Honours Thesis

The effects of catchment liming on the calcium budget of an acidified Nova Scotia watershed

Christine Angelidis
Department of Environmental Science
Supervisor: Dr. Shannon Sterling

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Acronyms

ALET	Atlantic Laboratory for Environmental Testing
ANC	Acid Neutralizing Capacity
BCAF	Bluenose Coastal Action Foundation
CaPMON	Canadian Air and Precipitation Monitoring Network
CEC	Cation Exchange Capacity
DFO	Department of Fisheries and Oceans
EC	Environment Canada
HRG	Hydrology Research Group
MAGIC	Model of Acidification of Groundwater In Catchments
SOM	Soil Organic Matter
SWNS	South West Nova Scotia

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Abstract

Acidification of South West Nova Scotia's (SWNS) watersheds from acid rain deposition has led to the depletion of base cations from catchment soils (Clair & Hindar 2005). This has led to a reduction in the acid neutralizing capacity (ANC) of the catchments, acidification of surface waters, and the release of aluminum ions (Al_i) into surface waters, which can cause deleterious changes to aquatic ecosystems, and can be particularly harmful to *Salmo salar* smolts (Clair & Hindar, 2005). There are decreasing trends in calcium concentration in acidified watersheds as calcium is released into streams as a result of ion exchange (Clair, 2004). Catchment liming, the addition of neutralizing compounds such as calcium carbonate ($CaCO_3$), to acidified watersheds has been demonstrated to be an effective mitigation strategy to assist in the recovery of such environments (Clair & Hindar, 2005). The application of 30 tonnes of $CaCO_3$ to an acidified watershed in SWNS in 2012 has been attempted in order to artificially replenish the depleted base cations from the soil and to mitigate the effects of acid rain deposition.

This research examined, using a mass balance approach, the calcium budget of an acidified watershed in SWNS. The study addressed the following questions: What were the annual exports and imports of Ca at the Maria Brook catchment, and were they balanced? And did catchment liming change the calcium budget of the Maria Brook catchment in SWNS?

Using data from The Canadian Air and Precipitation Monitoring Network (CAPMoN) and from grab samples of the catchment drainage waters, a pre-liming and post-liming calcium budget was constructed. A stage-velocity model was constructed to estimate drainage of water from the system both pre- and post-liming. The nutrient balance was determined from calcium entering the system through precipitation and leaving the system through drainage water (Bormann and Linkens, 1967).

It was found that the pre-liming Ca budget was negative, demonstrating that Ca is continually being depleted from the system and that inputs were insufficient to balance exports. The application of 30 tonnes of $CaCO_3$ resulted in increased Ca export from the system and increased stream water Ca concentrations; however these increases only represented a fraction of the Ca added to the system, suggesting that the remainder was taken up by vegetation or was stored in the soil pool. It is recommended that further liming applications be conducted and monitored in order to assess efficacy of catchment liming in remediating the detrimental effects to aquatic communities (Clair et al., 2004) and in replenishing Ca-depleted soils that potentially decrease forest productivity (Yanai, 2005).

1. Introduction

1.1. Motivation

Acid deposition in Eastern North America and Europe, resulting from sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emissions, has depleted base cations from soils and contributed to the acidification of surface waters (Clair & Hindar, 2005; Yanai et al., 1999). As base cations are depleted, aluminum ions (Al^{n+}) are released from catchment soils and are carried into surface waters where they negatively affect aquatic communities (Reuss, Cosby, & Wright, 1987). Furthermore, base cation depletion hinders the ability of the soil to buffer acid inputs and stored sulphur in the system, decreasing the pH of the overall system. Base cation depletion, particularly of calcium (Ca), has a detrimental effect on forest health and productivity and is largely responsible for observed declines in forest growth rates and nutrient losses from soils in Eastern North America (Yanai, et al., 2005; Hamburg et al., 2003; Baes & McLaughlin, 1984; Jeziorski et al., 2008). Furthermore, such depletion can hinder the recovery of acidified surface waters even in light of decreased acid deposition (Watmough & Dillon, 2003).

Southwest Nova Scotia (SWNS) is particularly vulnerable to acidification and base cation depletion (Hindar, 2001). The unique geology and low neutralizing capacity of SWNS, combined with an abundance of wetlands in the region and the deposition of acidifying sea salts, have prevented SWNS from showing the improvements in surface water acidity and soil chemistry that have been observed in Europe and North America in response to recent decreases in sulfur emissions (Clair, Dennis, & Vet, 2011; Whitfield, Aherne, Dillon, & Watmough, 2007). Minichiello (2014) has found similar results in the river record of SWNS. Chronic acidification of SWNS is thought to be the primary cause of the extirpation of Atlantic salmon (*Salmo salar*) (DFO, 2013), as well as a contributing factor to decreasing terrestrial and aquatic ecosystem productivity and health (Bradley & Ormerod, 2002; Watt, 1987; Rosseland & Staurnes, 1994). It is unlikely that Atlantic salmon populations will be able to recover without human intervention, as it has been predicted by Clair et al. (2004) that Ca concentration in SWNS rivers will decrease by as much as 15% over the next 40-50 years, and may not recover for as long as 90 years if acidification continues at the present rate (Clair T. A., Dennis, Amiro, & Cosby, 2004). The Department of Fisheries and Oceans (DFO, 2013) has predicted that Atlantic salmon populations in SWNS will be highly vulnerable to further extirpation without human intervention. However reduction of the Ca deficit and of pH extremes may allow successful re-establishment of *Salmo salar* populations in the region (DFO, 2013).

Catchment liming, a method demonstrated to be effective in mitigating the effects of acid rain in Europe, replenishes Ca in watershed soils by adding Ca-based liming agents such as limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) to the watershed soils, thereby improving the capacity of soils to neutralize acid deposition and to reduce toxicity. A better understanding of the Ca budget and cycling in an acidified system, and how this budget changes in response to liming, is necessary for the development of more effective management and mitigation strategies and will assist in determining whether catchment liming can be used to successfully replenish soil base cations in SWNS.

The current research examined, using a mass balance approach, the calcium budget of an acidified watershed in SWNS and further examined its response to catchment liming.

1.2. Background

1.2.1. Acidification

Eastern North America and Northern Europe have been subject to increased acid deposition for the past 50 years (Clair & Hindar, 2005). Sulfuric (H_2SO_4) and nitric (HNO_3)

acids produced from the release of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from smelting, transportation, and power generation are oxidized and result in acid deposition (Equation 1 and 2). In SWNS, SO_2 is the primary acidifying agent as it has a great range of transport than NO_x due to its longer mean residence time (Driscoll et al., 2003; Seinfeld & Pandis, 1998).

$$SO_2 + O_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4 \qquad (1)$$

$$NO + \frac{1}{2} O_2 \rightarrow NO_2 + H_2O \rightarrow HNO_3 + NO \qquad (2)$$

Acid deposition delivers H^+ to catchment soils where ion exchange occurs at soil cation exchange sites, releasing Ca^{2+} and Mg^{2+} into surface waters and depleting base cations from the catchment soils (Clair et al., 2004; Clair & Hindar, 2005; Christophersen, Seip, & Wright, 1982). Base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) increase the pH of water when released in solution from mineral weathering and ion exchange reactions (Bailey et al., 1996). Relative to other base cations stored in soils, Ca^{2+} is preferentially exchanged with H^+ and as such plays an important role in buffering soils from acid inputs (Clair et al., 2004). When H^+ inputs exceed available base cations, the soils become depleted of base cations and H^+ will instead exchange with Al^{n+} in order to maintain the electro-neutrality of soils (Clair et al., 2004; Dennis & Clair, 2012) . The Al is leached from soils and released into surface waters where it can have toxic effects on aquatic communities, particularly Atlantic salmon (Kroglund, et al., 2007). Depletion of base cations also results in a reduction of the acid neutralizing capacity (ANC) of the catchments, and Clair et al. (2004) projected that there will be a steady reduction in Ca concentrations in acidified watersheds as Ca is released into streams to buffer continued acid deposition.

The ANC of a catchment is a measure of acidification calculated by subtracting the sum of the concentrations of strong acid anions (SO_4^-, Cl^-, NO_3^-) from the sum of the concentrations of available base cations (Reuss, Cosby, & Wright, 1987). A simplified equation that can be used to calculate ANC is shown in Equation 3 (modified from Reuss, 1987).

$$ANC \approx [Ca^{2+} + Mg^{2+}] - [SO_4^{2-} + NO_3^{-}] \qquad (3)$$

In the latter part of the 20th century, Scandinavia and parts of the United Kingdom were severely affected by acidification as a result of the predominance of the slow-weathering underlying bedrock and its proximity to sulfur and nitrogen sources (Clair et al., 2004), and this has led to significant depletion of some species of fish and a reduction of biodiversity (Hesthagen, Sevaldrud, & Berger, 1999). Eastern North America has experienced similarly significant losses of Ca from soils as a result of acid deposition and forest harvest (Yanai, et al., 2005; Watmough & Dillon, 2003). Declines in fish populations and aquatic ecosystem productivity in North America are the result of the combined effects of low pH (as a result of elevated H^+ concentrations), toxic levels of Al, and low Ca concentrations (Rosseland & Staurnes, 1994; Cronan & Schofield, 1979). This net loss of base cations may slow the recovery of acidified surface water chemistry even with decreased emissions and acid inputs (Clair T. A., Dennis, Amiro, & Cosby, 2004).

SWNS is thought to be one of the most vulnerable regions to acid rain deposition in North America because of its unique combination of slow-weathering bedrock, proximity to oceans (resulting in acidic deposition from sea salt spray), down-wind location from sulfur emission sites, and abundance of wetland environments (Hindar, 2001). Despite reductions in acid rain deposition over the past 20 years (Stoddard, et al., 1999) the lake record for SWNS has shown little evidence of improvement in water chemistry (Clair, Dennis, & Vet, 2011).

1.2.2. Major pools and fluxes of calcium in a forested catchment

In forested catchments, Ca can be found in a number of major pools. It moves among these pools as a result of natural cycling processes. The major pools of Ca are: soil, live wood, foliage, plant reproductive tissues, root systems, and litter, where soil represents the largest pool (Whitaker, 1970). The annual inputs of Ca to the catchment are derived from bulk deposition and bedrock weathering, while the major losses of Ca from the system result from stream and ground water loss (Whitaker, 1970). Fluxes of Ca among pools within the system are dominated by biotic factors such as plant uptake, litterfall, net primary production (foliage, new twigs, reproductive tissues) and decomposition. Ca plays a crucial role in the growth and development of vegetation, and is particularly important in cell wall and cell membrane structure and function, as well as in regulating the kinase family of enzymes (Hepler, 2005; Harper, Breton, & Harmon, 2004). Kinases control key events of cell function, particularly regarding cell division, and are responsible for adding phosphate groups to other proteins (Pierce, 2012). Furthermore, Ca plays a vital role in vertebrate and invertebrate physiology. It functions in the maintenance of cell membrane permeability, assists in regulation of blood coagulation, and assists in the formation of internal and external skeletal components (Robertson, 1941).

The weathering flux is important as the capacity of an ecosystem to buffer acid inputs depends on the content and availability of base cations in the soils. Base cations in soils are derived from the underlying bedrock through weathering processes, and their abundance and availability depend partially on these processes. Chemical weathering of bedrock releases base cations into the overlaying soils (Clair et al., 2002; Christophersen, Seip, & Wright, 1982). Different forms of bedrock vary in Ca content and weathering characteristics. These differences are reflected in the overlaying soils. Slow-weathering bedrock, as well as bedrock that is low in

Ca content, release base cations slowly, resulting in lower soil concentrations and a reduced ability to buffer incoming H^+ (Clair et al., 2004). As such, the leaching and depletion of base cations from soils in regions underlain by slow-weathering bedrock and exposed to acid rain is accelerated. The majority of SWNS is underlain by slow-weathering Devonian granites, containing less than 1% CaO that provide little buffering capacity to soils and surface waters (Charest, 1976). Therefore, despite the fact that acid deposition has decline in recent decades, Ca release by weathering is insufficient to replace lost base cations (Whitfield et al., 2007; Clair, Ehrman, Ouellet, Brun, & Lockerbie, 2002; Charest, 1976).

1.2.2.1. Depletion of Ca in soil and surface water

Calcium-depleted soils can limit the productivity of terrestrial ecosystems. Since Ca is an essential nutrient for all organisms (Jeziorski et al., 2008) the depletion of Ca reduces forest productivity and increases stress and mortality in a number of trees species such as Sugar Maple (*Acer saccharum*) and Red Spruce (*Picea rubens*), which are abundant in the forests of SWNS (Yanai, et al., 2005; Hamburg et al., 2003; Driscoll et al., 2003). Calcium limitation can have particularly negative effects on populations of calcifying organisms, such as snail populations, which in turn is detrimental to passerines that feed on them (Graveland et al., 1996). Large losses of Ca from soils and the depletion of exchangeable pools of Ca (the pool of Ca that is readily available for ion exchange) result in forest vegetation that is more sensitive to acid deposition. This depletion has negative implications for the ability of soils and stream waters to recover from acid deposition (Watmough & Dillon, 2003; Likens, et al., 1998). The decline of Ca concentration in catchment soils and surface waters results in reduced buffering capacity and ANC.

The depletion of Ca in soils also has implications for the water cycle. Green et al. (2013) found that watersheds in the Hubbard Brook Experimental Forest (HBEF) in New Hampshire were so depleted of nutrients, particularly of Ca, that lower rates of photosynthesis were observed in response to the nutrient limitation. As a result, evotranspiration decreased and despite decreases in rainfall, water discharge increased. The experimental application of wollastonite, a calcium-silicate mineral, replenished Ca to the soils to pre-acidification levels and resulted in increases in evotranspiration relative to a reference watershed (Green, et al., 2013).

Acid-induced depletion of Ca from soils results in reduced Ca in aquatic habitats. This reduction has detrimental effects on the development of fish eggs, as increased Ca concentrations in freshwater environments have been found to increase egg survival, in addition to contributing to increased surface water toxicity and acidity (Sayer, Reader, & Morris, 1991a). Once base cations are depleted from soils, continued acid input causes the mobilization of Al ions. These Al ions are released from aluminosilicate minerals into surface waters in order to maintain electro-neutrality in the soils (Reuss, Cosby, & Wright, 1987). Al ions are toxic to many aquatic organisms (Cronan & Schofield, 1979) including the Atlantic salmon, currently recommended by the Committee on the Status of Endangered Wildlife in Canada (COSEIWC) for listing as endangered under the Species At Risk Act (SARA) (COSEWIC, 2010). Positively charged Al ions accumulate on negatively charged fish gill surfaces and interfere with gas exchange (Gensemer & Playle, 1999). Aluminum is particularly toxic when there is insufficient dissolved organic carbon (DOC) to render Al biologically unavailable, and where there is insufficient Ca in the water to occupy the negative exchange sites on fish gills (Lacroix & Kan, 1986). Freshwater crustacean zooplankton such as Daphnia also suffer from the effects of Ca depletion, as they require a minimum of 1.5 mg L^{-1} of Ca to survive (Jeziorski, Paterson, Desellas, Turner, & Jeffries, 2008).

Clear cutting and harvesting accelerate losses of Ca from soils and contribute to Ca depletion. Clear cutting can result in the loss of as much as 200-1100 kg Ca ha^{-1} as a result of the increased nitrification of soils generated by harvesting (Likens, et al., 1998; Federer, et al., 1989).

1.2.3. Catchment liming

Catchment liming, the addition of neutralizing compounds such as calcium carbonate ($CaCO_3$) to acidified watershed soils, artificially replenishes base cations and effectively mitigates the acidification and resulting toxic effects of freshwater Al by replenishing Ca. The neutralizing agent increases the availability of cations for exchange with incoming H^+ from acid deposition, and therefore reduces the release of Al into surface waters, as Ca is preferentially exchanged over Al (Equation 4) (Clair & Hindar, 2005; Dennis & Clair, 2012).

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3 \qquad (4)$$

As a result, catchment liming has been shown to increase Ca concentrations in soils and in surface waters (Hindar et al., 2003), and to retain toxic Al (Hindar & Wright, 2005). This replenishment of Ca to depleted soils benefits terrestrial and aquatic ecosystems (Sayer, Reader, & Dalziel, 1993; Cronan & Schofield, 1979; Yanai, et al., 2005; Hamburget al., 2003; Driscoll et al., 2003), increases surface water pH, and decreases the concentration of toxic Al in surface waters (Clair & Hindar, 2005). In acidified watersheds with low ANC, Mant et al. (2013) found that catchment liming helped restore aquatic communities.

Catchment liming has been demonstrated to be effective in Europe (Clair & Hindar, 2005; Bradley & Ormerod, 2002) but has until recently remained untested in SWNS and as such little is known about its effectiveness in mitigating the effects of acid deposition, base cation depletion, and acidification of surface waters in a Nova Scotian acidified system.

1.3. Knowledge gaps

Given that catchment liming has never been attempted in SWNS, there are several knowledge gaps that must be addressed. Ion mass balances and seasonal fluxes were measured for four acidic streams in SWNS between January 1981 and December 1983 and revealed that Ca represented only 6% of total cation equivalent inputs through precipitation and represented 16% of cation equivalents in stream waters (Freedman & Clair, 1987); however little else is known of Ca budgets in Nova Scotia, such as how Ca budgets will be affected by catchment liming. Of particular importance is if and how the export of Ca will change with the addition of $CaCO_3$. More generally, an understanding of how the system is responding to the liming, and whether the additional Ca is reaching surface waters, is crucially important to assess whether catchment liming is effective in SWNS. This information can then be used to determine whether catchment liming can assist in the recovery of acidified environments and to assess how much Ca is needed to in order to make catchment liming effective in remediating the effects of acidification. It is currently unknown how Ca pools and fluxes will change with the addition of $CaCO_3$, and what changes will be observed in water and soil chemistry.

1.4. Research questions

Understanding the Ca budgets of acidified watersheds in SWNS and how they change in response to catchment liming will allow for more effective mitigation strategies to be developed for the region. The current research aimed to increase the understanding of Ca budgets in acidified watersheds in SWNS. This was done by developing a Ca budget for an acidified watershed in SWNS using a mass balance approach. The research was an analytic, retrospective and prospective exploratory study that compared pre- and post-liming Ca budgets for the Maria Brook watershed in SWNS. The following research questions were addressed:

1. What are the annual exports and imports of Ca at the Maria Brook catchment, and are they balanced?
2. How does catchment liming change the Ca budget of the Maria Brook catchment?
    a. What proportion is the Ca added (through catchment liming) in comparison with the estimated volume of Ca lost from the catchment?
    b. Is there a significant difference between the Ca budget of the catchment pre-liming and post-liming? Is there evidence that the Ca is delivered in a continuous release to the stream, or does it remain in the system (stored in soil or biomass pool)?
    c. How soon after the liming process will a difference be observed in the calcium budget?

1.5. Hypotheses

It was hypothesized that catchment liming will have a measurable impact on the Ca budget of the Maria Brook watershed. The associated hypotheses for the above mentioned research questions are:

1. It is expected that the pre-liming Ca budget will be negative, meaning that the rate of loss from the system exceeded the rate of input, based on the significant acid deposition and poor weathering quality of substrates in the system, as well as the predicted base cation depletion.

2. The catchment liming will result in increased soil and water Ca concentrations, and therefore in a greater flux of Ca through the system as the additional Ca will be leached from the soil by the acid deposition from precipitation inputs.
    a. Post-liming, there will be a significant increase in Ca export from the system, while inputs from natural sources will remain the same. Inputs from deposition and weathering will not be affected by the addition of Ca to the catchment soils, however the additional Ca cations made available by liming will be released into the surface waters to buffer acid inputs and will be exported from the system in surface water discharge. The amount of Ca exported from the system will depend on the proportion of added Ca that will be stored in depleted pools.
    b. Within the first year of addition of $CaCO_3$to the catchment, there will be a noticeable difference in the Ca budget. This will provide sufficient time for additional Ca to be released into surface waters in order to buffer acid inputs.

1.6. Summary of approach

Using data from The Canadian Air and Precipitation Monitoring Network (CAPMoN), water chemistry grab samples, and in-situ continuous monitoring data of stage and conductivity of the catchment drainage waters, and the literature where local values were not available, pre-liming and post-liming Ca budgets were constructed. A stage-discharge relation was constructed in order to estimate annual water discharge based on stage data from the system both pre- and post-liming. The nutrient balance was determined from Ca entering the system through precipitation and weathering, and leaving the system through drainage waters (Likens et al., 1967). The pre- and post-liming Ca budgets were compared and this comparison, in combination with comparisons to modeled Ca budgets of the catchment pre-acidification, provided a first step in the evaluation of the potential of catchment liming in mitigating the effects of acidification in SWNS.

2. Literature review

This literature review summarizes the body of knowledge of biogeochemical cycling, nutrient budgets, and mass balances of Ca in forested watersheds. In particular, this literature review will investigate Ca budgets in acidified watersheds and on comparative studies of paired watersheds. The aim of this review is to illustrate the complexity of Ca budgets in small watersheds, and to demonstrate the current trends in Europe and eastern North America of decreasing Ca concentrations and availability in catchment soils. Furthermore, this review will demonstrate the key role of catchment liming in replenishing depleted soil Ca and will analyze the changes to Ca budgets in watersheds that have undergone catchment liming. Finally, this review will identify any gaps in knowledge.

This literature review was conducted using several databases, in particular ScienceDirect and Web of Science. The following key words were used to search the available literature for relevant information: calcium budget, watershed, acidification, acid deposition, mass balance, catchment liming.

2.1. Properties of calcium

Ca plays an integral role in the biogeochemistry of forested catchments. Understanding its chemical and physical properties facilitates the understanding of its behaviour in nutrient cycling in acidified watersheds (Likens, et al., 1998). Calcium is the most common alkaline earth element in the Earth’s crust (Wedepohl, 1995). It is present in relatively low concentrations in igneous rock, such as granite, and is easily released by weathering (Likens, et al., 1998). The rate of weathering of Ca depends on soil solution pH, and therefore acid precipitation can contribute to changes of Ca concentration in soil solutions (Likens, et al., 1998). When Ca is weathered from underlying bedrock, it moves into soil solution where it can be adsorbed onto negatively charged clay minerals or soil organic matter (SOM) as a result of cation exchange. It can be taken up by plants or microbial organisms, or leached out of the system (Likens, et al., 1998; Yuan, Gammon, & Leighty, 1967). The cation exchange capacity (CEC) of a soil represents the availability of adsorbed cations for ion exchange with soil solution (Mengel D. B., n.d.). The CEC of a soil is determined by the abundance of silicate clay minerals present, as these minerals possess a net negative charge to which cations can bond (Schlesinger & Bernhardt, 2013). The higher the CEC, the less readily soils lose Ca^{2+} (Bowen, 1979). The availability of Ca for use by organisms depends on inputs from atmospheric deposition, rock weathering, mineralization of SOM, and on losses of Ca through leaching, stream water discharge, and plant uptake (Likens, et al., 1998). Ca cycles among the biotic and abiotic components of a system through plant uptake and litterfall mineralization processes (Likens, et al., 1998). The depletion of Ca from acidified soils therefore alters the biogeochemistry of entire systems through this cycling process.

Calcium is an essential nutrient for all organisms and a particularly important macronutrient for plants (Bowen, 1979; Mengel & Kirkby, 1979). Calcium is a major constituent in skeletal elements of invertebrates and vertebrates (Robertson, 1941; Bowen, 1979). It helps to maintain the function and permeability of cell membranes, is required for muscle contraction, and contributes to the transmission and propagation of nerve impulses (Campbell & Reece, 2005). It is also a crucial nutrient for vegetation as it is an important component of cell wall and membrane structure and function (Mengel & Kirkby, 1979). Furthermore, Ca is important in regulating plant growth and development, and is an important constituent of the kinase family of enzymes (Hepler, 2005; Harper, Breton, & Harmon, 2004; Bowen, 1979). In prokaryotes, Ca plays an integral role in signal transduction (Shemarova & Nesterov, 2005; Dominguez, 2004). As in plant cells, Ca is an important contributor to the development and growth of cell walls in fungi, particularly in the hyphae. It is also important in active and passive transport processes in all eukaryotic organisms (Jackson & Heath, 1993; Pitt & Ugalde, 1984).

2.2. The role of calcium in watersheds

Ca plays a complex and vital role in watershed systems. Ca ions in soils are preferentially exchanged with incoming H^+, and as such act as important buffers to acid inputs through ion exchange with soil carbonates (Clair T. A., Dennis, Amiro, & Cosby, 2004; Christophersen, Seip, & Wright, 1982). This exchange results in the release of base cations from soils into surface waters (Clair T. A., Dennis, Amiro, & Cosby, 2004). Although the depletion process is primarily acute in the early stages of acidification, where acid deposition is chronic base cations eventually become depleted from soils, and this depletion may be particularly problematic where slow weathering bedrock provides insufficient Ca^{2+} inputs to replace depleted cations. Cation depletion results in forests that are more sensitive to acid inputs from atmospheric deposition (Clair & Hindar, 2005; Likens, et al., 1998). When base cations have been depleted, incoming H^+ is instead exchanged with Al^{n+}, which has been found to be toxic to aquatic and terrestrial communities (Dennis & Clair, 2012; DFO, 2013; Likens, et al., 1998). Christophersen et al. (1982) observed positive correlations between H^+ and Al^{n+} concentrations at the Birkenes field site in Norway, demonstrating that as acid deposition increases and base cations are depleted, H^+ exchanges instead with Al^{n+} in order to maintain electro-neutrality in soils. An inverse relationship was observed between Al concentrations and base cation concentrations in surface waters (Christophersen, Seip, & Wright, 1982).

While it has been widely documented that Al is detrimental to aquatic and terrestrial ecosystems (Cronan & Schofield, 1979; Rosseland & Kroglund, 2011); until recently its threat to SWNS Atlantic salmon populations was underestimated, as it was believed that dissolved organic carbon (DOC) rendered the Al biologically inaccessible (Lacroix & Kan, 1986; Lacroix et al. , 1990; Lacroix & Townsend, 1987; Watt et al., 2000; Rosseland & Kroglund, 2011). Denis and Clair (2012) have however demonstrated that in several acidified rivers in SWNS, DOC was insufficient to render Al inaccessible, and therefore Al reached levels that were toxic to aquatic ecosystems. Biologically accessible Al ions bind to the negatively charged gills of Atlantic salmon and disrupt gas exchange (Dennis & Clair, 2012).

As mentioned previously, Ca is also a vital nutrient for terrestrial and aquatic communities, and the productivity and health of ecosystems is negatively affected by Ca depletion (Yanai, et al., 2005).

2.3. Methods used to study calcium budgets

Nutrient budgets are based on the differences between nutrient inputs and outputs into and from ecosystems and are useful tools for quantifying the fluxes and changes in nutrient pool sizes over time (Bormann & Likens, 1967). A budget is considered to be balanced when the quantity of outputs is equal to the nutrient inputs into the system (Shober, Hochmuth, & Wiese, 2013). A balanced budget indicates that no net accumulation or depletion is occurring at the catchment scale (Ranger & Turpault, 1999). If nutrients are accumulating in the system, the budget is considered positive, while if nutrients are being depleted from the system, it is considered to be negative (Ranger & Turpault, 1999). The impact of any imbalanced budget on a system varies widely depending on the available nutrient stock (Ranger & Turpault, 1999; van der Heijden, et al., 2013; Watmough, et al., 2005; Watmough & Dillon, 2003; Likens, et al., 1998). When conducting nutrient budgets, it is important to consider all potential sources of inputs into and exports from the ecosystem in order to accurately assess the budget (Likens G. E., Bormann, Johnson, Fisher, & Robert, 1970). The mass balance approach is a method of developing nutrient budgets by applying the theory of conservation of mass to estimate mass flows of nutrients within systems (Himmelblau & Riggs, 2012).

Studying Ca budgets and analyzing system trends requires a holistic, ecosystem approach to quantifying Ca pools, inputs, and outputs. There are several of methods used to study changes in nutrient pool sizes overtime.

2.3.1. Sampling techniques

2.3.1.1. Soil calcium sampling

Soil sampling can be used to estimate the size of the soil nutrient pool. Changes in soil nutrient pool size can be studied by sampling and resampling soils and comparing nutrient values (van der Heijden, et al., 2013). There is a large spatial variability of nutrients in soil pools, and as such it can be difficult to effectively sample soils (Likens et al., 1967; Ranger & Turpault, 1999). It is therefore important to design a soil sampling program to be representative of the entire study area in order to estimate as accurately as possible the size of the nutrient pool.

Several sampling designs exist, including statistical approaches using measures of central tendency and dispersion, convenience sampling, and probability based sampling (Canadian Society of Soil Science, 2008). The topography of the terrain may dictate the type of sampling used. On level terrain, or on sloped terrain with no significant across-slope variation, transect sampling can be used to capture a representative sample. However in sloped terrain that is more variable and includes across-slope curvature, it is more important to capture the spatial heterogeneity of the topography and therefore grid sampling may be preferable. Furthermore, it is important to consider the timing and depth of sampling (Canadian Society of Soil Science, 2008). When conducting nutrient inventories of soils, the accuracy of the soil tests in estimating the nutrient pool is more dependent on the way the sample was collected and handled than on error from laboratory analysis (Canadian Society of Soil Science, 2008).

At the HBEF, Johnson et al. (1991b) measured the available pool of soil Ca by extracting soils with 1 M NH_4Cl in a mechanical-vacuum extractor. Further measurements used at the HBEF sites for measuring exchangeable Ca and Ca fluxes included collection of forest floor samples, stream water grab samples, soil solution samples, canopy foliage, and throughfall measurements.

2.3.1.2. Calcium in biomass

Chemical analyses of plant tissues may be used to estimate biomass accumulation from canopy foliage, and tree cores and cross sections may be used to determine the chemical composition of softwood (Johnson, Johnson, & Siccama, 1991b). Foliar concentrations of Ca appear to remain relatively constant through time, and as such biomass accumulation can be used to estimate of addition of Ca to the biomass pool. Plant growth rate estimates can be used to estimate the rate of calcium accumulation in biomass (Likens, et al., 1998; Likens et al., 1970). Plant uptake rates can then be estimated based on the difference in the biomass pool size over time (Likens, et al., 1998).

2.3.2. Modeling fluxes and input-output nutrient budgets

Nutrient budgets can be determined by modeling fluxes using empirical and processed-based models. With appropriate hydrological measurements, relatively precise estimates of chemical precipitation inputs and stream water discharge can be obtained (van der Heijden, et al., 2013). Although input-output budgets can be useful in describing trends in nutrient budgets, they have several disadvantages. Constructing these budgets is often labour-intensive and expensive. Furthermore, modelled fluxes and input-output budgets are generally site-specific and time-specific, and provide little information about the causative mechanisms for the observed changes in budgets (Ranger & Turpault, 1999). For example, insufficient understanding of the relationship between nutrient availability and forest productivity implies that it is not possible to accurately quantify changes in productivity based on observed nutrient depletion (Ranger & Turpault, 1999).

In order to produce an accurate input-output budget, it is necessary that all components of the budget be measured independently and that spatial heterogeneity and temporal variation be considered. The difficulty in acquiring precise measurements of all inputs and outputs, particularly with regards to weathering rates, may result in imprecise estimates of fluxes, and therefore unrealistic budgets (Hodson & Lagan, 1999; Nilsson & Grennfelt, 1988). This difficulty is reflected in discrepancies between predications made using flux modeling and estimates based on soil sampling methods. Models of cation budgets are often based on hydrologic and anion submodels, and therefore it can be difficult to determine where the discrepancies originate, and whether or not discrepancies exist between observed and simulated cation concentrations (Christophersen, Seip, & Wright, 1982). Furthermore, there are uncertainties present in input-output budgets as a result of incorrect flux calculations, and the difficulty of validating input-output budgets (van der Heijden, et al., 2013)

2.4. *Calcium pools*

Calcium is stored in several pools in ecosystems, and these pools are influenced by a number of interacting factors such as elevation, soil properties and drainage, and vegetation structure and composition (Likens, et al., 1998). In order to understand the complete Ca budget of a watershed, an intimate knowledge of the existing pools within the system is essential.

2.4.1. Soil

Soil is a major pool of exchangeable Ca, with typical pools varying considerably in size (61 to 829 kg ha^{-1}) and spatial distribution depending on the system (van der Heijden, et al., 2013; Watmough & Dillon, 2003; Watmough, et al., 2005; Likens, et al., 1998). As much as 92% of Ca present in an ecosystem is held in the soil pool; however much of this is inaccessible to organisms (Likens, et al., 1998). Calcium is primarily found in the A and B horizons of soil, however in regions of slow weathering inputs, the majority of exchangeable Ca is found in the organic layer (O horizon), with only a negligible proportion found in deeper soils (Likens, et al., 1998; van der Heijden, et al., 2013; Watmough, et al., 2005). The majority of Ca enters the O horizon through direct precipitation, throughfall, litterfall, remineralization by microorganisms, and root exudates that decompose. The Ca entering the soil from these sources is then available for uptake by plants and microorganisms (Likens, et al., 1998). The concentration of Ca in the soil pool may also be a function of elevation, as Likens et al. (1998) observed lower concentrations of Ca at higher elevations as a result of differences in hydrologic flowpaths, and that softwood trees at higher elevations also contained lower concentrations of Ca.

2.4.2. Biomass

Biomass is the second major Ca pool, and is variable in size depending on community compositions. In forested catchments across North America and Western Europe, typical Ca pool sizes in above-ground biomass range between 64 to 960 kg ha^{-1} (Watmough, et al., 2005; van der Heijden, et al., 2013). Calcium accumulates in the biomass pool through plant uptake of available Ca from the soil pool, and the net accumulation of Ca in vegetation is directly related to the decreasing content of exchangeable Ca in soils (Johnson, et al., 1988b). Calcium is stored preferentially in branches (41%) with only 26% of Ca stored in bark, 19% in root systems, and relatively little stored in standing dead tress (Likens, et al., 1998). Availability of Ca is important for the growth and health of vegetation because of its role as a macronutrient, and long-term changes in this availability may have significant impacts on forest ecosystems (Federer, et al., 1989).

Plant uptake removes as much as 30% of available Ca per year from the soil exchangeable pool. The majority (97%) of this Ca is returned to the soils as a result of annual fluxes, such as litterfall, with only 3% accumulating in plant tissues (Likens, et al., 1998). This demonstrates the importance of Ca cycling within a system in maintaining Ca stocks despite limited inputs and significant exports.

Although plant biomass represents a large proportion of the Ca biomass pool, it is not the only biotic pool of Ca. Burton and Likens (1975) have estimated the biotic stocks of Ca of fauna from several taxonomic groups in the HBEF. Mammals on average represented a stock of 27.5 g Ca ha^{-1}, while birds represented a smaller proportion at an average of 6.9 g ha^{-1} (Burton & Likens, 1975). No published estimates for invertebrate or microbial stocks were found.

2.5. Calcium inputs, outputs, and fluxes

Ca flows into and out of the above-described pools from a number of sources, and moves among these pools through intrasystem cycling. In order to understand the complete Ca budget of a system, an intimate knowledge of the existing fluxes driving the system is essential.

2.5.1. Atmospheric deposition

Atmospheric deposition is a source of Ca for ecosystems, and can be subdivided into two forms. Wet deposition includes all Ca inputs derived from rainfall or snowfall, while dry deposition consists mainly of sedimentation, as Ca has no gaseous phase (Watmough, et al., 2005; Lindberg et al., 1986). The concentration of Ca in atmospheric deposition can be affected by such processes as soil erosion, proximity to industrial emissions, forest fires, and sea-salt aerosols (Brahney, Ballantyne, Sievers, & Neff, 2013).Wet deposition can be directly measured by capture of rain and snowfall and analysis of water chemistry (Ranger & Turpault, 1999). Christophersen et al. (1982) observed only minor inputs of Ca from precipitation at the Birkenes field site in Norway. Watmough et al. (2005) measured average bulk deposition (both wet and dry deposition) of Ca for forested catchments in North America and Europe as 2.27 kg $ha^{-1}yr^{-1}$. In south west Scotland, Tervet and Harriman (1988) observed a higher average deposition of Ca at 8 kg $ha^{-1}yr^{-1}$ for wet deposition alone. Several investigators have observed a decline in the concentration of Ca bulk deposition in North America, paralleling the decline in sulfur deposition resulting from more stringent emissions controls (Likens, et al., 1998; Watmough, et al., 2005; van der Heijden, et al., 2013; Gimeno et al., 2001; Hedin, et al., 1994). Likens et al. (1998) observed an average decline in bulk deposition of Ca of 1.9 kg $ha^{-1}yr^{-1}$Ca over 30 years at six watersheds at HBEF. The decline in Ca deposition has been correlated with declines in emissions from cement producing factories and solid waste incineration. (Likens, et al., 1998). It has been suggested that this decline of base cation deposition may offset the benefits of decreased sulfur deposition (Gimeno et al., 2001; Hedin, et al., 1994).

Throughfall and stemflow (the proportion of precipitation that is intercepted and flows down the truck of vegetation) contain higher concentrations of Ca than that observed in bulk precipitation. This is due to throughfall and stemflow collection of Ca particles that have been deposited on the canopy and trunk through dry deposition (Likens, et al., 1998). Availability of Ca to the system as a result of throughfall depends largely on the amount of Ca that is leached from the canopy, and this leaching is influenced by the pH of precipitation, where more acidic precipitation was found to promote foliar leaching in Sugar maple (*Acer saccharum*) (Wood & Bormann, 1975; Lovett & Hubbell, 1991). This foliar leaching demonstrates the indirect effect of acid deposition on Ca availability in ecosystems.

2.5.2. Weathering

Weathering of Ca-bearing bedrock and soil minerals contributes a small quantity of Ca to soil pools each year, and is one of several geochemical processes that release Ca into soil solution (Likens, et al., 1998; Ranger & Turpault, 1999; Christophersen, Seip, & Wright, 1982). The rate of weathering depends both on the parent material and on the pH of the soil solution, and can be difficult to estimate; however it is believed that weathering rates remain relatively constant over time in unperturbed systems (Ranger & Turpault, 1999; Likens, et al., 1998). As a result, the PROFILE model, as developed by Sverdrup and Warfvinge (1988) is often used by investigators to estimate the contribution of Ca from weathering. Watmough et al. (2005) calculated a range of Ca weathering rates between 1.2-13.9 kg ha^{-1} yr^{-1} using the PROFILE model, and found that generally the weathering of bedrock contributed less than 6 kg ha^{-1} yr^{-1}.

Likens et al. (1998) calculated similar rates of weathering as Watmough et al. (2005) in a northern hardwood forest ecosystem underlain by mostly by granitic bedrock (2.1 kg ha^{-1} yr^{-1}).

Other methods of estimating the contribution of weathering to nutrient budgets includes laboratory models, which tend to generally oversimplify and overestimate weathering rates, and mass balance studies (Ranger & Turpault, 1999). One of the most common methods used to estimate weathering input is to combine estimates of soil mineral concentrations, weathering fluxes, and estimates from geochemical models (Fichter, Dambrine, Turpault, & Ranger, 1998; Ranger & Turpault, 1999).

Weathering rates have remained relatively constant over the past 50 years, and contribute less than 50% of the net release of Ca from soils, although the effects of climate change and of more acidic rain from increased atmospheric CO_2 on weathering rates is not yet clear (Kump, Brantley, & Arthur, 2000). Changes in net soil release of Ca or in-stream water chemistry are therefore likely the result of changes in other geochemical processes. These processes include the release of Ca into soil solution by the displacement of Ca from soil exchange sites and the mineralization of Ca associated with SOM (Likens, et al., 1998).

2.5.3. Stream water discharge

Stream water discharge represents the only major export of Ca from an ecosystem. Watmough et al. (2005) estimated that stream flow exports of Ca in forested catchments ranged from 3.6 to 39.7 kg ha^{-1} yr^{-1}, while Likens et al. (1998) found similar values with an average range of 10.1 to 24.1 kg ha^{-1} yr^{-1}. In SWNS, Ca concentrations in stream water discharge ranged from 0.47 to 6.93 mg L^{-1} with a mean of 1.26 mg L^{-1} (Clair et al., 2004). Variation in concentrations of dissolved Ca ions in stream waters has generally been found to be positively correlated to the rate of discharge (Likens, et al., 1998; Johnson et al., 1968). However, Christophersen et al. (1982) observed the opposite relationship between cation concentration and discharge, where base cation concentrations tended to decrease with increasing discharge, possibly because during periods of high flow (high input of H^+) water only passes through the upper-most layers of the forest floor, which generally have a lower concentration of exchangeable base cations (Christophersen, Seip, & Wright, 1982). Furthermore, discharge of Ca is a function of the rate of chemical weathering and the origins of the water. There exists a positive relationship between the concentration of Ca in stream water discharge and the size of the exchangeable soil pool (Watmough, et al., 2005). Therefore, the depletion of Ca from soils has a direct effect on the concentration of Ca present in discharge waters. A corresponding decline of Ca concentration in stream discharge over time was observed by both Likens et al. (1998) and Watmough et al. (2005), decreasing on average by 0.0319 mg L^{-1} yr^{-1} between 1970-2001, suggesting a depletion of the soil pool; however Minichiello (2014) found no change in [Ca] stream water in SWNS between 1980 and 2011, suggesting that depletion occurred prior to the 1980s.

Stream discharge of Ca is also influenced by land use change. Whole-tree harvesting and clear cutting significantly increase stream water export of Ca if biomass is left on site, as well as directly remove the Ca stored in harvested vegetation. These activities increase the nitrification of soils, where nitrate anions then exchange with Ca^{2+} and result in increased Ca^{2+} release into stream waters. The combination of acid deposition and repeated harvests increase the amount of Ca^{2+} exported from a system and reduce the amount available for biological uptake (Yanai, et al., 2005).

Concentrations of Ca^{2+} in stream waters are generally greater than those of bulk deposition as a result of the accumulation in stream waters of other sources of Ca including dry deposition, cation exchange in soils, mineralization of organic matter, and weathering inputs (Likens, et al., 1998). In addition to dissolved Ca export in stream water, Ca held in particulate matter is also exported. The majority (74%) of Ca exported in this manner is held in inorganic particulate matter (Bormann & Likens, 1967). Likens et al. (1998) observed a positive correlation between the concentration of Ca in stream water and the concentration of SO_4^{2-} and NO_3^-, although this relationship is complicated by soil types and variations in SO_4^{2-} and NO_3^- inputs (Likens & Bormann, 1995).

The net export from stream waters results from the interaction of several processes including the inputs of Ca from deposition and the storage of Ca in biomass, and as a result stream water outputs vary depending on weather and plant activity (Likens, et al., 1998).

2.5.4. Biotic fluxes

Plant uptake is a major internal flux of Ca within a system, and is the dominant mechanism for increasing the biomass Ca pool. Annually, plants uptake an average of 26-30% of the available exchangeable Ca from the soil pool (Likens, et al., 1998). The rate of plant uptake of Ca depends on both the age and productivity of vegetation, as well as on the extent of nutrient depletion. Uptake is greater in forests that are actively growing than in mature forests, and there is a correspondingly greater accumulation of Ca in litter in young forests than in older forests, (Bailey, Buso, & Likens, 2003; Yanai, et al., 2005; Hamburg et al., 2003). Yanai et al. (2005) estimated plant uptake from mineral soils in young northern hardwood forests as 12 to 23 kg Ca $ha^{-1}yr^{-1}$ in young forests and only 2 to 8 kg Ca $ha^{-1}yr^{-1}$ in old growth forests. Similar values were calculated by Huntington et al. (1999) in Eastern North America. Plant uptake and accumulation of Ca is influenced by root processes in below-ground biomass, and by the availability of Ca from the soil pool (Likens, et al., 1998). It is not yet well understood how young stands acquire Ca from soils at rates that are not observed in old stands.

The primary flux of Ca between the vegetation pool and the soil pool results from uptake-litterfall-mineralization processes, as Ca is not easily leached directly from live foliage (Likens, et al., 1998). The availability of Ca to biomass depends on rates of atmospheric deposition, cation exchange in soils, mineral weathering, mineralization of SOM, and losses of Ca from the system through leaching and accumulation in biomass. Recent studies have found that annual net uptake of Ca by vegetation has declined by as much as 74% (Likens, et al., 1998), possibly as a result of the depletion of the exchangeable pool of Ca in soils (Bondietti et al., 1990).

Litterfall represents another biological flux of Ca within a forested system. The release of Ca from litter to the forest floor closely mirrors the loss of litter mass through decomposition, as the concentration of Ca in plant tissues that make up litter remains relatively constant (Gosz, Likens, & Bormann, 1973).

Movement of fauna into and out of systems also acts as a small flux of Ca. This flux is difficult to estimate and is inherently dependent on the species present, population sizes, and migration rates (Sturges, Holmes, & Likens, 1974).

2.6. Trends in calcium budgets

A number of trends have been observed over the past 50 years in Ca budgets across a large number of studies spanning North America and Western Europe.

2.6.1. Depletion of soil pool

Across several regions of North America and Europe, Ca exports have been observed to be greater than inputs from deposition and weathering, resulting in a continual depletion of Ca pools (Watmough, et al., 2005; Likens, et al., 1998; Watmough & Dillon, 2003; Christophersen, Seip, & Wright, 1982). Between 1983 and 1984, Watmough and Dillon (2003) observed a decline in the exchangeable pool of Ca of as much as 40%, as estimated from mass balance calculations and soil and stream water measurements, across a number of catchments in eastern North America. There remains some controversy, however, over whether the observed depletion of Ca from the soil pools are the result increased leaching associated with acid deposition, or changes in inputs (Watmough & Dillon, 2003). It was initially believed by many investigators that this depletion was the result of biomass accumulation (Johnson, et al., 1988b; Johnson, Andersen, & Siccama, 1994); however several studies have since demonstrated that depletion of the exchangeable soil pool is the result of increased leaching from the soil (Likens, Driscoll, & Buso, 1996; Bailey, Hoenbeck, Driscoll, & Gaudette, 1996). In Eastern North America, it was found that the average loss of Ca from soil leaching was 2.71 kg ha^{-1} yr^{-1} (Huntington, et al., 2000). Watmough and Dillon (2003) demonstrated that soil Ca depletion could not be explained by decreases in deposition or weathering inputs, and further estimated that the losses of Ca from the soil pool would have been even greater in mature forests that were not accumulating Ca in new biomass. In Morvan, France, pools of Ca have been decreasing since 1963 by an average of 1 kg ha^{-1} yr^{-1}, resulting in Ca-depleted soils (van der Heijden, et al., 2013). Watmough and Dillon (2003) observed comparable losses of Ca from soil pools in eastern North America. Similar depletion has also been observed at the HBEF since the early 1960’s as a result of leaching of base cations in response to acid deposition and decreases in inputs. As a result, the available pool of Ca in soil at HBEF has been reduced to the point that ecosystems are Ca-limited (Likens, et al., 1998).

Depletion of the soil pool may lead to nutrient-limited forest systems, potentially resulting in declines in growth rates (Likens G. E., et al., 1994) and changes to the water cycle (Green, et al., 2013); however it is not yet fully understood how vegetation will adapt to this limitation. Likens et al. (1998) suggest that vegetation may be able to take up Ca that is more strongly bound than the readily exchangeable Ca in soil pools, while Green et al (2013) have suggested that nutrient limitation may decrease the rate of photosynthesis and therefore affect the rate of evotranspiration.

2.6.2. Total budget trends

At the HBEF, between 1963 and 1992, the annual Ca budget was negative, indicating a net loss of Ca from the system (Likens, et al., 1998). During this period, it was also found that inputs from bulk precipitation were less than outputs from stream water export, contributing to the negative Ca budget (Likens, et al., 1998). This trend has been observed in other sites across Eastern North America (Yanai, et al., 2005; Watmough, et al., 2005; Huntington, et al., 2000). Between 1969 and 1992, net biomass uptake in a northern hardwood forest ecosystem decreased by a total of 3.86 kg ha^{-1}, while total inputs into the system from atmospheric deposition decreased by 1.52 kg ha^{-1} and stream export decreased by 1.76 kg ha^{-1} over the same time period, reflecting the depletion of the soil pool and decreases in atmospheric inputs (Likens, et al., 1998). The total forest floor and mineral soil pool declined from 10,369 kg ha^{-1} to 9,917 kg ha^{-1}, quantifying the soil depletions (Likens, et al., 1998). Depletion of the soil pool was largely the result of increased acid deposition, decreased deposition of Ca, and biomass accumulation. Only the biomass pool experienced an increase in Ca storage over this time period (as a result of accumulation in plant tissues); however as mentioned previously, the rate of uptake decreased.

2.7. Calcium budgets and catchment liming

Catchment liming is a method used to mitigate the effects of acidification by replenishing lost base cations to the exchangeable soil pool through the addition of a powdered acid neutralizing agent to catchment soils (Ivahnenko, Renton, & Rauch, 1988). There exist several neutralizing agents including: limestone ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), calcined lime (CaO), calcined dolomite (CaO-MgO), hydrated lime ($Ca(OH)_2$) and caustic soda ($NaOH$) (Clair & Hindar, 2005; Cho, Driscoll, & Blum, 2009). Limestone is used most often because its chemical composition ($CaCO_3$) replenishes Ca^{2+} which, as previously described, is an important base cation for neutralization. Furthermore, limestone occurs naturally in most soils and is comparatively inexpensive (Clair & Hindar, 2005). The Ca^{2+} dissociates from the limestone and exchanges with H^+ ions in soil solution or in surface waters (Equation 5), which decreases acidity by raising pH (Cho, Driscoll, & Blum, 2009).

$$CaCO_3 + 2H^+ = Ca^{+2} + H_2CO_3 \qquad (5)$$

Catchment liming is a relatively low maintenance approach to mitigating effects of acidification, as lime does not need to be applied frequently, and once applied the benefits to the catchment and stream waters are uninterrupted (Clair & Hindar, 2005). Furthermore, it addresses the proximate cause of aquatic ecosystem acidification by replenishing soil base cations and increasing Al retention (Clair & Hindar, 2005). Ca budgets have not yet been extensively used to determine liming dosages required in catchment liming applications.

The addition of neutralizing compounds such as $CaCO_3$ to acidified watersheds can result in significant increases Ca concentrations and pH in stream waters (Bradley & Ormerod, 2002; Rundle, Weatherley, & Ormerod, 1995; Traaen, et al., 1997). Several studies have reported such results in catchments in Europe (Miller et al, 1995; Howells, 1995; Hindar et al., 2003; Fransman & Nihlgaard, 1995; Wilander et al., 1995). In Norway, Traaen et al. (1997) measured the changes in the Ca budget after catchment liming. The exchangeable soil pool of Ca increased significantly, as 75% of the Ca added was stored in the soils, and only 15% was lost through runoff. Ten percent of the applied Ca remained unaccounted for. Fewer catchment liming studies have been conducted in North America; however Driscoll et al. (1996) observed similar increases in pH and Ca concentration in stream waters after a liming project in Eastern North America.

More research exists on the changes to Ca budgets by direct in-lake or in-stream liming, where the neutralizing agent is applied directly into the lake or stream waters. Teveret and Harriman (1988) tested the application of limestone to lake waters. Prior to the limestone application, the Ca budget for the system was balanced. The limestone application to the lake resulted in changes to the Ca budget where outputs exceeded input by an equivalence of 46% of the applied limestone, demonstrating that the lake sediments were acting as a Ca sink (Tervet & Harriman, 1988). A similar study was conducted in Nova Scotia, where it was found that 60% of the Ca added by a limestone application to the test lake was exported in outflow, demonstrating again the role of lake sediments in Ca-depleted environments as Ca sinks (White, Watt, & Scott, 1984). In both cases, the application of limestone directly to lake waters resulted in a negative Ca budget.

The addition of Ca to an acidified watershed has the potential to affect a number of biogeochemical processes, fluxes, and pools. Likens et al. (1998) presented the potential influences of the addition of $CaCl_2$ (used in order to isolate the Ca depletion problem without affecting the pH of the system) to a watershed at HBEF, including increases in stream output of Ca, increased tree growth, and increased abundance of soil invertebrates. Calcium budgets have not been used extensively as tools for calculating the quantities of neutralizing agents required to compensate for Ca losses in ecosystems affected by acid deposition.

2.8. Southwest Nova Scotia

South West Nova Scotia is one of the most acid-sensitive regions in North America. Despite significant decreases in acid emissions since the 1970s, the lake record in SWNS has not yet demonstrated recovery from acidification (Clair, Dennis, & Vet, 2011). This lack of recovery was also observed in the river record in SWNS (Minichiello, 2014).

SWNS possesses a unique set of physical and chemical characteristics that have made the region particularly vulnerable to Ca depletion. The granitic bedrock underlying SWNS is slow-weathering and therefore contributes a limited quantity of base cations to overlying soils. As a result, these soils possess little buffering capacity (Watt et al., 2000). The proximity of SWNS to the coast results in the deposition of acidifying sea salts, and the region also supports a high abundance of acidic wetlands (Whitfield et al., 2007; Clair, Dennis, & Vet, 2011). Sea salt spray and precipitation contain chloride which contributes to the acidification of freshwater and surface soils (Wright, 2008). Wetlands also contribute to the acidification of surface waters and soils. They have the potential to store large quantities of sulfur that can be mobilized as sulphuric acid (H_2SO_4) by the high concentrations of DOC present in wetlands, and that may be leached into surrounding soils and surface waters (Clair, Dennis, & Vet, 2011). Surface water chemistry has not recovered as expected from reduced acid deposition that has resulted from improved air quality standards (Clair, Dennis, & Vet, 2011). Soils depleted of base cations have a reduced buffering capacity; even if acidification were halted within the next 50 years, soil base cations are predicted not recover for 60-100 years, and freshwater communities may be unable to recover without human intervention. (Clair & Hindar, 2005).

Continued acidification from upwind fossil fuel emissions has further contributed to the decline in base cation concentration in catchment soils and surface waters in SWNS. This has resulted in lost buffering capacity of catchments and in decreased ANC, which has in turn led to decreases in pH and increases in Al concentrations in surface waters. As described previously, these changes can be detrimental to aquatic ecosystems (Clair, Dennis, & Vet, 2011). Of particular concern in SWNS are the negative effects of acidification to Atlantic salmon populations. Acidification has been identified as the major cause of Atlantic salmon extirpation in SWNS (Bradley & Ormerod, 2002; Watt, 1987; Rosseland & Staurnes, 1994), as the positively charged Al ions accumulate on the negatively charged gills of the salmon (Dennis & Clair, 2012). By replacing the depleted Ca through catchment liming, it may be possible to increase the availability of base cations for exchange with H^+ from acid deposition, and to therefore reduce the amount of toxic Al released into stream waters (Clair & Hindar, 2005).

Catchment liming has been demonstrated to be effective in mitigating the effects of acidification, and is currently being tested in SWNS. The addition of neutralizing substances to SWNS catchments may accelerate the recovery of stream water chemistry and soils by replenishing depleted base cations and buffering acid inputs. It is currently unknown how much Ca must be added to a catchment to effect sufficient change in surface water chemistry to mitigate the negative impacts of acidification.

2.9. Summary of knowledge gaps

Calcium budgets in forested and acidified ecosystems are reasonably well understood; however there remain several gaps in knowledge. Input-output budgets inherently contain high levels of uncertainty as a result of inaccurate estimates of fluxes within the system (van der Heijden, et al., 2013). Furthermore, validation of these inputs and outputs, and of the budget as a whole, can be difficult (van der Heijden, et al., 2013). Uncertainty remains around whether the observed trends in declining exchangeable soil pools of Ca are the result of loss from the exchangeable pool, or are instead the result of changes in Ca deposition (Watmough & Dillon, 2003). There remains a lack of understanding of how this depletion will affect concentrations of Ca in stream runoff, as Watmough et al. (2005) demonstrated a positive relationship between the concentration of Ca present in stream runoff and the size of the exchangeable pool in soils.

Freedman and Clair (1987) examined the ion mass balances and fluxes of four rivers in SWNS; however no complete Ca budgets have been completed for this region of the province. Clair et al. (2002) observed declines in Ca concentrations in Nova Scotian lakes between 1982 and 1997 which demonstrates that Ca depletion is occurring in SWNS. More recently, Clair et al. (2007) estimated the water chemistry of acid-sensitive lakes across eastern Canada and found that Ca concentration in stream waters were significantly higher during the peak acid deposition in 1975, and that have since decreased. This peak during the mid 1970’s is likely the result of increased acid deposition, which in turn increases the concentration of base cations in runoff waters (Stumm, Sigg, & Schnoor, 1987). Without a comprehensive Ca budget of acidified watersheds, however, this understanding remains incomplete. Calcium budgets have not yet been extensively used to determine liming dosages required in catchment liming applications, and therefore it remains unknown how much Ca must be added to a SWNS catchment in order to effectively mitigate the effects of acidification.

3. Methods

3.1. Overview

The technique of catchment liming has only recently been introduced to SWNS. In 2010, the Hydrology Research Group (HRG) of Dalhousie University, in partnership with the Bluenose Coastal Action Foundation (BCAF) and with support from the Donner Foundation and Environment Canada, implemented the first catchment liming experiment in SWNS. Ninety tonnes of crushed limestone ($CaCO_3$) was applied to the acidified watershed of Maria Brook (Fig. 1) in an attempt to replenish the depleted base cations from the soil and to mitigate the effects of acid precipitation deposition. The limestone was applied in two phases to the Maria Brook catchment. The first test application of 30 tonnes was applied in May 2012, with an average of 13 tons of limestone applied per hectare over 2.04 ha on the west side of the catchment. A second application of 60 tonnes was completed in August 2013 on the east side of the brook. This research concentrates on the effects of the first application of 30 tonnes of $CaCO_3$ to the Maria Brook watershed.

The Maria Brook watershed is mostly forested with well-defined hypsometry and is located in a typical SWNS environment underlain by leucomonzogranite.

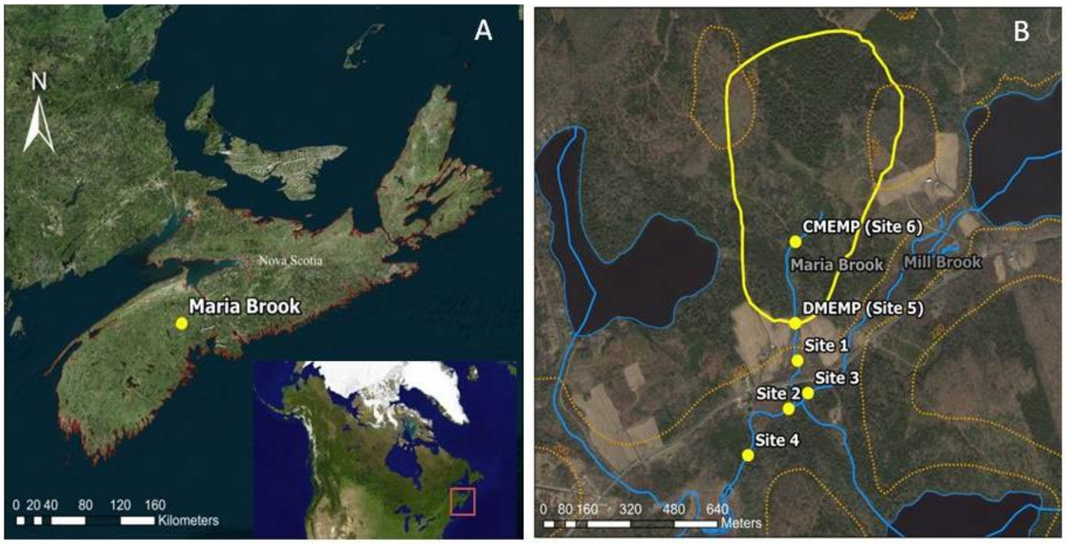


Figure 2 A) Maria Brook study site in South West Nova Scotia. B) The Maria Brook catchment (yellow contour) and the six field monitoring sites.

Using data from The Canadian Air and Precipitation Monitoring Network (CAPMoN) and from water chemistry grab samples, and in-situ continuous monitoring data of stage and conductivity of the catchment drainage waters, pre-liming and post-liming Ca budgets were constructed. A stage-discharge model was developed to estimate drainage of water from the system both pre- and post-liming. The Ca budget was determined from Ca entering the system through deposition and exported from the system through drainage water (Bormann and Linkens, 1967).

3.2. Site description

The Maria Brook watershed is an acidified watershed located in SWNS and is mostly forested, with well-defined tear-drop hypsometry and an area of 50 hectares underlain by leucomonzogranite. It is located 6.4 km east of the town of New Ross, and approximately 24 km from the southwest coast of Nova Scotia, with an elevation ranging between 190-225 m above sea level. No invasive species have been identified within the catchment. The catchment is composed of mixed forest, dominated by native Red spruce (*Picea rubens*), Balsam fir (*Abies balsamea*), and White spruce (*Picea glauca*) ranging in age from 5 to over 100 years.

The Maria Brook watershed was selected for several reasons. It is a typical SWNS forested watershed that is well connected to important Atlantic salmon habitats in the larger Gold River watershed. Furthermore, the watershed is located on private land with land owners who are supportive of the project, and is not divided by roads or developments.

3.3. Geology

Two drumlins border the brook on the east and west sides. The site is underlain predominately by the South Mountain batholith, composed of leucomonzogranite, containing less than 1% CaO (Charest, 1976). This low concentration of Ca results in little contribution of Ca by weathering to soils and surface waters. Soil pits revealed that the upslope region of the catchment is composed of well-drained sandy-loam soils, while the toe-slope region is composed of poorly drained stony soils with a shallow organic layer (10-20 cm) (Yanni, et al., 2000). BCAF collected 15 soil samples in August, 2011 from various sites within the Maria Brook catchment and recorded an average pH of 5.14, with a high of 5.75 and a low of 3.90. In September 2011, two more samples were collected to measure Ca concentrations in soils, 457 kg ha^{-1} and 834 kg ha^{-1} respectively (Fig. 3).

Figure 2: Soil sample sites at the Maria Brook catchment, SWNS. Courtesy of Andrew Breen (BCAF).

3.4. Climate

The climate in SWNS is typical mid-latitude maritime, with an average annual temperature of 7.5°C, ranging from an average of 17°C in the summer months and -5°C in the winter. The average precipitation ranges between 1400-1500 mm y^{-1} with average snow cover during the winter months of 60mm y^{-1} (Environment Canada, 2013).

3.5. Stream ecology

The Maria Brook is a lotic depositional environment characterized by a low abundance and diversity of stream invertebrates but relatively large numbers of worms (BCAF, 2011). Most invertebrates identified belonged to the *Chironomidae* family. Maria Brook has high levels of DOM and is a feeder stream of the Gold River system which is an important Atlantic Salmon habitat (BCAF, 2011).

3.6. Experimental Design

In order to understand the effect of catchment liming on the Ca budget of Maria Brook, pre-liming and post-liming calcium budgets were constructed and compared (Fig. 16 and 17). A stage-discharge model was constructed to estimate drainage of water from the system both preand post-liming (Fig. 3; equation 7). The nutrient balance was determined from Ca inputs to the system through precipitation and outputs through drainage water (Bormann & Likens, 1967; Likens, et al., 1998). The mass balance for Ca in the system was calculated using equation 6 adapted from Likens et al. (1994).

$$\text{Mass balance} = P_{Ca} + W_{Ca} - S_{Ca} \qquad (6)$$

where P represents atmospheric input, W is weathering input, and S is stream export.

3.6.1. Measuring inputs

The assumption was made that major inputs of Ca into the system were restricted to atmospheric deposition and weathering processes following Christophersen et al. (1982) and Likens et al. (1967). Atmospheric deposition of Ca was estimated using precipitation chemistry data from CAPMoN. Precipitation data from CAPMoN was available until 31 December 2011. Data for 2012 was unavailable and was therefore modeled based on past trends in precipitation inputs.

CAPMoN only provided data on wet deposition, which resulted in underestimation of the bulk deposition of Ca to the system by excluding dry deposition (Likens, et al., 1998). Atmospheric depositional inputs were adjusted by estimating dry deposition rates based on the relationship determined by Likens et al. (1998) between wet and dry deposition (Table 6).

Weathering inputs were approximated using estimates from the literature (Table 7). Watmough et al. (2005) estimated annual base cation weathering rates for the Moose Pit catchment in SWNS (using the PROFILE model) of 3.3 kg Ca ha^{-1}. This estimate was used for both pre- and post-liming budgets, and was assumed to remain constant through time (Likens, et al., 1998; Ranger & Turpault, 1999)

3.6.2. Measuring outputs

The assumption was made that stream discharge was representative of major exports of Ca from the system following Ranger & Turpault (1999) and Christophersen et al. (1982). In order to determine discharge chemistry, grab samples were collected bi-weekly for water chemistry analysis at Maxxam Analytics in order to ascertain Ca concentration in stream waters (Christophersen, Seip, & Wright, 1982). The grab samples were analyzed for metals content, pH, and DOC. Stream water discharge was estimated by developing a stage-discharge relationship. The relationship was developed by taking stream velocity measurements using a velocity meter (Global Water Model FP101), and measuring the cross-sectional area of the stream. In-situ monitoring provided real-time stage data, and once the relationship was developed between stage and discharge, discharge data was estimated using the real-time stage data. In-situ stage was measured with an OTT compact bubbler sensor and the data was collected on a data logger from Campbell Scientific (CR1000). The data was then downloaded in the lab for analysis. The discharge and the concentration of Ca obtained from the grab sample chemical analysis was then used to calculate the total output of Ca from the system as a result of stream discharge.

3.6.3. Measurement sites

The grab samples for water chemistry analysis were collected from six sites (1-6) (Fig. 1). There were two control sampling sites. Site 6 was located upstream of the limed zone of the Maria Brook catchment. Site 3 was located on Mill Creek, which acted as a comparison watershed. The four treatment sampling sites (sites 1, 2, 4, and 5) were located along Maria Brook and Mill Creek. Site 1 was located 520 m downstream of site 6; site 2 was located downstream of the junction between Maria Brook and Mill Creek; site 4 was located 1020 m farther downstream of site 2 along Maria Brook; and site 5 was located on Maria Brook, 320 m downstream of site 6 (control site). Velocity measurements were taken bi-weekly between sites 5 and 6 at 50 m intervals in order to produce a profile of stream discharge, and weekly at the culvert located at site 6. CAPMoN precipitation data was collected daily at the Kejimkujik National Park weather station located approximately 100 km from the experimental site.

3.6.4. Lime application

The 30 tonnes of $CaCO_3$ was applied to the hydraulic source area, which was divided into 20 x 20 m quadrats, and was not placed within 1 m of the stream. The powdered limestone was applied by hand to a total of 51 quadrats, covering a total of 2.04 ha of the Maria Brook catchment, with an average of 13 t/ha. This application was concentrated near the bottom of the watershed, along the east bank of the brook. The lime application was conducted during the late spring as this season tends to be drier and generally experiences reduced overland flow. It was hoped that this would allow for more uptake of the limestone by plants or for greater storage in soil, and would reduce the amount of limestone lost by overland flow caused by heavy storms.

3.7. Limitations and delimitations

This research was limited in several ways. Grab samples collected prior to the fall of 2013 were analyzed by the Atlantic Laboratory for Environmental Testing (ALET), while samples taken in September 2013 and later were analyzed by Maxxam Analytics. Consistency in analysis techniques may not have been maintained during this transition. Standard operating procedures differed between the two water quality testing labs, and as a result, some inconsistency may be present in the data. Grab samples were taken bi-weekly; however samples were not always collected on the same day and time. The velocity meter used to measure stream water velocity was not always sensitive enough to record the velocity in slow-moving segments of the stream. As a result, errors in velocity measurements may be present and may affect the stage-discharge relationship. Precipitation data for 2012-2013 were not available from CAPMoN, and as such it was necessary to estimate the inputs of Ca from this source based on past trends. Weathering fluxes are inherently difficult to obtain, and estimates from the literature were approximations only (Bailey, Buso, & Likens, 2003).

This study was also delimited by several factors. The Ca budgets developed did not include measurements of plant uptake of Ca as time and resources did not permit collection of required data. The research only compared the changes in Ca budgets between pre-liming at Maria Brook and post-liming of the first application of lime (2012-2013) as insufficient data were available to produce and compare Ca budgets with the second application of limestone in 2013.

4. Results

4.1. Stage-Discharge Relationship

Stage data was available in real-time at 15-minute intervals from in-situ monitoring stations. A stage-discharge relationship was developed in order to use this high-frequency stage data as an estimate of total water discharge from the system ($R^2=0.46$; N=37) (Equation 9).

$$\text{Discharge } (m^3/s) = 0.239 \text{ Stage } (m) - 0.0102 \tag{7}$$

Figure 3 illustrates the relationship between stage and discharge. Data were collected from August to October 2013, and measurements were taken along a 320 m transect the length of the brook segment between the control and treatment monitoring sites (sites 6 and 5 respectively). Descriptive statistics for the stage-discharge relationship are described in Table 1.

Table 1: Descriptive statistics of the stage-discharge relationship. Measurements collected at site 5, August-October 2013.

Variable	N	Mean	StDev	Minimum	Median	Maximum
Stage (m)	37	0.23	0.14	0.07	0.17	0.66
Discharge (m3/s)	37	0.044	0.049	0	0.031	0.26

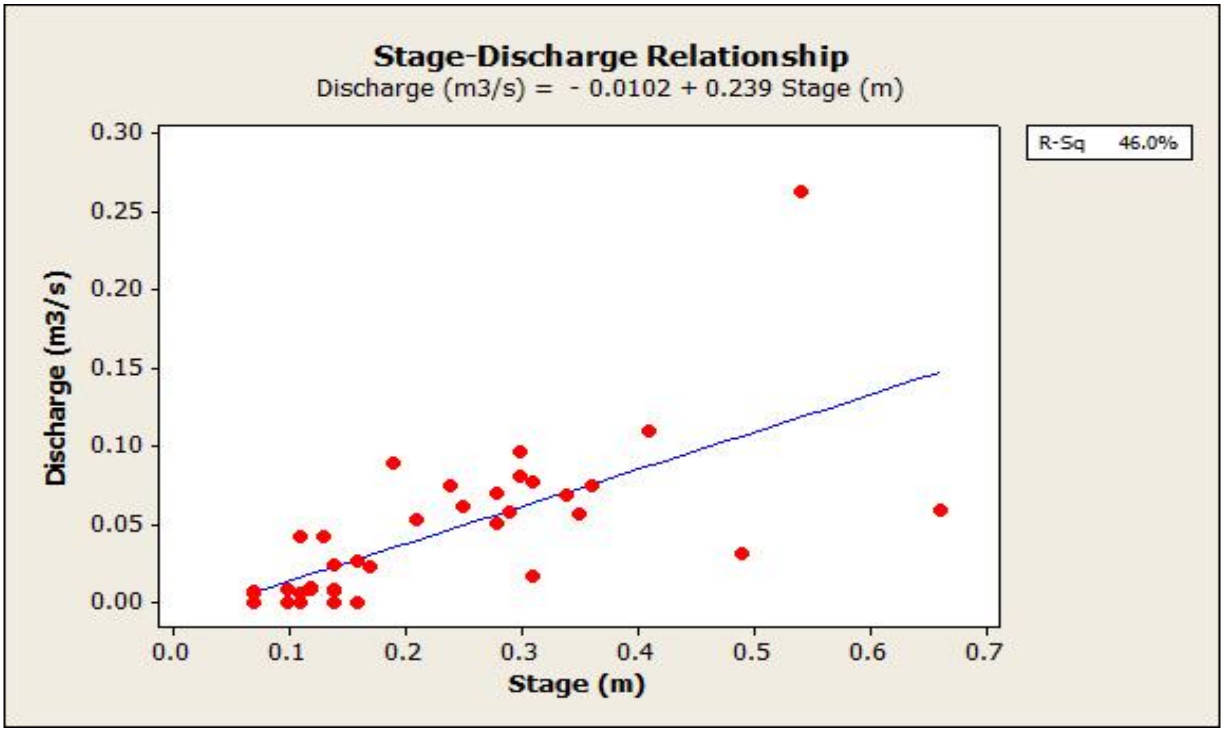


Figure 3. Stage (m) – discharge (m^3/s) relationship at the Maria Brook watershed. N = 37. Data collected between August and October 2013.

Real-time stage data was used from the treatment site 5. Gaps in data were adjusted using a relationship developed between the stage data from the control site 6 and from site 5 (Appendix B) (R^2= 0.72; N =5046). The relationship is described in Equation 10.

Site 5 stage (m) = 0.4279 site 6 stage (m) +0.1738 (8)

Total stream water discharge pre-liming (2.16 x 10^8L) was greater than during the post-liming phase (1.57 x 10^8L) (Table 2). Discharge was greatest in September 2011 (3.15 x 10^8L), and September 2012 (2.29 x 10^8L) and lowest in June and December 2012 (0.62 x 10^8L) (Fig. 4). Of particular importance is the significant discharge in July-September 2012, in the months immediately following the $CaCO_3$ application. The high discharge in September 2011 corresponds to high levels of precipitation during this same time (Fig. 5). During periods of low flow, there was a general decrease in precipitation. However, during December 2012 there was significant precipitation and little discharge. This was likely due to the fact that the soils were frozen and precipitation fell as snow which accumulated on the surface as opposed to running into surface waters. Stage data was not available prior to September 2011, and therefore discharge values for June-September 2011 (during the pre-liming phase) were estimated from monthly averages of 2011 (red points in Fig. 4).

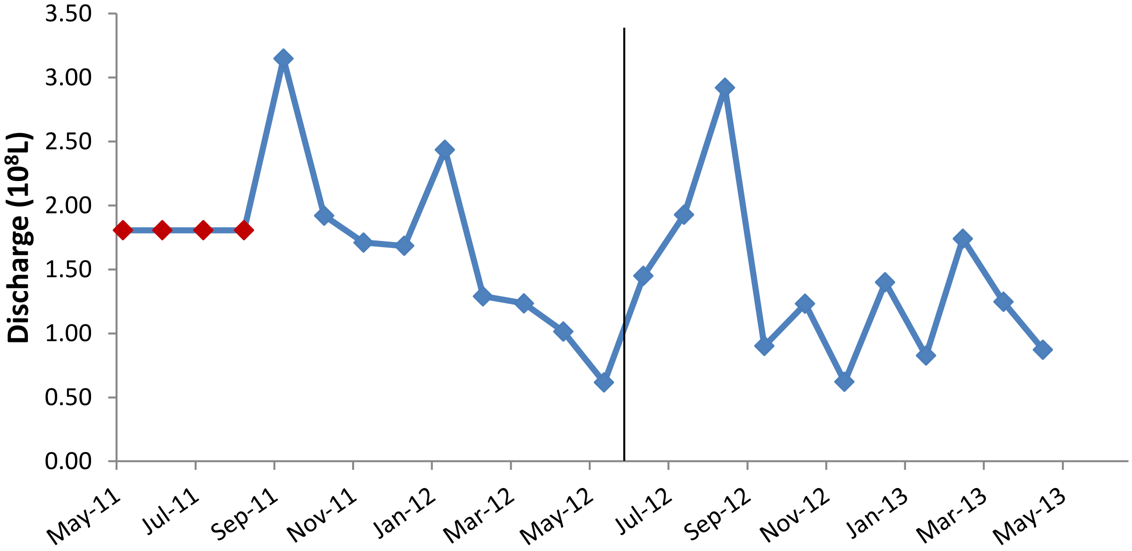


Figure 4. Stream water discharge (10^8L) pre- and post-liming estimated using the stage-discharge relation and real-time 15 minute stage data from site 5. Vertical black line denotes $CaCO_3$ application. Red points are estimates of discharge based on monthly averages of 2011 discharge.

Pre-liming monthly mean discharge was 1.8 x 10^7 L, while post-liming the monthly mean discharge was 1.3 x 10^7 L (Table 2). Post-liming monthly discharge was also more variable than during the pre-liming phase.

Table 2. Stream water discharge (10^9 L) pre-liming (June 2011-May 2012) and post-liming (June 2012-May 2013) as calculated for site 5.

	Pre-liming (10^9 L)	Post-liming (10^9 L)
Total	2.16	1.57
Monthly mean	0.18	0.13
SD	0.056	0.066

Discharge trends at site 5 were similar to precipitation trends (Fig. 5); however the relationship was not strong (R^2 = 0.12) (Appendix G).

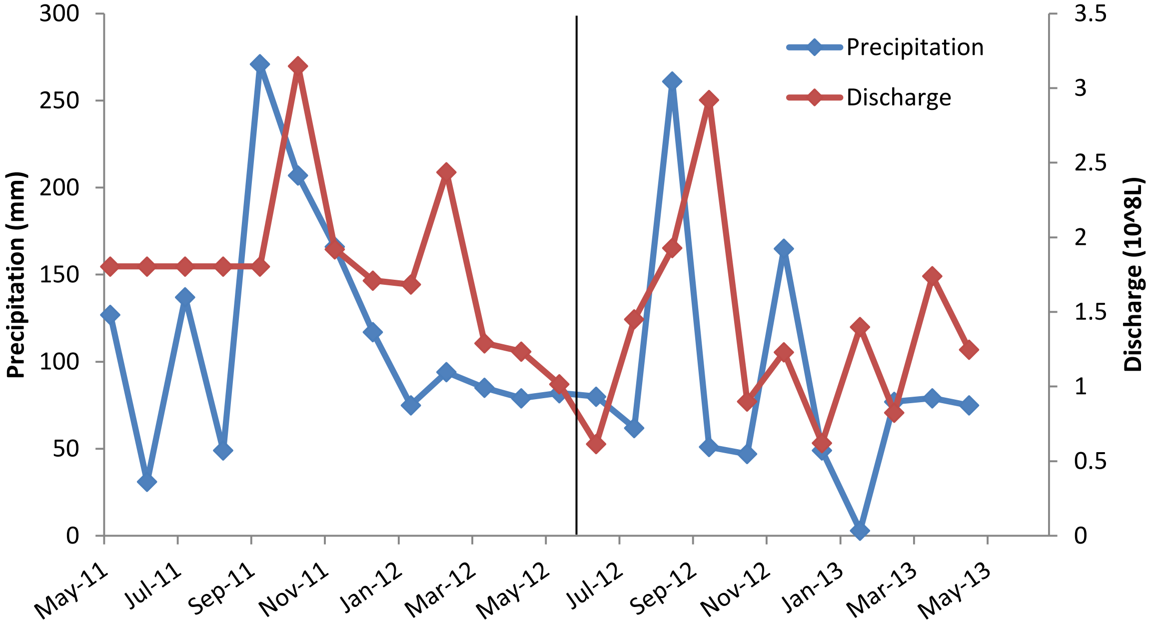


Figure 5. Monthly pre- and post- liming precipitation (mm) and discharge (10^8 L). Vertical black line denotes application of $CaCO_3$. Precipitation data from Environment Canada.

4.2. Stream water calcium concentration

Stream water Ca concentration varies with season (Likens, et al., 1998), where plant uptake of Ca from the soil pool and transpiration rates are greatest during late spring and summer when plants are most active. During this period, soil water loss, discharge, and Ca export tend to be lowest. Ca export and stream water concentrations are greatest during the early spring when temperatures rise and leaching increases as a result of snow melt. Because plants are still largely dormant during this period, Ca export is particularly high (Likens, et al., 1998). Similar trends were observed by Minichiello (2014) of long term seasonal patterns of Ca ion exports from Kejimkujik National Park in SWNS.

Conductivity data was available in real-time at 15-minute intervals from in-situ monitoring stations at the experimental site. A Ca-conductivity relationship (Equation 11) (R^2=0.71; N=19) was previously developed by the Hydrology Research Group (HRG) and was used in order to utilize the high-frequency conductivity data as a proxy for stream water Ca concentration (Appendix C) (Sterling, et al., 2014).

$$[\text{Ca}]\ (\text{mg L}^{-1}) = 0.079\ \text{conductivity}\ (\mu\text{S cm}^{-1}) - 0.897 \tag{9}$$

Real-time conductivity data from site 5 was used to calculate pre- and post-liming stream water Ca concentration (Fig. 6). Site 5 stream water Ca concentration was not significantly different from the control site 6 (R^2=0.71; p=0.00) (Appendix H). Descriptive statistics for site 5 are described in Table 3. Post-liming, mean stream water Ca concentration is greater (1.51mg L^{-1}) than pre-liming values (1.01mg L^{-1}) (Table 3). Maximum Ca concentration was measured on 7 September 2012 during the post-liming phase (2.75mg/L). The minimum Ca concentration during the post-liming phase (0.31mg L^{-1}) was also greater than the minimum Ca concentration pre-liming (0.31mg L^{-1}), and post-liming stream water Ca concentration was slightly more variable among months (SD = 0.39) than during the pre-liming phase (SD = 0.36).

Table 3. Descriptive statistics for pre-liming (June 2011-May 2012) and post-liming (June 2012-May 2013) stream water [Ca] (mg L^{-1}), Ca export (kg ha^{-1} $month^{-1}$), precipitation (mm $month^{-1}$) and bulk deposition (kg ha^{-1} $month^{-1}$). Values based on weekly estimates of [Ca] from real-time in-situ conductivity data and stream water discharge estimated from real-time in-situ stage measurements. Precipitation data from Environment Canada.

	N	Mean	StDev	Minimum	Maximum	Annual Total
Stream Water [Ca] (mg L^{-1})						
Pre-liming	52	1.01	0.36	0.31	1.59	
Post-liming	52	1.51	0.39	1.03	2.75	
Ca Export (kg ha^{-1})						
Pre-liming	12	3.77	2.10	1.52	7.715	46.11
Post-liming	12	4.52	3.23	1.40	13.10	58.41
Precipitation (mm)						
Pre-liming	12	119.8	68.4	31	271	1483
Post-liming	12	85.9	66.6	3	261	1033
Ca Bulk Deposition (kg ha^{-1})						
Pre-liming	12	0.22	0.12	0.04	0.46	2.66
Post-liming	12	0.20	0.08	0.10	0.31	2.48

Prior to the application of $CaCO_3$ in May 2012, a general decline in Ca concentration in stream waters was observed between September 2012 and March 2012, followed by an increase in Ca concentration leading up to the liming in May 2012 (Fig. 6). Post-liming, the rising trend in Ca concentration continued until September 2012, after which a sharp decline was observed followed by a levelling of Ca concentration which remained steady between October and April 2012. Calcium concentration increased again slightly in the spring of 2013.

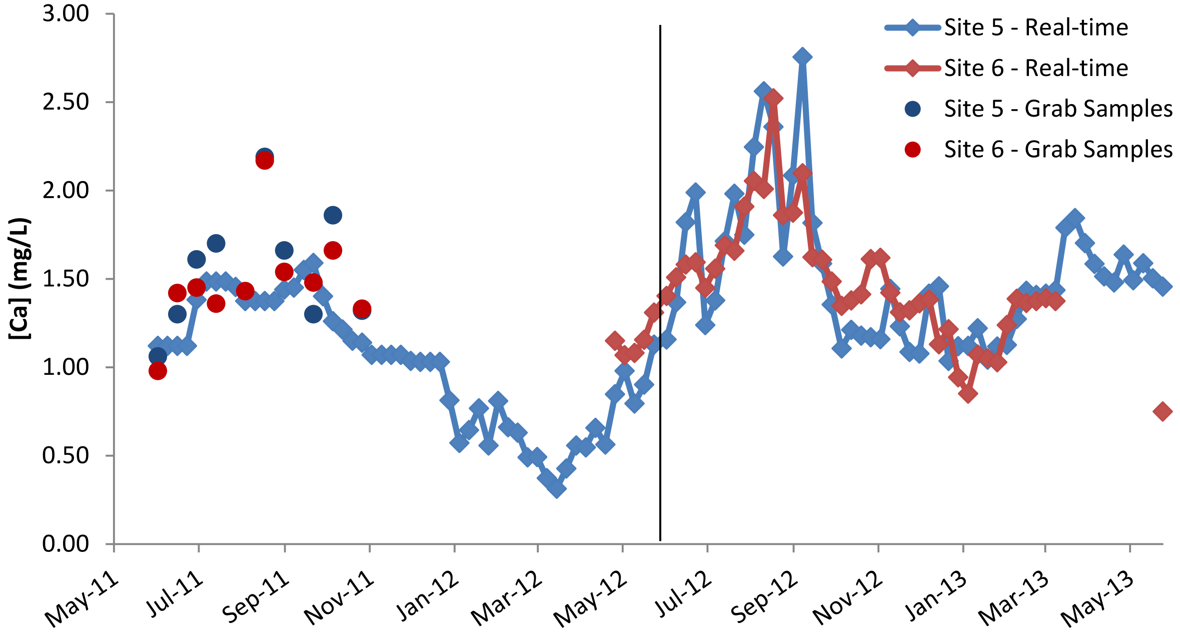
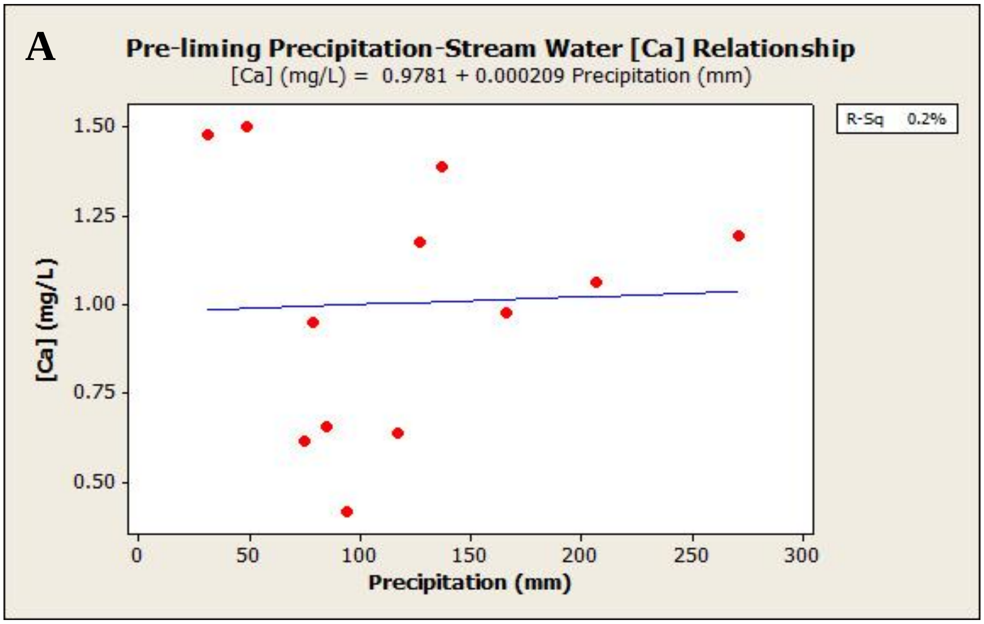


Figure 6. Pre- and post-liming stream water [Ca] (mg L^{-1}). Black vertical line denotes $CaCO_3$ application. Data calculated from real-time conductivity measurements (site 5) and equation 11.

Gaps in real-time conductivity data were filled using two methods. When grab samples were available for site 5, Ca concentration from the grab samples was used to fill any gaps. When grab samples were unavailable for site 5 (prior to 5 May 2012), the relationship (Equation 12) developed between site 1 grab sample Ca concentration and site 5 grab sample Ca concentration was used (R^2=0.85; N=11; p=0.00) (Appendix D). Grab samples for site 1 are available beginning in December 2010.

$$\text{Site 5 [Ca] (mg L}^{-1}\text{) = 0.29 site 1 [Ca] (mg L}^{-1}\text{) +0.73} \qquad (10)$$

Pre-liming, stream water Ca concentration had no significant relationship with precipitation (R^2=0.00; p-value = 0.942) (Fig. 7). Post-liming there was also no significant relationship between these two parameters, however the relationship was stronger (R^2 = 0.12; p-value = 0.267).



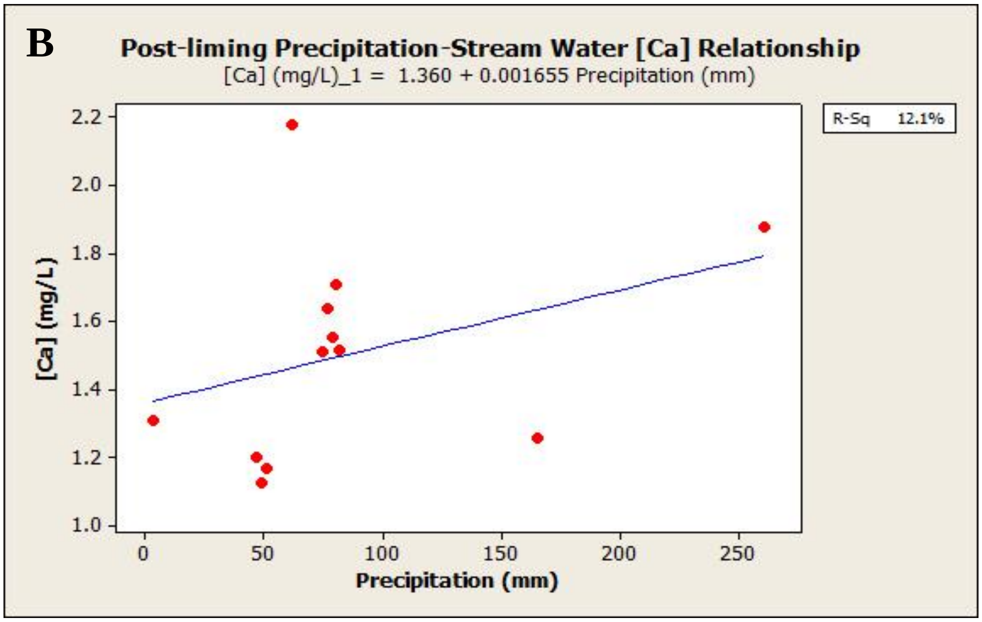


Figure 7. A) Pre-liming relationship between precipitation (mm/month) and mean monthly stream water [Ca] (mg L^{-1}) ($R^2 = 0.00$ p-value = 0.903). B) Post-liming relationship between precipitation (mm $month^{-1}$) and mean monthly stream water [Ca] (mg L^{-1}) ($R^2 = 0.12$; p-value = 0.267).

Measurements were compared to estimates of stream water Ca concentration made using the Model of Acidification of Groundwater In Catchments (MAGIC). The MAGIC model is a simulation model of hydrobiogeochemistry that is used to estimate the long-term effects of acidification on soils and surface water chemistry (Cosby et al., 1985). In 2004, Clair et al. used this model to estimate Ca concentration in surface waters in SWNS under several conditions. Pre-acidification stream water Ca concentration was estimated for the year of 1860, while 1975 represented the onset of acidification with large Ca exports (Table 4). The chronic acidification stage is represented by 1990 estimates. During both years of measurement at the Maria Brook watershed during the current research, stream water Ca concentration is greater than predicted by the model (Table 4).

Table 4 Predictions by Clair et al. (2004) of stream water [Ca] using the MAGIC model (assuming no change in SO_4 deposition since 1985) for the Gold River (located in SWNS) and actual measurements of mean annual stream water [Ca] from site 5 at Maria Brook using grab samples and the relationship developed between [Ca] and stream water conductivity (Equation 9).

Year	MAGIC predictions (mg Ca L^{-1})	Maria Brook Measurements (mg Ca L^{-1})
1860	1.03	-
1975	1.14	-
1990	1.06	-
2011	1.02	1.18
2012	1.02	1.20
2013	1.02	1.42

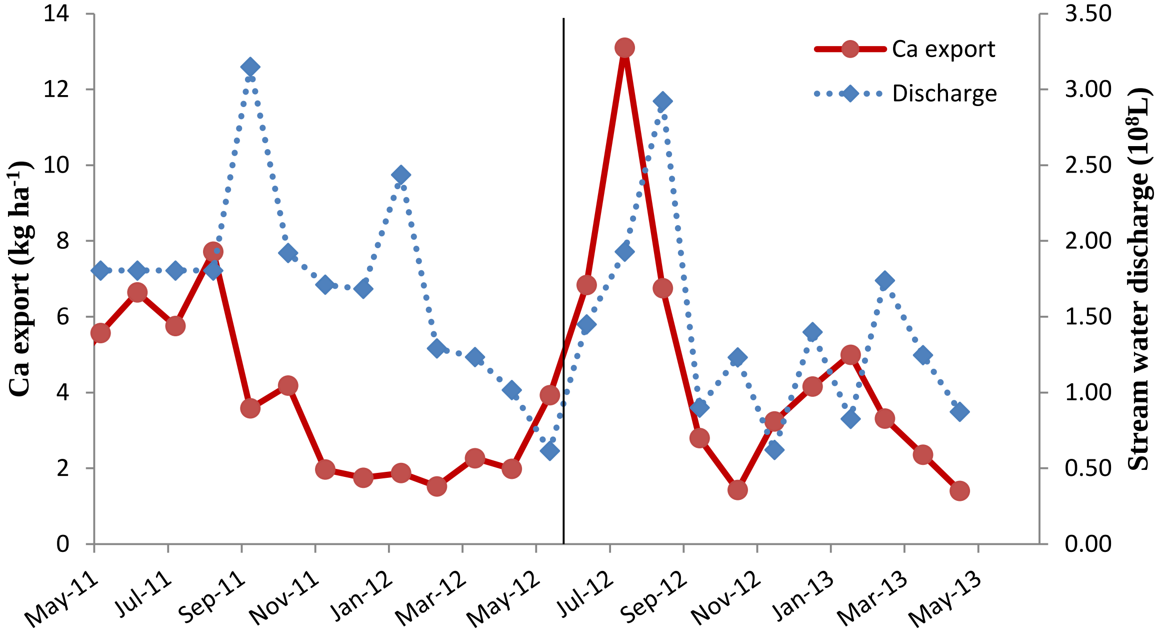


Figure 8. Ca export (kg ha^{-1}) (red) and stream water discharge (10^{8}L) (blue). Vertical black line denotes CaCO^{3} application.

4.3. Ca Export

Monthly Ca export (kg ha^{-1}) was estimated from stream water Ca concentration and stream water discharge (Fig. 8). Post-liming there was a large peak in Ca export, corresponding with a peak in stream water discharge, in the months immediately following the application of $CaCO_3$. Similar to Ca concentration, Ca export demonstrated a decreasing trend between September and December 2011 after which export levelled off before drastically increasing in the summer months (June-Sept 2012) immediately after the liming.

Monthly mean Ca export (kg ha^{-1}) was greater and more variable during the post-liming phase (Table 3). The minimum Ca concentration export during the post-liming phase (1.40 kg ha^{-1}) was slightly lower than during the pre-liming phase; however the maximum export post-liming was nearly twice as large as the greatest pre-liming Ca export (Table 3). Post-liming there is a strong positive relationship between stream water discharge and Ca export (R^2 = 0.73) (Fig. 9). Pre-liming there was no significant relationship between these two parameters (R^2 = 0.00).

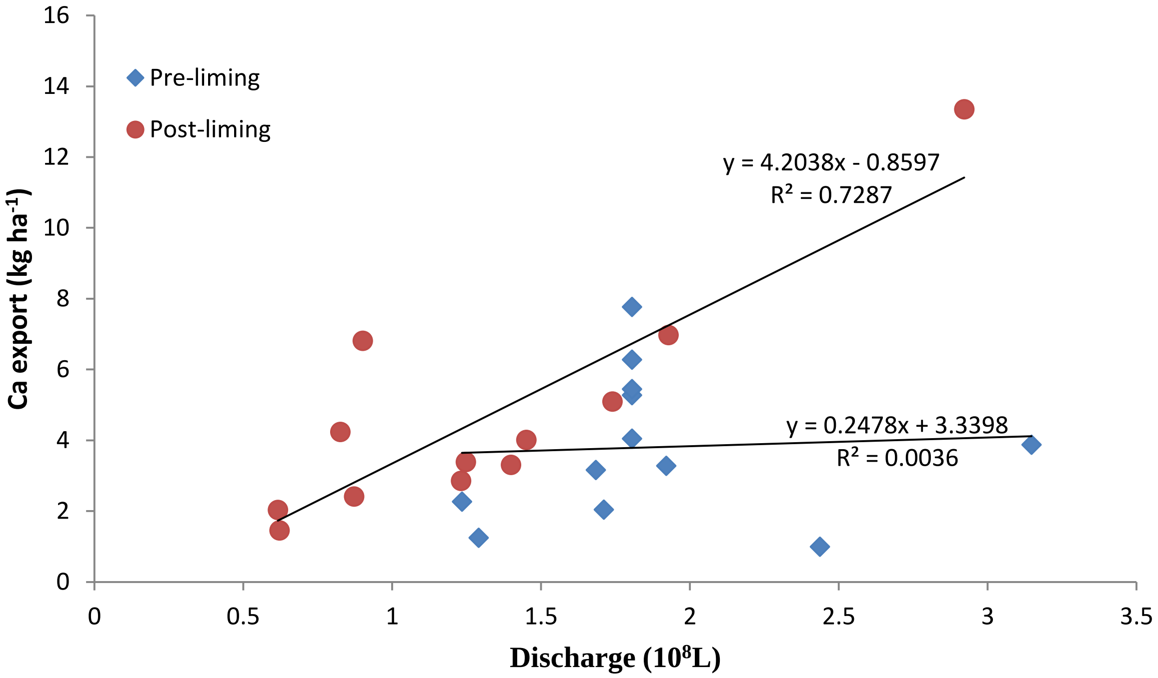


Figure 9. Ca export (kg ha^{-1}) and discharge (10^8L) relationship pre- and post-liming for site 5 using monthly means of Ca export calculated from real-time in-situ conductivity data and stream water discharge estimated from real-time in-situ stage measurements.

Calcium export (kg ha^{-1}) demonstrated similar trends as stream water Ca concentration (Fig. 10). Greatest Ca export was observed when stream water Ca concentration was highest. There was a reasonable relationship between stream water Ca concentration (mg L^{-1}) and Ca export (kg ha^{-1}) from the system (R^2=0.34; N = 24; p-value = 0.003) (Appendix E). Ca export was less well related to precipitation (Fig. 11). Total Ca export from the system pre-liming was 46 ± 2.10 kg ha^{-1}, and was greater post-liming (58 ± 3.23 kg ha^{-1}) (Table 3).

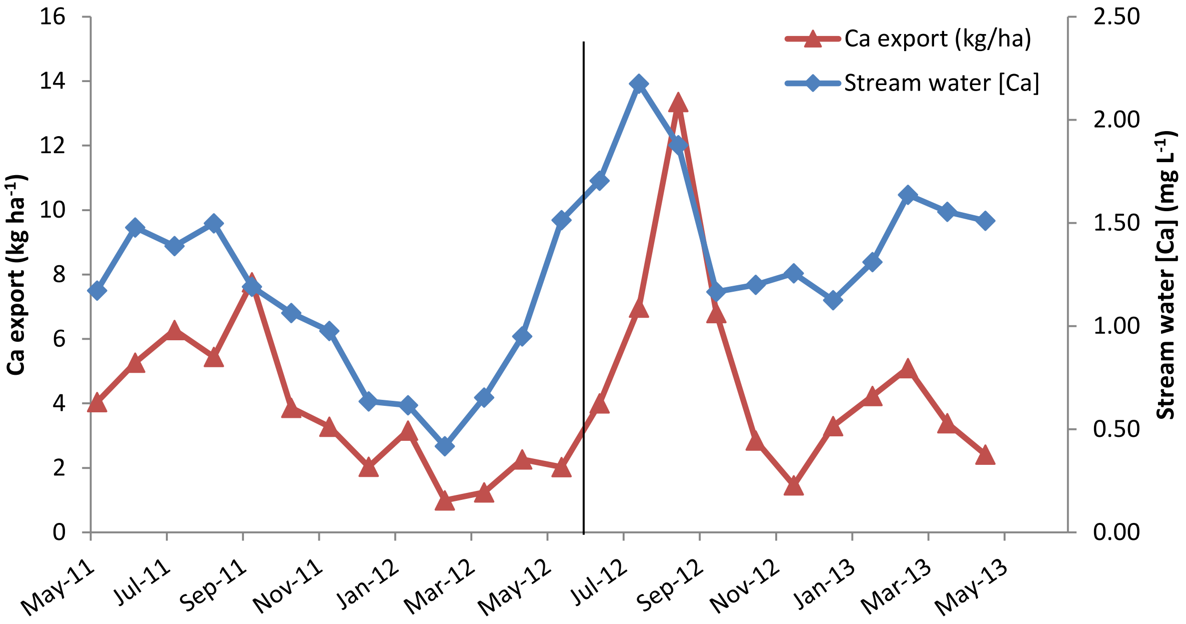


Figure 10. Stream water Ca export (kg ha^{-1}) and stream water [Ca] (mg L^{-1}) at site 5. Calculated from real-time in-situ conductivity data and stream water discharge estimated from real-time in-situ stage measurements. Black vertical line denotes application of CaCO$_3$.

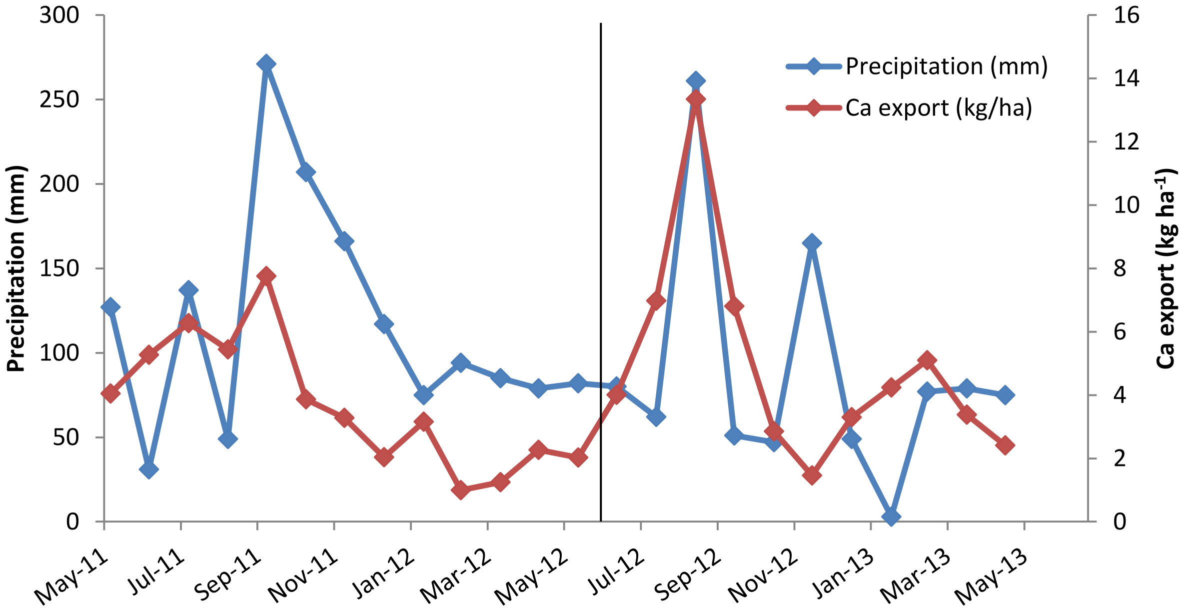


Figure 11. Precipitation (mm) and Ca export (kg ha^{-1}). Precipitation data from Environment Canada database.

4.4. Ca Deposition

Bulk Ca deposition was calculated from wet deposition in precipitation, and dry deposition based on a relationship developed by Likens et al. (1998). Total precipitation was greater during the pre-liming phase, as was the mean monthly precipitation (Table 3). Variability in precipitation was also slightly greater during the pre-liming phase. During both phases, the months of September and October experienced the greatest precipitation (Fig. 12).

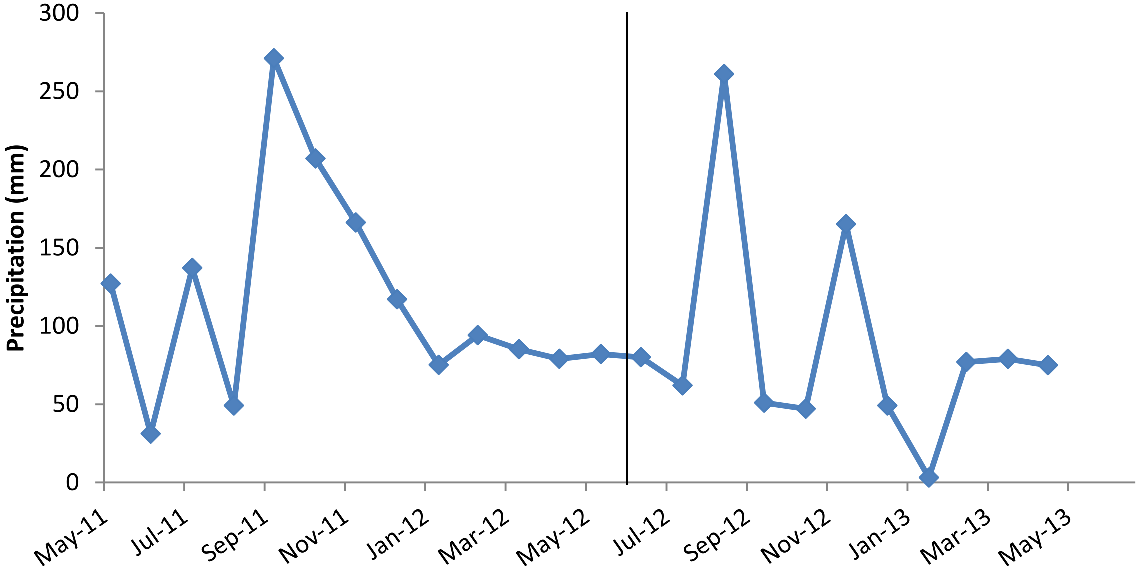


Figure 12. Pre- and post-liming precipitation (mm). Black vertical line denotes application of $CaCO_3$. Data from Environment Canada).

Wet deposition was calculated from CaPMON precipitation chemistry data the Kejimkujik National Park monitoring site in SWNS. Precipitation data were unavailable for 2012-2013. In order to fill this data gap, monthly means of Ca deposition (kg ha^{-1}) were calculated for 2001 to 2011 and were compared to one another using a one-way ANOVA (Table 5). No significant difference was found between monthly means (p-value=0.642) during these years. Monthly means between 2001 and 2011 were then used to estimate Ca deposition for 2012 and 2013.

Table 5 One-way ANOVA comparing differences in annual Ca deposition (mg L^{-1}) between 2001 to 2011. Data from CaPMON.

Source	DF	SS	MS	F	P
Year	10	0.05578	0.00558	0.79	0.642
Error	121	0.85868	0.0071		
Total	131	0.91445			

Mean monthly wet deposition for both pre- and post-liming phases was not significantly different than past deposition (between 2001 and 2011) (Fig. 13). The total wet deposition pre-liming was 2.10 ± 0.09 kg Ca ha^{-1} for a total deposition of 100.5 to 109.5 kg deposited to the Maria Brook watershed (Table 6). Post-liming, wet deposition was 1.95 ± 0.06 kg Ca ha^{-1} for a total of 94.5 to 100.5 kg Ca deposited (Table 6). Based on the relationship developed by Likens et al. (1998), dry deposition of Ca due to sedimentation was estimated from wet deposition (where Likens et al. estimated that dry deposition accounts for approximately 21% of bulk deposition). Dry deposition during the pre-liming phase was slightly greater (0.56 kg Ca ha^{-1}) than during the post-liming phase (0.52 kg Ca ha^{-1}). Dry deposition was greatest during the fall and winter months (Fig. 14). Bulk deposition of Ca pre-liming was approximately 2.66 ± 0.12 kg ha^{-1}, while post-liming it was slightly less at 2.47 ± 0.08 kg ha^{-1} (Table 6).

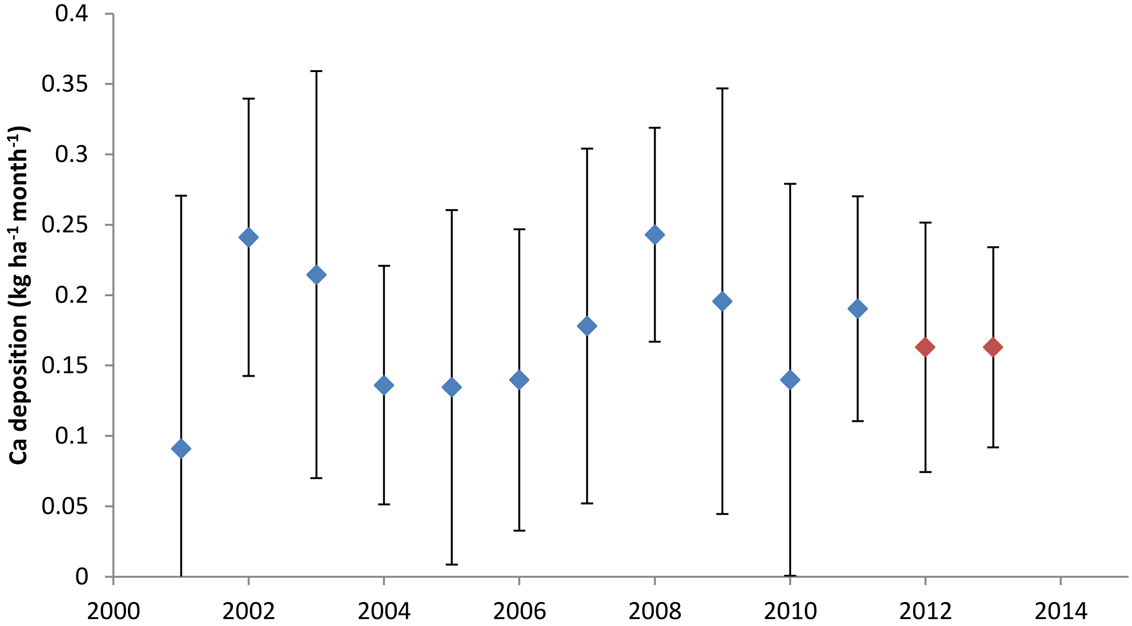


Figure 13. Mean historical wet deposition of Ca (kg ha^{-1} month^{-1}). Red points indicate estimated values. Data from CaPMON monitoring site in Kejimkujik National Park.

Table 6 Pre-liming (June 2011-May 2012) and post-liming (June 2012-May 2013) Ca deposition. Data from CaPMON precipitation chemistry database

	Pre-liming	Post-liming
Wet deposition (kg ha^{-1})	2.10 ± 0.09	1.95 ± 0.06
Dry deposition (kg ha^{-1})	0.56 ± 0.03	0.52 ± 0.02
Bulk deposition (kg ha^{-1})	2.66 ± 0.12	2.47 ± 0.08
Total deposition (kg)	127.00 – 139.00	119.50 - 127.50

During both phases, Ca deposition was lowest during the summer months (June-September) (Fig. 14). There was a sharp increase in deposition in October 2011 corresponding with an increase in precipitation (Fig. 14). A second lesser peak in deposition was observed in October 2012, also corresponding with precipitation. Furthermore, periods of low Ca deposition corresponded with periods of low precipitation.

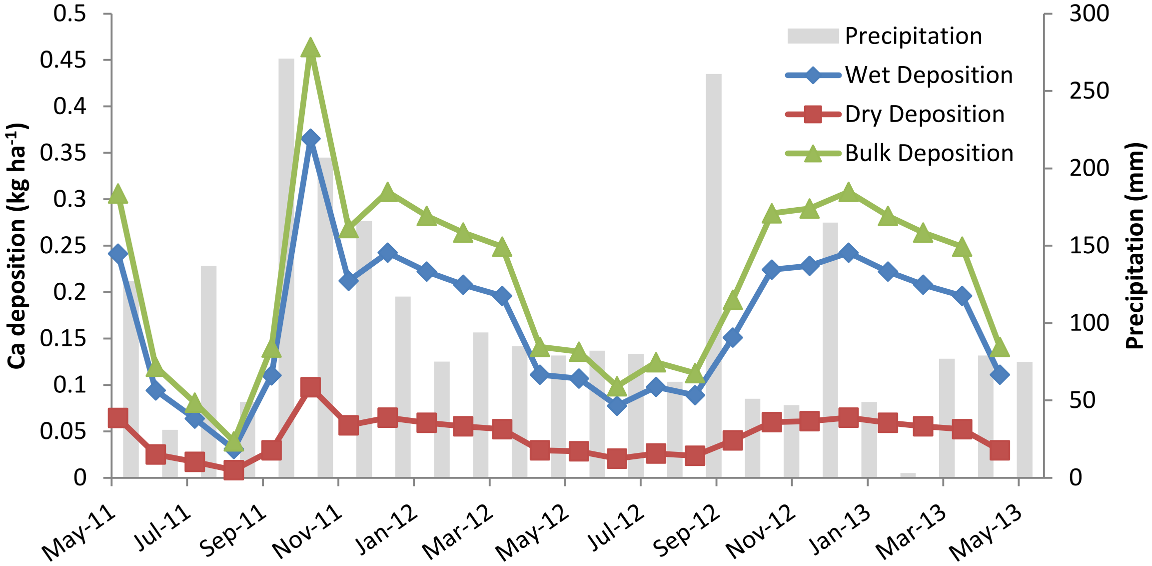


Figure 14. Ca deposition (kg ha^{-1}) per month; wet, dry, and bulk, and precipitation (mm).

Pre-liming, bulk deposition accounted for only 6% of total Ca lost from the system, while post-liming it accounted for only 4%. When combined with weathering inputs, total Ca inputs pre-liming only replaced a total of 14% of Ca lost from the system through export. Post-liming, inputs were even less successful at replacing lost Ca, where only 11% was replaced.

4.5. Ca Budgets

Throughout the entire two years of study, Ca export was always greater than total Ca inputs (from weathering and bulk deposition) (Fig. 15). Both pre- and post-liming budgets were found to be negative (Table 7; Fig. 16). Pre-liming loss of Ca from the system was 40.15 ± 2.22 kg ha^{-1}, and increased by approximately 24% to 52.63 ± 3.31 kg ha^{-1}. This increase represents a total of 5.2% of the total Ca added during the distribution of $CaCO_{3.}$ Above ground biomass and soil pool size ranges were estimated from literature values (Watmough, et al., 2005). These estimates provided a large range of possible pool sizes. It is likely that at the Maria Brook site, the above ground biomass pool and exchangeable soil pool most closely resembled that estimated for the Moose Pit watershed in SWNS by Watmough et al. (2005) (263 kg ha^{-1} and 324 kg ha^{-1} respectively).

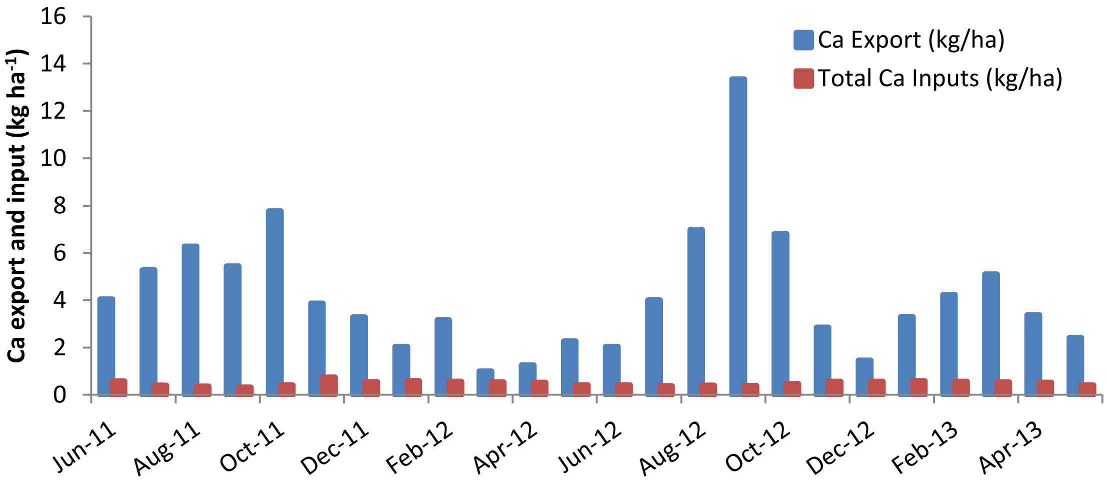


Figure 15. Total Ca export (kg ha^{-1}) and total Ca inputs (weathering and bulk deposition) (kg ha^{-1}) per month, pre- and post-liming.

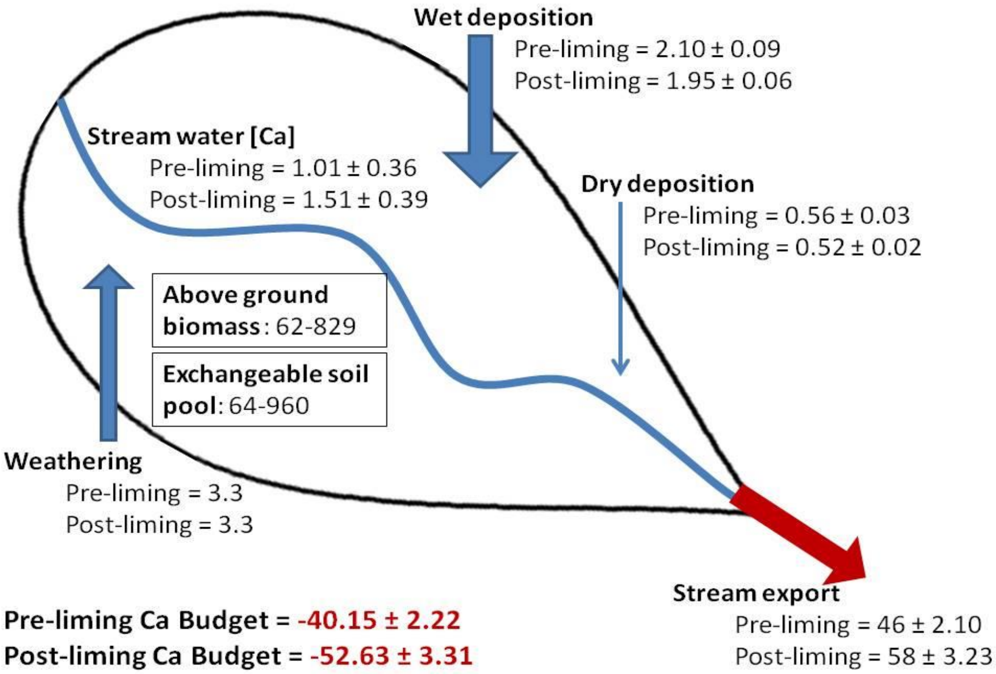


Figure 16. Annual pre- and post-liming Ca budgets for the Maria Brook watershed, excluding the $CaCO_3$ input of Ca. All values are in kg Ca ha^{-1}, except the stream water Ca concentration which is in mg L^{-1}. Stream water Ca concentration represents the mean concentration of the pre- or post-liming phase. Above ground biomass and exchangeable soil pool measures from Moose Pit (located in SWNS) following Watmough et al. (2005).

When including the applied 240 kg Ca ha^{-1}, the budget is positive (Fig. 17). A surplus of 187.37 ± 3.31 kg Ca ha^{-1} was added with the application of $CaCO_3$ (Table 7). Total Ca export pre-liming was 46.11 ± 2.10 kg ha^{-1} (Table 7). Total inputs (weathering and bulk deposition) replaced 13% of this loss during the pre-liming phase. Bulk deposition was responsible for replacing only 5.7% of total Ca lost during this same time. Post-liming, total Ca export was 57.34 ± 3.23 kg ha^{-1} (Table 7). During this time, total inputs replaced 10% of Ca exported. Bulk deposition replaced 4% during the post-liming phase. Based on these measures of export, the 240 kg of Ca added to each hectare potentially replaced approximately 500% of Ca being exported from the system pre-liming.

Table 7 Pre- and post-liming budgets. All values are in kg Ca ha^{-1}. Weathering estimate from (Watmough, et al., 2005).

	Pre-liming	Post-liming (no $CaCO_3$)	Post-liming (with $CaCO_3$)
Outputs			
Export	-46.11 ± 2.10	-57.34 ± 3.23	-57.34 ± 3.23
Inputs			
Bulk Deposition	2.66 ± 0.12	2.47 ± 0.08	2.47 ± 0.08
Wet Deposition	2.10 ± 0.09	1.95 ± 0.06	1.95 ± 0.06
Dry Deposition	0.56 ± 0.03	0.52 ± 0.02	0.52 ± 0.02
Weathering	3.3	3.3	3.3
$CaCO_3$	-	-	240
Total Budget	-40.15 ± 2.22	-52.63 ± 3.31	+187.37 ± 3.31

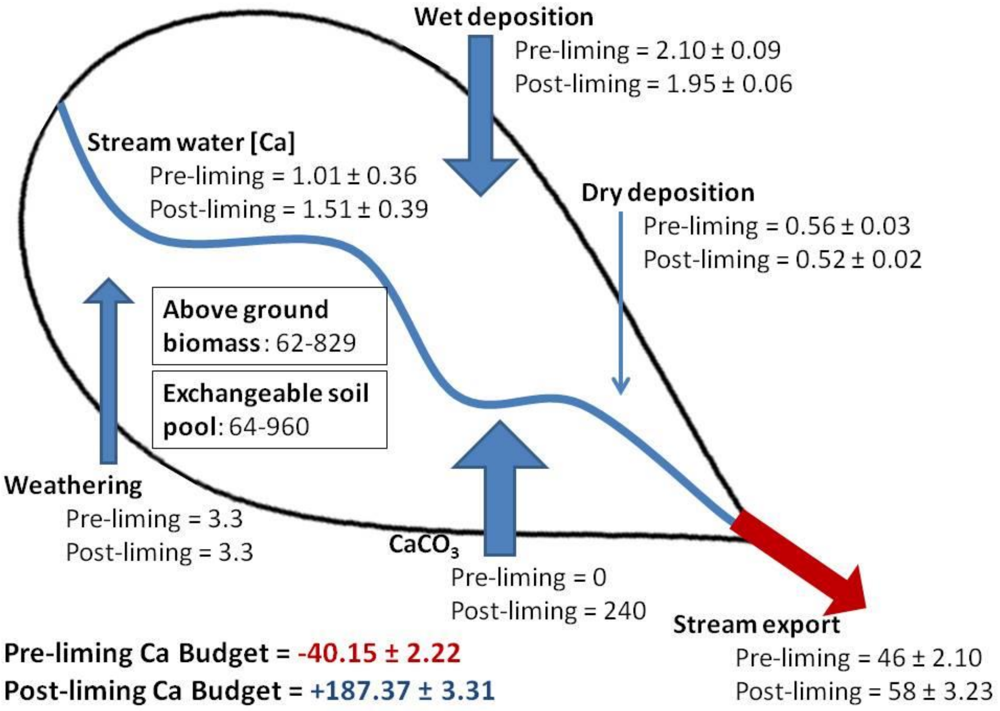


Figure 17. Post-liming Ca budget for the Maria Brook watershed, including the $CaCO_3$ input of Ca. All values are in kg Ca ha^{-1}, except the stream water Ca concentration which is in mg L^{-1}. Stream water Ca concentration represents the mean concentration of the post-liming phase.

5. Discussion

5.1. Stage-Discharge Relationship

The stage-discharge relationship was developed in order to use the high-frequency, real-time stage data as a proxy for stream-water discharge. The relationship between stage and discharge at site 5 was fairly strong (R^2=0.46) (Fig. 3); however the velocity meter used for measuring stream water velocity was not sufficiently sensitive to collect measurements during periods of low flow. When velocity measurements were recorded as 0.0 m s^{-1} but visible flow was observed by the field technician, the measurement was adjusted to 0.09 m s^{-1}, as this is the lower range of the velocity meter. This adjustment may explain why the relationship was not stronger. It is recommended that this relationship be further investigated with a more sensitive instrument before pursing future research into the Ca budget at Maria Brook, as a more reliable estimate of discharge will yield more accurate estimates of Ca export and therefore more valid budgets.

Total stream water discharge was greater during the pre-liming phase than during the post-liming phase (Table 2). This was likely the result of the greater rainfall during the pre-liming phase (1483 mm) than during the post-liming phase (1033 mm) (Environment Canada, 2014). However, this difference in discharge may also be the result of errors in the estimates of discharge that were used for June-September 2011 because stage data was not available during this time.

Peaks in discharge generally corresponded with peaks in precipitation (Fig. 5); however the relationship was not strong (R^2 = 0.12) (Appendix G). Other factors that may have contributed to uncertainty in discharge include the saturation of the soil, as well as the state of the soil (i.e. whether or not it was frozen). There were greater discrepancies between precipitation and discharge during the winter months, suggesting that frozen soils contributed to high surface runoff. Alternatively, precipitation during these winter months likely fell as snowfall and may have remained on the soil surface before later melting and being discharged. Finally, during the coldest months, a significant proportion of the surface water froze over, directly reducing the ability to relate precipitation to discharge. It is also important to note that estimates of discharge were made for the months of June – September 2011 (Fig. 4, red points), as stage data was not available during this time and these may have weakened the relationship between discharge and precipitation. Future modelling may be able to develop a relationship between precipitation and stream-water discharge, and it is recommended that this possibility be explored further.

Of particular interest was the significant discharge during the months of July-September 2012, the months immediately following the application of $CaCO_3$ (Fig. 4). This was the result of significant rainfall during these months (Fig. 12). The high precipitation during these months was beneficial to the project as a whole as it contributed to transporting the Ca from the $CaCO_3$ on the surface soil into soil solution, and further releasing it into surface waters. However, this high precipitation may also have washed away a large portion of the $CaCO_3$ in overland flow before the powdered lime had time to leach into the soil pool and replenish this pool. These months also corresponded with the highest stream water Ca concentrations and the greatest levels of Ca export (Fig. 6 and 8). This will be discussed further in the following sections.

5.2. Stream water calcium concentrations

A strong relationship was developed between stream-water Ca concentration and conductivity (Equation 11) (R^2=0.71). This allowed in-stream real-time measurements of conductivity to be used as estimates of stream water Ca concentration. Mean stream water Ca concentration was greater during the post-liming phase (Fig. 6; Table 3), suggesting that the Ca added from the $CaCO_3$ was exchanging with incoming H^+ , being leached from the soils, and being released into surface waters. This concept is important because it suggests that the lime application increased the availability of Ca such that more Ca was being exchanged with incoming acid cations, potentially reducing the abundance of toxic Al^{n+} that were being released into surface waters to maintain electro-neutrality in soils. However, because no significant difference was observed between the stream water Ca concentration at the upstream control site 6 and the experimental downstream site 5 (Fig. 6; Appendix H), it cannot effectively be argued that the increase in Ca concentration was the result of the lime application. This increase may instead have been the result of greater acid inputs, possibly from more acidic precipitation than during the pre-liming phase, which required greater cation exchange with incoming H^+ and resulted in more Ca^{2+} release into surface waters. Alternatively, it is possible that the $CaCO_3$ applied to downstream catchment soils did in fact affect the water chemistry at the upstream monitoring site as a result of unexpected hydrologic drainage. The catchment of Maria Brook is not heavily sloped, so it is possible that some of the Ca from the $CaCO_3$ was released into surface waters upstream of the control site. Of particular importance, however, is that post-liming stream water Ca concentrations (Table 3) were raised to the target level of 1.50 mg L^{-1} as suggested by Jeziorski et al. (2008) in order to meet requirements for aquatic life.

In Clair et al. (2004)'s hindcast of stream water Ca concentration (Table 4), it was estimated that Ca concentration during pre-acidification periods was lower (1.03 mg L^{-1}) than during the height of acid deposition. Pre-acidification, less Ca^{2+} was exchanging with incoming H^+, as precipitation was less acidic and therefore less Ca was being released into surface waters. During the mid-1970's, when acid deposition was severe, Ca concentrations in stream waters were high because the rate of cation exchange increased in response to increased H^+ deposition (Table 4). By the 1990's, after several decades of chronic acidification, Clair et al. (2004) estimated that stream water Ca concentration would decrease again, as by this time soils would be severely depleted, resulting in insufficient Ca present to exchange with H^+. Using the MAGIC model, Clair et al. (2004) predicted that if SO_4 inputs remained constant, by 2012 and 2013 stream water Ca concentrations in the Gold River (located in SWNS) would be 1.02 mg L^{-1} and would continue to decrease as soils were further depleted of Ca. During both years of monitoring (pre-liming and post-liming) at the Maria Brook site, stream water Ca concentration was found to be greater than predicted by Clair et al. (2004) (Table 4). This is as expected, as the first application of $CaCO_3$ began in May of 2012 and will have contributed to the increased Ca concentration in stream waters (1.20 mg L^{-1}). By 2013, the concentration of Ca in the water increased further (1.42 mg L^{-1}) as more Ca from the liming reached the surface waters. This suggests that the catchment liming at Maria Brook partially replenished the depleted soil Ca pool and that consequently a greater abundance of Ca cations were able to exchange with incoming H^+ and were released into surface waters in response to acid deposition.

The large amounts precipitation and discharge observed during the months immediately following the lime application (Fig. 5) corresponded with increases in stream water Ca concentration. This rainfall likely contributed to the observed increase in Ca concentration both by assisting in transporting the powdered $CaCO_3$ applied to surface soils into the soil solution and by causing leaching of the Ca into surface waters. Furthermore, the heavy rainfall would also have loaded the system with H^+, requiring greater cation exchange in the soil surface and contributing to greater leaching of Ca into the surface waters.

The variability in stream water Ca concentration was also greater during the post-liming phase, perhaps suggesting an improved ability to respond to acid deposition. The stronger relationship between precipitation and stream water Ca concentration post-liming (Fig. 7) suggests that the system may be better responding to acid inputs as a result of the lime application and the partial replenishment of the soil pool.

5.3. Ca Export

Pre- and post-liming, there was a weak positive relationship ($R^2 = 0.18$; $p = 0.04$) between the amount of Ca exported from the system and the deposition of H^+ in precipitation (Appendix F). This suggests that, as expected, the amount Ca released into surface waters and exported from the system depended on the deposition of H^+ into the system. This relationship should be further explored for the second application of $CaCO_3$ (August 2013), as it is possible that the relationship will be stronger when the availability of Ca in the soil pool is greater and the ability of the system to respond to acid deposition through cation exchange increases.

Post-liming there was a much stronger relationship between stream water discharge and Ca export than pre-liming (Fig. 9). This suggests that Ca export prior to the lime application was not dependent on discharge and H^+ inputs, but that it was instead limited by the size of the exchangeable pool of Ca in the soil. Post-liming, the relationship between Ca export and discharge was significantly stronger (Fig. 9); supporting that pre-liming Ca export was limited by Ca availability. This may signify that prior to liming there was insufficient Ca available in soils for exchange with incoming H^+, highlighting the extreme depletion of base cations from the soils as predicted by Clair et al. (2004).

Total stream water discharge post-liming was less than during the pre-liming phase (Fig. 4; Table 2); however, total Ca export from the system was greater during this same phase than during the pre-liming phase. This demonstrates that the increased Ca export post-liming was not simply a result of increased stream water discharge from the system, but also of greater concentrations of Ca in the stream water (Fig. 6; Table 3). This suggests greater Ca exchange with incoming H^+ and greater release of Ca into surface waters as a result of cation exchange, likely due to the additional available cations from the lime application. It should be investigated whether Al concentrations in stream water decreased in tandem with increasing Ca concentrations, as based on the hypothesis that Ca will leach from soil preferentially to Al in response to H^+ input from acid precipitation. Aluminum will not be leached in order to maintain the electro-neutrality of soils when preferred base cations such as Ca are available for exchange.

There was a large peak in Ca export in the three months following lime application (June-August 2012), which corresponded both with increased stream water discharge and increased precipitation. The increase in stream water discharge and precipitation had a two-fold effect on the Ca export. Firstly, discharge is related to precipitation and Ca export (Fig. 5; Fig. 9; Appendix G). Consequently, greater precipitation and stream water discharge correspondingly exports larger volumes of Ca from the system. Secondly, the increased precipitation during these months would have deposited more H^+ into the system, requiring more cation exchange with incoming acid ions in order to maintain soil electro-neutrality. This demand for cation exchange would therefore result in greater release of Ca from the soil, observed as increases in stream water Ca concentrations and finally as increased Ca export.

During both pre- and post-liming phases, the state of the soil seemed to contribute to total Ca export. In winter months, Ca export was lower than during the warm and wet spring and summer months. This is likely the result of frozen soils, which would have prevented the release of Ca into surface waters. This will be an important consideration when undertaking future catchment liming applications. Ca export was less well related to precipitation than expected, as it was expected that increases in H^+ would trigger the release of more Ca into surface waters. This may also have been related to the state of the soils, where precipitation would either runoff on the surface of frozen or saturated soils, or fall as snow. In both cases the additional H^+ would not have been absorbed into the surface soils and would not have instigated cation exchange and release of Ca into surface water. Alternatively, it may signify that the soil pool has not yet been sufficiently replenished to respond to high levels of H^+.

Both pre-liming Ca export (46.11 ± 2.10 kg ha^{-1}) and post-liming Ca export (57.34 ± 3.23 kg ha^{-1}) were larger than the greatest measurements of annual Ca export from 31 forested watersheds in North America, where the greatest export was found at the Turkey Lakes in Southern Ontario (39.7 kg ha^{-1}) (Watmough et al., 2005). While the export was higher than expected, it may have been the result of the more acidic environment of SWNS, as demonstrated by the abundance of wetlands, or the greater acid deposition in SWNS as a result of proximity to upwind smelting plants and large megalopolises such as New York City and Boston.

5.4. Ca Inputs

Weathering estimates are notoriously difficult to calculate (Ranger & Turpault, 1999). Due to the limited temporal and financial scope of this research, weathering rates were estimated from literature values (Watmough, et al., 2005). This weathering rate replaced only 8% of total Ca lost from the system pre-liming and 6% lost during the post-liming phase, demonstrating that this input was insufficient to replace Ca loss from the system. Despite the low concentrations of Ca in the bedrock, weathering represented the largest natural input of Ca.

There was greater bulk deposition of Ca during the pre-liming phase than post-liming (Table 6), indicating that any increases in stream export of Ca were not due to increases in deposition post-liming. During both phases, wet deposition represented the majority of depositional inputs of Ca in to the system. Sedimentation contributed only 21% of total Ca deposition and 9% of total Ca inputs during both the pre- and post-liming phase. This demonstrates that bulk deposition is also insufficient to remediate the depletion of Ca from catchment soils.

In an assessment of 17 forested catchments, Watmough et al. (2005) found that the average bulk deposition of Ca was 2.03 kg ha^{-1}. This is similar to the findings of the current research of 2.10 kg ha^{-1} pre-liming and 1.95 kg ha^{-1} post-liming. However, Watmough et al. (2005) found that Ca bulk deposition in Moose Pit (located in SWNS) was only 1.09 kg ha^{-1}, lower than the findings of this research by between 0.86 – 1.01 kg Ca ha^{-1}. This difference may be due to the fact that Watmough et al. (2005)'s findings were concluded based on depositional data from the 1990's, two decades prior to the current research. It may also be the result of a source point, either industrial or natural, of Ca near SWNS that has resulted in higher-than-expected Ca deposition. Finally, this may also have simply been the result of annual variations in precipitation, and therefore corresponding variation wet deposition of Ca.

5.5. Ca Budget

Both pre- and post-liming Ca budgets were found to be negative (Table 3; Fig. 16), demonstrating that in both phases, Ca export from the system surpassed inputs. This is as expected, as chronic acidification of SWNS has depleted base cations from the soil, and continued H$^+$ from precipitation, combined with insufficient Ca inputs, has resulted in the continued depletion of Ca from the system (Clair et al., 2004).

When excluding the 240kg Ca ha^{-1} added through the application of $CaCO_3$, Ca export was always greater than total Ca inputs (from weathering and bulk deposition) (Fig. 15), demonstrating further that natural inputs are insufficient to replace exported Ca.

If it is assumed that the observed increase in Ca export from the system during the post-liming phase was the result of the addition of $CaCO_3$ to the watershed, then this increase represents only 5.2% of the total Ca added during the distribution of $CaCO_3$. This suggests that the unaccounted 228 kg Ca ha^{-1} remains on the surface of the soil and has not been yet integrated into the system, is being stored in the soil pool, or has been taken up by vegetation. If it is assumed that all the unaccounted for Ca from the lime application is stored in the soil pool, then it will have replaced between 23-356% of the depleted Ca from soils (Fig. 16). Using the Moose Pit estimate of soil pool size (Watmough, et al., 2005), which may be the most accurate estimate for SWNS, the 228 kg Ca ha^{-1} unaccounted for in Ca export will have replaced 70% of the Ca depletion. If, however, it is assumed that all the unaccounted for Ca from the lime application is stored in the above ground biomass pool, then it will have replaced between 27-368% of the depleted Ca from biomass (Fig. 16). However, given that Yanai et al. (2005) estimated annual plant uptake of Ca as being between 12-23 kg ha^{-1}, it is unlikely that the majority of the unaccounted Ca was taken up by vegetation. If we assume a soil pool size similar to that measured at Moose Pit of 324 kg Ca ha^{-1} and annual plant uptake as described by Yanai et al. (2005), this suggests that in order to successfully replenish the soil pool at the Maria Brook catchment, and an additional 75 to 84 kg Ca ha^{-1} should be added to the system through future catchment liming. Soil analyses and measures of foliar Ca concentration in the future will help to identify where the remaining Ca is being stored and to more accurately assess how much additional Ca must be applied to restore the watershed.

When including the 240 kg Ca ha^{-1} added through the liming process, the post-liming budget is found to be positive, with a surplus of 187.37 ± 3.31 kg Ca ha^{-1} still remaining in the system (Fig.17, Table 7). If the rate of depletion remains constant, the remaining 187.37 ± 3.31 kg Ca ha^{-1} should balance the export of Ca for four more years before it is depleted. However, it is difficult to include the Ca from the lime application in the budget, as it remains uncertain how much of the added Ca is being stored in the soil pool and what fraction is being taken up by Ca-limited vegetation. More importantly, it is not presently known how much of the Ca in the $CaCO_3$ is actually *in* the system, as visual observation of the experimental site have revealed a large proportion of lime still sitting on the soil surface. In order to be considered in the budget, this additional Ca must be in soil solution or surface waters. While sitting on the soil surface, it is not directly interacting with the system, until it has been leached by rainfall into the soil or surface waters. In order to produce a more accurate and complete budget, soil analysis will be essential in order to identify where the added Ca is being stored.

6. Conclusion

The aim of this research was to gain a better understanding of how the Ca budget of an acidified watershed in SWNS responds to catchment liming by determining the annual exports and inputs of Ca into the system, and to determine the pre- and post-liming Ca budgets.

Pre-liming, the Ca budget of Maria Brook was found to be negative, demonstrating that Ca is contiunally being depleted from the system as a result of chronic acidification. Weathering inputs of Ca replaced approximately 7% of Ca lost from the system and bulk deposition replaced only approximately 5% of Ca exported the during both phases, demonstrating that natural inputs are insufficient to replace depleted base cations from the catchment. Pre-liming Ca inputs were not sufficient to replace the Ca being lost from the system, establishing the need for anthropogenic intervention to mitigate the problem. Our results were similar to those obtained by Watmough et al. (2005), where in 21 watersheds in Northa America, all were found to have negative Ca budgets.

The application of 30 tonnes of $CaCO_3$ to the catchment soils resulted in increased export of Ca from the system and higher stream water Ca concentrations. The increased Ca concentration in stream waters (Fig. 6) represented only a fraction of the total Ca added to the system, which suggests that a portion of Ca from the applied $CaCO_3$ is being released into surface waters, while the remainder of the added Ca is either being stored in soils, being taken up by vegetation, or has not yet leached through the soil surface into soil solution. When including the 240 kg Ca ha^{-1} added to the catchment during the lime application, the post-liming budget was found to be positive, with a surplus of 187.37 ± 3.31 kg Ca ha^{-1}. This suggests that 52.63 kg ha^{-1} of the applied Ca was exported from the system in the year following the catchment liming, and that the remaining 187.37 kg Ca ha^{-1} were stored in the soil pool or were taken up by vegetation. The assumption that all of the 240 kg Ca ha^{-1} are included in the system may be incorrect, as some of the limestone particulates have not yet been leached into soil solution, and may still remain on the soil surface. It has been estimated that, if the current rate of depletion remains constant, the first application of $CaCO_3$ to the Maria Brook watershed should balance the export of Ca for four more years before it is depleted, and that in order to effect long term improvements to water quality, further liming applications will be required.

7. Recommendations

I suggest continuing to monitor the system for long-term assessment of the benefits of catchment liming, and to evaluate the effects of a second application of $CaCO_3$ (August 2013). The relationship between stage and discharge should be further investigated using a more sensitive instrument for velocity measurements in order to develop more reliable estiamtes of discharge and therefore more accurate estimates of Ca export. Future modelling may be possible in order to develop a relationship between precipitation and stream water discharge, but should take into consideration soil state (i.e. frozen) and temperature. Greater understanding of the effect of frozen soils on Ca transport within the system is needed, as this will be an important consideration for future catchment liming applications. I further suggest monitoring the aluminum concentration in surface waters in order to assess whether Ca is effectively being replenished in soils and is reducing the release of toxic Al into the system.

The effects of Ca limitation on calcifying organisms, primary productivity, and vegetative sensitivity to acid deposition should further be investigated in SWNS in conjunction with investigations on the efficacy of liming as a mitigation stratgey for water quality improvement. Furthermore, the effects of Ca limitation on the water cycle, as identified by Green et al. (2013), should be investigated in SWNS. The reduced rates of photosynthesis and resulting decreases in evotranspiration result in increased water discharge. It is possible that in a watershed already severely depleted of Ca, this increased discharge will further reduce the available pools of Ca in soils, exacerbating the problem. As in Green et al. (2013), it is recommended that evotranspiration rates be monitored at the Maria Brook watershed, and that the response to liming be evaluated. As it has been estimated that the current application of $CaCO_3$ will only balance the budget for the next four years, I recommend that future liming applications be conducted in order to effect more long term benefits. Specifically, I suggest that 75 to 84 kg Ca ha^{-1} should be added to the system through future catchment liming to replenish the soil pool. Finally, I suggest collecting measurements of soil and foliar Ca concentration in order to identify where the additional Ca is being stored, and if vegetation is benefiting from the liming.

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9. Appendix A

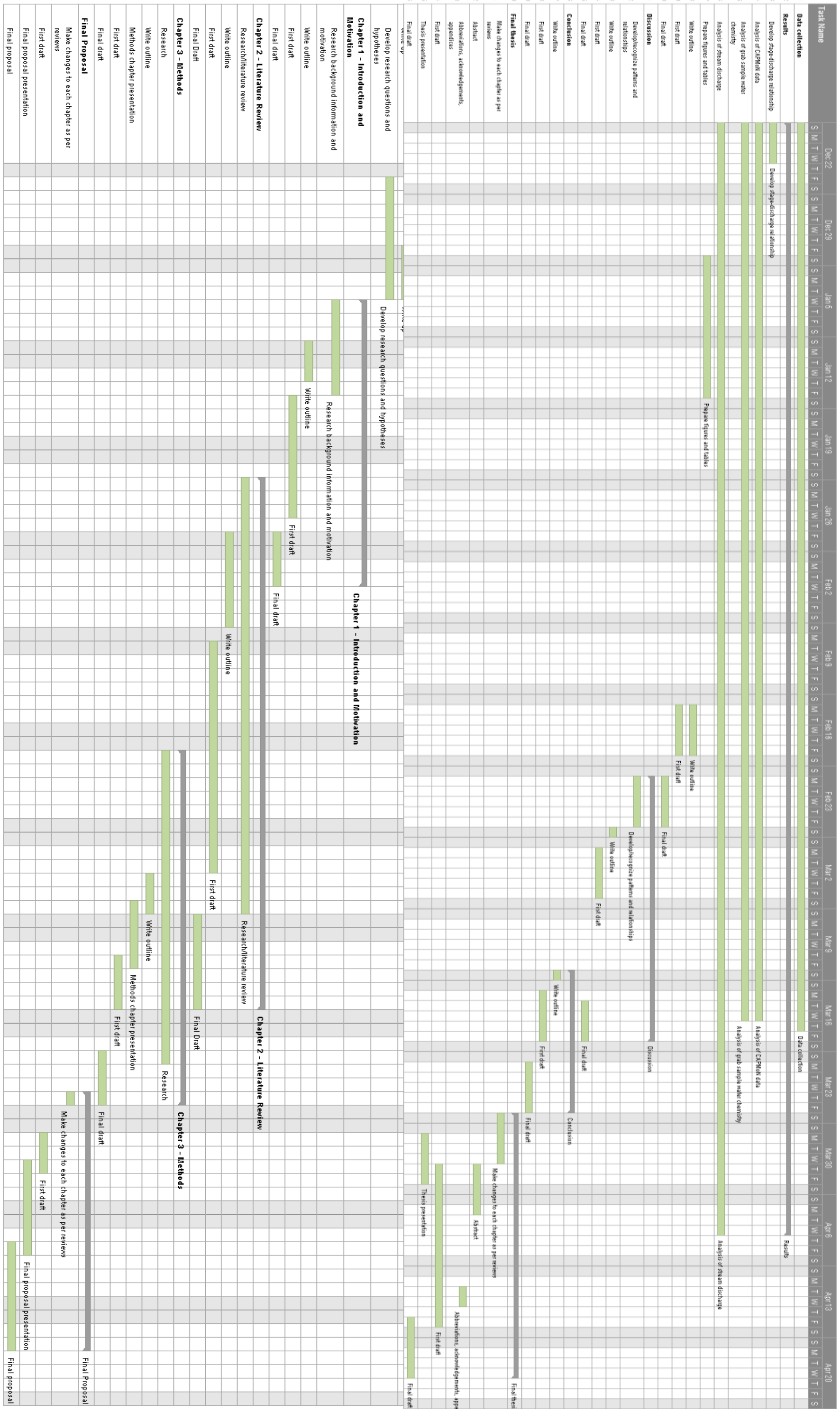

Figure 18. Gantt chart outlining the schedule for completion of the thesis project

10. Appendix B

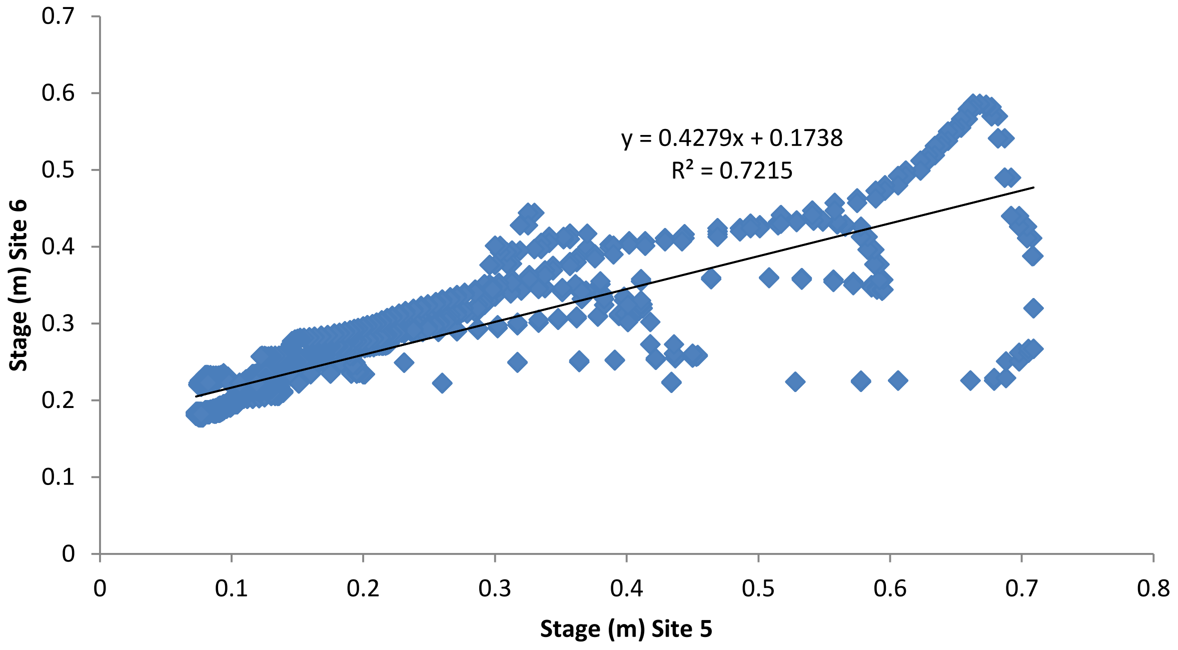

Figure 19. Relationship between site 5 and site 6 stage (m).

11. Appendix C

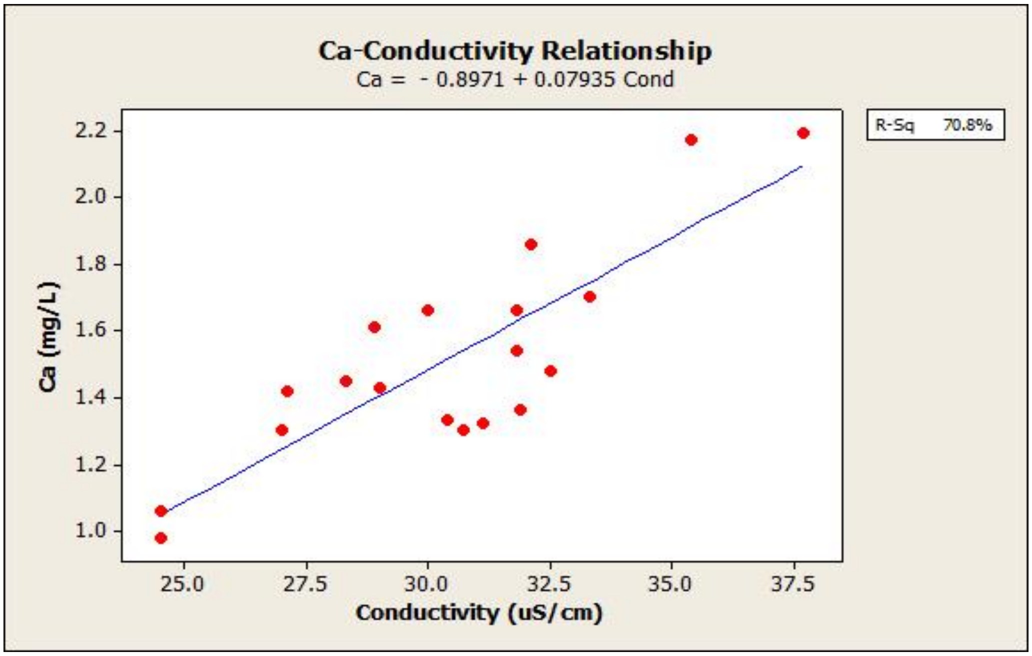

Figure 20. Relationship between calcium (mg L^{-1}) and conductivity (µS cm^{-1}). $R^2 = 0.71$; p-value = 0.00; N = 19.

12. Appendix D

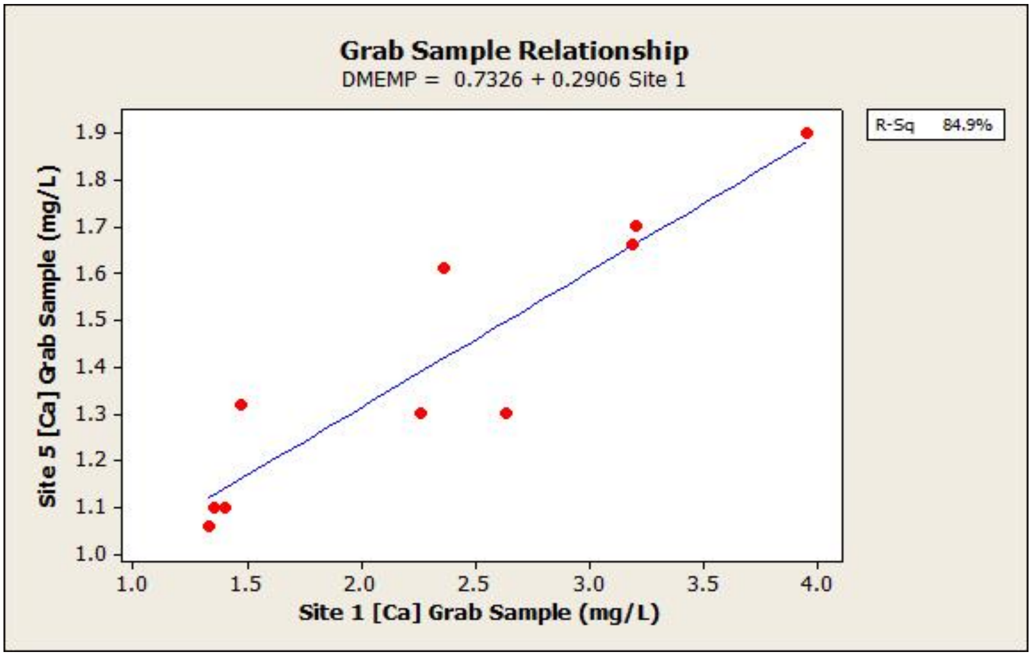

Figure 21. Relationship between site 1 and site 5 grab sample [Ca] (mg L^{-1}). $R^2 = 0.85$; p-value = 0.00; N = 10.

13. Appendix E

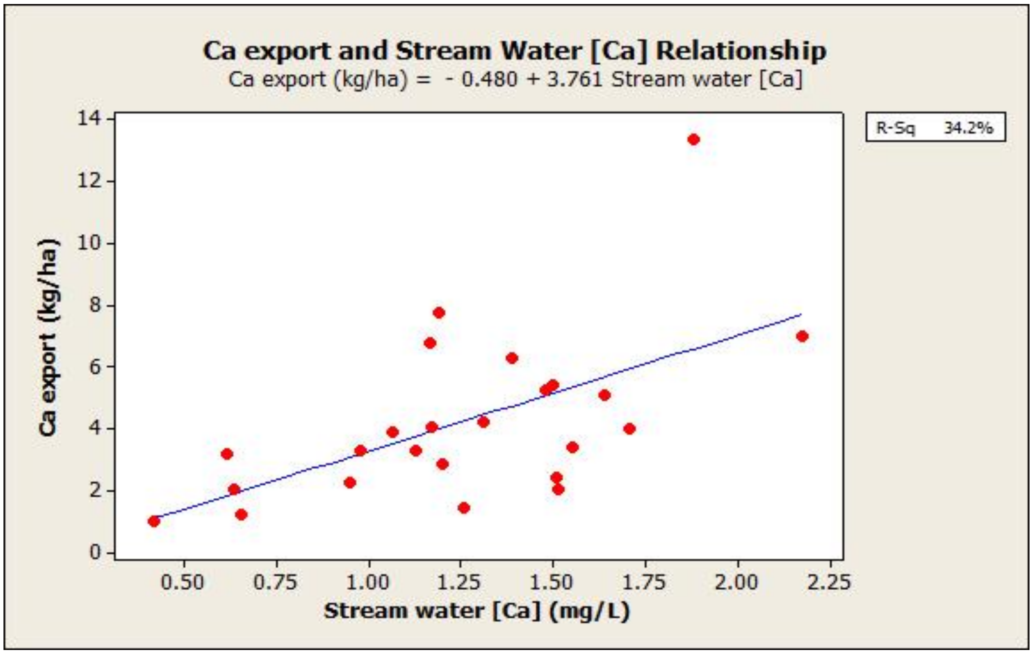

Figure 21. Relationship between Ca export (kg ha^{-1}) and stream water [Ca] (mg L^{-1}). $R^2 = 0.34$; p-value = 0.00; N = 24.

14. Appendix F

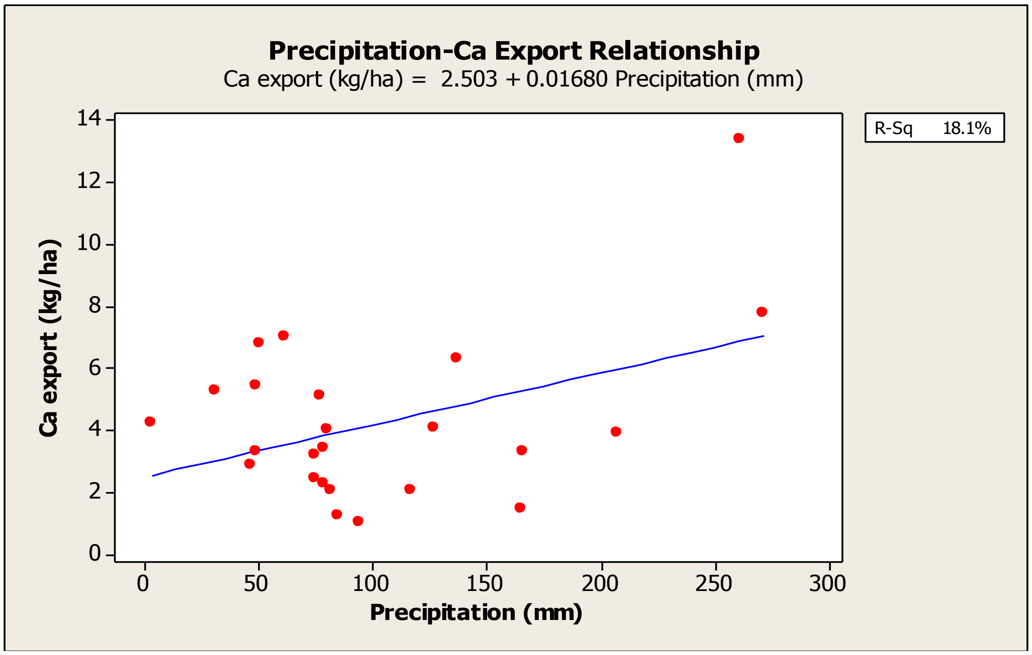

Figure 22. Relationship between precipitation (mm) and Ca export (kg ha^{-1}); $R^2 = 0.18$; p-value = 0.04; N = 24.

15. Appendix G

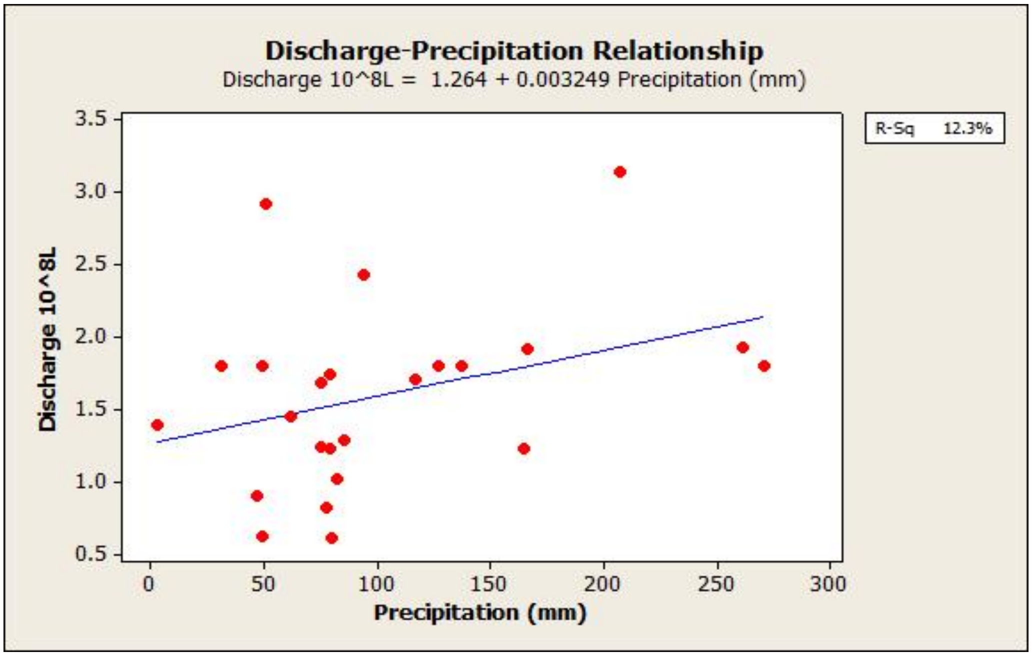

Figure 23. Relationship between discharge (10^8L) and precipitation (mm). $R^2 = 0.12$; p-value = 0.09; N = 25.

16. Appendix H

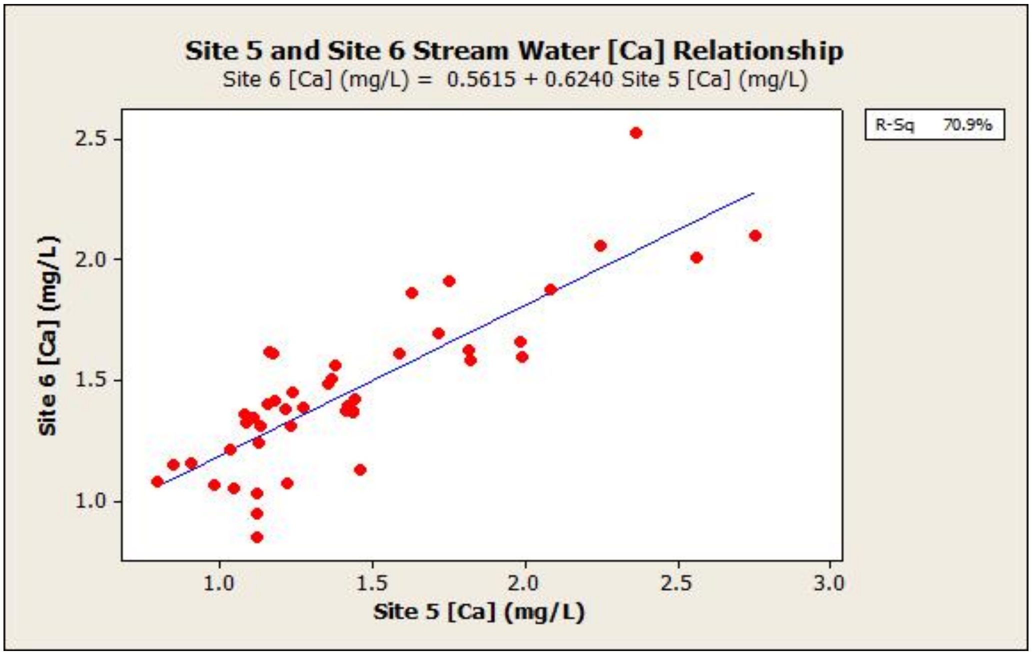

Figure 24. Relationship between site 5 stream water [Ca] (mg L^{-1}) and site 6 stream water [Ca] (mg L^{-1}). $R^2 = 0.71$; p-value = 0.00; N = 45.