pit Brook	90.0	-7.38	-6.14	**-1.24**	0.22	4
Moose Pit Brook	83.2	-6.89	-6.05	**-0.84**	0.22	4
Moose Pit Brook	96.7	-7.50	-6.14	**-1.36**	0.22	4
Moose Pit Brook	79.8	-6.56	-5.88	**-0.68**	0.22	4
Moose Pit Brook	109.4	-7.09	-6.05	**-1.04**	0.22	4
Moose Pit Brook	89.4	-6.97	-5.88	**-1.09**	0.22	4
Moose Pit Brook	88.0	-6.89	-5.88	**-1.01**	0.22	4
Pine Marten Stream	85.7	-6.78	-6.05	**-0.73**	0.22	4
Pine Marten Stream	72.5	-6.54	-6.14	**-0.40**	0.22	4
Pine Marten Stream	99.3	-7.04	-6.14	**-0.90**	0.22	4
Pine Marten Stream	73.9	-7.28	-6.05	**-1.23**	0.22	4
Pine Marten Stream	79.0	-7.02	-6.14	**-0.88**	0.22	4
Pine Marten Stream	75.3	-7.28	-6.05	**-1.23**	0.22	4
Pine Marten Stream	89.7	-6.67	-6.09	**-0.58**	0.22	4
Pine Marten Stream	82.4	-7.16	-6.05	**-1.11**	0.22	4
Pine Marten Stream	100.4	-6.97	-6.05	**-0.92**	0.22	4
Pine Marten Stream	92.0	-7.29	-5.88	**-1.41**	0.22	4
Pine Marten Stream	92.5	-7.20	-5.88	**-1.32**	0.22	4

The range of δ^{37}Cl values from atmospheric deposition samples collected during this study are comparable to the values of wet precipitation samples from Bay D'Espoir, Newfoundland which range from 0.0 ‰ to -3.1 ‰ and an amount weighted annual average (N=17) of -1.3 ‰ (Koehler and Wassenaar 2010).

Fig. 4.7 represents an important observation from the results of this study; the isotopic composition of stream water is distinct from rainfall. This observation implies rainfall alone does not account for all the chloride in stream water, which is consistent with observations from long term monitoring by EC.

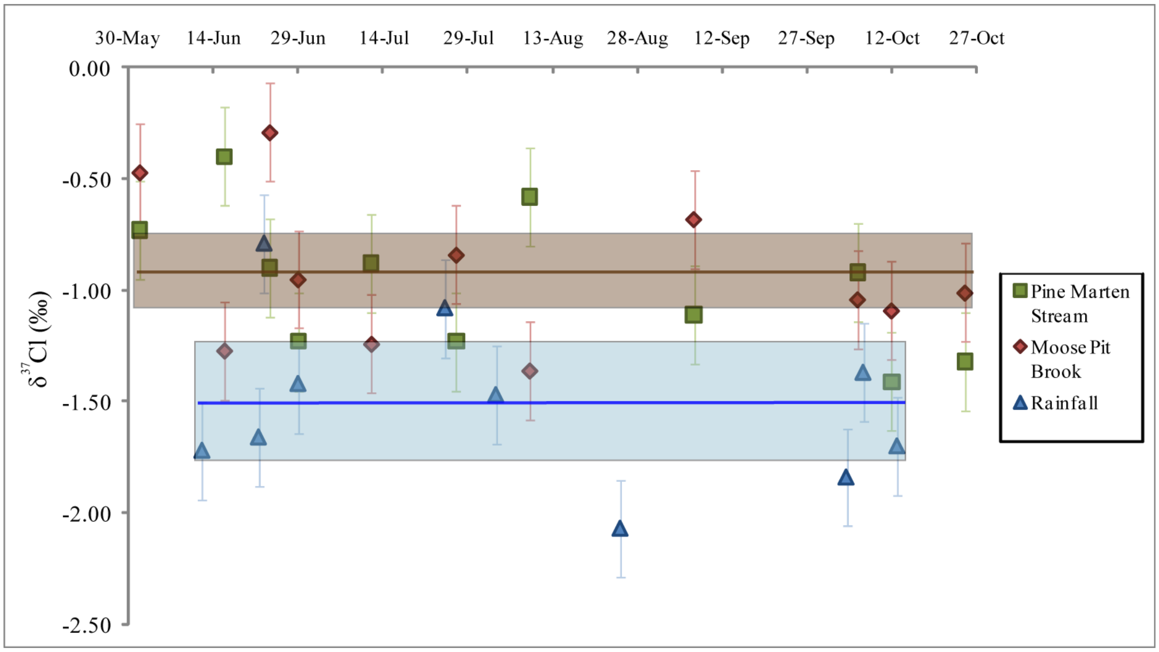


Figure 4.7: Chlorine stable isotope compositions of stream and rainfall samples with error bars representing analytical uncertainty. Colored lines with boxes represent the mean and 95 % confidence interval of the means of streams (brown) and rainfall (blue). Error bars represent analytical uncertainty based on repeat analyses of seawater samples.

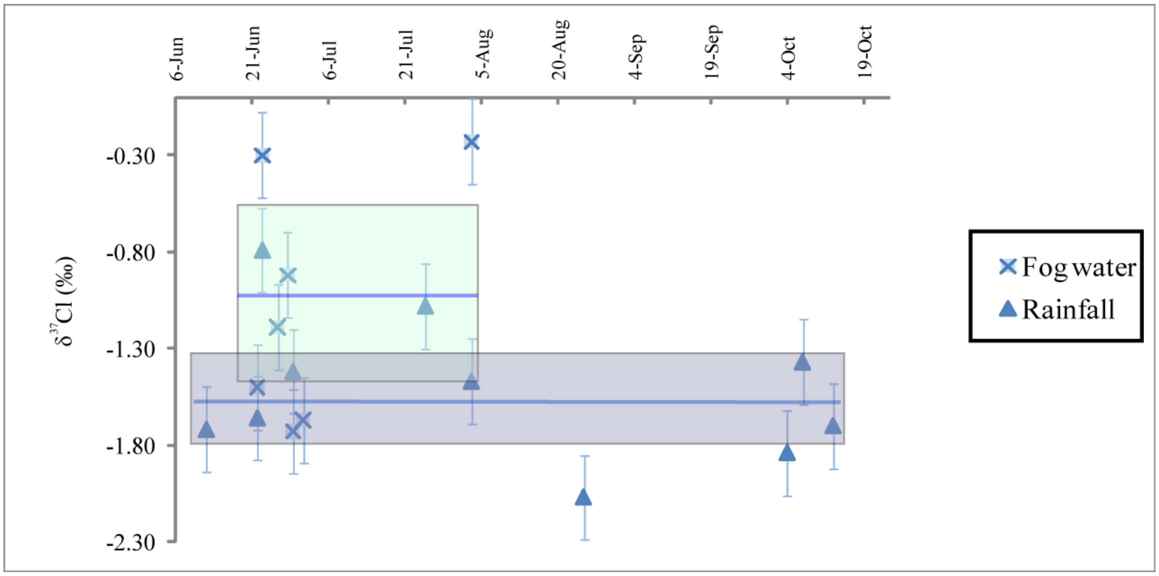


Figure 4.8: Chlorine stable isotope composition of atmospheric deposition samples during the course of the study. Blue box represents fog water 95 % confidence interval of the mean (blue line). The red line and box represent the mean and 95 % confidence interval of the mean for rainfall samples. Error bars represent analytical uncertainty based on repeat analyses of seawater samples.

Table 4-6:Concentration and δ^{37} Cl values of fog and rainwater samples. Analytical and relative uncertainties represent 1 σ of seawater analyses. Weather systems describe in section 3.1.2.

ID #	Sample type	Sampling date	Weather system	Cl ueq/L	Na ueq/L	Cl / Na	Raw δ^{37}Cl (‰)	Daily SMOC (‰)	**δ^{37}Cl (‰)**	Analytical uncertainty (‰)	Relative uncertainty (%)
9078	Fog	22-Jun	MS	n/a	n/a	n/a	-7.59	-6.09	**-1.50**	0.22	4
9079	Fog	23-Jun	MS	929.7	896.9	1.04	-6.44	-6.14	**-0.30**	0.22	4
9076	Fog	26-Jun	MS + Con	n/a	n/a	n/a	-7.28	-6.09	**-1.19**	0.22	4
9081	Fog	28-Jun	MS	94.5	100.0	0.94	-7.06	-6.14	**-0.92**	0.22	4
9080	Fog	29-Jun	MS	32.4	32.2	1.01	-7.87	-6.14	**-1.73**	0.22	4
9075	Fog	1-Jul	MS +Con	n/a	n/a	n/a	-7.76	-6.09	**-1.67**	0.22	4
9077	Fog	3-Aug	MS	n/a	n/a	n/a	-6.37	-6.14	**-0.23**	0.22	4
9064	Rainfall	12-Jun	MS + Con	26.2	27.8	0.94	-7.60	-5.88	**-1.72**	0.22	4
9065	Rainfall	22-Jun	MS	29.9	27.0	1.11	-7.54	-5.88	**-1.66**	0.22	4
9067	Rainfall	23-Jun	MS	11.0	12.2	0.90	-6.93	-6.14	**-0.79**	0.22	4
9068	Rainfall	29-Jun	MS	3.1	3.5	0.89	-7.56	-6.14	**-1.42**	0.22	4
9069	Rainfall	25-Jul	MS + Con	57.8	56.1	1.03	-7.17	-6.09	**-1.08**	0.22	4
9270	Rainfall	3-Aug	MS	n/a	n/a	n/a	-7.61	-6.14	**-1.47**	0.22	4
9070	Rainfall	25-Aug	MS	4.5	7.0	0.65	-7.95	-5.88	**-2.07**	0.22	4
9071	Rainfall	4-Oct	MS + Con	9.0	10.0	0.90	-7.72	-5.88	**-1.84**	0.22	4
9072	Rainfall	7-Oct	MS	7.6	7.4	1.03	-7.25	-5.88	**-1.37**	0.22	4
9073	Rainfall	13-Oct	MS	10.2	8.3	1.23	-7.58	-5.88	**-1.70**	0.22	4

4.2.3 Chlorine Stable Isotopes in Soil

Analyses were completed of soil solution samples of the B and C horizons of each of 6 soil sampling pits, as well as silicate mineral bound chloride (chloride released following HF dissolution) of three C horizon samples (Table 4-7). The three C horizon samples chosen for HF dissolution and analysis, (stony till drumlin, silty till drumlin and granite clast till 2) are samples selected to be representative of the different soil/till types (Fig. 4.8).

Soil solutions, extracted by immersing sieved and dried samples in water, have δ^{37}Cl values that are within a similar range as atmospheric deposition (Fig. 4.8). Silicate mineral bound chloride of two C horizon samples (silty drumlin and granite clast till) are in the same range as soil solution and meteoric water, while the silicate mineral bound chloride of the C horizon of the stony drumlin is more enriched in heavy isotopes compared to other soil samples. There is not a consistent relationship, within the analytical uncertainty, between increasing depth (from B horizon to C horizon) and change in δ^{37}Cl (Fig. 4.9). In the stony till drumlin (DRSS1) and the biotite monzogranite clast till (GRSS2) the δ^{37}Cl values of silicate mineral bound chloride are heavier than the soil solutions, and in the silty till drumlin (DRSS2) the δ^{37}Cl values of silicate mineral bound chloride is lighter than soil solution.

Table 4.7: Chloride concentrations (where applicable) and chlorine stable isotope values of soil solution chloride and silicate mineral bound chloride (HF).

ID #	Sample type	Sample Description	Sampling Depth (cm)	Cl (μeq/L)	Uncorrected δ^{37}Cl (‰)	Average SMOC (‰)	δ^{37}Cl (‰)	Analytical error (‰)	Relative error (%)
9014	Soil solution	Stony Drumlin B horizon (DRSS1)	-25	186.7	-8.04	6.45	-1.59	0.22	3
9005	Soil solution	Stony Drumlin C horizon (DRSS1)	-155	15.5	-7.93	6.45	-1.48	0.22	3
9082	Soil HF	Stony Drumlin C horizon (DRSS1)	-155	n/a	-6.48	6.83	0.35	0.17	2
9033	Soil solution	Granite Clast Till B horizon (GRSS2)	-15	62.1	-7.28	6.45	-0.83	0.22	3
9006	Soil solution	Granite clast Till C horizon (GRSS2)	-130	16.1	-7.63	6.45	-1.18	0.22	3
9083	Soil HF	Granite clast Till C horizon (GRSS2)	-130	n/a	-7.75	6.83	-0.92	0.17	2
9027	Soil solution	Hornfels clast Till B horizon (SLSS1)	-20	271.6	-7.41	6.45	-0.96	0.22	3
9008	Soil solution	Hornfels clast Till C horizon (SLSS1)	-120	17.8	-7.97	6.45	-1.52	0.22	3
9009	Soil solution	Granite Clast Till B horizon (GRSS3)	-25	356.5	-7.43	6.45	-0.98	0.22	3
9024	Soil solution	Granite clast Till C horizon (GRSS3)	-90	42.9	-7.87	6.45	-1.42	0.22	3
9028	Soil solution	Slate Clast Till B horizon (SLSS2)	-20	271.6	-7.67	6.45	-1.22	0.22	3
9013	Soil solution	Silty Drumlin B horizon (DRSS2)	-10	122.7	-7.67	6.83	-0.84	0.17	2
9042	Soil solution	Silty Drumlin C horizon centrifuged (DRSS2)	-100	n/a	-7.35	6.45	-0.9	0.22	3
9043	Soil solution	Silty Drumlin C horizon filtered (DRSS2)	-100	n/a	-7.64	6.45	-1.19	0.22	3
9084	Soil HF	Silty Drumlin C horizon (DRSS2)	-100	n/a	-7.79	6.83	-0.96	0.17	2

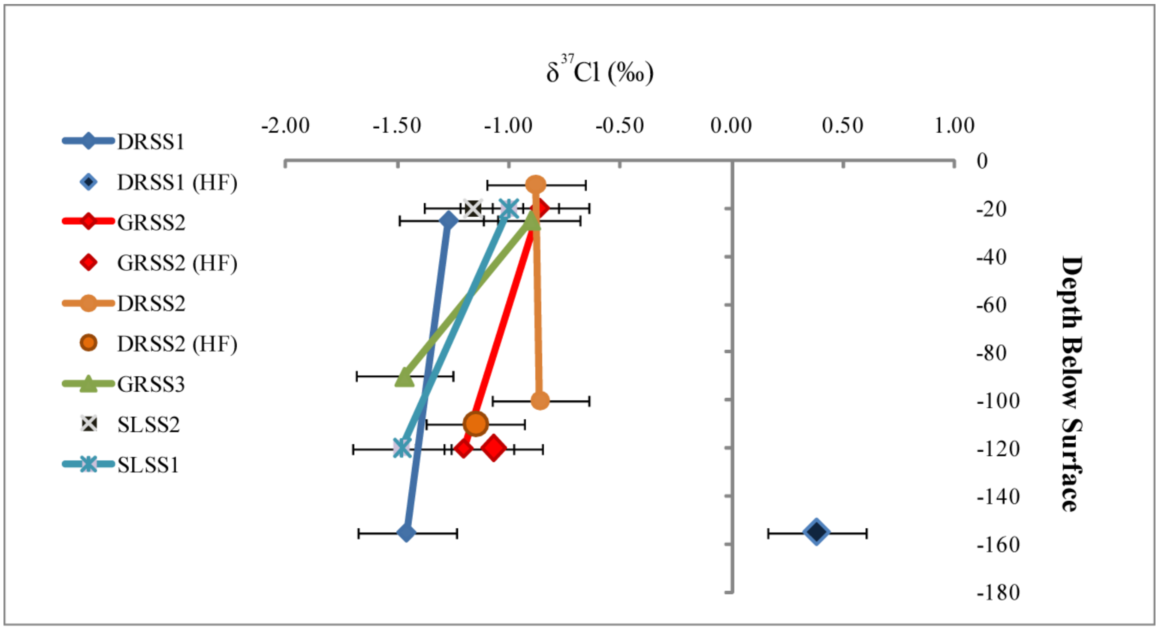


Figure 4.9: Chlorine stable isotope results of soil solution and silicate mineral bound chloride in B and C horizon samples. Stony till drumlin (DRSS1), Granite clast till (GRSS2), Silty drumlin (DRSS2), Granite clast till 3 (GRSS3), hornfels clast till (SLSS1) and Slate clast till (SLSS2). HF denotes samples subject to HF dissolution. The span of the bars represents 1 σ of all seawater analysis.

4.2.4 Silicate Mineral Bound Chloride in Soils and Bedrock

Three C horizon samples, three bedrock samples and two bedrock mineral separations were decomposed using HF and the extractable chloride was measured for chlorine stable isotope composition and the results are summarized in Fig. 4.10. Samples of the C horizon of granite clast till pit 2 (-1.07 ± 0.22 ‰) and silty drumlin (-1.15 ± 0.22 ‰) are close to the mean of stream water (-0.97 ± 0.19 ‰ Pine Marten Stream, -0.93 ± 0.20 ‰ Moose Pit Brook), while the C horizon of the stony drumlin (+0.38 ‰) is much higher than any of the aqueous samples. Like the soil sediment, the mineral bound chloride of the rock samples is enriched in heavy isotopes compared to atmospheric deposition. The hornfels sample (-0.35 ± 0.22 ‰) with a total chloride concentration of 40 ppm and one biotite monzogranite sample (-0.30 ± 0.22 ‰, 160 ppm) are more enriched in heavy isotopes than many of the aqueous samples. The other biotite monzogranite sample (0.78 ± 0.22 ‰, 320 ppm) is enriched in heavy chlorine isotopes compared to precipitation and stream water. The biotite monzogranite sample with 320 ppm was split using Franz mineral separation (1.0 mA) methods which isolated non-magnetic (feldspars and quartz) from iron rich minerals (magnetite, biotite). The splits of these samples (1.14 ± 0.22 ‰ non magnetic and 2.47 ± 0.22 ‰ magnetic) are higher than the whole sample they were split from (0.78‰) and much higher than all aqueous samples.

Average values of silicate mineral bound chloride are variable depending on which group of samples is used. If the three bedrock samples plus the mineral separations are used, the mean is +0.75 ‰. The mean of all the HF decomposition samples is +0.24 ‰, while the mean δ^{37}Cl of the three whole bedrock samples is +0.04 ‰. Using the whole bedrock samples and the C horizon samples the mean is -0.29 ‰. The uncertainties associated with these means are unstated, but large (> 10% at 1 σ) because of large ranges of values and small sample sizes.

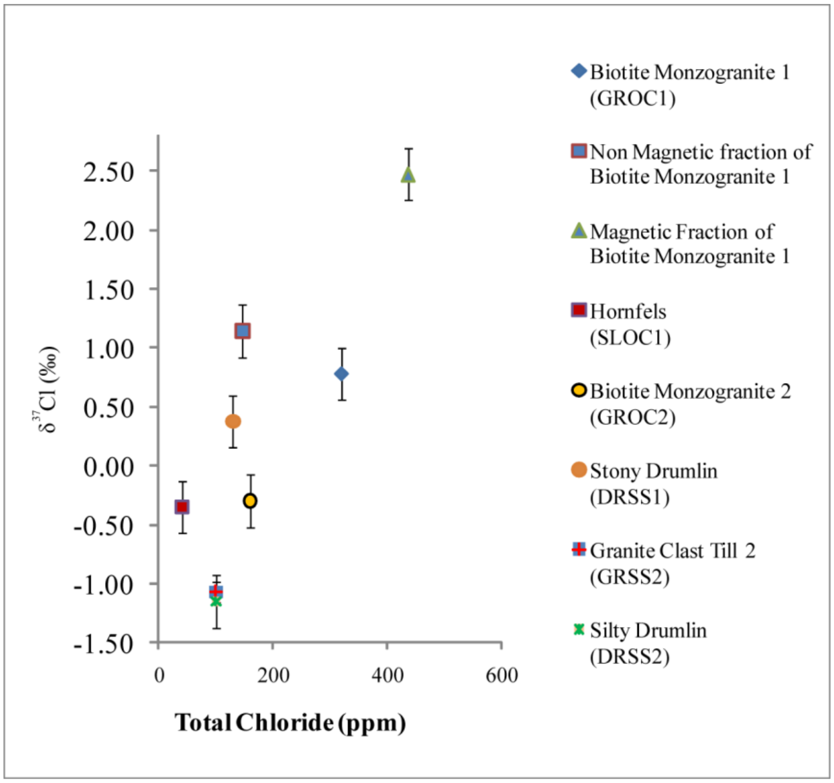


Figure 4.10: Total chloride and δ^{37}Cl in soil and bedrock samples. The span of error bars indicate analytical uncertainty.

4.2.5 Summary

Chlorine stable isotope analyses of 60 samples in this study yielded a range of δ^{37}Cl values from -2.07 ‰ to + 2.47 ‰ (Fig. 4.11). Atmospheric deposition is isotopically light with mean δ^{37}Cl values of -1.51 ‰ for rainfall and -1.08 ‰ for fog water. Stream water samples are isotopically light compared to seawater, but both streams are heavier than atmospheric deposition (Moose Pit Brook -0.93 ‰ and Pine Marten Stream -0.97 ‰). The difference between δ^{37}Cl values of rainfall and stream water indicates that an isotopically heavy source of chloride is contributing to the stream chloride budget. Soil solution samples are heavier than atmospheric deposition and similar to stream water. Silicate mineral bound chloride in soils and bedrock are isotopically the heaviest reservoirs of chloride in the system.

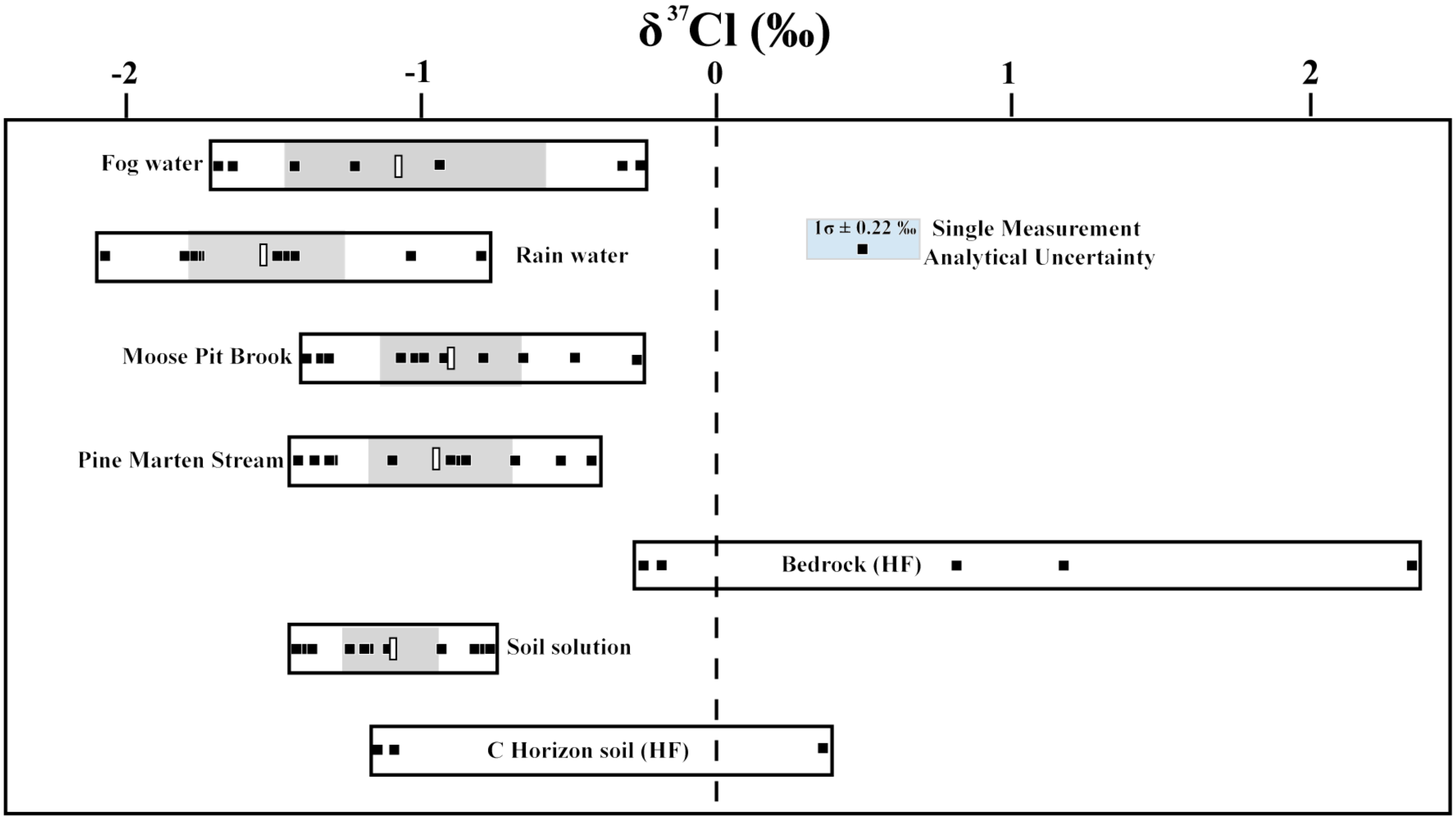


Figure 4.11: Summary of chlorine stable isotope results of this study. Small black squares represent individual samples, small white rectangles represent the mean, grey rectangles represent the 95 % confidence interval of the mean and black boxes represent the range of the samples.

Chapter 5 : Interpretation and Discussion

The results indicate that the chlorine compositions of stream water and rainfall are isotopically distinct, implying a source of chloride in stream water other than rainfall (Fig. 4.11). Assuming fog water contributes at least a small proportion to the stream chloride budget, silicate mineral bound chloride in combination with fog water appears to compensate for the disparity in δ^{37}Cl values between streams and rainfall. In an attempt to quantify the contributions from fog and rock/water interactions to the stream chloride flux of Moose Pit Brook, an isotope balance approach is used. The chloride flux attributed to rock/water interactions based on the isotope mass balance approach is compared to a chloride flux based on weathering rate release of chloride. For Pine Marten Stream catchment, a different approach is used to suggest geologic sources of chloride. This approach includes a discussion of the isotopic and ionic results of each component (fog, rainfall, soil solution, mineral chloride and streams) as well as a comparison of physical features between the two catchments.

5.1 Isotope Mass Balance

Within the constraints of this study, which include limited samples and coarse analytical precision, an attempt is made to isotopically fingerprint each chloride component and use these values in an isotopic mass balance approach. In the mass balance, the value used to represent each component is a mean value and standard error of the mean is used to represent uncertainty. The uncertainty is combined in the equations for mass balance using the rules of error propagation in Taylor (1983). To indicate the portrayal of uncertainty represented by the standard error, the standard error of the mean is compared to 95% confidence intervals for each of the components in Table 5-1.

Table 5-1: The mean values of each component with 95 % confidence intervals and standard errors.

Component	Mean δ^{37}Cl (‰)	95 % Confidence Interval (± ‰)	Standard Error (± ‰)
Moose Pit Brook	-0.93	0.20	0.10
Pine Marten Stream	-0.97	0.19	0.10
Rainfall	-1.51	0.23	0.12
Fog water	-1.08	0.46	0.23
Mineral bound chloride	0.13	0.53	0.27

Because the majority of soil and bedrock sampling occurred in Moose Pit Brook catchment, δ^{37}Cl values that represent silicate mineral bound chloride for that catchment are available, but not for Pine Marten Stream catchment. Therefore, the mass balance will consider the inputs and outputs of Moose Pit Brook catchment and Pine Marten Stream isotopic composition will be considered in relation to ionic data and in comparison to Moose Pit Brook. The mean isotopic values used for rainfall, streams and fog water are the mean of all the samples for each component. However before delving into the mass balance, it is necessary to discuss the range of δ^{37}Cl values in silicate mineral bound chloride of this study and provide reasoning for including or excluding values from the mean used for the isotope mass balance.

Chloride released from bedrock and soil samples following hydrofluoric acid dissolution represents silicate mineral bound chloride that has potential to enter stream systems via rock /water interactions. The range of δ^{37}Cl values from silicate mineral bound chloride in this study is lowest at -1.15 ‰ and highest at +2.47 ‰. The average value chosen to be used in the isotopic mass balance has a wide range depending on the values used to represent silicate mineral bound chloride (Table 5-1).

The lightest soil sourced δ^{37}Cl values are -1.15 ± 0.22 ‰ from the C horizon of a silty drumlin, and -1.07 ± 0.22 ‰ from the C horizon of a granite clast till (Table 4-7). These δ^{37}Cl values are indistinguishable from the average values of stream water. These values could represent silicate mineral bound chloride of mafic fragments incorporated into the till. Bonifacie et al. (2007) provide examples of δ^{37}Cl values from altered and glassy MORBs that are consistently lighter. Mafic clasts were not identified from the pits where the soil samples were collected, but a large exposure of a drumlin near Moose Pit Brook catchment revealed weathered basaltic clasts. Transport of these clasts from the North Mountain Basalt which lies less than 50 km to the northwest of the study area is probable given the projected glacial flow vectors of the Calendonia Phase of the last glacial period (Refer to section 2.4.2). However, another explanation of the low δ^{37}Cl values is that meteoric chloride was not completely removed from the soils during the weak acid rinsing. The rinse leachate was not analyzed for chloride content at any of the steps of rinsing. It cannot be determined which of the two explanations is most likely cause of the isotopically light values, therefore the samples will not be included in the mean value of silicate mineral bound chloride.

The silicate mineral bound chloride of a C horizon sample from the stony drumlin is enriched in heavy isotopes compared to SMOC and other C horizon samples with a δ^{37}Cl value of + 0.38 ± 0.22 ‰. The enrichment of heavy isotopes may be from chloride in minerals that contain higher proportions of ^{37}Cl, but lacking a detailed analysis, the mineral source is unknown. It seems unlikely that a non-geological source could account for the isotopic composition; therefore this value will be used in the mean of the silicate mineral bound chloride that is used for the isotope mass balance.

The hornfels δ^{37}Cl value is -0.35 ± 0.22 ‰ and the total chloride content is low (40 ppm). The protolith of the hornfels is an interbedded slate to fine grained sandstone which was deposited in the offshore of a passive margin. The chloride may have been incorporated into the sediment from seawater during deposition or it could be silicate mineral bound chloride within the sedimentary fragments. If the chloride in the hornfels has a marine source, then a δ^{37}Cl value similar to SMOC could be inferred. The slight deviation from SMOC could be a result of one of the following; fractionation during one of the stages of metamorphism, the seawater had a different isotopic composition during the Cambrian, contamination from meteoric water or the difference is not a significant deviation from SMOC. If the chloride in the hornfels is from silicate mineral bound source, the δ^{37}Cl value of the hornfels could reflect the isotopic composition of the parent material. Any of these explanations are plausible and it seems appropriate to include it in the mean of silicate mineral bound chloride.

The silicate mineral bound chloride in the two biotite monzongranite samples have distinct chlorine stable isotope compositions. The sample GROC1 is from a medium grained outcrop located within 500 m of the contact with the country rock and has lower total chloride concentrations (160 ppm) and a negative δ^{37}Cl value (-0.30 ± 0.22 ‰). The sample GROC2 has higher total chloride (320 ppm) and a positive δ^{37}Cl value (+0.78 ± 0.22 ‰), is coarse grained and is more than 1 km from the contact. Thin section observations display a higher proportion of apatite grains in the sample with the positive δ^{37}Cl values. The difference in isotopic composition of two samples from the same lithology could be a result of increasing incorporation of chloride from the country rock with decreasing distance from the contact or it may reflect heterogeneity in the pluton. The large difference in both total chloride and δ^{37}Cl values is indicative of the poor constraints achieved using only two samples to characterize the distribution of compositions that occur in chemically heterogeneous lithologies. However, for the purpose of an isotope mass balance, there is no apparent reason to exclude either of these samples from the mean of silicate mineral bound chloride.

The biotite monzogranite sample with higher total chloride (320 ppm) and heavy δ^{37}Cl (+0.78 ± 0.22 ‰) was selected as a sample to attempt to identify mineral sources of chloride within the rock. The sample was split using Franz separation to compare the δ^{37}Cl values of magnetic (biotite) minerals to non magnetic (apatite and quartz). The magnetic mineral separate has a δ^{37}Cl value of + 2.47 ± 0.22 ‰ and the non-magnetic mineral separate has a δ^{37}Cl value of + 1.14 ± 0.22 ‰. A simple isotope mass balance cannot resolve the mineral separates which in combination are more enriched in heavy isotopes than the whole rock analysis. One explanation of this is there was contamination or analytical error that overwhelmed one of the sample sets. Another explanation is the size of the sample split (37 g of each) was not large enough to account for the heterogeneities of the coarse grained biotite monzogranite. While contamination or analytical error is a possibility that cannot be definitively excluded, the bias introduced by the small sample size appears to be a reasonable explanation. If this explanation is valid, then the isotopically heavy analyses increase the range of possible δ^{37}Cl value from silicate mineral bound chloride. However, no evidence can be provided to support either explantion, therefore these values will be excluded from the optimum δ^{37}Cl value to represent silicate mineral bound chloride.

The range of δ^{37}Cl values from HF decomposition of soils and bedrock includes samples that may be influenced by meteoric water and includes samples that are inexplicably enriched in heavy isotopes. The best representation of silicate mineral bound chloride from samples collected in Moose Pit Brook is a mean of the hornfels, the two whole rock biotite monzongranite samples and the stony till drumlin C horizon, +0.13 ± 0.18 ‰ . However, a range of values including the isotopically light and heavy samples will be used to demonstrate possible ranges in the isotope mass balance.

Considering the definitions, assumptions and steps outlined in section 3.4 and in reference to the calculation details in Appendix D where the subscripts p, s and e refer to precipitation, stream and excess chloride respectively, the isotope mass balance of Moose Pit Brook is as follows:

Using equation 1:

$$\delta^{37}Cl_s = (X_p)\, \delta^{37}Cl_p + (X_e)\, \delta^{37}Cl_e$$

and the values

$X_p = 0.39 \pm 12$ % and $X_e = 0.61 \pm 8$ %, and

$\delta^{37}Cl_s = -0.93$ ‰ ± 1%, and $\delta^{37}Cl_p = -1.51$ ‰ ± 2 %,

equation 1 can be rearranged to solve for the isotopic composition of the excess chloride:

$$\delta^{37}Cl_e = -0.56 \text{ ‰} \pm 14 \text{ \%}$$

which can be estimated to be -0.56 ± 0.99 ‰.

The estimated isotopic composition of the excess chloride for each catchment is summarized in Table 5-2.

Table 5-2: Estimated isotopic compositions of excess chloride in each of the streams.

Stream Sampled	$\delta^{37}Cl_s$ (‰)	Proportional Rainfall Contribution	$\delta^{37}Cl_p$ (‰)	Proportional contribution of Excess Chloride	$\delta^{37}Cl_e$ (‰)
Moose Pit Brook	-0.93	0.39	-1.51	0.61	-0.56
Pine Marten Stream	-0.97	0.39	-1.51	0.61	-0.62

In Moose Pit Brook catchment, an assumption is made that the dissolution of halite is not a contributor to the chloride stream budget, implying the remaining chloride contributors are fog water ($\delta^{37}Cl_f$) and mineral/water interaction ($\delta^{37}Cl_w$). Another possible approach would be to assume the dissolution of halite also contributes to geologic sources of chloride and include a $\delta^{37}Cl$ value of 0 ‰ into the mass balance equation. However, Moose Pit Brook chloride fluxes are less than Pine Marten Stream (Fig. 1.1) and during base flow conditions the sodium to chloride ratio deviates further from the seawater ratio (Fig. 4.5) suggesting a minimal influence of halite. Therefore the dissolution of halite is excluded from the Moose Pit Brook isotope mass balance.

The upper and lower estimates of $\delta^{37}Cl_w$ of chloride from silicate minerals can be used to provide a range of proportions. The upper limit estimate is from bedrock plus mineral separates $\delta^{37}Cl_{ws} = +0.75$ ‰ ± 7%, and the lower limit estimate is from bedrock and soils $\delta^{37}Cl_{wbs} = -0.29$ ‰ ± 5 %. Table 5-3 provides a summary of estimated contributions from fog water and mineral/water interactions based on a range of $\delta^{37}Cl_w$ values.

When the upper limit of $\delta^{37}Cl_{ws} = +0.75$ ‰ ± 7% is used to represent silicate mineral bound chloride isotope values with $\delta^{37}Cl_e = -0.56$ ‰ ± 15 %, $\delta^{37}Cl_f = -1.08$‰ ± 3%, an estimate of the proportional contributions of fog water and mineral/water interactions can be made using equation 3:

$$X_f = (\delta^{37}Cl_e - \delta^{37}Cl_w) / (\delta^{37}Cl_f - \delta^{37}Cl_w)$$

$X_f = 0.71$ ± 18 % and $X_w = 0.29$ ± 18 %, which represent proportions of the 0.61 ± 8 % of chloride in streams that is from a source other than precipitation. This results in a lower limit estimation of chloride from mineral/water interactions at 18 ± 4 % and an upper limit estimate of chloride from fog water at 43 ± 9 %.

Using the isotopic composition of silicate mineral bound chloride most enriched in light isotopes, $\delta^{37}Cl_{wbs}$ = -0.29 ‰ ± 5 % an upper limit estimation of chloride from mineral/water interactions is 40 ± 8 % and 21 ± 4 % from fog.

The chlorine stable isotope composition thought to best represent silicate mineral bound chloride in Moose Pit Brook, the mean of the hornfels, the two whole rock biotite monzongranite samples and the stony till drumlin C horizon, is +0.13 ‰ ± 3 %. The use of the best representation produces an estimate of 26 ± 5 % of chloride in stream water results from mineral/water interactions of and 35 ± 6 % of stream chloride fluxes are from fog water deposition.

Table 5-3: Range of fog and silicate mineral bound chloride contributions to stream fluxes based on variety of silicate mineral bound chloride values ($\delta^{37}Cl_w$).

Samples included to estimate $\delta^{37}Cl_w$	$\delta^{37}Cl_w$ (‰)	$\delta^{37}Cl_e$ (‰)	$\delta^{37}Cl_f$ (‰)	X_w	X_f	Proportion of Stream Chloride from Rock/Water Interactions	Proportion of Stream Chloride from Fog	Proportion of Stream Chloride From Rainfall
Bedrock and Mineral Separates	0.75	-0.56	-1.08	0.28	0.72	0.17	0.44	0.39
All HF decomposition samples	0.31	-0.56	-1.08	0.37	0.63	0.23	0.38	0.39
Bedrock samples	0.2	-0.56	-1.08	0.41	0.59	0.25	0.36	0.39
Bedrock and soils	-0.29	-0.56	-1.08	0.66	0.34	0.40	0.21	0.39
Optimal value	0.13	-0.56	-1.08	0.43	0.57	0.26	0.35	0.39

The best estimate of chloride contributions from mineral/water interactions can be used to produce an estimate of the flux from Moose Pit Brook during the months of June to October. Using the mean value of the monthly chloride flux from Moose Pit Brook in Table 3-4 of 1.06 kg/ha/month, an estimate of 0.28 kg/ha/month could be attributed to chloride release from mineral/water interactions using the isotope mass balance approach.

5.2 Estimate of Chloride Contributions from Weathering

The isotope mass balance provides an estimate of chloride flux from mineral/water interactions. This flux is compared to an estimate of chloride flux using weathering rates calculated for Moose Pit Brook (Whitfield et al. 2006). The approach follows a methodology similar to Lovett et al. (2005), where an estimate of chloride contributions to stream water from the weathering of bedrock is based on mineral weathering estimates combined with chemical analyses of specific minerals in Deer et al. (1963). The estimated chloride weathering flux in catchments of Hubbard Brook Experimental Forest in New Hampshire is 2.8 mol Cl ha/yr which is approximately 0.1 kg/ha/yr. This represents less than 5 % of the yearly chloride catchment flux of Hubbard Brook catchments.

An estimate of chloride weathering flux for Moose Pit Brook can be made using base cation weathering rates and an approximation of chloride to base cation ratio in the bedrock and tills (Tables 5-1 and 5-2). An estimate of base cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) fluxes from weathering for Moose Pit Brook catchment provides a range of weathering fluxes based on different methodological approaches (Whitfield et al. 2006). For the purposes of this study an approximation of the smallest base cation fluxes (~ 10 mmol/m/ yr) estimated using soil profiles (Zr depletion, clay content and PROFILE model) and the larger fluxes estimated (~ 70 mmol/m/yr) from catchment based methods (MAGIC model and catchment mass balance deficit) are used to estimate chloride flux from weathering.

Table 5-1: Values used to calculate chloride flux from weathering rates.

Base Cation wt %	Base Cation ppm	Chloride ppm	Proportion of Chloride to Base Cation	Average Chloride to Base Cation ratio
10.43	104300	240	0.0023	0.0014
7.7	77000	40	0.0005	

Table 5-2: Range of chloride fluxes based on weathering rates and approximations of chloride to base cation ratios.

	Chloride to Base Cation ratio	Base Cation Weathering Rate (mmol/m/yr)	Base Cation Weathering Rate (kg/ha/yr)	Chloride Weathering Rate (kg/ha/yr)
Best approximation using both lithologies	0.0014	10	13	0.02
Best approximation using both lithologies	0.0014	70	86	0.1
Highest approximation	0.0031	10	13	0.04
Highest approximation	0.0031	70	86	0.3

Chloride to base cation ratios can be approximated by the using total chlorine results of this study (Table 4-4) and base cation analyses of biotite monzogranite of the South Mountain Batholith (Ham et al. 1990) and Cunard formation (White 2010). The mean base cation content in biotite monzogranite is 10.43 wt % or 104300 ppm and in the Cunard formation base cations comprise 7.7 wt % or 77000 ppm. From the results of this study, the total chloride content of hornfelsic Cunard is 40 ppm and the average total chloride of two biotite monzogranite samples is 240 ppm. It is assumed that the proportion of chloride to base cations in the bedrock of Moose Pit Brook catchment is representative of tills in the catchment and the release of chloride and base cations during weathering processes occurs at the same rate. It is also assumed that the Cunard rocks and biotite monzogranite contribute equally to the weathering flux of the catchment, resulting in a chloride to base cation ratio 1.4 x 10^{-3} part chloride to 1 part base cation. Using the best approximation of chloride to base cation ratio (Table 5-2) and the weathering rate estimates, a probable range of chloride fluxes are 0.02 kg/ha/yr to 0.1 kg/ha/yr. However, an upper limit estimate of chloride flux can be calculated by using the highest chloride concentratio (320 ppm) in a bedrock sample and assuming that all the flux is coming from the weathering of material with ratio of biotite monzogranite. This upper limit estimate is 0.3 kg/ha/yr. These are first order estimates and not meant to represent a precise description of chloride flux values, but they offer a basis of comparison for the flux estimated from the isotope mass balance.

The largest chloride flux estimate from the weathering rates is 0.3 kg/ha/yr and more reasonable estimates are an order of magnitude less. Yet the best approximation of a monthly chloride flux for the months of June to October is 0.3 kg/ha/month based on the isotope mass balance approach. Even if a large portion of weathering flux occurs during summer months, the monthly rate is greater than the reasonable yearly rates. This disparity implies either an underestimation of weathering rate flux, a process that could release chloride from geological materials at a different rate than the weathering rate of base cations, or an over-estimation of chloride flux using the mass balance approach.

The use of isotope mass balance equations is an attractive method to quantify relative contributions of sources of chloride. However, it appears to contradict the chloride flux estimate based on weathering rates. The estimate of the chloride flux using the base cation weathering rates and the proportions of chloride to base cations in bedrock could be underestimated as a result of a flawed approach. First, the range of base cation weathering rates provided by Whitfield et al. (2006) are large, reflecting the uncertainty in weathering rate estimates which could produce inaccurate estimates. Second, the ratios of chloride to base cations are from only three samples within Moose Pit Brook catchment while the mean base cation values are approximated from the samples across the South Mountain Batholith. A ratio produced by such different sample populations could introduce a large error. However, only when the highest ratios and weathering rates are used to estimate a chloride flux, does the flux become comparable to the flux estimate from the isotope mass balance. The extreme measures needed to resolve the inconsistency indicates that either some biophysical process may release chloride from bedrock and soils at different rates than the base cations, or the isotopic mass balance approach may be overestimating the chloride flux from geological materials.

The chloride flux estimate derived from weathering rates assumes that chloride is released from soils and bedrock at the same rate. This assumption could be invalid if the weathering rates of minerals hosting chloride are different from the weathering rates of minerals with base cations. This study did not include an investigation of mineral hosts of chloride, but biotite, apatite and fluid inclusions in quartz are the most likely (Refer to section 1.1.2). The minerals hosting the majority of base cations are feldspars in the biotite monzogranite. If the weathering rate of chloride hosting minerals is greater than base cation hosting minerals, the chloride flux based on weathering rates could be under estimated. This is possible considering the phosphate minerals are more soluble than feldspars and the weathering of micas can occur at a greater rate than feldspars. Also, if ion retention and release rates in soils are different for base cations and chloride, then the chloride flux estimate using weathering rates could be inaccurate.

An over-estimate of the chloride flux using the isotope mass balance approach could be produced from inaccurate characterization of the components or by not including all sources of chloride in the mass balance equation. An inaccurate characterization of the δ^{37}Cl values of the components could produce an over-estimate of chloride flux. For instance, the mean δ^{37}Cl value of selected samples was used, but if the apparent linear trend of δ^{37}Cl values and chloride concentration in Fig. 4.10 is a result of mixing between two end members, then a heavier value could be used to represent silicate mineral bound chloride. A heavier value would result in a lower estimation of chloride flux using the isotope mass balance approach. If significant sources of stream water chloride are not included in the isotope mass balance, an overestimation of chloride flux from geologic materials could occur. Potential sources of stream chloride that are not included in this study are dry deposition and biological chloride. Dry deposition is composed at least partly of marine aerosols and marine aerosols have been identified as a source of chloride enriched in heavy isotopes (Volpe and Spivack 1994). Biological cycling of chloride can contribute significantly to stream chloride fluxes (cf. section 1.1.3) and the mineralization of chloride from organic matter may be a source of chloride enriched in heavy isotopes (cf. 1.3.7). If sources of heavy chloride have been omitted from the isotope mass balance, then the chloride flux attributed to silicate mineral bound chloride is over estimated.

It is unclear which factors or combination of factors account for the discrepancy between the chloride flux estimates based on weathering rates and the chloride flux estimates based on the isotope mass balance approach. Further investigations of chlorine stable isotopes in dry deposition and biological cycling of chloride may provide insight to the discrepancy.

The best estimate of chloride flux from silicate mineral bound chloride is 26 % of chloride in stream water of Moose Pit Brook. While this estimate may be inflated as a result of the sampling and analysis constraints of the study, it implies a significant flux of stream chloride is not accounted for by atmospheric deposition. This implication suggests that chloride in stream water may not be a valid proxy for marine-derived sulphate in southwestern Nova Scotia.

5.3 Pine Marten Stream

Discussion of stream isotopic results, ionic results and the physical features of the two catchments are presented in the context of a hypothesis that the sources of excess chloride to Pine Marten Stream are different from those of Moose Pit Brook. This is followed by a discussion of isotopic results that are not directly applicable to identifying sources of chloride to stream water and a discussion of methods.

5.3.1 Isotopic Composition of Pine Marten Stream

The mean and range of δ^{37}Cl values from Pine Marten Stream samples are similar to Moose Pit Brook (Fig. 4.10), but are slightly lighter, although not significant. The proportional contribution of wet deposition chloride flux to stream chloride flux is estimated to be the same as Moose Pit Brook during the study period (Table 3-4). The fog water and rainfall samples collected for isotopic analysis are from locations near to both catchments (Fig. 1.2). It is assumed the similar topography and similar distance from the ocean of the two catchments would result in the isotopic composition of atmospheric deposition being the same for Pine Marten Stream catchment as Moose Pit Brook catchment. However, this assumption could be validated by sampling of atmospheric deposition within both catchments. The same mass balance approach used for Moose Pit Brook is applied to Pine Marten Stream to estimate the isotopic composition of the excess chloride (Appendix 4). An estimate of the δ^{37}Cl value of the geological chloride in Pine Marten is + 0.01 ‰ ± 27 %. The uncertainty is extremely large, restricting the reliability of the estimate, but the value is indistinguishable from what would be expected from the dissolution of halite. This provides a testable hypothesis for future investigations of chloride in Pine Marten Stream catchment and it does not contradict the working hypothesis of dissolution of halite being the source of the geological chloride.

5.3.2 Comparing Ionic Fluxes of the Two Catchments

The chlorine stable isotope data of this study is effective at characterizing differences in chloride of atmospheric deposition, streams and geologic chloride, but within the precision of the results, the chlorine stable isotopes do not indicate a difference between the two streams. However, a comparison of ionic fluxes and concentrations between the two catchments suggests different sources of chloride. Long term average fluxes from the catchments show that the flux of chloride from Pine Marten Stream is consistently greater than Moose Pit Brook (Fig. 1.1). For example, in a comparison of yearly fluxes, Pine Marten Stream mean flux is 36 kg/ha/yr and Moose Pit Brook mean flux is 28 kg/ha/yr. In keeping with observations from the long term monitoring data set, a similar observation is made when comparing the mean monthly fluxes from June to October. From Table 3-4, the mean monthly flux from Pine Marten is 1.5 kg/ha/month and Moose Pit Brook is 1.1 kg/ha/month. If the atmospheric deposition is the same for the two catchments, then the difference must be due to a terrestrial source.

Assuming the atmospheric deposition to both catchments is adequately represented by the measured wet deposition and fog water, differences between streams ionic output are interpreted to reflect differences within the catchments. The calcium input from atmospheric deposition is minimal; while the atmospheric deposition of sulphate contributes a large proportion to the stream fluxes (Figs. 4.2 and 4.3). Geological sources of calcium would primarily be derived from the weathering of feldspars and/or from the dissolution of gypsum. Geological sources of sulphate would come from the weathering of sulphide minerals and/or dissolution of evaporites. The calcium and sulphate concentrations and fluxes of the two catchments are comparable, but examination of relationships between the two ions offers potential for speculation of different sources for each catchment. The stronger correlation between calcium and sulphate in Pine Marten Stream compared to Moose Pit Brook (Fig. 4.4) suggests the release of the two ions may occur during the same processes for Pine Marten Stream catchment, but are decoupled for Moose Pit Brook catchment. The slope of the trendlines of Pine Marten Stream (3.9) and Moose Pit Brook (2.9) are also different from one another, suggesting different sources for either or both calcium and sulphate (Fig. 4.4B). The bedrock, regolith and tills of Moose Pit Brook have a high proportion of plagioclase rich biotite monzogranite, which is a source for calcium, and it also has sulphide rich, hornfelsic, bedrock and till fragments. The weathering of bedrock and tills in Moose Pit Brook would produce both calcium and sulphide, but perhaps at different rates and time periods. The bedrock, regolith and tills of Pine Marten Stream have sulphide rich metasedimentary rocks, similar to the protolith of Moose Pit Brook, which are likely a source of sulphides. However, Pine Marten Stream catchment is lacking an identifiable source of calcium, yet the flux of calcium from Pine Marten Stream catchment is similar to Moose Pit Brook. Therefore a source of calcium to Pine Marten Stream catchment other than what is represented by the bedrock and locally derived tills must be present within the catchment, potentially the dissolution of gypsum. The differences in the tills and bedrock, along with ionic flux observations from long term monitoring offer grounds for speculation that the fluxes from Pine Marten Stream may be influenced by the dissolution of evaporites.

Atmospheric deposition is a major source of both sodium and chloride for both catchments (Fig. 4.3), yet the fluxes of these ions are different for the two catchments. The correlation between chloride and sodium in yearly fluxes and concentration of individual samples is stronger in Pine Marten Stream than Moose Pit Brook, but the slopes are essentially the same suggesting that both catchments are controlled by similar inputs, predominantly seawater or halite. However, the intercept on the y-axes (sodium) is higher for Moose Pit Brook (3.4 kg/ha/yr) than Pine Marten Stream (2.8 kg/ha/yr). Also, Fig. 4.4 shows the variation in sodium to chloride ratios as monthly averages. During the summer months when baseflow has a larger influence on stream fluxes, the ratio of Pine Marten Stream approaches that of seawater, suggesting a halite source. The sodium to chloride ratio of Moose Pit Brook increases during baseflow conditions implying weathering of biotite monzogranite has more of an influence on the stream flux. These ionic relationships, coupled with the observation that both sodium and chloride fluxes are greater in Pine Marten Stream suggest that Pine Marten stream catchment has a larger influence from halite dissolution.

Differences of ionic fluxes of the two catchments suggest that dissolution of evaporites may have a larger influence on Pine Marten Stream catchment than Moose Pit Brook catchment. This is supported by observations from Rogers Brook catchment near Pine Marten Stream catchment, which display higher pH and higher calcium fluxes than surrounding catchments (Yanni 1995). These conditions permit buffering of acid water to an extent where it is a preferential and protected catchment for aquatic life. These favourable conditions have been suggested to be a result of the dissolution of evaporites entrained in the surrounding drumlins (Clair et al. 1989).

5.3.3 Influence of Catchment Physical Features on Chloride Fluxes

Field observations, soil sampling, geological features and hydrological data indicate that the two catchments of this study have different physical features which may provide a mechanism to explain the different chloride outputs of the streams. A general characterization of the two catchments could describe them as thin soils and tills in between large drumlins. However, an examination of some of the details of the catchments reveals important differences. The primary difference in physical features that could influence stream chemistry is the grain size distribution of soils and tills of the two catchments. Field observations and soil sampling allowed observation of sandy, well drained soils in Moose Pit Brook, while observations in Pine Marten Stream catchment showed silt and clay rich soils.

The difference in grain size controls the permeability of the soils which could influence stream chemistry in two ways; change the soil / water interactions and change the bedrock / water interaction. The moderately permeable soils of Moose Pit Brook permit greater infiltration of water to the soils than in Pine Marten Stream catchment where the clay rich soils would facilitate shallower throughflow, which is a possible explanation of the longer mean transit time (Godsey et al. 2010) and larger proportion of baseflow. The greater permeability of soils could also influence the likelihood of evaporite dissolution contributing to the stream water. Glacial erosion and dispersion of evaporite deposits from the Windsor Basin or other Carboniferous basins could have incorporated evaporite clasts into the drumlins of southern Nova Scotia. If it is possible that evaporite clasts were incorporated into the drumlins and exposed to meteoric water for the past 14,000 years, the likelihood of them still influencing stream chemistry would be partly controlled by the soil permeability. Therefore, the sandy, well drained soils of Moose Pit Brook may have permitted the rapid dissolution of entrained evaporite clasts resulting in little to no current contribution to the stream flux. The lower permeability of the clay rich Pine Marten Stream soils may permit a slower, longer lasting dissolution of evaporites that may still influence stream chemistry.

Differences between the catchments in both soil permeability and the underlying bedrock likely produce very different situations of bedrock and water interactions. The low permeability soils of Pine Marten Stream catchment would decrease the volume of meteoric water that could reach the bedrock. The bedrock of Pine Marten Stream catchment is one lithology that is in the limb of an anticline (Fig. 2.6). The meteoric water that would reach the bedrock may have some pathways to allow water interaction with the bedrock such as small fractures and cleavage, but as a whole the bedrock and meteoric water interactions would be limited. The moderate permeability of the soils in Moose Pit Brook catchment would permit a larger proportion of meteoric water to reach the bedrock surface. The bedrock of Moose Pit Brook catchment comprises two lithologies with an intrusive contact bisecting the catchment. Regional bedrock mapping infers the trace of a regional scale fault zone to the north west of the catchment. Field observations of jointed and fractured igneous rocks as well as the regional scale features indicate the bedrock is likely more fractured than the bedrock in Pine Marten Stream catchment. The increased permeability of the soils in Moose Pit Brook would provide a mechanism for greater till and bedrock interaction with meteoric water than in Pine Marten Stream.

A comparison of hydrological properties suggests a difference in physical features of the catchments. Moose Pit Brook has a larger proportion of baseflow and a longer mean transit time than Pine Marten Stream catchment. A difference in the area of the catchments is a feature that could influence mean transit time and baseflow without influencing the stream chemistry. However, the difference in baseflow, coupled with the observations of soil and bedrock features indicates that different physical features may be impacting processes that influence stream water chemistry.

In Pine Marten Stream catchment, a set of observations are consistent with the possibility that the dissolution of halite may contribute to its stream chloride output. The first observation is the higher chloride outputs of Pine Marten Stream than Moose Pit Brook. Assuming the atmospheric deposition of the two catchments is the same, the disparity between the two catchments must be due to a terrestrial source. The bedrock and surficial deposits of the two catchments are considerably different with potential for distinct geochemistry and hydrology. In addition, catchments nearby Pine Marten Stream catchment have anomalous stream chemistry attributed to the dissolution of evaporites

(Clair et al. 1989). If Pine Marten Stream catchment has a halite source of chloride, it would likely have an isotopic composition similar to SMOC. The best estimate of a δ^{37}Cl value for non-atmospheric chloride in Pine Marten Stream catchment is -0.04 ‰ ± 14%, which is indistinguishable from SMOC. In summary, a halite source of chloride for a portion of Pine Marten Stream output is clearly possible and this hypothesis merits further investigation and provides a reason to caution the use of chloride as conservative tracer ion in this catchment.

5.4 Additional Results

Many of the observations and results of this study fit into the context of determining stream chloride sources. Some results do not directly relate to the specific problem of the study, but nevertheless merit a brief discussion. This includes a discussion of the isotopic composition of atmospheric deposition and the isotopic composition of soil solutions. This is followed by discussion of the methods used during this study including sample collection, preparation and analysis.

5.4.1 Isotopic Composition of Atmospheric Deposition

Atmospheric deposition samples from this study include chlorine stable isotope analysis of 10 rainfall with δ^{37}Cl values between – 2.07 and -0.79 ‰ and seven fog water samples with δ^{37}Cl values between -1.73 and -0.23 ‰. A detailed account of processes that contribute to the enrichment of light isotopes in precipitation is provided in Koehler and Wassenaar (2010). In brief, chloride in marine generated aerosols can be volatilized by $HNO_{3(g)}$ and $H_2SO_{4(g)}$ to produce isotopically light $HCl_{(g)}$ which is quickly dissolved in rainwater and deposited as isotopically light precipitation. Due to the removal of isotopically light HCl, the remaining marine aerosols become isotopically enriched (Volpe and Spivack 1994). Evidence of atmospheric chloride enriched in heavy isotopes was not observed during this study, likely a result of sampling only wet deposition.

Rainfall samples of this study are enriched in light isotopes which is consistent with results from Koehler and Wassenaar (2010). The range of values depicts summer time rainfall with different proportions of isotopically light HCl. Many of the samples were collected during rainfall events when the weather system was predominantly

Atlantic Ocean sourced, while two samples were collected from weather systems that passed over the eastern United States. There is a lack of correlation between increasing enrichment of light isotopes with continental influence of weather systems (Table 4-6). However, sampling over longer time periods and more detail portrayals of weather systems and air pollution outputs may be useful to explain variations in the chlorine stable isotope composition of rainfall.

Fog water samples of this study are higher in chloride concentration and are enriched in heavy isotopes compared to rainwater samples (Fig. 4.11). The negative δ^{37}Cl values indicate the fog events sampled likely contain volatilized HCl from marine aerosols. Assuming marine aerosols are close to SMOC or enriched in heavy isotopes (Volpe and Spivack 1994) the higher chloride concentration and higher proportion of heavy isotopes in fog samples compared to rainwater suggest the fog deposition has a greater influence of marine aerosols. The high degree of variability of δ^{37}Cl values in fog water is consistent with the high variability of chloride concentration of these samples and previous work (Reynolds et al. 1997). While the mean of seven samples with a large range of concentration and δ^{37}Cl values does not provide a complete characterization of fog deposition, the results are not anomalous compared to the rainwater samples or what would be expected from previous studies, therefore no reason exists to invalidate these results.

The variability of chlorine stable isotope compositions in atmospheric deposition reflects the dynamic systems that control this flux of chloride and exemplifies the complexity of these systems. However, the range of values presents an opportunity to thoroughly investigate patterns and explain processes that control chlorine stable isotope variation in atmospheric deposition.

5.4.2 Isotopic Composition of Soil Solutions

Soil solutions of B and C horizons from five soil pits produced δ^{37}Cl values that fall within the range of atmospheric deposition, indicating that meteoric chloride is the dominant source in soils up to a depth of 1.7 m. The analytical uncertainty of the measurements produces ambiguity in the variations with depth. However, if the reported are taken at face value, a few trends can be identified. Results from the Silty Drumlin, both the Granite Clast Tills and the Hornfels Clast Till all display a trend of decreasing δ^{37}Cl values with depth, while the Stony Drumlin displays increasing δ^{37}Cl values with depth (Fig. 4.9). The samples were collected at different times during the summer, introducing the variable of different cumulative atmospheric deposition and differences in duration since atmospheric deposition events. These temporal differences make interpretations of depth patterns based on physical and chemical properties of the soils difficult. Considering the overall distribution of soil solutions, it appears that meteoric chloride controls the isotopic composition of the soils. Evaporite sources of chloride were not directly identified in the upper portions of the tills. The chloride in these soil samples does not appear to be a source of chloride, but rather is an intermediate host of meteoric chloride within the hydrologic cycle.

5.4.3 Lower than Average Chloride Concentrations in Stream Water

Chloride concentrations of stream water samples collected during this study are less than the monthly averages for both streams (Figs 4.1C and D). The rainfall volume during the study was greater than normal, and the concentration of the majority of rainfall samples was lower than average. An examination of correlation between monthly rainfall volumes and average stream chloride concentration ($R^2 < 0.05$) over a period of 15 years or more reveals no relationship between months with high rainfall and low stream chloride concentrations. A lack of correlation is somewhat unexpected because it seems reasonable to postulate that an increase in rainfall would result in a dilution of stream water by preventing concentration of meteoric chloride in soils. However, processes such as soil retention of chloride (Chen et al. 2002) or incorporation or ‘pre-event’ water which contribute to the dampening of the atmospheric chloride signal in streams (Kircher et al. 2000, Neal and Kirchner 2000) could also disturb the connection between high rainfall and low chloride concentrations.

Perhaps biological cycling could account for the lower than average stream chloride concentrations during this sampling period. Logging of forests within both catchments has occurred during the past ten years, disturbing the steady state of biomass needed to assume no net flux of biological chloride. In vegetation manipulation experiments of catchment deforestation, Lovett et al. (2005) observe a dramatic increase in chloride outputs following deforestation and the increased chloride outputs remained elevated for four years. Four years following the deforestation, chloride outputs were less than the output of undisturbed catchments including a seasonal pattern of low chloride output in summer which was not present in undisturbed catchments. The lower chloride output is attributed to an increase of vegetative uptake of chloride as the forest recovers. This process may be affecting the chloride outputs of Moose Pit Brook and Pine Marten Stream, but no direct evidence is provided to substantiate this. The impact of vegetative uptake on chlorine stable isotopes is not known and may provide an opportunity for research to quantify biomass accumulation of chloride and contribute to the discussions (Öberg 2002) regarding the impact of biological cycling of chloride on the ‘conservative’ nature of chloride in the hydrological cycle.

5.5 Sampling and Analytical Methods

Through the implementation of sampling, preparation and analysis of this study, a series of observations were made that highlight areas for improvement for future studies. A discussion of fog sampling methods and isotopic analysis is provided to clarify sources of error and uncertainty, as well as provide insight for further investigations.

5.5.1 Fog sampling

The fog interception screen used for this study was a rudimentary device that effectively sampled fog water during ideal conditions. Advantages of using this system include the limited cost (< $100), ease of transport and set-up. The required equipment fits easily into most small cars and could be carried distances of kilometers, if needed. One person can quickly (<15 minutes) set-up the screen once the optimum site procedure has been established. Short comings of the apparatus include inefficient sampling and contamination effects. More than 10 fog events occurred at the field area during the sampling season where no sample was collected because of the inefficiency of the sampler. As a result of the high drip threshold of the screen a substantial volume of water is needed to be on the screen before the mass of the water droplets overcomes the tension keeping the water suspended on the screen. Ionic results of the process blanks of the fog interceptor show chloride concentrations 2 to 3 times greater than detection limits were being washed off the screen prior to sampling. This is likely a result of incomplete rinsing of the screen between sampling events. The double screen hinders a complete rinsing with a spray bottle, indicating a more thorough method of cleaning the screen is needed to prevent contamination.

Future fog sampling studies should consider the costs and benefits of using a simple fog sampler such as the one constructed for this study. A more elaborate system with a cooled metal plate to facilitate the condensation of fog water would address the efficiency issue, but may not be ideal because it would sample moisture other than the intended fog water. Active fog water sampling devices with a fan forcing air past suspended Teflon strings (Demoz et al. 1996) designed at Caltech (Caltech Active Strand Cloudwater Collector, CASCC) have shown to be effective instruments. Variations of the CASCC can segregate different sized fractions of water droplets which could be useful in detailed studies of the chlorine stable isotope composition of fog water. The cost of this method would likely be higher, but it may address the issues of efficiency and contamination that were observed with the fog screen.

Despite the disadvantages of the methods outlined, the method and apparatus has proven to be effective to collect inland fog samples to evaluate the contributions of fog chloride to stream water. The sampling of fog water in Southwestern Nova Scotia is an improvement on the previous estimates of inland fog water deposition which were based on fog sampling near the Atlantic Coast (Yanni et al. 2000). The analyses of the chlorine stable isotope composition of fog water in this study is the first reported and signifies a contribution to the developing literature of chlorine stable isotopes and displays an opportunity to contribute to understanding atmospheric cycling of chloride.

5.5.2 Chlorine Stable Isotope Analysis

Concerns and challenges encountered during the sample processing and isotopic analysis illustrate opportunities for refinement in methodology. Improvements in the methodology of chlorine stable isotope analysis of this study could be implemented by investigation of potential fractionation processes during sample preparation, the use of process blanks and effective use of standards.

One of the processes known to fractionate chlorine stable isotopes is the volatilization of HCl (Volpe et al. 1998, Koehler and Wassenaar 2010). In two separate steps of sample preparation, potential volatilization occurred that was not controlled or tested for fractionation effects. Potential for fractionation occurred as HNO_3^- was added to a chloride bearing solution and the solution was heated to 80°C. Future studies should consider including experimental design to test if these steps produce an enrichment of isotopically heavy solution as a result of HCl volatilization. The ion fractionation experiment carried out in this study to test the filtering methods used was not conclusive, but displayed proof of concept of fractionation during filtering through a clay membrane using a pressure gradient. A more detailed investigation of this experiment could improve future methods.

The method of HF decomposition of silicate samples was not tested for contamination of samples by the use of process blanks. In this study, it was assumed the acids would not contribute to the chloride content of the AgCl extracted from solution. However, the grade of HF used for silicate decomposition states the chloride content is < 5 ppm. If the acid contained up to 5 ppm, and complete transfer of chloride from HF to the sample precipitate occurred, a systematic error could have been introduced. For example, the largest volume of HF used was 180 mL, which could contain up to 30 µmol of chloride. The same sample contained 115 µmol of chloride which means 26 % of the AgCl extracted for analysis could have come from the HF. Process blanks of a volume of HF could be used to evaluate the effects of this method.

The analytical process used to evaluate Standard Mean Ocean Chloride (SMOC) resulted in incomplete and ineffective evaluation of analytical precision. The analytical uncertainty in the measurement of samples is a nested design with three levels of uncertainty. Internal reproducibility of the instrument is tested daily by automated injections of the laboratory standard CH_4Cl gas and this method of testing internal precision of the instrument is effective. Two different measures of uncertainty could be attained by repeated injections of seawater samples. Repeat injections of individual seawater samples could provide a measure of uncertainty which would represent the variability associated with manual injections. Analysis of replicate seawater samples would provide a measure of uncertainty representing the variability of sample preparation. If each of these is adequately known, an analysis of error could be properly undertaken. During the course of this study, a well defined system of seawater replicate analysis was not implemented. For example, on some days only two seawater samples were analyzed, with different number of repeat injections. The distribution of the results in some cases did not approximate a normal distribution, but rather a bimodal distribution. This makes the daily estimate of the standard deviation unlikely to represent the true analytical uncertainty. Also, three seawater samples were analyzed on separate days, while the remaining five were only analyzed on single days (Table 3-3). The stated analytical uncertainty in this study is the mean of eight seawater means, which is the best approximation of uncertainty reflecting repeated injections and sample preparation. However, because of the weak analytical design, a complete quantification of the individual sources of error is problematic. In order to fully evaluate the levels of uncertainty in this nested design, numerous seawater samples should have been analyzed daily. A more effective approach would have been to use 10 to 20 seawater samples that could have each been analyzed each day.

The lab standard of methyl chloride gas (CH_4Cl) is used as the internal reference standard for the instrument. Manual injections of CH_4Cl are also used to evaluate the variability of $\delta^{37}Cl$ values produced by differences in the volume of sample injected. In previous studies (Wassenaar and Koehler 2004, Shouakar-Stash 2008) a strong linear correlation ($R^2 > 0.95$) was observed between increasing area under the major curve (representing $CH_3{}^{37}Cl$) and increasing $\delta^{37}Cl$ values. This linearity was used as a correction on all samples analyzed. However during the course of this study, the correlation was not as strong (R^2 ranging from 0.53 to 0.88) and as a result introduced a measure of uncertainty that was greater than the error being corrected. This failure to optimize the linearity is likely a major contributor to the high level of analytical uncertainty (0.22 ‰) compared to recent publications (< 0.10 ‰) (e.g Godon et al. 2004a, Wassenaar and Koehler 2005).

Optimization of the instrument also occurs with adjustment of the intensity of the ion beam in the mass spectrometer. Tuning of the instrument (changing the current) between the first day of analysis and the second, may have improved the instrument precision, but also introduced a measure of uncertainty in the population of measurements that has not been properly evaluated.

Chapter 6 : Conclusion

The primary objective of this thesis was to identify and quantify sources of stream chloride in excess of rainfall contributions using ionic and isotopic data in conjunction with a detailed investigation of geological features of the catchments of interest. Previous to this research, it was unclear if significant differences in the isotopic composition of natural stream waters and atmospheric deposition would permit the use of chlorine stable isotopes to distinguish between sources of chloride. An important result from this study indicates stream water of these two catchments, during baseflow conditions, has a distinct isotopic composition from rainfall permitting further investigation of sources of the excess chloride using chlorine stable isotopes. Using long term monitoring fluxes and an isotopic mass balance approach, the best estimate of the sources of chloride to Moose Pit Brook catchment for the months of June to October are 39 % from rainfall, 34 % from occult deposition and 27 % from mineral/water interactions, with an error of ± 10 % for each of the components. In the case of Pine Marten Stream catchment, differences in the ionic fluxes and physical characteristics compared to Moose Pit Brook catchment indicate distinct geological sources of chloride that are not apparent using isotopes alone.

The conclusion of a significant geological source of chloride questions the use of chloride as a marine tracer ion. Specifically within these catchments, chloride has been used as a marine tracer and proxy to estimate the quantity of marine sulphate in stream water and distinguish it from anthropogenic atmospheric pollution. If the conclusions of this study are accurate, the proportion of stream sulphate previously attributed to marine source has been overestimated. This implies that anthropogenic sources of sulphate are greater than previously supposed.

6.1 Suggestions for Future Research

In addition to the recommendations for refinement of methods in the discussion, a set of recommendations for further research are made both to better address the problem of this study and for applications beyond the scope of this project. One of the limitations of this study is the short sampling period and small number of samples used to characterize each of the components. A way to improve on this would be to include chlorine stable isotope analysis into the long term wet deposition and stream monitoring by EC. The bi-weekly stream sampling and per event precipitation sampling would provide results to examine seasonal variations and produce a framework for more detailed investigations of sources of chloride.

Chlorine stable isotope analysis of short interval stream sampling coupled with long term atmospheric deposition results could provide a means to evaluate the transit times and quantify the proportions of ‘old’ water in stream chloride fluxes. This may indirectly assist the investigation of the problem of this study, but the primary usefulness may be in addressing the ‘double paradox’ of Kircher (2003) by fingerprinting depositional events and modeling their incorporation through the catchment to understand the movement and incorporation of ‘old’ water into stream fluxes.

Long term sampling of stream and wet precipitation should be coupled with multiple years of occult sampling for ionic and isotopic analysis. In this study, occult deposition displayed a wide range of ionic concentrations and isotopic compositions. To get an accurate portrayal of the chemical composition of this form of deposition, sampling throughout the year and for multiple years is necessary. A suitable method for accomplishing this may be to have a passive strand collector sampling a combination of dry deposition and fog water throughout the sampling program. This would provide a more accurate portrayal of the variability of occult deposition. In addition to this, samples of exclusively dry deposition should be collected for isotopic analysis to investigate whether dry deposition may be a source of chloride enriched in heavy isotopes. Chlorine stable isotope analysis of long term sampling of atmospheric deposition would also provide results to examine relationships between trajectories of weather patterns and isotopic composition, testing the hypothesis that atmospheric deposition that has been exposed to acidic pollutants would be enriched in light isotopes compared to marine systems.

The survey style sampling of silicate mineral bound chloride in this study provided a range of δ^{37}Cl values that could contribute to stream chloride. However, the results have potentially erroneous results due to incomplete rinsing of meteoric water from soils and small samples of heterogeneous bedrock. These issues could be addressed by a larger group of samples and a set of procedures to determine the best method to ensure all meteoric chloride is removed from the soils. Also, an examination of the location of chloride within rocks and soils is necessary to evaluate where the sources isotopically heavy chloride are. This would include microprobe analysis of rock and soil samples to determine how much of the chloride is in fluid inclusions, apatites, micas. This information would be useful to understand processes that facilitate the release of silicate mineral bound chloride to solution. Examination of chlorine stable isotopes in the biotite monzogranite of the South Mountain Batholith will be useful for the chloride stream budget issue, but it may also be useful for understanding igneous processes and origins. Identification of sources of chloride enriched in heavy isotopes within the biotite monzogranite produces questions regarding sources of heavy isotopes. Is the isotopically heavy chloride mantle derived? Is there an igneous process that fractionates chloride? Can the variation of chlorine stable isotope compositions of the granite be attributed to the incorporation of country rock that is relatively enriched in light isotopes? These questions and many others could be addressed by more detailed investigations of silicate mineral bound chloride.

This study did not examine the potential impact of groundwater on stream chloride. Chlorine stable isotope analysis of groundwater may provide insight to the degree of infiltration of meteoric water to groundwater systems as well as the influence of mineral/water interactions on stream water. A survey sampling of wells in the area would provide data to compare to stream and atmospheric deposition. This could be followed by drilling and pumping of groundwater from drumlins and bedrock to determine if isotopic variation occurs. Survey and detailed sampling of groundwater would be aided by a thorough investigation of ground water movement in and through the South Mountain Batholith which could address issues of residence time of water and flow pathways.

The biological cycling of chloride is acknowledged to potentially alter chloride primary chloride cycling (eg. Öberg 2002). The isotopic composition of stream water in this study may have been affected by biological uptake and release of chloride.

Hypotheses of the effects are included in Section 1.3.7, but sampling was not conducted to test them. A simple and useful beginning to an investigation of biological cycling of chloride could be carried out by sampling throughfall and soil solutions of organic soil layers. A comparison of chlorine stable isotope compositions of atmospheric deposition and throughfall could be useful to determine whether uptake or release of chloride through the foliage occurs. The chlorine stable isotope composition of soil solutions of organic soils would offer an initial investigation of the release of chloride through the mineralization of organic matter. The mineralization of chloride and its effects on the chlorine stable isotope composition of soil solution could be investigated in more detail by controlled laboratory experiments such as those used by Bastviken et al. (2007). Related to the biological cycling of chloride are the potential effects of the high organic content of the streams and lakes of the region on chloride transport and chlorine stable isotopes. Could the difference between the isotopic composition of rainfall and stream water be accounted for by a fractionation process driven by complexation of chloride with DOC? Laboratory experiments could be designed to test the potential effects of organic matter on chlorine isotopes.

The results of this study open the door to a new set of problems that chlorine stable isotope analysis can be used to investigate. It is with consternation that some researchers approach the use of chlorine stable isotopes because of the precision needed in analysis and the small natural variations. However, the relative minimal use of chlorine stable isotopes along with an increasing understanding of processes that facilitate isotopic variations offers a broad range of research opportunities with specific and large scale implications.

References

Ambler, D.C. 1983. Surface water hydrology Kejimkujik calibrated catchment program on the aquatic and terrestrial effects of the long-range transport of air pollutants. Report # IWD-AR-WRB-83-43.

Barnes, J.D., Sharp, Z.D., Fischer T.P. 2008. Chlorine isotope variations across the Izu-Bonin-Mariana arc. Geology, **36**(11): 883-886.

Bastiviken, D., Sandén, P., Svensson T., Ståhlberg, C., Magounakis, M., Öberg, G. 2006. Chloride retention and release in a boreal forest soil: Effects of soil water residence time and nitrogen and chloride loads. Environmental Science and Technology, **40**(9): 2977-2982.

Bastviken, D., Thomsen, F., Svensson, T., Karlsson, S., Sandén, P., Shaw, G., Matucha, M., Öberg, G. 2007. Chloride retention in forest soil by microbial uptake and by natural chlorination of organic matter. Geochimica et Cosmochimica Acta, **71**: 3182-3192.

Bonifacie. M., Charlou, J.L., Jendrzejewski, N., Agrinier, P., Donval, J.P. 2005. Chlorine istopic composition of high temperature hydrothermal vent fluids over ridge axes. Chemical Geology, **221**: 279-288.

Bonifacie, M., Jendrzejewski, N., Agrinier, P., Coleman, M., Pineau. F., Javoy, M. 2007. Pyrohydrolysis-IRMS determination of silicate chlorine stable isotope compositions. Application to oceanic crust and meteoric samples. Chemical Geology, **242**: 187-201.

Bonifacie, M., Jendrzejewski, N., Agrinier, P., Humler, E., Coleman, M., Javoy, M. 2008. The chlorine isotope composition of Earth's mantle. Science, **319**: 1518-1520.

Campbell, D.J. 1985. Fractionation of stable chlorine isotopes during transport through semipermeable membranes. MSc. thesis, The University of Arizona.

Chan, W. H., Lusis, M. A., Stevens, R.D., Vet, R.J. 1983. A precipitation sampler intercomparison. Water, Air and Soil Pollution, **23**: 1-13.

Chen, J., Wheater, H.S., Lees, M.J. 2002. Identification of processes affecting stream chloride response in the Hafren catchment, mid-Wales. Journal of Hydrology, **264**: 12-33.

Clair, T.A., Schwarcz, H.P., Kramer, J.R., 1989. The origins of sulfur in waters from four Nova Scotian basins, Canada. Applied Geochemistry, **4**: 93-98.

Clair, T.A., Ehrman, J.M., Ouellet, A.J., Brun, G., Lockerbie, D., Chul-Un, R. 2002. Changes in freshwater acidification trends in Canada's Atlantic provinces: 1983-1997. Water, Air, and Soil Pollution, **135**: 335-354.

Clair, T.A., Dennis, I.F., Scuton, D.A., Gilliss, M. 2007. Freshwater acidification research in Atlantic Canada: a review of results and predictions for the future. Environmental Reviews, **15**, 153-167.

Clarke, D.B., and Halliday, A.N., 1980. Strontium isotope geology of the South Mountain Batholith, Nova Scotia. Geochimica et Cosmochimica Acta, **44**: 1045-1058.

Demoz, B.B., Collett Jr., J.L., Daube Jr., B.C. 1996. On the Caltech active strand cloudwater collectors. Atmospheric Research, **41**: 47-62.

Desaulniers, D.E., Kaufmann, R.S., Cherry, J.A., Bentley, H.W. 1986. ^{37}Cl-^{35}Cl variations in a diffusion-controlled groundwater system. Geochimica et Cosmochimica Acta, **50**: 1757-1764.

Eastoe, C.J., Guilbert, J.M. 1992. Stable chlorine isotopes in hydrothermal systems. Geochimica et Cosmochimica Acta, **56**: 4247-4255.

Eastoe, C.J., Peryt, T.M., Petrychenko, O,Y., Geisler-Cussey, D. 2007. Stable chlorine isotopes in Phanerozoic evaporites. Applied Geochemistry, **22**: 575-588.

Eggenkamp, H.G.M. 1994. δ^{37}Cl: the geochemistry of chlorine isotopes. PhD thesis, Ultrecht University.

Eggenkamp, H.G.M., and Schuiling, R.D. 1995. δ^{37}Cl variations in selected minerals: a possible tool for exploration. Journal of Geochemical Exploration, **55**: 249-255.

Eggenkamp, H.G.M., and Coleman, M.L. 2009. The effect of aqueous diffusion on the fractionation of chlorine and bromine stable isotopes. Geochimica et Cosmochimica Acta, **73**: 3539-3548.

Elsner, M. and Hunkeler, D. 2008. Evaluating chlorine isotope effects from isotope ratios and mass spectra of polychlorinated molecules. Analytical Chemistry, **80**: 4731-4740.

Environment Canada. 2006. Satellite Imagery – Environment Canada. http://www.weatheroffice.gc.ca/satellite/index_e.html.

Environment Canada. 2010. Air – CAPMoN – Precipitation chemistry. http://ec.gc.ca/rs-mn/default.asp?lang=en&n=42D909F1-1

Erickson, D.J., and Duce, R.A. 1988. On the global flux of atmospheric sea salt. Journal of Geophysical Research, **93**(C11): 14079-14088.

Farrell, E.P. 1995. Atmospheric deposition in maritime environments and its impact on terrestrial ecosystems. Water, Air and Soil Pollution, **85**: 123-130.

Finck, P.W., Stea, R.R. 1995. The compositional development of tills overlying the South Mountain Batholith, Nova Scotia. Nova Scotia Department of Mines and Energy, Paper 95-1.

Freedman, B. and Ogden, J.D. 1981. Sources and consequences of acid rain in Nova Scotia. Nova Scotia Research Council.

Fuge, R. 1979. Water-soluble chlorine in granitic rocks. Chemical geology, **25**: 169-174.

Gates, A.D. 1973. The tourism and outdoor recreation climate of the maritime provinces. Publications in Applied Meteorology, REC-3-73.

Godon, A., Jendrzelewski, N., Eggenkamp, H.G.M., Banks, D.A., Ader,M., Coleman, M.L., Pineau, F. 2004a. A cross-calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. Chemical Geology, **207**:1-12.

Godon, A., Jendrzelewski, N., Castrec-Rouelle, M., Dia, A., Pineau, F., Boulègue, J., Javoy, M. 2004b. Origin and evolution of fluids from mud volcanoes in the Barbados accretionary comlex. Geochimica et Comsochimica Acta, **68**(9): 2153-2165.

Godsey, S., Aas, W., Clair, T., de Wit, H., Fernandez, I., Kahl, J., Malcom, I., Neal, C., Neal, M., Nelson, S., Norton, S., Palucis, M., Skjelkvale, B.L., Soulsby, C., Tetzlaff, D., Kirchner, J. 2010. Generality of fractal 1/f scaling in catchment tracer time series, and its implications for catchment travel time distributions. Hydrological Processes (in press).

Graedel, T.E. and Keene, W.C. 1996. The budget and cycle of Earth's natural chlorine. Pure and Applied Chemistry, **68**(9): 1689-1697.

Ham, L., Corey, M., Horne, R., MacDonald, M. 1990. Lithogeochemistry of the western portion of the South Mountain Batholith, Nova Scotia. Nova Scotia Department of Mines and Energy, Open file report ME 1990-007.

Hendry, M.J., Wassenaar, L.I., Kotzer, T. 2000. Chloride and chlorine isotopes (^{36}Cl and δ^{37}Cl) as tracers of solute migration in a thick, clay-rich aquitards system. Water Resources Research, **36**(1): 285-296.

Hoering, T.C., and Parker, P.L. 1961. The geochemistry of the stable isotopes of chlorine. Geochimica et Cosmochimica Acta, **23**: 186-199.

Horne, R.J., MacDonald, M.A., Corey, M.C., Ham, L.J. 1992. Structure and emplacement of the South Moutain Batholith, southwestern Nova Scotia. Atlantic Geology, **28**: 29-50.

Hrachowitz, M., Soulsby, C., Tetzlaff,D., Dawson, J.J.C., Dunn, S.M., Malcolm, I.A. 2009. Using long-term data sets to understand transit times in contrasting headwater catchments. Journal of Hydrology, **367**: 237-248.

Hunkeler, D., Breukelen, B.M., Elsner, M. 2009. Modeling chlorine isotope trends during sequential transformation of chlorinated ethenes. Environmental Science and Technology, **43**: 6750-6756.

Jamieson, R.A., Tobey, N.W., ERTH 3020. 2005. Contact metamorphism of the Halifax Formation on the southeastern margin of the Halifax Pluton, Halifax, Nova Scotia: in Halifax 2005, Geological Association of Canada, Mineralogical Association of Canada, Canadian Society of Petroleum Geology, Canadian Society of Soil Science Joint Annual Meeting, Halifax, Nova Scotia, Abstract **30**: 95.

Johns, W.D. and Huang, W.H. 1967. Distribution of chlorine in terrestrial rocks. Geochimica et Cosmochimica Acta, **31**: 35-49.

Kaufmann, R.S. 1984. Chlorine in ground water: Stable isotope distribution. PhD thesis, University of Arizona.

Kennedy, G.W. and Drage, J.M. 2008. Groundwater regions map of Nova Scotia [1:500 000]. Nova Scotia Department of Natural Resources, Open file map ME 2008-003.

Kennedy, G.W., Garroway, K.G., Finlayson-Bourque, D.S. 2010. Estimation of regional groundwater budgets in Nova Scotia. Nova Scotia Department of Natural Resources, Open file illustration ME 2010-002.

Kirchner, J.W., Feng, X., Neal, C. 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. Nature, **403**(3), 524-526.

Kirchner, J.W. 2003. A double paradon in catchment hydrology and geochemistry. Hydrological Processes, **17**: 871-874.

Koehler, G. and Wassenaar, L.I. 2010. The stable isotopic composition (^{37}Cl/^{35}Cl) of dissolved chloride in rainwater. Applied Geochemistry, **25**: 91-96.

Kuroda, P.K. and Sandell, E.B. 1953. Chlorine in igneous rocks: Some aspects of the geochemistry of chlorine. Bulletin of the Geological Society of America, **64**: 879-896.

Lim, K.J., Engel, B.A., Tang, Z., Choi, J., Kim, K.S., Muthikrishnan, S., Tripathy, D. 2005. Automated web GIS based hydrograph analysis tool, WHAT. Journal of the American Water Resources Association, **41**(6): 1407-1416.

Long, A., Eastoe, C.J., Kaufmann, R.S., Martin, J.G., Wirt, L., Finley, J.B. 1993. High-precision measurement of chlorine stable isotope ratios. Geochimica et Cosmochimica Acta, **57**: 2907-2912.

Lovett, G.M., Nolan, S.S., Driscoll, C.T., Fahey, T.J. 1996. Factors regulating throughfall flux in New Hampshire forested landscape. Canadian Journal of Forest Research, **26**: 2134-2144.

Lovett, G.M., Likens, G.E., Buso, D.C., Driscoll, C.T., Bailey, S.W. 2005. The biogeochemistry of chlorine at Hubbard Brook, New Hampshire, USA. Biogeochemsitry, **72**: 191-232.

MacDougall, J.I., Nowland, J.L., Hilchey, J.D. 1969. Soil survey of Annapolis County. Nova Scotia Soil Survey, Report #16.

Neal, C. and Kirchner, J.W. 2000. Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. Hydrology and Earth System Sciences, **4**(2): 295-310.

Nordstrom, K., Ball, J.W., Donahoe, R.J., Whittmore, D. 1989. Groundwater chemistry and water-rock interaction at Stripa. Geochimica et Cosmochimica Acta, **53**: 1727-1740.

NSDNR 2010. Nova Scotia Department of Natural Resources Forest Inventory. http://www.gov.ns.ca/natr/forestry/gis/licence.asp?url=../gis/forest-inventory.asp

Öberg, G. 2002. The natural chlorine cycle – fitting the scattered pieces. Applied Microbiology Biotechnology, **58**: 565-581.

Page, T., Beven, K.J., Freer, J., Neal, C. 2007. Modelling the chloride signal at Plynlimon, Wales, using a modified dynamic TOPMODEL incorporating conservative chemical mixing (with uncertainty). Hydrological Processes, **21**: 292-307.

Peters, N.E. 1991. Chloride cycling in two forested lake watersheds in the west-central Adirondack Mountains, New York, U.S.A. Water, Air, and Soil Pollution, **59**: 201-215.

Phillips, F.M. and Bentley, H.W. 1987. Isotopic fractionation during ion filtration: I. Theory. Geochimica et Cosmochimica Acta, **51**: 683-695.

Reynolds, P.H., Zentilli, M., Muecke, G.H. 1981. K-Ar and ^{40}Ar/ ^{39}Ar geochronology of granitoid rocks from southern Nova Scotia: its bearing on the geological evolution of the Meguma Zone of the Appilachians. Canadian Journal of Earth Sciences, **18**: 386-394.

Reynolds, B. and Pomeroy, A.B. 1988. Hydrogeochemistry of chloride in an upland catchment in mid-Wales. Journal of Hydrology, **99**: 19-32.

Reynolds, B., Fowler, D., Smith, R.I., Hall, J.R. 1997. Atmospheric inputs and catchment solute fluxes for major ions in five Welsh upland catchments. Journal of Hydrology, **194**: 305-329.

Schauble, E.A., Rossman, G.R., Taylor Jr., H.P. 2003. Theoretical estimates of equilibrium chlorine-isotope fractionations. Geochimica et Cosmochimica Acta, **67**(17): 3267-3281.

Schenk, P.E. 1997. Sequence stratigraphy and provenance on Gondwanna's margin; the Meguma Zone (Cambrian to Devonian) of Nova Scotia, Canada. Geological Society of America Bulletin, **109**(4): 395-409.

Shaw, R.W. 1979. Acid precipitation in Atlantic Canada. Environment Science Technology, **13**: 406-411.

Sharp, Z.D. and Barnes, J.D. 2008. Comment to "Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean" by Wei et al. A review of the Cl isotope composition of serpentinites and the global chlorine cycle. Earth and Planetary Science Letters, **274**: 531-534.

Sharp, Z.D., Barnes, J.D., Brearley, A.J., Chaussidon, M., Fischer, T.P., Kamenetsky, V.S. 2007. Nature, **446**: 1062-1065.

Shields, W.R., Murphy, T.J., Garner, E.L., Dibeler, V.H. 1962. Absolute isotopic abundance ratio and the atomic weight of chlorine. Journal of the American Chemical Society, **84**(9): 1519-1522.

Shouakar-Stash, O. 2008. Evaluation of stable chlorine and bromine isotopes in sedimentary formation fluids. PhD thesis, University of Waterloo.

Sie, P.M.J. and Frape, S.K. 2002. Evaluation of the groundwaters from the Stripa mine using chlorine stable isotopes. Chemical Geology, **182**: 565-582.

Soulsby, C. 1995. Influence of sea salt on stream water chemistry in an upland afforested catchment. Hydrological Processes, **9**: 183-196.

Soulsby, C. and Tetzlaff, D. 2008. Towards simple approaches for mean residence time estimation in ungauged basins using tracers and soil distributions. Journal of Hydrology, **363**: 60-74.

Stea, R.R. and Brown, Y. 1989. Variation in drumlin orientation, form and stratigraphy relating to successive ice flows in southern and central Nova Scotia. Sedimentary Geology, **62**: 223-240.

Stea, R.R., Piper, D.J.W., Fader, G.B.J., Boyd, R. 1998. Wisconsinan glacial and sea-level history of Maritime Canada and the adjacent continental shelf: A correlation of land and sea events. Geological Survey of America Bulletin, **110**(7): 821-845.

Stea, R.R., Conley, H., Brown, Y. 2006. Surficial geology map of the province of Nova Scotia, Digital version. Nova Scotia Department of Natural Resources, Map ME 1992-3.

Stewart, M.A. and Spivack, A.J. 2004. The stable-chlorine isotope compositions of natural and anthropogenic materials. Reviews in Mineralogy and Geochemistry, **55**: 231-254.

Sturchio, N.C., Böhlke, J.K., Beloso Jr., A.D., Streger, S.H., Heraty, L.J., Hatzinger, P.B. 2007. Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: laboratory results and implications for forensics and natural attenuation studies. Environmental Science and Technology, **41**: 2796-2802.

Taylor, J.A. 1982. An introduction to error analysis: The study of uncertainties in physical measurements. University Science Books.

Underwood, J.K., Waller, D.H., Thirumurthi, D. 1987. The influence of the ocean on the chemistry of precipitation in Nova Scotia. Atmosphere-Ocean, **26**: 467-479.

Urey, H.C. 1947. The thermodynamic properties of isotopic substances. Journal of Chemistry Society, **69**: 562-581.

van Staal, C.R. 2007. Pre-Carboniferous tectonic evolution and metallogeny of the Canadian Applalachians. *In* Mineral resournces of Canada: A synthesis of major deposit types, distinct metallogeny, the evolution of geological provinces and exploration methods. *Edited by* W.D. Goodfellow, Geological Association of Canada, Mineral Deposits Division, Special Publications **5**: 793-818.

Vet, R.J., Sukloff, W.B., Still, M.E., Gilbert, R. 1986. Canadian air and precipitation monitoring network (CAPMoN) precipitation chemistry data summary. Environment Canada Atmospheric Environment Service, Report AQRB-86-001-M.

Viers, J., Dupre, B., Braun, J.J., Frydier, R., Greenberg, S., Ngoupayou, J.N., Nkamdjou, L.S. 2001. Evidence for non-conservative behavior of chlorine in humid tropical environments. Aquatic Geochemistry, **7**: 127-154.

Volpe, C. and Spivack, A.J. 1994. Stable chlorine isotopic composition of marine aerosol particles in the western Atlantic Ocean. Geophysical Research Letters, **21**(12): 1161-1164.

Volpe, C., Wahlen, M., Pszenny, A.A.P., Spivack, A.J. 1998. Chlorine isotopic composition of marine aerosols: Implications for the release of reactive chlorine and HCl cycling rates. Geophysical Research Letters, **25**(20): 3831-3834.

Wadleigh, M.A., Schwarcz, H.P., Kramer, J.R. 1994. Sulphur isotope tests of seasalt correction factors in precipitation: Nova Scotia, Canada. Water, Air, and Soil Pollution, **77**: 1-16.

Wassenaar, L.I. and Koehler, G. 2004. On-line technique for the determination of the δ^{37}Cl of inorganic and total organic Cl in environmental samples. Analytical Chemstry, **76**: 6384-6388.

Watmough, S.A., Aherne, J., Alewell, C., Arp, P., Bailey, S., Clair, T., Dillon, P., Duchesne, L., Eimers, C., Fernandez, I., Foster, N., Larssen, T., Miller, E., Mitchell, M., Page, S. Sulphate, nitrogen and base cation budgets at 21 forested catchments in Canada, the United States and Europe. Environmental Monitoring and Assessment, **109**: 1-36.

Watt, W.D., Scott, D., Ray, S. 1979. Acidification and other chemical changes in Halifax County lakes after 21 years. Limnology Oceanography, **24**: 1154-1161.

Wei, W., Kastner, M., Spivack, A. 2008. Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean. Earth and Planetary Science Letters, **266**: 90-104.

White, A. 2008. Quantitative approaches to characterizing natural chemical weathering rates. *In* Kinetics of Water-Rock Interaction, *Edited by* S.L. Brantley and E.E. Roden. Springer New York, pg 469-543.

White, C.E. 2007. Preliminary bedrock geology of the Kejimkujik Lake map area (NTS 21A/06), southern Nova Scotia. 2007. Nova Scotia Department of Natural Resources, Report ME 2007-1: 159-169.

White, C.E. 2010. Compilation of geochemical and petrographic data from the western and southern parts of the Goldenville and Halifax Groups, Nova Scotia. Nova Scotia Department of Natural Resources, Open File Report ME 2010-001.

White, C.E. 2010 in press. Stratigraphy of the Lower Paleozoic Goldenville and Halifax groups in southwestern Nova Scotia. Atlantic Geology.

White, C.E., Barr, S.M., Horne,R.J., Hamilton, M.A. 2007. The neoacadian orogeny in the Meguma terrane, Nova Scotia. *In* 42st Annual Meeting Geological Survey of America, Northeastern Section, Abstracts, **39**: 69.

Whitfield, C.J., Watmough, S.A., Aherne, J., Dillon, P.J. 2006. A comparison of weathering rates for acid-sensitive catchments in Nova Scotia, Canada and their impact on critical load calculations. Geoderma, **136**: 899-911.

Willimore, C.C., Boudreau, A.E., Spivack, A., Kruger, F.J. 2002. Halogens of Bushveld complex, South Africa: δ^{37}Cl and Cl/F evidence for hydration melting of the source region in a back-arc setting. Chemical Geology, **182**: 503-511.

Worgan, J. 1987. Acid mine drainage in reactive slates, “The Halifax Airport Case”. *In* Proceedings Acid Mine Drainage Seminar/Workshop, Halifax NS. Environment Canada, 127-136.

Yanni, S. 1995. Hydrogeochemical assessment of water in forested watersheds at Kejimkujik National Park: Discharge rates, chemical composition and ion fluxes. MSc thesis, University of New Brunswick.

Yanni, S., Keys, K., Clair, T.A., Arp, P.A. 2000. Fog and acidification impacts on ion budgets of basins in Nova Scotia, Canada. Journal of the American Water Resources Association, **36**: 619-631.

Yin, X. and Arp, P.A. 1994. Fog contributions to the water budget of forested watersheds in the Canadian Maritime provinces: A generalized algorithm for low elevations. Atmosphere-Oceans, **32**(3): 553-566.

Zhang, M., Frape, S.K., Love, A.J., Herczeg, A.L., Lehmann, B.E., Beyerle, U., Purtschert, R. 2007. Chlorine stable isotope studies of old groundwater, southwestern Great Artesian Basin, Australia. Applied Geochemistry, **22**: 557-574.

Appendix A: Extraction of Dissolved Chloride as AgCl.

The following is a detailed description of the procedure used for the extraction of chloride from solutions as AgCl. Changes have been made from procedures provided by Dr. Wassenaar (personal communication 2009) and as such, a detailed account may be useful for future applications.

1. Use BioRad Ag 4x4, free base, 20-50 mesh resin to isolate and concentrate chloride.
    a. Resin preparation: to convert the resin to a form that will adsorb the chloride, it requires pretreatment. 50-100 g of resin is placed in graduated beaker (500 mL or greater). Rinse the resin five times with deionized water. Add twice the mass of 0.8 M acetic acid to the resin and remain immersed for a minimum of one hour. Decant excess acetic acid and rinse with deionized water.
    b. Add 5 ml of prepared resin to 100 mL glass ion chromatography column. Rinse resin with 250 mL of DI water.
    c. Add up to 100 mL of sample to resin in column. Drain the sample at a rate of 1 mL/min (~ 1 drop every three seconds). Return the sample to the column and drain. Return the sample to column again and allow it to remain in the column for 8 hours or more. Drain supernant from column and keep in a clean, marked container.
    d. Elute the chloride from the resin using 1 M HNO_3. Add 30-35 mL dropwise to resin in the bottom of the column. Allow the eluent to drain at a rate of 0.5 mL/min into a 250 mL graduated beaker.
    e. Heat solution to 80°C on hotplate. Turn off overhead lights and turn on red light.
    f. Add 1 mL of 0.2 M $AgNO_3$ and examine for white precipitate (AgCl).
    g. Pre-weigh glass fiber filter GF/F papers.
    h. Filter sample using GF/F on a vacuum suction filter system.

i. Dry sample on filter paper in oven at 60°C. Reweigh the dried filter with sample to calculate the yield of sample
j. Sample yields > 90% is required for validation of effective procedure. This was completed with an NaCl solution of known concentration before field samples were used.

Appendix B: Chlorine Stable Isotope Repeat Analyses of Samples

Of the 60 samples analyzed for chlorine stable isotopes composition, 54 are the product of a single analysis. In 6 of samples, the reported values are the result of multiple analyses (Table B-1). However, the reported δ^{37}Cl is not always the mean of all the analyses because of exclusion of outlier values. Sample 9040, the δ^{37}Cl value of +3.14 ‰ was excluded because it is well outside two standard deviations of the other three analyses and sample 9079, the δ^{37}Cl value of +0.45 ‰ was excluded because it is outside two standard deviations of the other three samples and during the analyses a leak in the septum was detected following the analysis.

Table B- 1: Chlorine stable isotope results of samples with multiple analyses.

Sample	ID #	Raw δ^{37}Cl	Daily SMOC δ^{37}Cl	Single analysis δ^{37}Cl	Reported δ^{37}Cl	Analytical uncertainty (‰)	Relative uncertainty (%)
Hornfels (40 ppm)	9037	-6.62	-6.29	-0.33	-0.35	0.22	3
Hornfels (40 ppm)	9037	-6.42	-6.05	-0.37	-0.35	0.22	4
Bt Monzogrnt 2 (160 ppm Cl)	9038	-6.82	-6.29	-0.53	-0.30	0.22	3
Bt Monzogrnt 2 (160 ppm Cl)	9038	-6.26	-6.05	-0.21	-0.30	0.22	4
Bt Monzogrnt 2 (160 ppm Cl)	9038	-6.03	-5.88	-0.15	-0.30	0.22	4
Bt Monzogrnt 1 (320 ppm Cl)	9039	-5.44	-6.29	0.85	0.78	0.22	3
Bt Monzogrnt 1 (320 ppm Cl)	9039	-5.60	-6.29	0.69	0.78	0.22	3
Bt Monzogrnt 1 (320 ppm Cl)	9039	-5.48	-6.29	0.81	0.78	0.22	3
Non-Magnetic (btmz 1 split)	9040	-5.20	-6.29	1.09	1.14	0.22	3
Non-Magnetic (btmz 1 split)	9040	-5.17	-6.29	1.12	1.14	0.22	3
Non-Magnetic (btmz 1 split)	9040	-5.07	-6.29	1.22	1.14	0.22	3
Non-Magnetic (btmz 1 split)	9040	-3.17	-6.29	3.12	1.14	0.22	3
Magnetic (btmz 1 split)	9041	-3.84	-6.29	2.45	2.47	0.22	3
Magnetic (btmz 1 split)	9041	-3.70	-6.29	2.59	2.47	0.22	3
Magnetic (btmz 1 split)	9041	-3.91	-6.29	2.38	2.47	0.22	3
Fog June 23 (high Cl 33 mg/L)	9079	-6.37	-6.14	-0.23	-0.30	0.22	4
Fog June 23 (high Cl 33 mg/L)	9079	-5.69	-6.14	0.45	-0.30	0.22	4
Fog June 23 (high Cl 33 mg/L)	9079	-6.64	-6.14	-0.50	-0.30	0.22	4
Fog June 23 (high Cl 33 mg/L)	9079	-6.32	-6.14	-0.18	-0.30	0.22	4

Table B-1 provides an example of how the raw δ^{37}Cl value of each analysis is compared to the daily SMOC, but the analytical uncertainty is the standard deviation of all the seawater analyses during the multiple days of analysis.

Appendix C: Ion Filtration Experiment

In the standard methods of this study, soil solution is extracted from soils by centrifuging then filtering. The filtering process uses an air pump to produce a pressure gradient to draw the solution past a filter. Typically, sandy soils were sampled and these methods proved to be efficient at quickly removing suspended sediment. In situations where the solution contained colloids not removed during centrifugation, clays would build up on the filter paper and slow the filtering process from a period of second to a period of hours. The plugging of the filter paper by clay, set up a semipermeable membrane similar to the experiments of Campbell (1985). This membrane effectively removed the colloids from solution, but it also set up a pressure gradient with a higher pressure vacuum sucking the solution past the semipermeable membrane. It was this situation that was identified to possibly fractionate chlorine isotopes by ion filtration.

In Table 4-7, soil solution samples 9042 and 9043 are the results of an experiment testing the influence of a step of sample preparation procedures. The soil samples collected from the silty drumlin site (DRSS2 in Fig. 2.11) have a high clay content which prevented the standard soil solution method of centrifuging (10 min at 5000 rpm) and filtering (0.45 μm filter) from removing the colloids completely. The colloids could be removed from solution by increasing the centrifugation time and rpm and/or filtering through a filter that has a build-up of clay on it. Two samples were prepared in different ways to test if isotopic fractionation was occurring during the filtration of solution through a clay membrane. One sample had the colloids removed by centrifuging for 12 hours at 10000 rpm (9042) and a second sample had the colloids removed by filtering twice through a 0.45 μm which had accumulated approximately 1 mm of clay (9043). The experiment was meant to test the potential fractionation effects of ion filtration through a semi permeable membrane (Campbell 1985). The results of this experiment indicate that the sample passed through the filter is more enriched in light isotopes (-1.20 ± 0.22 ‰) compared to the sample that was centrifuged (-0.86 ± 0.22 ‰).

This small sub-set experiment indicates that isotopic fractionation may have occured while solutions were passed through a semi-permeable clay membrane. This is in accordance with previous investigations of chlorine stable isotope fractionation processes. Eggenkamp (1994) calculated that significant chloride stable isotope fractionation can occur in diffusive processes and studies (Desaulniers et al.1986, Eggenkamp 1994) show results that can be explained by diffusion based on concentration gradients. Eggenkamp and Coleman (2009) establish diffusive isotope fractionation factors of chloride by setting up concentration gradients with gels. Campbell (1985) conducted forced flow ion filtration experiments and observed isotopic fractionation resulting in solution passed through the membranes being enriched in heavier isotopes compared to the initial solution. The results were interpreted to be the product of back diffusion, where the greater inertial force of the heavier isotopes allows them to more readily approach the negatively charged clay surface and the light isotopes are more readily repulsed, resulting in isotopically heavier solution passing through the membrane. Of the two samples in the experiment, the sample filtered through the membrane produced an isotopically light solution (-1.20 ± 0.22 ‰) compared to the centrifuged sample (-0.86 ± 0.22 ‰). These results are different than would be predicted by the results of the Campbell (1985) experiments. The experiment in this study was different in methods, in that the filtering of the sample involved a solution on one side and a vacuum on the other, not a solution on the other side of the membrane. The gradient in this study was a pressure gradient, but also a difference in states on either side of the filter which would complicate diffusion arguments. The fractionation observed in this study could be a result of the light isotopes being drawn preferentially through the clay membrane, while the heavier isotopes may remain preferentially within the solution of the clay membrane. However, the results of this single experiment could be considered insignificant when the analytical uncertainty is considered or the results could be a product of the centrifugation or flocculation observed in the ion chromatography columns with these samples.

Regardless of the interpretation of processes producing these results, caution is recommended in development of procedures of soil solution extraction for chlorine stable isotope analysis. A more rigorous testing of this experiment may shed light on ion filtration processes and aid in the development of procedures that do not systematically fractionate samples.

Appendix D: Calculations

1. Moose Pit Mass Balance

Considering the definitions, assumptions and steps outlined in section 3.4, the isotope mass balance of Moose Pit Brook is as follows.

Using equation 1:

$\delta^{37}Cl_s = (X_p)\ \delta^{37}Cl_p + (X_e)\ \delta^{37}Cl_e$

and the values

$X_p = 0.39 \pm 12$ % and $X_e = 0.61 \pm 8$ % (from Table 3-4), and

$\delta^{37}Cl_s = -0.93$ ‰ ± 1%, and $\delta^{37}Cl_p = -1.51$ ‰ ± 2 %,

equation 1 rearranged to solve for the isotopic composition of the excess chloride:

$$\delta^{37}Cl_e = \{\delta^{37}Cl_s - [(X_p)\ \delta^{37}Cl_p]\} / (X_e)$$

$$= [-0.93 \text{ ‰} \pm 1\% - (0.39 \pm 12 \% * -1.51 \text{ ‰} \pm 2 \%)] / 0.61 \pm 8 \%$$

$\delta^{37}Cl_e = -0.56$ ‰

using the rules of uncertainty propagation in Taylor (1982), but keeping the uncertainty as relative uncertainty, the relative uncertainty simplifies to summation in quadrature:

$$E(\delta^{37}Cl_e) = (1^2 + 12^2 + 2^2 + 8^2)^{-2}$$

$$= 15 \%$$

Because the $\delta^{37}Cl_e$ value of -0.56 ‰ is a SMOC corrected value, an estimate of the uncorrected value can be made by adding the average SMOC value of -6.07 ‰ resulting in an uncorrected value of -6.63 ‰. The relative uncertainty, 15 % of -6.63 ‰ is 0.99 ‰.

Therefore the estimate of the isotopic composition of the excess chloride in Moose Pit Brook is -0.56 ± 0.99 ‰.

Proportions of Fog and Rock water interactions when most value most enriched in heavy isotopes is used.

When the upper limit of $\delta^{37}Cl_{ws}$ = +0.75 ‰ ± 7% is used to represent silicate mineral bound chloride isotope values with $\delta^{37}Cl_e$ = -0.56 ‰ ± 15 %, $\delta^{37}Cl_f$ = -1.08‰ ± 3%, an estimate of the proportional contributions of fog water and weathering can be made using equation 3:

$$X_f = (\delta^{37}Cl_e - \delta^{37}Cl_w) / (\delta^{37}Cl_f - \delta^{37}Cl_w)$$

$$= [(-0.56\ ‰ \pm 15\ \%) – (+0.75\ ‰ \pm 7\%] / [(-1.08‰ \pm 3\%) – (+0.75\ ‰ \pm 7\%)]$$

$$= 0.71$$

$$X_w = 1 - X_f$$

$$= 0.29$$

An estimate of the uncertainty for X_f is provided by

$$E(X_f) = (15^2 + 7^2 + 3^2 + 7^2)^{-2}$$

$$= 18\ \%$$

X_f = 0.71 ± 18 % and X_w = 0.29 ± 18 %.

These are the unit-less proportional contributions to the 0.61 ± 8 % of chloride in streams that is from a source other than precipitation. Therefore, of all the chloride in Moose Pit Brook, an estimate of the contribution from fog is:

$$0.71 * 0.61 = 0.43$$

And a measure of uncertainty is

$$E(fog) = (18^2 + 8^2)^{-2}$$

= 20 %

A lower limit estimate of the contribution from silicate mineral bound chloride is

0.29 * 0.61 = 0.18

E(ws) = 20 %

Given that the uncertainty is represented as a relative error, the estimates produced are 43 ± 9 % from fog and 18 ± 4 % from mineral/water interactions.

Upper limit estimate of silicate mineral bound chloride contributions

Using the isotopic composition of silicate mineral bound chloride most enriched in light isotopes, $\delta^{37}Cl_{wbs}$ = -0.29 ‰ ± 5 % with the values $\delta^{37}Cl_{e}$ = -0.56 ‰ ± 15 %, $\delta^{37}Cl_{f}$ = -1.08‰ ± 3%, an estimate of the proportional contributions of fog water and weathering can be made using equation 3:

$X_f = (\delta^{37}Cl_e - \delta^{37}Cl_w) / (\delta^{37}Cl_f - \delta^{37}Cl_w)$

$= [(-0.56 ‰ \pm 15 \%) – (-0.29 ‰ \pm 5\%] / [(-1.08‰ \pm 3\%) – (-0.29 ‰ \pm 5\%)]$

$= 0.34$

$X_w = 1 - X_f$

$= 0.66$

An estimate of the uncertainty for X_f is provided by

$E(X_f) = (15^2 + 5^2 + 3^2 + 5^2)^{-2}$

$= 17 \%$

$X_f = 0.34 \pm 17 \%$ and $X_w = 0.66 \pm 17 \%$.

These are the proportional contributions to the 0.61 ± 8 % of chloride in streams that is from a source other than precipitation. Therefore, of all the chloride in Moose Pit Brook, an estimate of the contribution from fog is:

$0.34 * 0.61 = 0.21$

And a measure of uncertainty is

$E(\text{fog}) = (17^2 + 8^2)^{-2}$

$= 19\ \%$

An upper limit estimate of the contribution from silicate mineral bound chloride is

$0.66 * 0.61 = 0.40$

$E(\text{ws}) = 19\ \%$

Given that the uncertainty is represented as a relative error, the estimates for an upper limit of chloride from mineral/water interactions is 40 ± 8 % and 21 ± 4 % from fog.

Optimal estimate of chloride contributions from silicate mineral bound chloride.

The chlorine stable isotope composition thought to best represent silicate mineral bound chloride in Moose Pit Brook is +0.13 ‰ ± 3 %. This value combined with the values $\delta^{37}Cl_e = -0.56$ ‰ ± 15 %, $\delta^{37}Cl_f = -1.08$‰ ± 3%, an estimate of the proportional contributions of fog water and weathering can be made using equation 3:

$X_f = (\delta^{37}Cl_e - \delta^{37}Cl_w) / (\delta^{37}Cl_f - \delta^{37}Cl_w)$

$= [(-0.56\ ‰ \pm 15\ \%) – (+0.13\ ‰ \pm 3\%] / [(-1.08‰ \pm 3\%) – (+0.13\ ‰ \pm 3\%)]$

$= 0.57$

$X_w = 1 - X_f$

$= 0.43$

An estimate of the uncertainty for X_f is provided by

$E(X_f) = (15^2 + 3^2 + 3^2 + 3^2)^{-2}$

$= 16\ \%$

$X_f = 0.57 \pm 16\ \%$ and $X_w = 0.43 \pm 16\ \%$.

These are the proportional contributions to the 0.61 ± 8 % of chloride in streams that is from a source other than precipitation. Therefore, of all the chloride in Moose Pit Brook, an estimate of the contribution from fog is:

$0.57 * 0.61 = 0.35$

And a measure of uncertainty is

$E(fog) = (16^2 + 8^2)^{-2}$

$= 18\ \%$

The best estimate of the contribution from silicate mineral bound chloride is

$0.43 * 0.61 = 0.26$

$E(wo) = 18\ \%$

Therefore the best estimation of chloride from mineral/water interactions is 26 ± 5 % and 35 ± 6 % from fog.

2. Isotopic Composition of Excess Chloride in Pine Marten Stream.

The isotopic composition of excess chloride in Pine Marten Stream is estimated using the same mass balance approach as Moose Pit Brook.

Using equation 1:

$\delta^{37}Cl_s = (X_p)\ \delta^{37}Cl_p + (X_e)\ \delta^{37}Cl_e$

and the values

$X_p = 0.39 \pm 19\ \%$ and $X_e = 0.61 \pm 12\ \%$ (from Table 3-4), and

$\delta^{37}Cl_s = -0.97\ ‰ \pm 1\%$, and $\delta^{37}Cl_p = -1.51\ ‰ \pm 2\ \%$,

equation 1 rearranged to solve for the isotopic composition of the excess chloride:

$\delta^{37}Cl_e = \{\delta^{37}Cl_s - [(X_p)\ \delta^{37}Cl_p]\} / (X_e)$

$= [-0.97 ‰ \pm 1\% - (0.39 \pm 19\ \% * -1.51 ‰ \pm 2\ \%)] / 0.61 \pm 12\ \%$

$\delta^{37}Cl_e = -0.62$ ‰

and the uncertainty is estimated to be

$E(\delta^{37}Cl_e) = (1^2 + 19^2 + 2^2 + 12^2)^{-2}$

$= 23\ \%$

Because the $\delta^{37}Cl_e$ value of -0.62 ‰ is a SMOC corrected value, an estimate of the uncorrected value can be made by adding the average SMOC value of -6.07 ‰ resulting in an uncorrected value of -6.69 ‰. The relative uncertainty, 23 % of -6.63 ‰ is 1.5 ‰.

Therefore the estimate of the isotopic composition of the excess chloride in Pine Marten Stream is -0.62 ± 1.53 ‰.

The composition of the excess chloride along with the estimates of proportional contributions from rain, fog and geological sources can be used to estimate the isotopic composition of the geological chloride.

Using the equation:

$\delta^{37}Cl_s = (X_p)\ \delta^{37}Cl_p + (X_f)\ \delta^{37}Cl_f + (X_g)\ \delta^{37}Cl_g$

where $\delta^{37}Cl_s = -0.97$ ‰ ± 1 %, $X_p = 0.39 \pm 19$ %, $\delta^{37}Cl_p = -1.51$ ‰ ± 2 %, $X_f = 0.35 \pm 18$ %, $\delta^{37}Cl_f = -1.08$ ‰ ± 3 %, $X_g = 0.26 \pm 5$ %.

$\delta^{37}Cl_g = \{(-0.97 ‰) – [0.39(-1.51 ‰)] – [0.35(-1.08 ‰)]\} / 0.26$

$= +0.01$ ‰

And the uncertainty is represented by:

$E(\delta^{37}Cl_g) = (1^2 + 19^2 + 2^2 + 18^2 + 3^2 + 5^2)^{-2}$

$= 27\ \%$

The uncorrected $\delta^{37}Cl_g$ would be -6.06 ± 1.6‰