

# WHAT IS THE DOSAGE OF POWDERED LIMESTONE NEEDED TO RAISE WATER QUALITY TO WITHIN TARGET LEVELS IN SOUTHWESTERN NOVA SCOTIA?

Combined Earth Science and Environmental Science Undergraduate Honours Thesis

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## Abstract

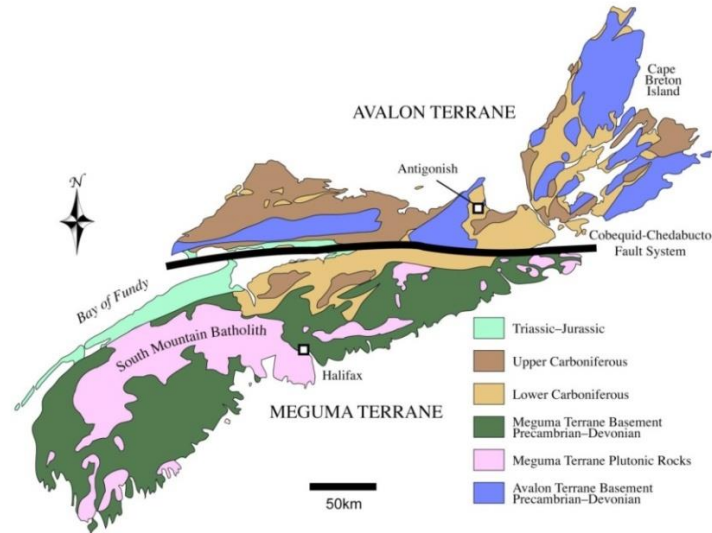
Acidification is a great problem for freshwater systems in Eastern Canada, but especially for Southwest Nova Scotia (SWNS) (Stoddard et al., 1999). This region's granite and slate bedrock is low in base cations ( $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) and weathers slowly, which leads to low Acid Neutralizing Capacity (ANC) in the soil produced from the weathering of this parent material (Clair et al., 2007). In turn, low ANC of soils give rise to low base cations in soil water, leading to surface waters that cannot effectively buffer acidic inputs (Clair et al., 2007). Chronic acidification was identified as a main cause of extirpation of Atlantic salmon (*Salmo salar*) during the 1980s and 1990s (Clair et al., 2004; DFO, 2013; Sterling et al., 2014-a). Population modelling suggests two of SWNS's larger *Salmo salar* populations have a high probability of extirpation (87 and 73 %) if habitat improvements are not made within the next 50 years (DFO, 2013; Sterling et al., 2014-a). Liming, the introduction of base cations via limestone or dolomite to an acidified catchment, has proved to be an effective mitigation strategy in Norway and Sweden (Brown, 1988). While there are many types of liming methods used for mitigation of freshwater acidification, one of the most promising types is terrestrial liming (Sterling et al., 2014-a). Terrestrial liming studies in Sweden and Norway have had success in improving water quality in multiple catchments for over a year. Two experimental terrestrial liming studies are conducted within SWNS; a BACI analysis is chosen to determine if terrestrial liming can improve water quality in SWNS catchments, with the overall goal to determine a range of doses for effective terrestrial liming in NS. In-situ pH trends increase over time for each individual study. Similarly, Ca concentrations increase throughout each study period, while DOC levels in both studies decrease over time. Lastly, total Al levels remain fairly constant in Maria Brook, while slightly decreasing from June to September, 2015 for Ted Creek (the window of time used for analysis of terrestrial liming effects at Ted Creek). Therefore, terrestrial liming has been effective at improving water quality in both Maria Brook and Ted Creek, at least in the short-term. An in-stream liming dose of  $375 \text{ t ha}^{-1}$  used to maintain a pH of 6.0 in WRSH is converted into a terrestrial liming application rate of  $0.012 \text{ t ha}^{-1} \text{ yr}^{-1}$ ; a reasonable rate for terrestrial liming standards. My research acts as a guideline for larger, future terrestrial liming projects in NS, and provides important information to stakeholders for the decision-making process regarding terrestrial liming. Helicopter application is recommended as the next step to better define the range of doses required for effective terrestrial liming in NS.

Key Words: *watershed liming, terrestrial liming, catchment liming, recovery from acidification, effective liming, improvements in water quality*

## 1.0 Introduction

### 1.1 Rationale

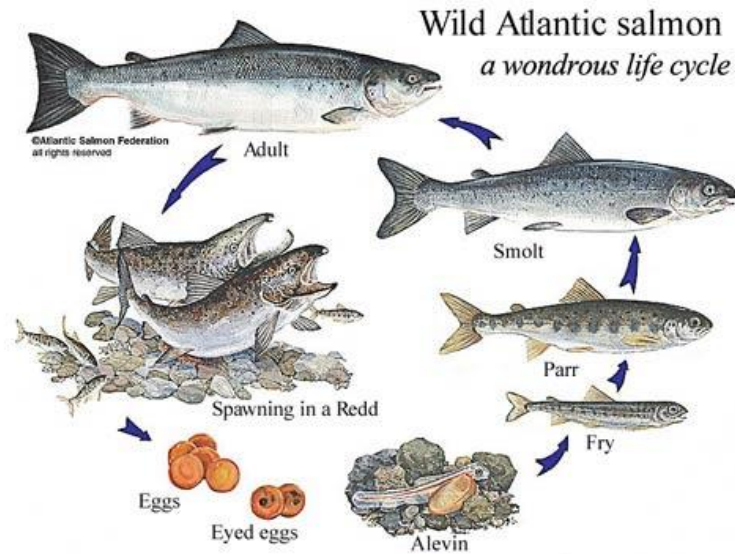
Acidification of surface waters is caused by the deposition of acid volatiles (sulphate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ )) into forest soils and in turn, into freshwater systems (Clair et al, 2007). Eastern Canada, specifically Southwest Nova Scotia, has some of the most highly acidified waters on the continent (Stoddard et al., 1999; Hindar, 2001). Contributing factors involve prevailing winds from central North America which transport emissions to the Maritimes, and Southwest Nova Scotia's (SWNS) granite and slate bedrock (Meguma Group in Figure 1) which have low base cations, producing soils with low Acid Neutralizing Capacity (ANC) (Clair et al., 2007), (ANC is the ability for a material to buffer or neutralize acidic inputs). Introduction of soil water with low ANC into surface waters of lakes or streams decreases the ability of these waterbodies to buffer acidic inputs (Clair et al., 2007) (e.g. acid precipitation). Despite emission reductions of sulphate following the United States Clean Air Act Amendments in 1990 (EPA, 2013), chronic freshwater acidification has not improved in many regions of North America (Sterling et al., 2014-a; Stoddard et al, 1999).



**Figure 1.** Generalized geologic map of Nova Scotia. The Meguma terrane includes the Halifax Formation and the Goldenville Formation, both of which are mainly composed of slates, as well as the plutonic rocks of the South Mountain Batholith (Schenk et al., n.d.).

Chronic acidification in SWNS threatens many aquatic species, predominantly Atlantic salmon (*Salmo salar*) populations (Clair et al., 2004). Typical values of pH in surface waters of SWNS are between 4 and mid-5's (Clair et al., 2007). At these pH values freshwater systems become too acidic for fish survival, and mobility of ionic Aluminum species can occur. The species of ionic Aluminum of concern are  $Al^{3+}$  and  $Al^{+}$ , as these are capable of binding to the negatively charged gill sites of *Salmo salar* and other fish species (Lydersen, 2002). Clogging of gills due to Aluminum toxicity can lead to decreases in gill function and ultimately suffocation. Immune system vulnerability of *Salmo salar* smolts can prove problematic during the stressful transition from freshwater to saltwater systems. Additional stress caused by Aluminum toxicity greatly increases mortality rates of *Salmo salar* smolts.





**Figure 2.** Life cycle of Wild Atlantic Salmon. Spawning, as well as life stages up to Parr, takes place in freshwater systems. The Smolt stage is when *Salmo salar* transition from freshwater into saltwater systems, where they spend their lives as an adult. To spawn, the adult *Salmo salar* travel, once again, to freshwater systems and lay their eggs, thus completing the cycle. [Atlantic Salmon Federation, 2012].

*Salmo salar* continue to undergo severe abundance reductions due to innerving acidification of freshwater systems in Nova Scotia. The Department of Fisheries and Oceans (DFO) (2013) have reported declines of 88% to 99% in four rivers in the Southern Upland region since the 1980's (Figure 3). Evidence for extirpation of *Salmo salar* has been observed in 50 rivers between 2000 and 2008/09 due to major declines in juvenile density. Southern Upland *Salmo salar* have been categorized as endangered by COSEWIC in 2010 (COSWIC, 2010; DFO, 2013), and if habitat improvements are not made within the next 50 years the probability of extirpation is 87% (DFO, 2013). Human intervention is needed to help improve water quality of SWNS watersheds, which are not expected to improve naturally for at least another 60 years (DFO, 2013; Clair et al., 2004).

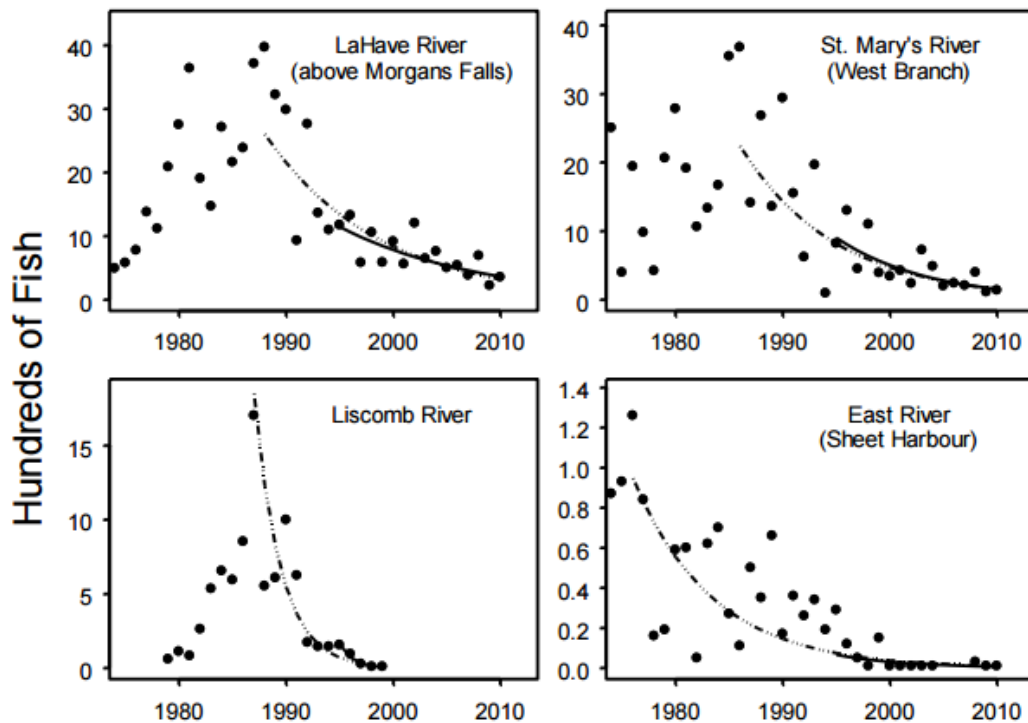


Figure 3. “Atlantic salmon adult abundance time series based on adult count data (points) for four rivers in the Southern Upland from 1974 to 2010. The lines show the trends estimated by log-linear regression over the previous 3 generations (solid lines) and from the year of maximum abundance (dashed lines)” [DFO,2013].

However, due to limited research on liming strategies in Canada, general information regarding terrestrial liming is unknown. For example, how effective terrestrial liming is to mitigating the effects of acidification can vary by location, the liming and application strategies implemented, the lime quality, and the chosen application rates (Hindar et al., 2003). All of which in turn, may vary depending on which parameter(s) are targeted for study (e.g., pH, Ca and/or Mg, Al, tree growth, forest health, etc.). Furthermore, liming doses for effective mitigation of freshwater acidification for varying catchment sizes are unknown and there is little information about how variables, such as calcium uptake by vegetation, affect liming success. Filling these knowledge gaps is essential for more effective terrestrial liming in SWNS.

Application of powdered limestone or dolomite to a catchment is the only mitigation method able to neutralize the system's surface water acidity. While there are many different types of liming methods used to improve water quality, two methods in particular are more commonly used. The first is in-stream liming, which is the addition of limestone or dolomite (i.e.  $\text{CaCO}_3$  or  $\text{MgCO}_3$ ) directly to a stream. This method provides immediate improvements in water quality with the increase of base cations into the system; however continuous application is required to keep results constant, and purchase, as well as maintenance of needed equipment (i.e. a lime doser) for application tends to be fairly expensive (Clair & Hindar, 2005). The second method is terrestrial liming, also known as catchment liming, is the application of base cations to the drainage basin soils in an acidified catchment (Clair & Hindar, 2005). Terrestrial liming is of interest because of its potential to have long-term improvements to water quality without the need for continuous re-application, its generally low cost compared to in-stream liming due to less requirements for heavy machinery, less-extreme water chemistry responses to acid episodes (Hindar, 2005), and reductions in  $\text{Al}_i$  and other metal concentrations hazardous to aquatic life (Clair & Hindar, 2005; Traaen et al, 1997). My thesis summarizes successful terrestrial liming studies completed in Norway and Sweden, and adds to the knowledge of catchment liming in Nova Scotia. I will also determine an updated dose for effective terrestrial liming of acidified catchments in SWNS, as well as provide a rough conversion of the dose currently used in in-stream liming practices within West River Sheet Harbour (WRHS) to an equivalent dose for terrestrial liming methods, that could be used to maintain current water quality standards.

## *1.2 Background*

### *1.2.1 Freshwater Acidification*

Acidification of freshwater systems was first studied in parts of Scandinavia and Eastern Canada during the 1970's (Clair & Hindar, 2005). The main causes of acidification are the transportation and

deposition of sulphur dioxide (SO<sub>2</sub>) and nitrogen oxide (NO<sub>2</sub>) that are produced from the emissions of industrial processes, such as the burning of fossil fuels for power generation. These contaminants are deposited in soils where ion exchange with carbonates occur, leading to the release of base cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) into surface waters (Geddes, 2015). The amount of base cations released depends on the Acid Neutralizing Capacity (ANC) of the soils, or the ability for the soils to buffer acidic inputs. Soils with a high ANC value tend to be more alkaline-rich and have a higher concentration of base cations, which in turn leads to higher levels of base cations in surface waters. High ANC is important for maintaining surface water pH values suitable for most aquatic life, and is necessary for the survival of Atlantic Salmon (*Salmo salar*) (Dennis and Clair, 2012). Soils with low ANC values have low base cations concentrations, therefore leading to inability of the soils to buffer against acidic inputs. This results in corresponding low concentrations of base cations in surface waters, causing both the soils and surface waters to have a low pH. Ionic Aluminum (Al<sub>i</sub>) is released from aluminosilicates, or clays, in soils at low pH values, where it becomes readily available to freshwater biota (Clair & Hindar, 2005). This is concerning as Al<sub>i</sub> has two chemical species, Al<sup>3+</sup> and Al<sup>+</sup>, and when they are not bound to organic matter in complexes they can affect the fitness of freshwater fish species, like *Salmo salar*, by binding to the negatively charged sites of gills (Lydersen, 2002; Dennis and Clair, 2012). This is known as Aluminum toxicity, which can eventually lead to increased rates of mortality in fish if gill clogging occurs due to the build-up of excess mucus (Dennis and Clair, 2012). Aluminum toxicity is especially fatal to *Salmo salar* smolts as it significantly raises stress levels during the already difficult transition from freshwater to saltwater systems. Peterson et al. (1980) looked at hatching rates of *Salmo salar* eggs when exposed to different surface water pH ranges, and found that hatching was prevented in a lower pH range of 4.0 to 5.5, with proper hatching of eggs occurring in a pH range of 6.6 to 6.8. Unfortunately, most of Southwest Nova Scotia's surface waters are in the range of the lower pH values noted above, which is cause for concern as this greatly impacts the integrity of freshwater fish species in Nova Scotia.

### 1.2.2 Freshwater acidification in SWNS

Southwest Nova Scotia has some of North America's most acidified surface waters (Clair et al., 2007; Stoddard et al., 1999; Sterling et al., 2014-a). The four primary factors of acidification in Nova Scotia are: 1) the combination of the eastward transportation of emissions from central North America by prevailing winds and their deposition in the Maritimes, 2) the continuous addition of sea spray to coastal soils, 3) the low levels of base cations of slowly weathered NS bedrock and corresponding low ANC of soils produced from this parent material (Clair et al., 2007), and 4) the slow recovery of NS surface waters and soils due to chronic acid precipitation (Sterling et al., 2014-a). Acid precipitation also affects how quickly and how well surface waters rebound after acid episodes, or events that cause surface water pH to decrease below base flow levels. Sometimes these events can not only lead to dangerously low pH levels, but also prolonged periods of low pH. Acid episodes usually occur after large run-off events, which can include periods of intense rainfall, introduction of snow melt-water in springtime, and even prolonged periods of light rainfall. Acid episodes are known to negatively affect many aquatic species in Nova Scotia, in particular *Salmo salar* populations (Bowlby et al., 2013; Armstrong, 2014).

Significant reductions in acid deposition and corresponding improvements in water chemistry have been seen in many parts of the western hemisphere due to the introduction of emission controls in North America and parts of Europe in the 1980's; like the amendments to the United States Clean Air Act in 1990 (EPA, 2013). However despite this fact, numerous authors (Clair et al., 2003; Mulder et al., 1991; Reuss et al., 1987) have shown that the rate at which some soils and surface waters are recovering is slow due to previous long-term acidification of terrestrial ecosystems (Clair & Hindar, 2005; Sterling et al., 2014-a). In fact according to Clair et al. (2004), even if acid deposition ended in the next 50 years, recovery of a number of Nova Scotia rivers to pre-acidification levels will not occur naturally for another

60-100 years. A model from Wright and Cosby (2003) predicts similar slow rates of recovery in parts of Europe as well. Therefore, human mitigation efforts for freshwater acidification are essential for the survival of many Nova Scotian fish species, particularly the endangered Southern Upland (SU) Atlantic salmon, as categorized by COSEWIC (2010).

### *1.2.3 Terrestrial liming*

One method towards increasing rates of ecosystem recovery is liming, which is the addition of base cations to freshwater systems to increase the overall buffering capacity of the system. Calcium carbonate in the form of limestone ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) are the two main source types used for base cation addition. These minerals are usually crushed into a powder to make it easy for dissolution in freshwater systems. While there are many types of liming methods used to raise base cations levels, the most common practices are in-stream liming and terrestrial liming. In-stream liming is the direct addition of base cations to surface waters, which involves continuous application of limestone or dolomite to the stream, and usually immediate improvements in water quality can be seen. Terrestrial liming is the addition of base cations to acidified soils of a catchment or drainage area, and does not require continuous liming efforts, but with delayed effects. The federal government and many community groups are interested in terrestrial liming because of its low maintenance requirements. Favourability of terrestrial liming over in-stream liming is also due to the fact that terrestrial liming strategies tend to have long-term improvements in water quality since base cations are slowly added to the system, as compared to instream-liming, where any improvements seen in surface waters disappear quickly after the addition of base cations to the stream ceases (Clair & Hindar, 2005). Hindar et al. (2003) estimates the effects of terrestrial liming could exceed 15 years after application based on a study in Norway. Another reason for interest in terrestrial liming practices is due to no requirements for heavy machinery, where in-stream liming usually involves a lime doser (generally quite expensive) which

delivers limestone or dolomite to the stream at rates based on readings of pH sensors upstream (Clair & Hindar, 2005). Lastly, Clair & Hindar (2005) demonstrates that successful terrestrial liming methods result in less variation in water chemistry during extreme acid episodes (periods of intense rain and acid precipitation) and subsequent high flow, which is important for the integrity of freshwater fish and other aquatic species.

Additionally, there are two types of terrestrial liming, whole catchment liming and local catchment or wetland liming. In whole catchment liming, powdered limestone or dolomite is applied to the whole catchment area. The application rate tends to be lower than local catchment liming because more area is treated. However, this method tends to be more effective as limestone is applied over the whole catchment, causing improvements to be longer lasting. Local catchment liming is when a fraction of the whole catchment is limed; usually close to the pour point of the stream (the point in which all of the water above it drains into). Therefore, local catchment liming is more cost effective; less catchment area requires treatment, resulting in the purchase of less limestone. Alternatively, the same amount of limestone used for whole catchment liming can be spread over a portion of the total watershed, and still remain low-cost when compared to whole catchment liming; less labour is required to manually spread the limestone due to a smaller percentage of the overall watershed being treated, leading to larger application rates. Water quality improvements resulting from this method tend to be observed at a faster rate than whole catchment liming, and tend to be greater in magnitude due to the ability for larger application rates; however, water quality improvements can potentially last a shorter duration than whole catchment liming due to less treatment of the total watershed.

#### *1.2.4 Effective terrestrial liming in SWNS*

Effective liming is a term used to describe the target levels of water quality parameters affected, and usually improved, following terrestrial liming. Due to lack of liming studies and research in Nova

Scotia, there are stipulations on what should be considered the correct target levels for these parameters. For example, Hindar (2001) states that “only rivers with pH > 5.4 have non-damaged” SU Salmon populations and therefore liming strategies are calculated for a “water quality target pH of 5.5”. However, Brown (1988) and Clair & Hindar (2005) define a successful terrestrial liming target pH of 6.0 and above, which is most likely due to immobility of ionic Al species at this pH range.

Terrestrial liming success can be negatively influenced by increased levels of Dissolved Organic Carbon (DOC) (mg/L) within surface waters, as well as the presence of Acid Rock Drainage (ARD) and close proximity of these sources to the study site. The main source of DOC in surface waters originates from the addition of leaf litter fall to streams and lakes, and the soils along their banks. DOC levels are highest in surface waters during the Fall, following seasonal vegetative leaf-loss and the accumulation of litter fall on the ground surface. DOC, “contains natural organic acids (NOAs) that increase water acidity” (Clair et al., 2007), which affects in-situ and grab sample measurements of pH. Similarly, ARD refers to the acidification of water as it flows through rock formations that contain sulphide minerals. When these sulphide minerals are exposed to water and air, they react to form sulphuric acid (Earthworks, n.d.).

General water quality improvements from terrestrial liming include increases in surface water pH, immobility of ionic Aluminum species, and higher Calcium (Ca) concentrations, which tend to benefit all types of vegetation and wildlife species within the catchment (Clair & Hindar, 2005). For this study target parameters are as follows: a pH of 6.0 or above, in order to be suitable for the presence of Atlantic Salmon in freshwater streams and to decrease Al concentrations below 15 mg/L, as defined by Macleod et al. (2015), and Ca concentrations above 2.5 mg/L.

### *1.3 Knowledge Gaps*



Research into terrestrial liming is limited, especially in Canadian catchments. Brown (1988) investigated the dose-response relationship of liming in multiple catchments; however results are broad and summarize over many different regions, leading to generalizations of catchments and parameters, with the main focus on liming strategies in Norway and Sweden. It also does not include information on important variables (e.g., were there Ca concentration increases, and/or decreases in  $Al_i$  concentrations in surface waters after liming application?), as it tends to focus only on pH trends. The research is also now outdated as it was published in 1988. As previously mentioned, another issue with determining a dose-response relationship for any type of liming application is that effectiveness varies by location and depends on which parameters are chosen to be the focus of the study (e.g., surface water and/or soil: pH levels, Ca and/or Mg concentrations,  $Al_i$  concentrations, catchment tree/vegetation growth, and forest health, etc.) (Hindar et al., 2003).

Variation in the type and quality of material used (i.e., limestone vs. dolomite, and the size of particles; where finer particles are considered better quality due to their faster rate of infiltration into groundwater systems than large particles) for liming strategies can also be seen in different parts of the world, like Norway (Hindar et al., 2003; Traaen et al. 1997), Sweden (Westling and Zetterberg, 2007) and Whales (Jenkins et al., 1991). These discrepancies can add to confusion over effective liming procedures. Furthermore, freshwater systems have many variables that can affect liming success, such as how much calcium originating from the applied limestone is consumed by vegetation. Determining which variables are important in each freshwater system (i.e., pH, Calcium,  $Al_i$ , DOC, etc.) can prove to be difficult because little is known about how many relatable variables there are, or how they generally behave and in turn, affect liming success. Without this knowledge, it is hard to know if liming efforts are effective outside of the determined variables chosen for that particular study.

My thesis details the only two terrestrial liming projects in Nova Scotia, Maria Brook and Ted Creek, which are two small catchments within the Gold River Watershed in New Ross where

experimental terrestrial liming projects are currently taking place (Sterling et al., 2014-a). Considering the gaps in knowledge surrounding liming strategies in general, there is a need for a more accurate terrestrial liming dose to support effective liming in Nova Scotia. In addition, a better definition of important environmental influences on terrestrial liming is needed (i.e., an analysis of calcium concentrations before and after treatment). My thesis will provide the information to fill-in these knowledge gaps.

#### *1.4 Research Goals and Objectives*

The objective of my research is to identify a likely range of liming doses that would be effective to restore water chemistry to levels needed to support *Salmo salar* populations. I will summarize the results of successful terrestrial liming studies completed in Sweden and Norway (because of comparable catchment characteristics), to define effective water quality targets. I will outline the results of two terrestrial liming studies currently taking place within New Ross, NS, in order to update the range of liming doses suitable for effective liming in NS. I will also provide a preliminary conversion of the present dose used for in-stream liming practices in the WRSR catchment, to an equivalent terrestrial liming dose that would maintain water quality targets currently met. In addition, my research will support decision making for larger terrestrial liming projects within Nova Scotia with expectations to promote recovery of Southern Upland salmon populations.

My thesis will use the following questions to determine a dose for effective terrestrial liming within SWNS catchments:

1. What is the dosage needed for effective terrestrial liming in SWNS?
  - a. What are the application rates and/or percentages of area limed that have been effective?
    - i. Using data collected from other areas of the world

1. What ranges of liming doses have been effective in other regions?
  2. Is there a clear target of what pH, Ca concentrations, and Al<sub>i</sub> concentrations are considered safe for freshwater species, mainly *Salmo salar*?
- ii. Using experimental catchments aimed to test liming effectiveness
1. Was a whole catchment rate of 2.50 t/ha of powdered limestone able to bring pH, Ca and Al concentrations to target levels in the Maria Brook experimental catchment? If not, then how much change in these variables did the dose produce?
  2. Will a dose of powdered limestone resulting in a local application rate of 9.41 t/ha increase the water quality (pH, Ca and Al concentrations) to target levels in the Ted Creek test site in the first year?
- b. In cases of instream liming, what would be the equivalent effective terrestrial liming dose?
- i. Using data from in-stream liming conducted in the West River Sheet Harbour catchment
1. What dose is needed for effective terrestrial liming of WRSB when the current in-stream liming application is converted?

The spatial scope of this study is restricted to experimental terrestrial liming of two small catchments within the Gold River Watershed in New Ross, NS. This research builds on data collected prior to the start of this study, between September 2011 and May 2014, with this research beginning in May 2014 and continuing to November 2015. The two primary limiting factors for this research are budget constraints and time, both of which restrict the scale and detail that is included within this project.

## *1.5 Summary of Approach*

My thesis focuses on determining a range of doses suitable for effective terrestrial liming in NS using four different lines of evidence: the results from successful experimental terrestrial liming studies in Sweden and Norway, both bi-weekly and weekly in-situ and grab sample analyses to compare the before and after effects of liming application for control and treatment sites in two experimental terrestrial liming catchments in New Ross, NS, and conversion of the current dose used for in-stream liming practices in WRSB to an equivalent terrestrial liming dose needed to maintain present water quality targets. Lastly, my research adds to the database of knowledge surrounding terrestrial liming in Nova Scotia, as well as in Canada, with the goal to reduce the risk of extirpation for Southern Upland (SU) Atlantic salmon.

A Before/After Control/Impact analysis was chosen as the study method for the Maria Brook catchment. This type of analysis is used to determine a base level of water quality measurements at a control and treatment site prior to limestone application (pre-liming), and compare the water quality measurements following treatment of the catchment area (post-liming) to the control site, and pre-treatment levels. A similar method was used to investigate the effects of terrestrial liming at Ted Creek; however larger application rates were used to help determine a range of doses for effective terrestrial liming in SWNS.

## 2.0 Methods

### *2.1 Terrestrial Liming in Other Areas of the World*

There are only a few other examples of terrestrial liming elsewhere in the world. One of which is a catchment at Tjonnstrond in Norway, where 75 t of limestone is applied to produce an application rate of 3 t ha<sup>-1</sup> to a catchment that also contains two lakes with a retention time (the average time a

molecule of water spends in a lake before exiting due to outflow) of 0.2 yr (Brown, 1988). Another example of terrestrial liming is located in the Esk Valley in Southwestern Cumbria, where 3000 t of limestone is applied to agricultural land at a local rate of  $5 \text{ t ha}^{-1}$ , or a whole catchment rate of  $0.45 \text{ t ha}^{-1}$ . A terrestrial liming study in the Solway River, Scotland, has 80 t of limestone applied to an area of 0.3 ha to produce a whole catchment rate of  $0.15 \text{ t ha}^{-1}$ . Lastly, a terrestrial liming study in the UK, the Loch Fleet Project, varies the application rates (up to  $30 \text{ t ha}^{-1}$ ) of numerous sub-catchments to determine the response of the lake(s) to a total catchment application of  $3 \text{ t ha}^{-1}$ .

Although these studies measure the success of terrestrial liming practices by the effects on water quality of the lake(s) present within the treated catchment, these experiments are still a guideline for terrestrial liming studies in SWNS because it can be assumed that water quality improvements detected in the lake(s) of a treated catchment can also be observed in the stream(s) flowing into the lake, as long as the streams are located downslope of the treated catchment area. Therefore, stream water quality analyses completed in the Maria Brook and Ted Creek experimental terrestrial liming catchments in New Ross, NS, are comparable to the lake water quality analyses of the experimental terrestrial liming studies summarized above.

## *2.2 Terrestrial Liming Catchments in SWNS*

There are currently only two experimental terrestrial liming studies taking place in NS. They are located in New Ross (Figure 4 and Figure 7), and are small sub-catchments of the larger Gold River watershed. Before initiation of each experiment, both sites were ground-truthed to determine if:

- 1) the site was accessible on foot and/or if a portion of the access trail was vehicle accessible (but with absent ARD),

2) the site had both wetland and forest environments present (characteristic of a NS catchment),

3) a stream was present and was large enough for grab sample collection (following the approximate size and location previously determined using ArcGIS and/or Google Earth software),

4) the stream was acidified and had an approximate water quality of a pH around low 4's to mid 5's, total Al around 300 to 400 µg/L, and Ca concentrations around 1.4 mg/L,

5) land owner permission existed. Additionally, priority would be given to catchment sites with fish present; however this factor was nondeterministic of site selection, as the main focus was on water quality improvements following terrestrial liming application.

### *2.2.1 Maria Brook*

#### *Study area*

The Maria Brook catchment is located in New Ross, NS (Figure 4). The original pre-liming water quality measurements of this study site include a pH in the high 4's to mid 5's., Ca concentrations around 1.0 mg/L, and average total Al levels of around 400 µg/L. It has a catchment area of 47 ha, consisting of forest and wetland, and a small abandoned Christmas tree lot. A man-made grown-over ATV trail runs through the catchment and is used as access to sampling sites. Powdered limestone was applied to the Maria Brook study catchment once every summer, starting in 2012 and ending to 2014, for a total of 3 applications, or 4 liming phases (Table 1). A Before/After Control/Impact (BACI) analysis was completed each year. Seven sampling sites (i.e. 2 controls and 5 treatments) (Table 2) with varying distances downstream of the applied liming area (Figure 5) were chosen to assess liming effectiveness. Of the seven sites, three sampling sites: site 5 (DMEMP), site 6 (CMEMP), site 7 (Control) were given priority due to their locations in the catchment. Site 5 (DMEMP) was the site downstream of all applied

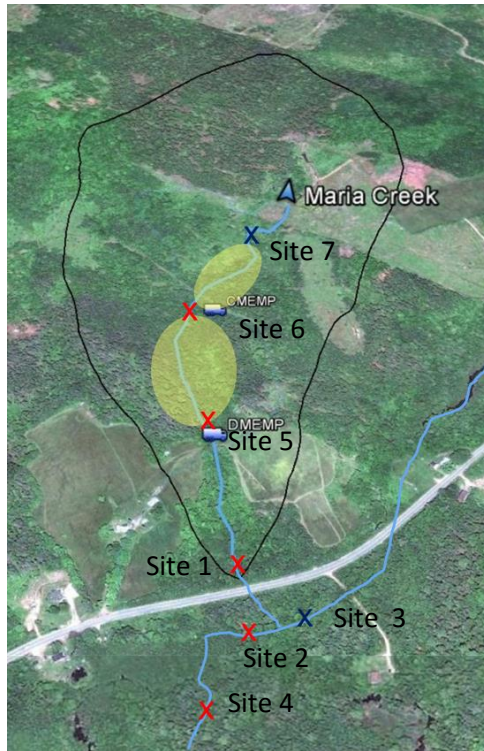
lime, site 6 (CMEMP) was initially the control and later became a treatment site; downstream of approximately 27 % of all lime, and site 7 was created as the new control and was above all applied lime.



**Figure 4.** Location of Maria Brook study catchment in New Ross, Nova Scotia.

**Table 1.** Liming phases and their corresponding information for Maria Brook, New Ross, NS.

Phase	Duration	Date of Application	Amount of Limestone	Notes
1	October 2010 and May 2012	N/A	N/A	Pre-liming phase.
2	June 2012 to May 2013	June 2012	27 tonnes	Post-liming begins.
3	June 2013 and May 2014	June 2013	60 tonnes	Raining during application, piles became cemented.
4	June 2014 and July 2015	June 2014	30 tonnes	Piles that had cemented the previous year were broken-up, also applied lime in Christmas Tree Lot.



**Figure 5.** Maria Brook catchment perimeter outlined in black, with the 7 sampling sites shown. Control sites are marked with a blue X and treatment sites with a red X. Yellow areas highlight parts of the stream where sub-transects are located: two between Site 7 and CMEMP, and 6 between CMEMP and DMEMP.

### *Liming Method*

A local catchment terrestrial liming method was chosen in combination with a Before/After Control/Impact analysis, which was completed in four phases. Phase 1 is also known as the pre-liming phase which took place between October 2010 and May 2012 (Table 1). Within this time sites 1 to 4 were chosen. Site 1 is a treatment site and it was chosen because it was downstream from the applied lime. Site 2 is a treatment site, which was chosen to determine if effects could be observed further downstream. Site 3 is a control and is located on another branch of the catchment and was chosen to compare its water chemistry to the treated branch. Site 4 is located downstream from Site 2 and was chosen to see how far downstream the effects of liming could be seen. Grab samples from each of the four sites began in October 2010, while in-situ data collection records began in September 2011. Sites 5 and 6 were created in November 2011, following installation of two Mobile Environmental Monitoring



Platforms (MEMPs). MEMPs can collect real-time data every 15 minutes, which includes solar and wind information, water quality information, like turbidity, pH, temperature, conductivity, Dissolved Oxygen (DO) percent and concentration in mg/L, total dissolved solids (TDS), and other valuable information like flow data and stage in meters (Nfld and Labrador, 2012).

Phase 2, or the first post-liming phase commenced with the application of powdered limestone in June 2012, purchased from Mosher Limestone. This phase took place from June 2012 to May 2013 (Table 1). 192 liming quadrats were flagged in May 2012, but limestone was applied at only 51 of the flags. The limestone was applied by Dalhousie and New Germany High School students and Bluenose Coastal Action Foundation (BCAF) volunteers via bucket dispersal (Figure 6). 27.3 t of limestone were applied to 2.08 ha, or 4.4% of catchment (Figure 6). This addition resulted in a local application rate of 13.1 t/ha and a whole catchment application rate of 0.58 t/ha.



**Figure 6.** New Germany, BCAF volunteers, and HSRG members during liming application in June 2012, Maria Brook catchment, New Ross, NS.

Phase 3, the second post-liming phase, took place between June 2013 and May 2014 (Table 1). 93 flagged quadrats of the previous 192 flags were limed, with the lime applied once again by Bluenose Coastal Action Foundation volunteers via bucket dispersal. This time 60.0 t of limestone was purchased from Mosher Limestone, and applied to 3.72 ha of the catchment, or 7.9% of the whole catchment area. This resulted in a local application rate of 16.13 t/ha and a whole application rate of 1.28 t/ha (Figure 6).

Unfortunately the limestone was not spread properly and major clumping issues occurred, causing the 2013 application to be almost ineffective.

Phase 4, the final post-liming phase, took place between June 2014 and July 2015. 21 new liming quadrats were flagged by Dalhousie and BCAF volunteers within the abandoned Christmas tree lot. Any clumps of limestone still visible from the previous year's application were broken up to allow the limestone to dissolve and enter the system. Limestone was purchased from Mosher Limestone once again, and 30.2 t were applied over 2.36 ha, or 5.0 % of whole catchment limed. This resulted in a local application rate of 12.79 t/ha and a whole catchment application rate of 6.4 t/ha (Figure 8). Therefore, the total dose of limestone applied over all four phases was approximately 117 t, and was spread over a total area of 8.16 ha, or 17.4 % of the entire catchment. This resulted in a local application rate of 1.4 t/ha and a whole catchment application rate of 2.5 t/ha.



**Figure 7.** BCAF volunteers during the June 2014 liming application at Maria Brook, New Ross, NS.

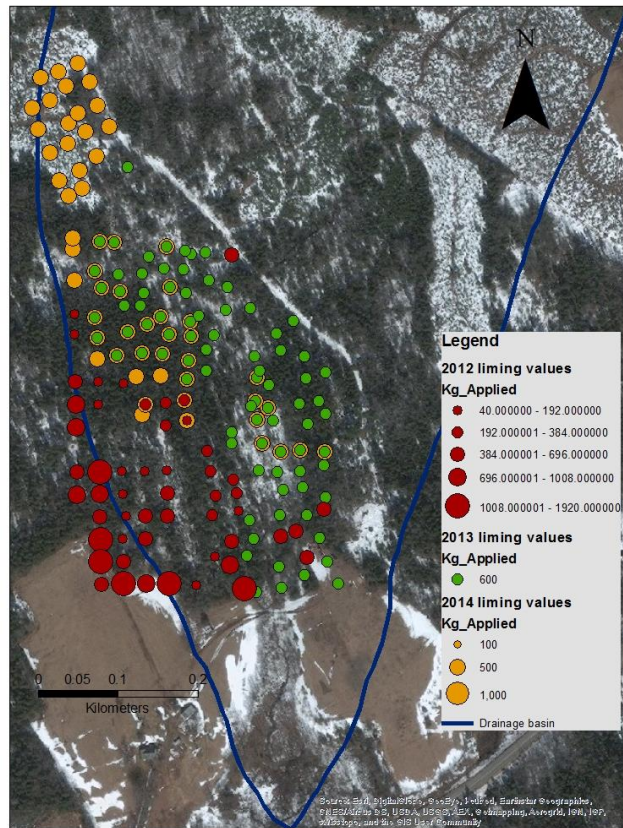


Figure 8. Location and amount of limestone (in kg) applied during 2012, 2013 and 2014 liming phases [produced by M. Geddes, 2014].

### Sampling Procedure

Table 2. List of sites 1 to 7 and their descriptions.

Site Number	Treatment or Control	Start Date	Description
Site 1	Treatment	Oct 2010	Test for how far downstream of lime effects can be seen
Site 2	Treatment	Oct 2010	Test for how far downstream of lime effects can be seen
Site 3	Control	Oct 2010	Test to see if connecting stream has similar water quality to control upstream
Site 4	Treatment	Oct 2010	Test for how far downstream of lime effects can be seen
Site 5 (DMEMP)	Treatment	September 2012	Test for how far downstream of lime effects can be seen

Site 6 (CMEMP)	Control→Treatment	September 2012	Initial control site; however became a treatment site after liming application in 2014, as it was downstream from 27% of the lime from this point forward
Site 7	Control	May 2014	New control site created in May 2014 before liming application in June 2014

Bi-weekly water grab samples of pH, Dissolved Organic Carbon (DOC), and dissolved metals were collected from all sites until May 2014, when weekly collection of grab samples from Site 1 to 7 began. This data collection continued until July 2014 when grab samples from Sites 1 to 7 returned to bi-weekly sampling, with grab sample collection at sites 5, 6 and 7 (i.e. priority sites) every other week due to budget restrictions. Weekly in-situ data collection of pH, temperature, DO%, and Conductivity were gathered using a YSI 600 data logger, in combination with a hand-help pH Ecosense meter. Real-time data was collected (i.e. rainfall, water pH, water temperature, water conductivity, wind speed, etc.) every 15 minutes by DMEMP and CMEMP Mobile Environmental Monitoring Platforms (MEMPs) following their installation in Nov 2011 and collected off-and-on until summer of 2015 when one MEMP was removed due to the sale of property where it was located, and the other MEMP underwent maintenance; however it was improperly re-installed and no longer transmitted data. For these reasons, MEMP data was not analyzed within the scope of this study, as data quality and integrity could not be assured.

#### *Data Analysis*

Grab samples were analyzed at the Atlantic Laboratory for Environmental Testing (ALET) in Moncton, NB until April 2013, when samples were then sent to Maxxam Analytics in Bedford, NS for the rest of the project duration. All information was sent to the Hydrology Sterling Research Group (HSRG) of Dalhousie University following laboratory analysis (Appendices A and B). Levels of pH, DOC (mg/L), Ca

concentrations (mg/L), and  $Al_t$  ( $\mu\text{g/L}$ ) will individually be plotted against time to observe trends during different times of the year.

### 2.2.2 Ted Creek

#### *Study area*

The Ted Creek study site is another small catchment within the Gold River Watershed, located off of Mill Rd, New Ross, NS (Figure 7). This site meets the selection criteria (e.g. pH around low 4's to mid 5's, total Al around 300 to 400  $\mu\text{g/L}$ , and Ca concentrations around 1.4 mg/L). This site has electrofishing data available, is accessible, and has landowner permission. The catchment has an area of 7.60 ha and is composed of forest and wetland area, with dirt road access to the catchment and an abandoned forestry lot making up one-third of the catchment area. Ted Creek was limed in the summer of 2015, for a total of one limestone application that resulted in larger local and whole catchment application rates than Maria Brook.

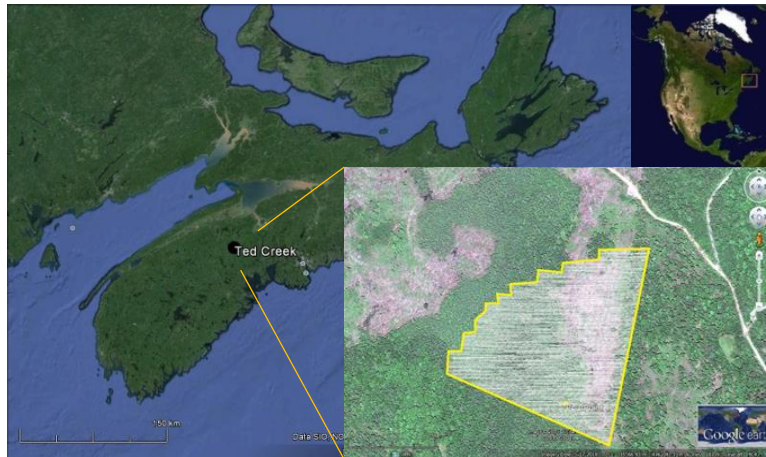


Figure 9. Location of Ted Creek study site, New Ross, NS.

#### *Liming Method*

A local catchment terrestrial liming method was selected for this study area, in which it was decided to use a larger application rate than Maria Brook's to a larger percentage of the total

watershed. This method was selected to help determine an accurate range of doses that could be used for effective terrestrial liming in SWNS. An ATV trail was created by BCAF volunteers as a way to make liming application easier. A dump truck unloaded the full load of limestone on a tarp on the main dirt road, and the ATV was used to create another smaller pile of limestone half-way into the catchment at the end of the ATV trail. Limestone was spread by manually carrying buckets to proper flags and spreading it evenly over the ground of the catchment. 33.89 t of limestone was purchased from Mosher Limestone and applied to 3.6 ha, or 47.3% of the total catchment (for limestone composition see Figure 11). This resulted in a local application rate of 9.41 t/ha and a whole catchment application rate of 4.46 t/ha (Table 3; Figure 10).

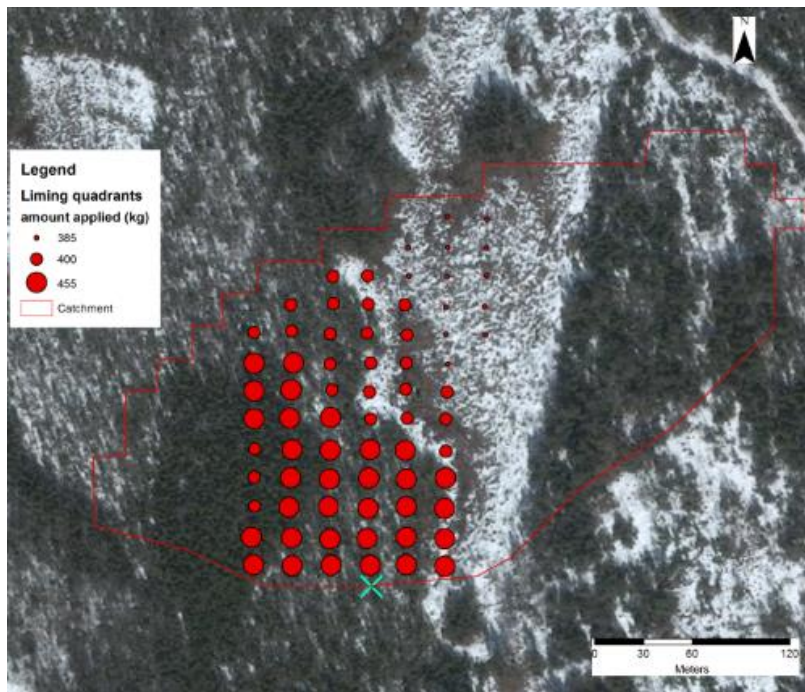


Figure 10. Locations and amount of limestone (in kg) applied in 2015 to each flag in 2015 [produced by M, Geddes, 2015].

Table 3. Maria Brook and Ted Creek liming application results for the 2015 experimental period.

Description	Maria Brook	Ted Creek
Catchment area	47.0 ha	7.6 ha

Limed area	8.16 ha	3.6 ha
% catchment limed	17.4	47.3
Total amount of lime applied	117.5 t	33.89 t
Ave local application rate	1.4 t/ha	9.41 t/ha
Whole catchment application rate	2.5 t/ha	4.46 t/ha

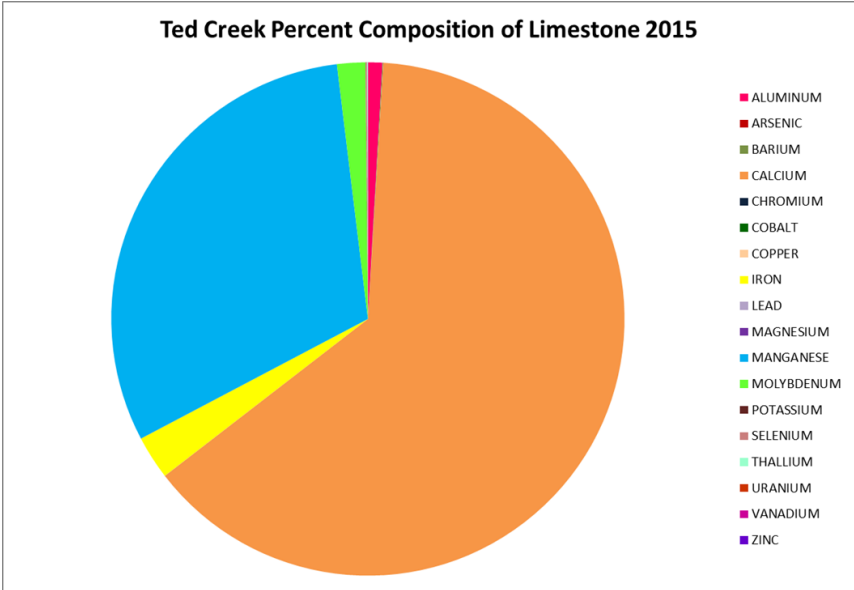


Figure 11. Limestone percent composition for 2015 material purchased from Mosher Limestone.

*Sampling Procedure*

Weekly grab samples of pH, DOC, and dissolved metals concentrations were taken at the pour point of the Ted Creek catchment from June 2015 to the end of November 2015. The control for this study site is the Site 7 control at Maria Brook, which is possible due to both site belonging to the same, larger Gold River Watershed. Weekly grab samples of the same water quality parameters were collected at this control site as well. In addition to this, weekly in-situ data collection at both sites of stream water pH, temperature, DO%, and Conductivity were taken during this time as well using a YSI Pro sonde, in combination with a hand-held Ecosense pH meter for comparison of the pH and temperature parameters.

### *Data Analysis*

Grab samples analysis took place at Maxxam Analytics in Bedford, NS. All information was then sent to the Hydrology Sterling Research Group of Dalhousie University following laboratory analysis. Similarly to Maria Brook, levels of pH, DOC (mg/L), Ca concentrations (mg/L), and  $Al_t$  ( $\mu\text{g/L}$ ) will independently be plotted against time to detect patterns in each parameter during different times of the year, as well as to note differences in initial and final levels of each parameter to judge the effectiveness of terrestrial liming at Ted Creek. Again, hydrograph positions are noted during data collection of in-situ data and grab samples (see sections 3.2.1 and 3.2.2 for corresponding Figures). Graphs of treatment parameters vs. control parameters (i.e., pH, Ca (mg/L),  $Al_t$  ( $\mu\text{g/L}$ ), and DOC (mg/L)) with their corresponding hydrograph positions are useful for observing changes in each hydrograph position, but my main focus will remain on changes in baseflow water quality parameters.

### *2.2.3 West River Sheet Harbour*

#### *Study area*

The West River Sheet Harbour catchment is located within West River Sheet Harbour, NS (Figure 12). The catchment is roughly 317,000 ha in area. The purpose of this site is to convert the current dose used for in-stream liming methods to an equivalent dose (i.e.  $\text{t ha}^{-1} \text{yr}^{-1}$ ) that could be used for terrestrial liming methods in order to maintain a pH of 6.0 for this study site.





**Figure 12.** West River Sheet Harbour study area location, extended on the right to show relation to major highways in the region.

### *Liming Method*

An in-stream liming method is presently used in this catchment, where a liming doser applies powdered limestone directly to stream for immediate results. A sensor upstream from the doser monitors the pH levels of the stream, and when the pH drops below 6.0, the doser automatically releases limestone into the stream until the target pH is acquired (Clair and Hindar, 2005). The average total dose of limestone applied is 375 t/year.

### *Sampling Procedure*

As previously mentioned, surface water pH levels are continuously monitored upstream from the doser, the doser then releases powdered limestone to the stream at a constant rate to maintain a target pH of 6.0. Other than this, there are no additional in-situ or grab sampling procedures completed within the West River Sheet Harbour catchment.

### *Data Analysis*

An average application rate (equation 1) is calculated and further analysis is finalized to determine if the current in-stream liming strategies could convert to reasonable terrestrial liming

strategies, with the objective to maintain the target pH of 6.0. Additionally, how much calcium is lost to system plays an important role when computing the proper amount needed for terrestrial liming application.

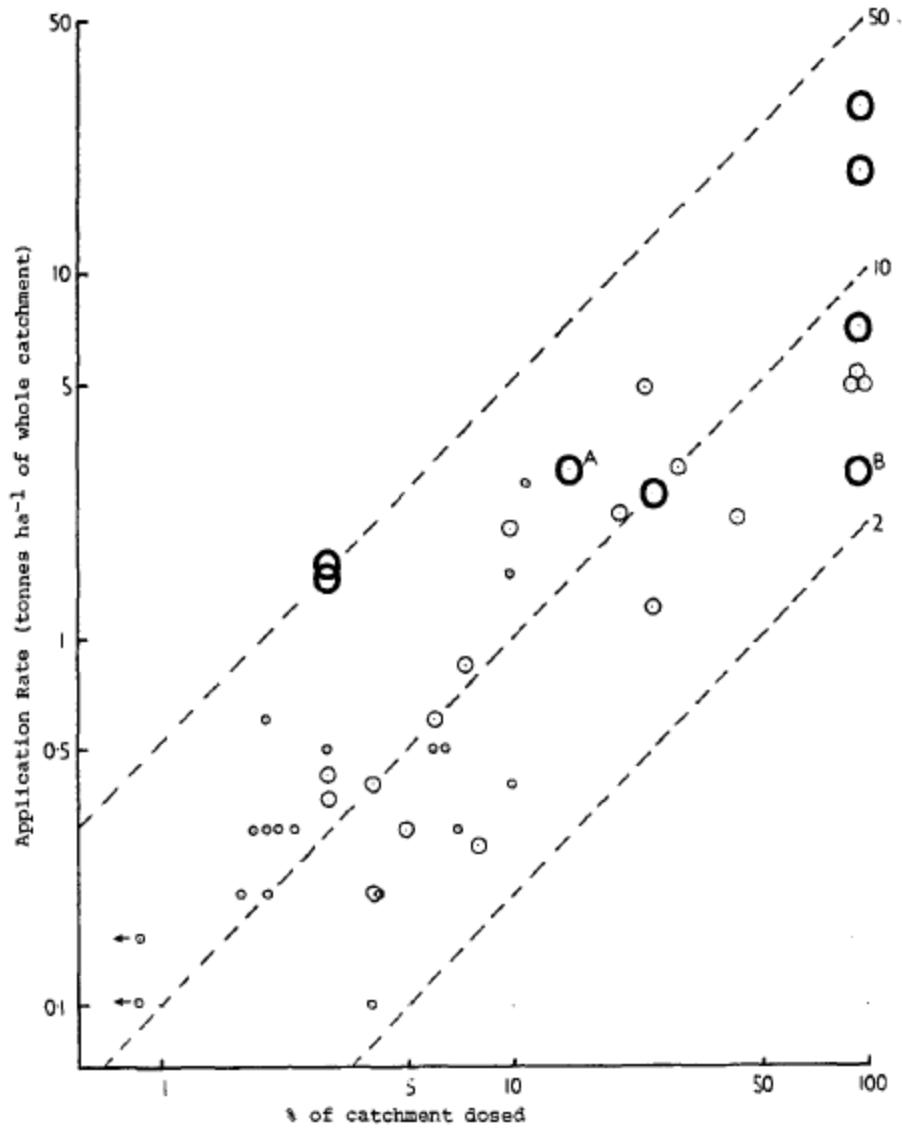
$$R_{ave} = L_{ave} / A_{total} \quad (\text{Equation 1})$$

Where  $R_{ave}$  is the annual average application rate in  $t\ ha^{-1}\ yr^{-1}$ ,  $L_{ave}$  is the tonnes of powdered limestone applied each year ( $t\ yr^{-1}$ ), and  $A_{total}$  is the total catchment area (ha).

## 3.0 Results

### 3.1 Literature Results

Water quality improvements were observed from the liming application in Tjonnstrond, Norway. These improvements remained 5 years after the initial application, with the effects expected to persist for many years to come (Brown, 1988; Traaen et al., 1995); even with a short lake retention time of 0.2 yr for the two lakes within the catchment. In the Esk Valley, Southwestern Cumbria, a significant and immediate pH increase was observed following terrestrial liming, and has remained throughout time (Brown, 1988). In the case of terrestrial liming in the Solway River catchment, in Scotland, no improvements in water quality were observed following liming application. Finally, terrestrial liming proved to be effective (pH held at 6.0 for longer than 1 yr) in the Loch Fleet Project for two cases where approximately 4 % of the catchment was treated with application rates of around  $2\ t\ ha^{-1}$ . Another successful case within the Loch Fleet Project was observed when limestone was applied to approximately 10 % of the catchment at a rate of around  $4\ t\ ha^{-1}$  (Figure 13). Additionally, an application rate of approximately  $3.5\ t\ ha^{-1}$  spread over ~25 % of the catchment area proved to be effective at improving water quality for over a year. However, when 100 % of the total catchment was limed, effective liming applications rates ranged from around  $4\ t\ ha^{-1}$  to  $25\ t\ ha^{-1}$  (Brown, 1988; Figure 13).



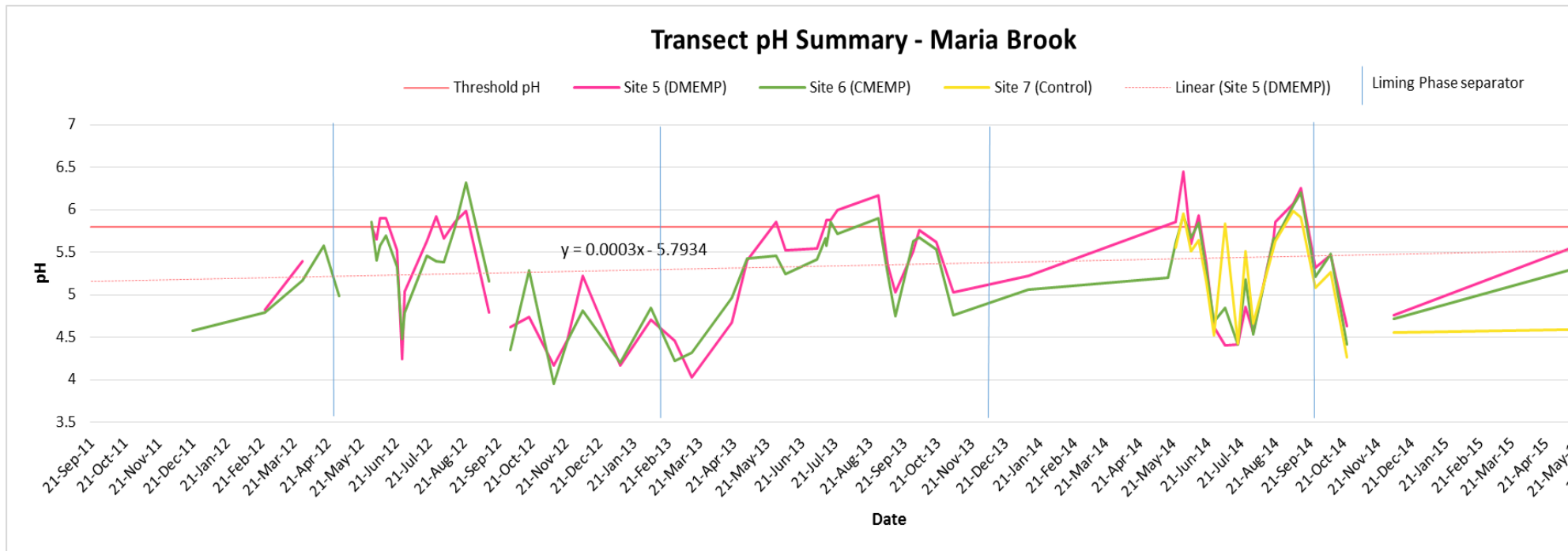
**Figure 13.** Terrestrial liming results from around the world; “Diagonal lines indicate average local application rates of 50, 10 and 2 tonnes ha<sup>-1</sup> respectively, o indicates no effect of treatment on surface water quality, O some short term positive effect on pH, O indicates pH being held above 6.0 for longer than 1 year. A and B are the whole lake experiments at Loch Fleet in Scotland and Tjonnstrond in Norway respectively. Other long term neutralisations are subcatchments within Loch Fleet and 2 streams on the Swedish West Coast” [Brown, 1988].

### 3.2 Maria Brook

#### 3.2.1 In-situ Data Results

Figure 14 shows pH trends throughout time; data was collected via in-situ methods. The three priority sites: 5 (Downstream of all lime - treatment), 6 (Downstream of ~27% of all lime – first control),

and 7 (Above all lime – Control) are given focus in order to determine notable differences in before and after liming application at control and treatment sites. In-situ data collection began December 25, 2010; however sampling of Site 5 and 6 priority sites did not begin until November 28, 2011, with the initiation of Site 7 on May 23, 2014. The initial pH at Site 5 before liming application in 2012 was 5.49, with the end pH following liming application in 2015 at 5.48 (Appendix A). Whereas, the initial control pH was 4.58, and was 4.24 at the end of the study. Average Site 5 pH over the duration of the study was 5.35, with an average control pH of 5.21. The trend-line of Site 5 (DMEMP - Downstream of all lime) suggests that in-situ pH has slightly improved throughout the course of the study; between November 28, 2011 and August 13, 2015 (Figure 14).



**Figure 14.** Insitu Transect pH results for Maria Brook from September 21, 2011 to August 13, 2015. Data collected via YSI 650 (September 21, 2011 to August 1, 2014) and YSIPro SONDE (August 19, 2014 to August 13, 2015); however priority sites: treatment (Site 5 – downstream of all lime) and first control (Site 6 - which became downstream of 27% of all lime) started to be sampled November 28, 2011, and the new control (site 7 – above all lime) became a sample site May 23, 2014.

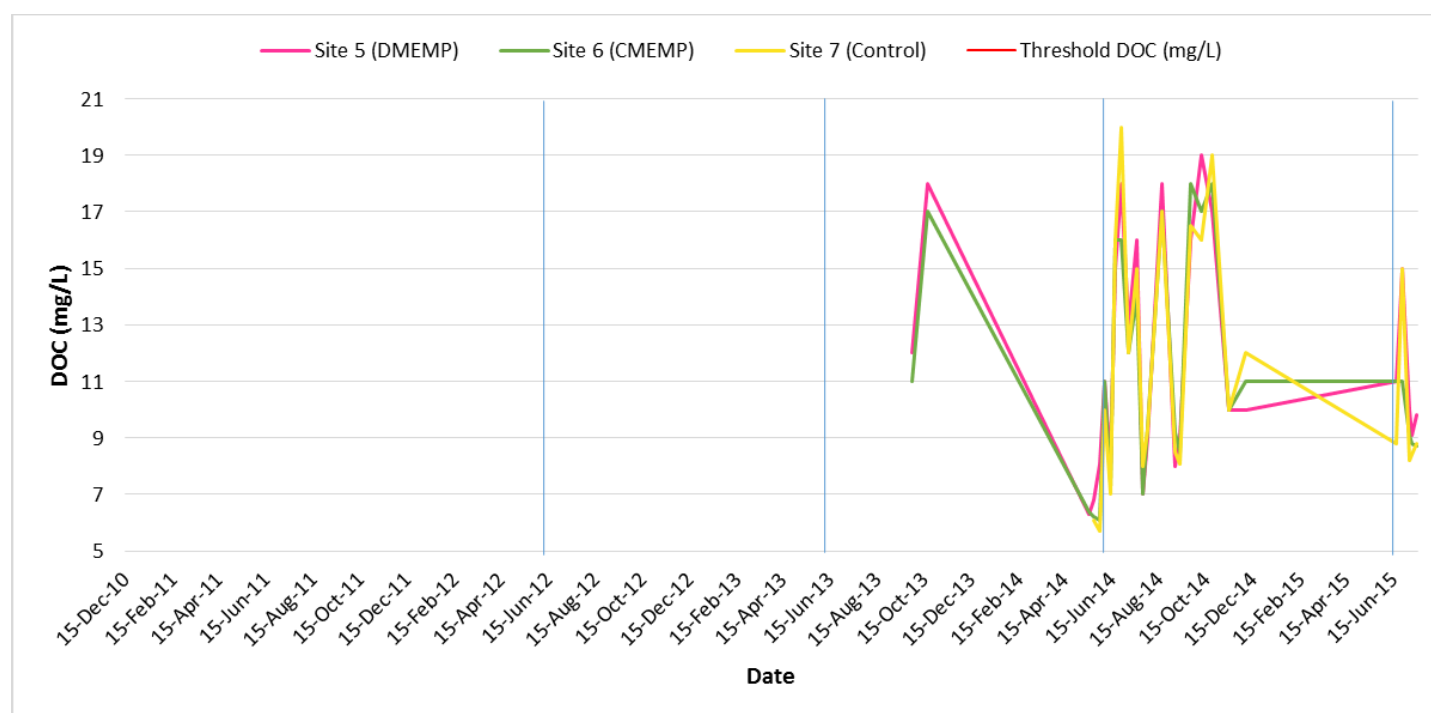
### 3.2.2 Maxxam Lab Data Results

Transect pH was also analyzed at Maxxam Analytics as grab samples throughout the study, to act as a comparison to the in-situ transect pH data. Data was collected and analyzed initially at the Atlantic Laboratory for Environmental Testing (ALET) from December 25, 2010 to April 17, 2013. Grab sample analysis then continued at Maxxam Analytics from July 12, 2013 to July 16, 2015, when the study finished. However, the priority sites 5 and 6 were not sampled for analysis until May 8, 2012, and grab sampled for Site 7 did not occur until May 23, 2014. The initial pH of Site 5 was 6.11, while the final pH was 6.14. Comparably, the initial control pH was 6.19 and final pH was 6.10 (Appendix A – Note: the control site began as Site 6, and finished as Site 7, so mentioned pH values correspond to correct control sites). The average pH for Site 5 during the experiment was 5.83, while the average control pH was 5.70 (Figure 15; Appendix A).



**Figure 15.** pH results of Maria Brook grab samples analyzed by ALET (Dec 15, 2010 to April 17, 2013) and by Maxxam Analytics (July 12, 2013 to July 16, 2015); however priority sites: treatment (Site 5 – downstream of all lime) and first control (Site 6 - which became downstream of 27% of all lime) started to be sampled May 8, 2012, and the new control (site 7 – above all lime) became a sample site May 23, 2014. Blue lines represent liming phase separators.

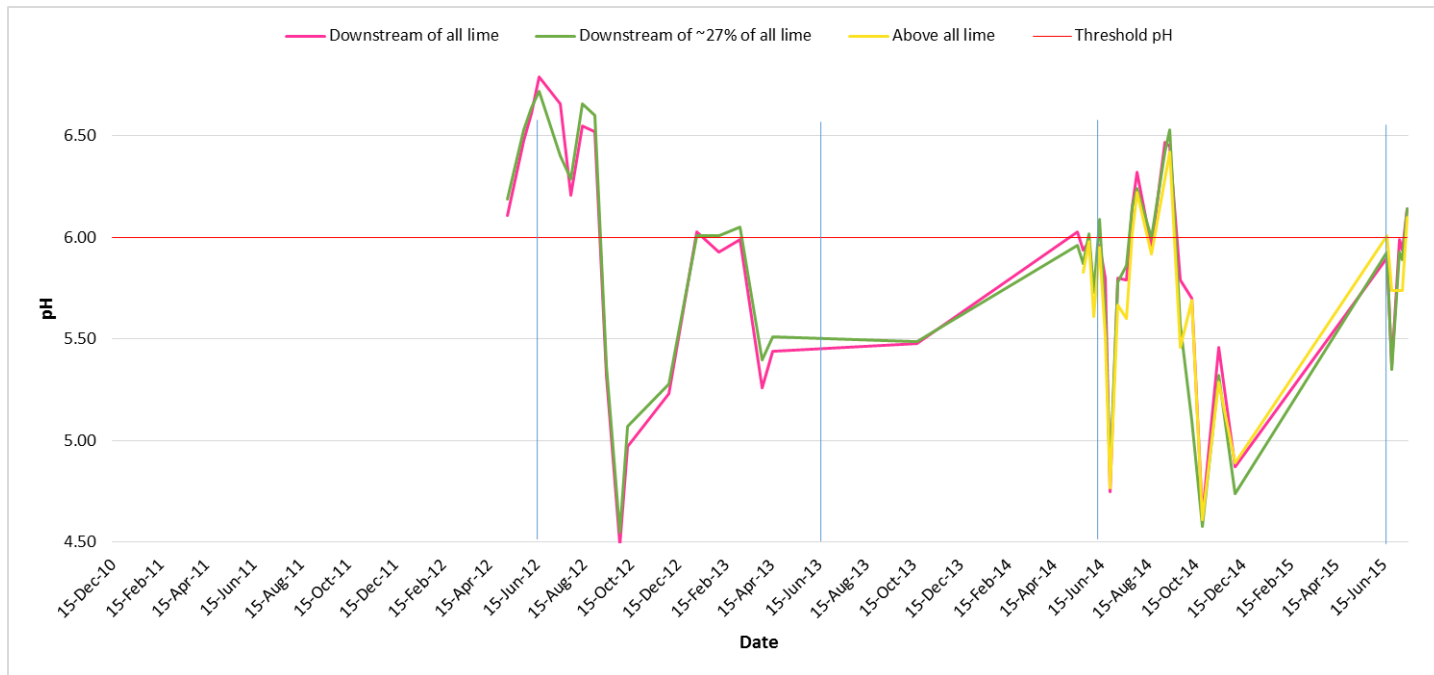
In addition to grab sample analysis of pH, Dissolved Organic Carbon (DOC) in mg/L was also analyzed at Maxxam Analytics; however analysis began on Sept 29, 2013, which explains the vacancy of data up until this point. The initial level of DOC for Site 5 was 12.0 mg/L, but end the value of DOC was 9.8 mg/L. The Initial control DOC value was 6.1 mg/L and end value was 8.8 mg/L. Both Site 5 and the control have similar average DOC values, 11.9 mg/L and 11.5 mg/L, respectively. A decrease in DOC levels can be observed throughout the study period (Figure 16; Appendix A).



**Figure 16.** DOC (mg/L) results of Maria Brook grab samples analyzed by ALET (Dec 15, 2010 to April 17, 2013) and by Maxxam Analytics (July 12, 2013 to July 16, 2015); however priority sites: treatment (Site 5 – downstream of all lime) and first control (Site 6 - which became downstream of 27% of all lime) started to be sampled May 8, 2012, and the new control (site 7 – above all lime) became a sample site May 23, 2014. Blue lines represent liming phase separators.

Grab sample analysis for  $Al_t$  at Sites 5 (Downstream of all lime) and 6 ((Downstream of ~27% of all lime) began on May 8, 2012, and was conducted at Maxxam Analytics until the end of the study, July 16, 2015.  $Al_t$  grab sample analysis did not begin for Site 7 (Control) until the site was created on May 23, 2014. Ignoring the periodic spikes,  $Al_t$  seems to stay fairly constant throughout the study period (Figure

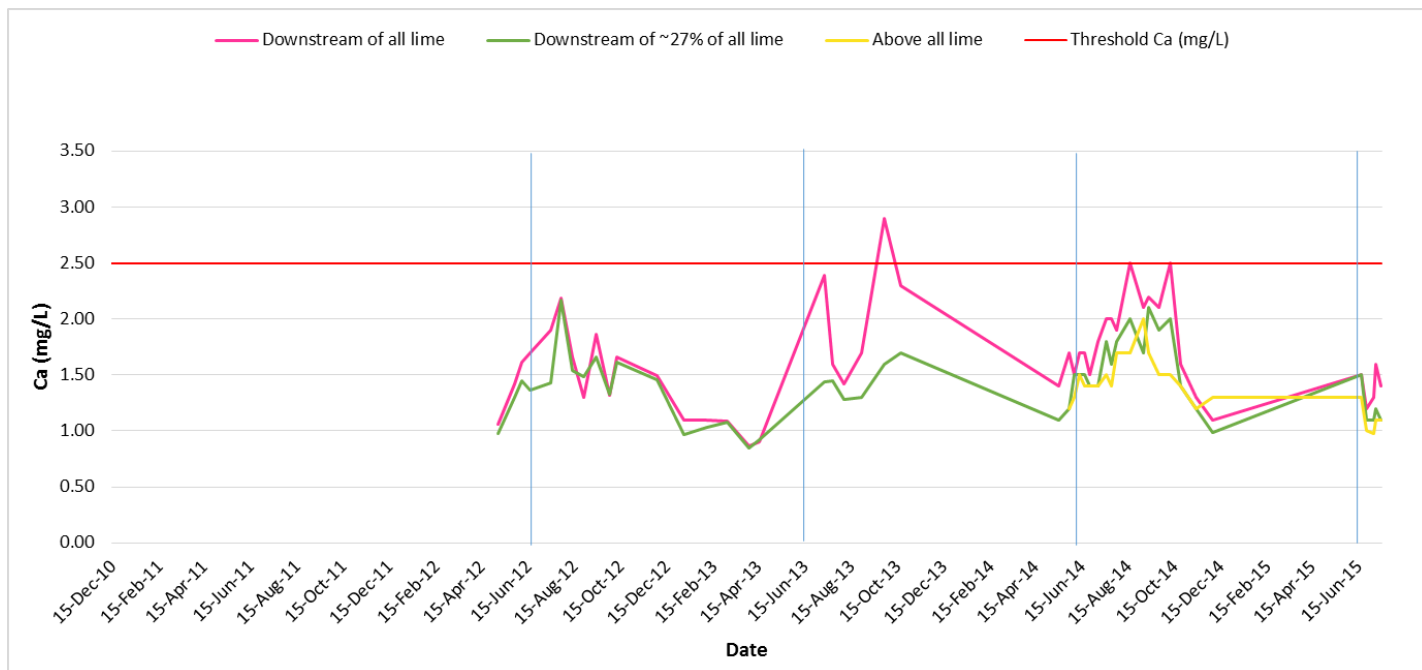
17). The initial  $Al_t$  for Site 5 is 221.8  $\mu\text{g/L}$ , while the final value is 410.0. The original control value for  $Al_t$  is 235.9  $\mu\text{g/L}$ , with an end value of 330.0  $\mu\text{g/L}$  (Appendix A). The average value for Site 5  $Al_t$  is 465.4  $\mu\text{g/L}$ , with an average control value of  $Al_t$  of 553.6  $\mu\text{g/L}$ . Additionally, total Al levels did not make it below the suggested target of 1.5 mg/L suitable for *Salmo salar* population stability.



**Figure 17.** Total Aluminum ( $\mu\text{g/L}$ ) results for Maria Brook grab samples analyzed by ALET (Dec 15, 2010 to April 17, 2013) and by Maxxam Analytics (July 12, 2013 to July 16, 2015); however priority sites: treatment (Site 5 – downstream of all lime) and first control (Site 6 - which became downstream of 27% of all lime) started to be sampled May 8, 2012, and the new control (site 7 – above all lime) became a sample site May 23, 2014. Blue lines represent liming phase separators.

Again, grab sample analysis for Ca (mg/L) for priority sites 5 and 6 began on May 8, 2012, with Site 7 grab sample analysis beginning on May 23, 2014. The initial Site 5 Ca concentration was 1.06 mg/L, with the final concentration at 1.40 mg/L. The original control value for Ca was 0.98 mg/L, while the end concentration for Ca was 1.10 mg/L. The average Ca concentration for Site 5 was 1.66 mg/L, with the average Ca control concentration at 1.39 mg/L (Appendix A). Ca concentrations (mg/L) have increased throughout the duration of the study period; however levels were far below the suggested 2.5 mg/L target level for surface water Ca concentrations (Figure 18).



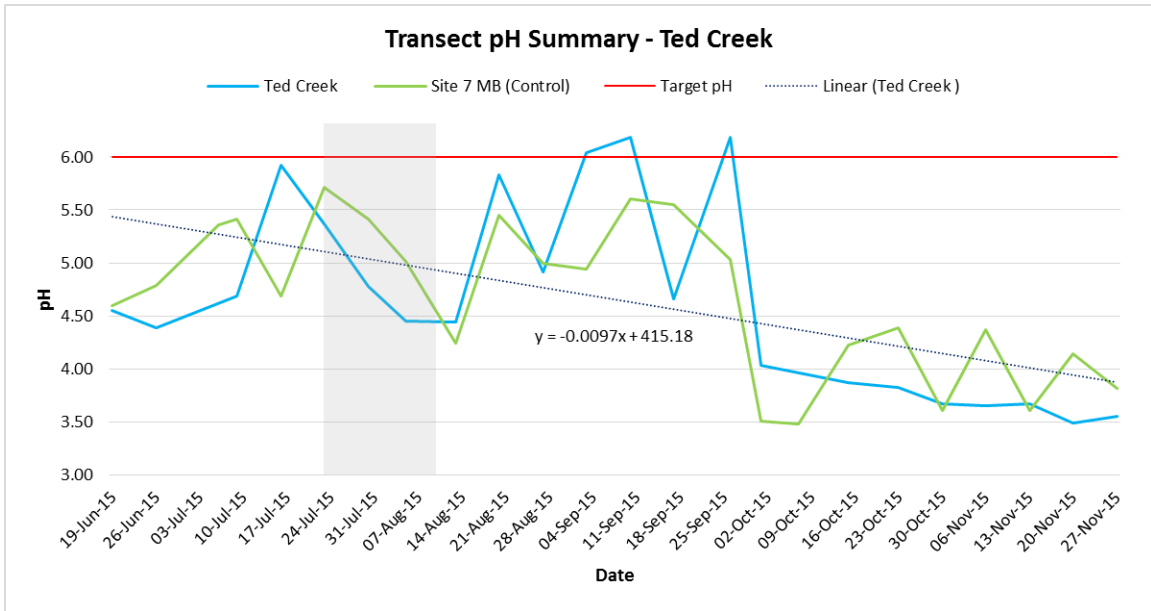


**Figure 18.** Calcium concentration (mg/L) results of Maria Brook grab samples analyzed by ALET (Dec 15, 2010 to April 17, 2013) and by Maxxam Analytics (July 12, 2013 to July 16, 2015); however priority sites: treatment (Site 5 – downstream of all lime) and first control (Site 6 - which became downstream of 27% of all lime) started to be sampled May 8, 2012, and the new control (site 7 – above all lime) became a sample site May 23, 2014.

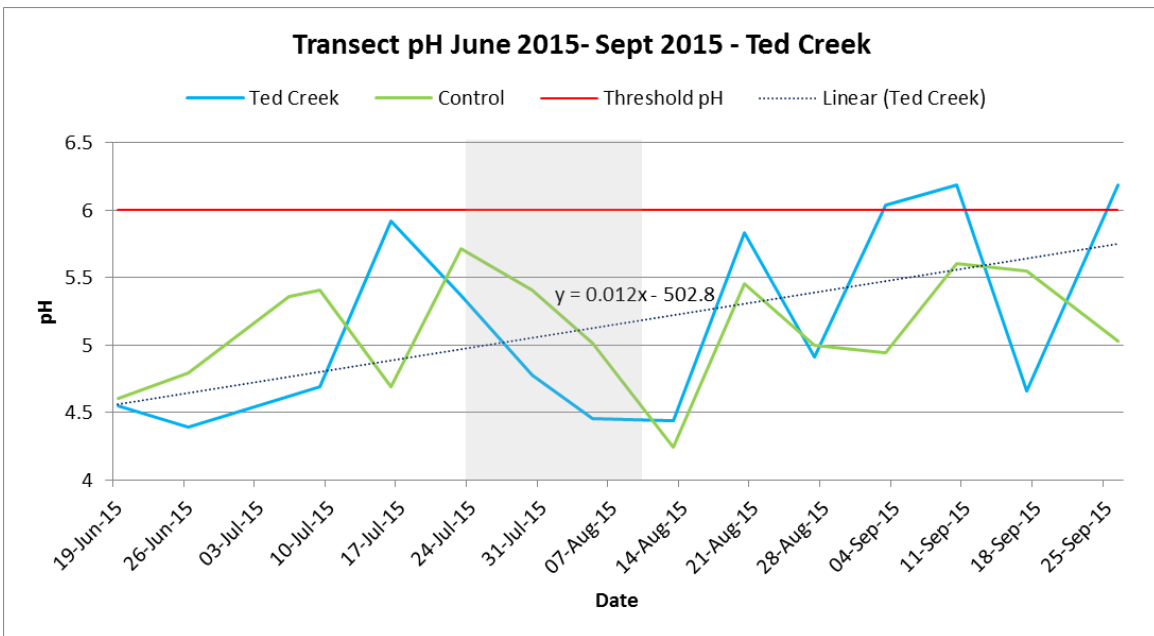
### 3.3 Ted Creek

#### 3.3.1 Insitu Data Results

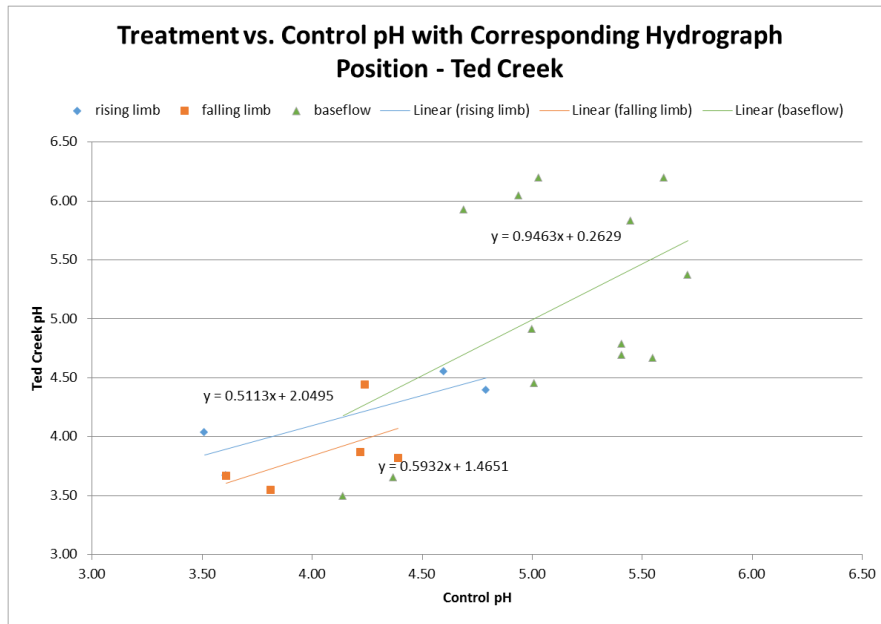
In-situ transect data collection began June 19, 2015, with liming application taking place between July 24, 2015 and August 11, 2015, represented by the shaded section (Figure 19). The trend line for pH decreases throughout the study period (Figure 19). However the trend from June to September, pH increases significantly (Figure 20). The treatment pH for the start of the study was 4.55, and at the end of September, 2015, it was 6.19. Whereas, the starting pH for the control was 4.60 and the pH at the end of September, 2015 was 5.03. The average pH for the treatment site from June to September, 2015, was 5.17 (Appendix B). The trend line for the baseflow treatment pH vs. control pH increases over time (Figure 21).



**Figure 19.** Insitu Transect pH results from June 19, 2015 to November 27, 2015. Data collected via YSI Pro SONDE.



**Figure 20.** Insitu Transect pH Ted Creek June 19, 2015 to September 26, 2015. To provide pH results before the Fall rain. Data collected via YSI Pro SONDE.



**Figure 21.** Treatment vs. Control pH with Corresponding Hydrograph Position. Data collected via YSI Pro SONDE from June - September 2015 at Ted Creek, New Ross, NS.

### 3.3.2 Maxxam Lab Data Results

Grab sample analysis of pH was completed at Maxxam Analytics throughout the duration of the study, from June 19, 2015 to November 27, 2015. The trend for pH is comparable to the decreasing trend observed in the in-situ pH data for Ted Creek (compare Figure 19 to Figure 22). However, similarly to the perceived increasing trend in the in-situ pH between June and September 2015, Maxxam lab pH also mirrors this trend (compare Figure 20 to Figure 23). The initial pH of the treatment site was 4.87, with a final pH of 6.79 at the end of September, 2015. The original control had a pH value of 6.01, and a value of 6.39 at the end of September, 2015. The average pH for the treatment site between June and September, 2015 was 5.67, where the average control pH during this period was 6.05 (Appendix B; Figure 23).

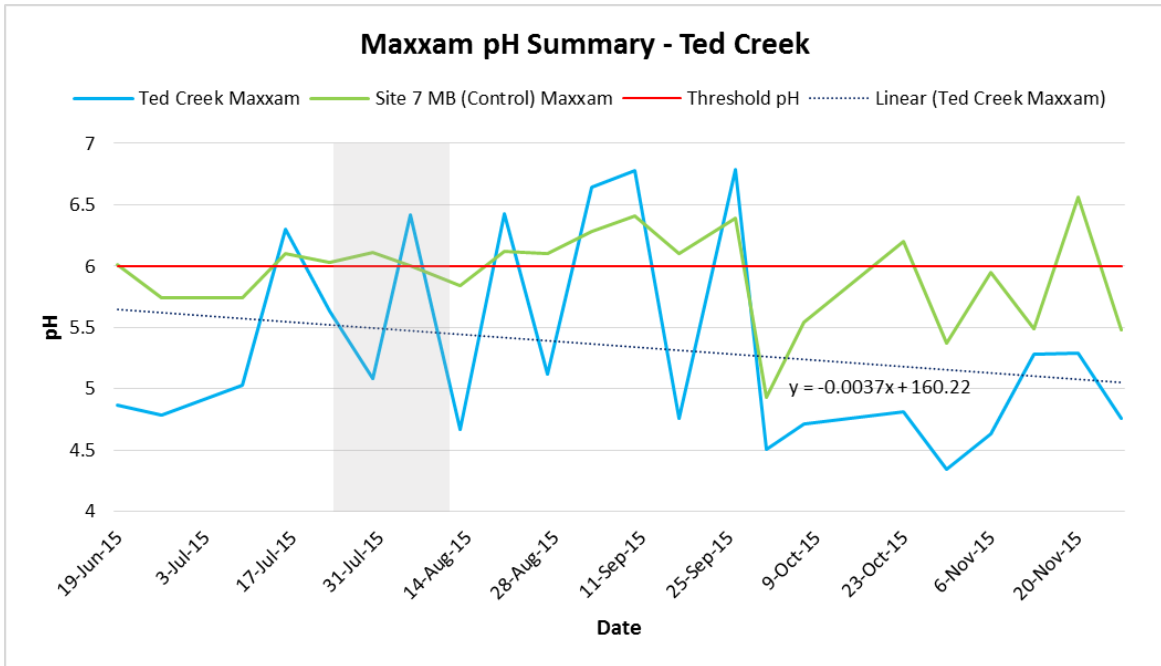


Figure 22. pH results from Ted Creek grab samples analyzed from Maxxam Analytics, June 2015 to November 2015.

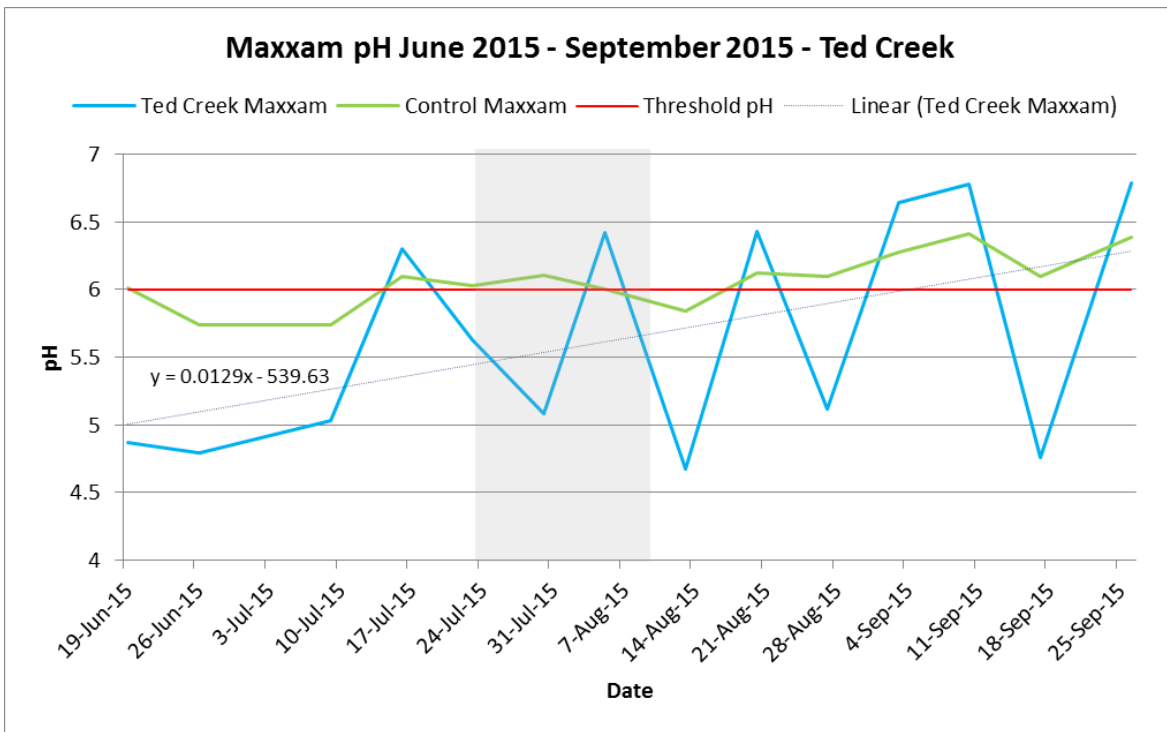


Figure 23. pH results from Ted Creek grab samples from June 2015 to September 2015 to give a better representation of pH response from terrestrial liming.

DOC (mg/L) was also analyzed at Maxxam Analytics during the study period, from June 19, 2015 to November 27, 2015; results are shown in Figure 24 and Appendix B. The overall trend of DOC increases over time; however further analysis of the data from June to September, 2015, actually demonstrates DOC (mg/L) to be decreasing before it significantly increases during September to October, 2015. The initial value of treatment DOC is 16.90 mg/L, with an end value of 4.89 mg/L in September, 2015. The corresponding DOC values for the control site are 8.77 mg/L and 7.47 mg/L, respectively. The average value for DOC at the treatment site from June to September, 2015, is 15.22 mg/L, whereas the average control value during this period is 10.28 mg/L (Appendix B; Figure 24).

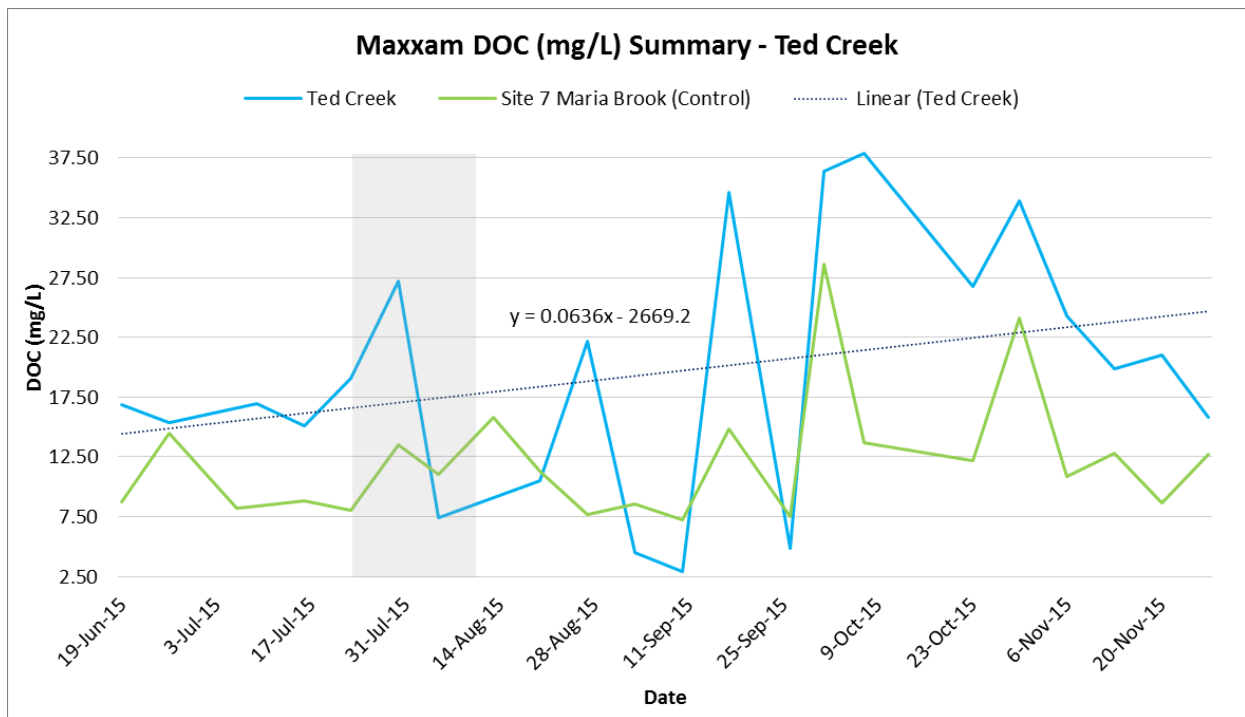


Figure 24. DOC (mg/L) results from Ted Creek grab samples analyzed by Maxxam Analytics, June 2015 to November 2015.

Grab sample of total Al ( $\mu\text{g/L}$ ) were also analyzed at Maxxam Analytics for the duration of the study; June 19, 2015 to November 27, 2015. The trend line for  $\text{Al}_t$  slightly decreases over time; however remains fairly constant (Figure 25). The initial value for  $\text{Al}_t$  at the treatment site is 270  $\mu\text{g/L}$ , with a

September, 2015, value of 95 µg/L. The corresponding original control value for Al<sub>t</sub> is 1040 µg/L, with a final value for September, 2015, of 322 µg/L (Appendix B; Figure 25).

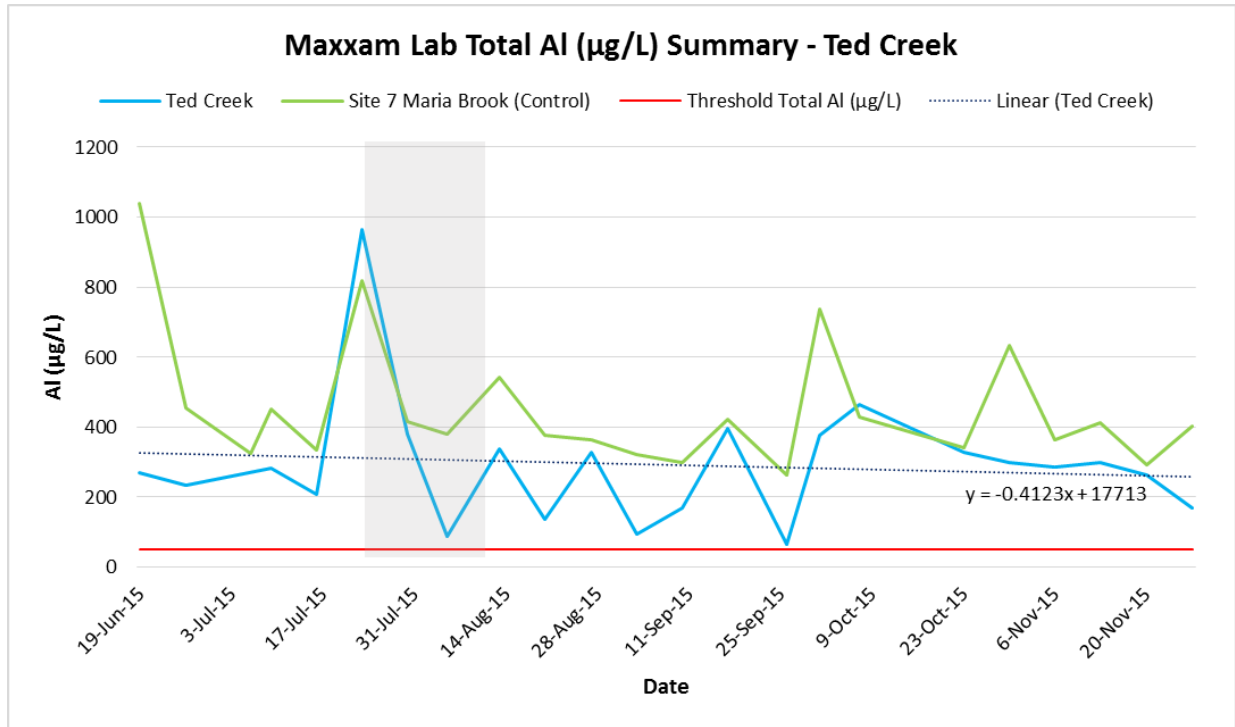


Figure 25. Total Aluminum results from Ted Creek grab samples analyzed from Maxxam Analytics, June 2015 to November 2015.

Lastly, grab sample analysis of calcium (Ca) concentrations (mg/L) were completed at Maxxam Analytics for the study period, June 19, 2015 to November 27, 2015. The trend for Ca concentrations increases over the duration of the study. The initial Ca concentration for the treatment site was 0.924 mg/L, while the end result in September, 2015, was 5.6 mg/L. The original Ca concentration for the control site was 1.290 mg/L, and the final Ca concentration in September, 2015, was 1.580 mg/L. The average Ca concentration for the treatment site during June and September, 2015, was 2.960 mg/L, while the average value for the control was 1.370 mg/L (Appendix B; Figure 26).

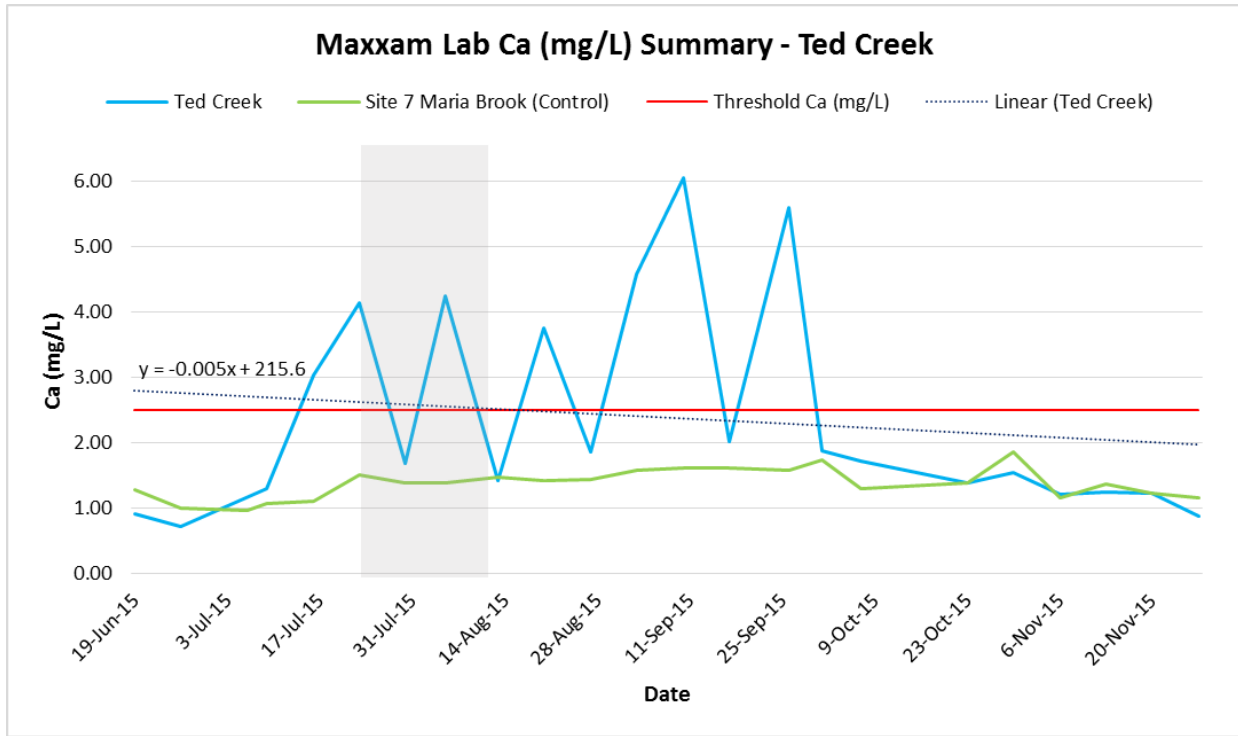


Figure 26. Calcium (mg/L) results from Ted Creek grab samples analyzed from Maxxam Analytics, June 2015 to November 2015.

### 3.4 West River Sheet Harbour

As previously stated, current in-stream liming practices for West River Sheet Harbour (WRSH), NS, include the yearly addition of 375 tonnes of powdered limestone via lime doser into the stream to maintain a pH of 6.0. The WRSH catchment has an area of 317,000 ha, and using Equation 1, an equivalent terrestrial liming dose can be calculated (Equation 2). This dose translates into an application rate of  $0.0012 \text{ t ha}^{-1}$  per year, which is reasonable for terrestrial liming practices. Therefore, the in-stream liming methods currently taking place at WRSH could alternatively be completed by terrestrial liming procedures.

$$R_{\text{ave}} = L_{\text{ave}} / A_{\text{total}} = 375 \text{ t yr}^{-1} / 317,000 \text{ ha} = 0.0012 \text{ t ha}^{-1} \text{ yr}^{-1} \quad \text{(Equation 2)}$$

### 3.5 Terrestrial liming Range of Doses

117.5 t was the total amount of limestone applied to Maria Brook over the full duration of the study from October, 2010 to July, 2015. The total area of the catchment is 47 ha, with a limed area that is 17.4 % of the total catchment or 8.16 ha. Therefore, the whole application rate was 2.5 t ha<sup>-1</sup>, and the local application rate was 1.4 t ha<sup>-1</sup> (Table 3). For Ted Creek, 33.89 t of limestone was applied at a local catchment rate of 9.41 t ha<sup>-1</sup>, and at a whole catchment rate of 4.46 t ha<sup>-1</sup>. The total area was 7.6 ha, with a limed area that is 47.3 % of the total catchment, or 3.6 ha (Table 3). Both Maria Brook and Ted Creek data was added to the following Figures (Figure 27 for whole catchment application rates and Figure 28 for local catchment application rates) to update the range of doses that are effective for terrestrial liming.

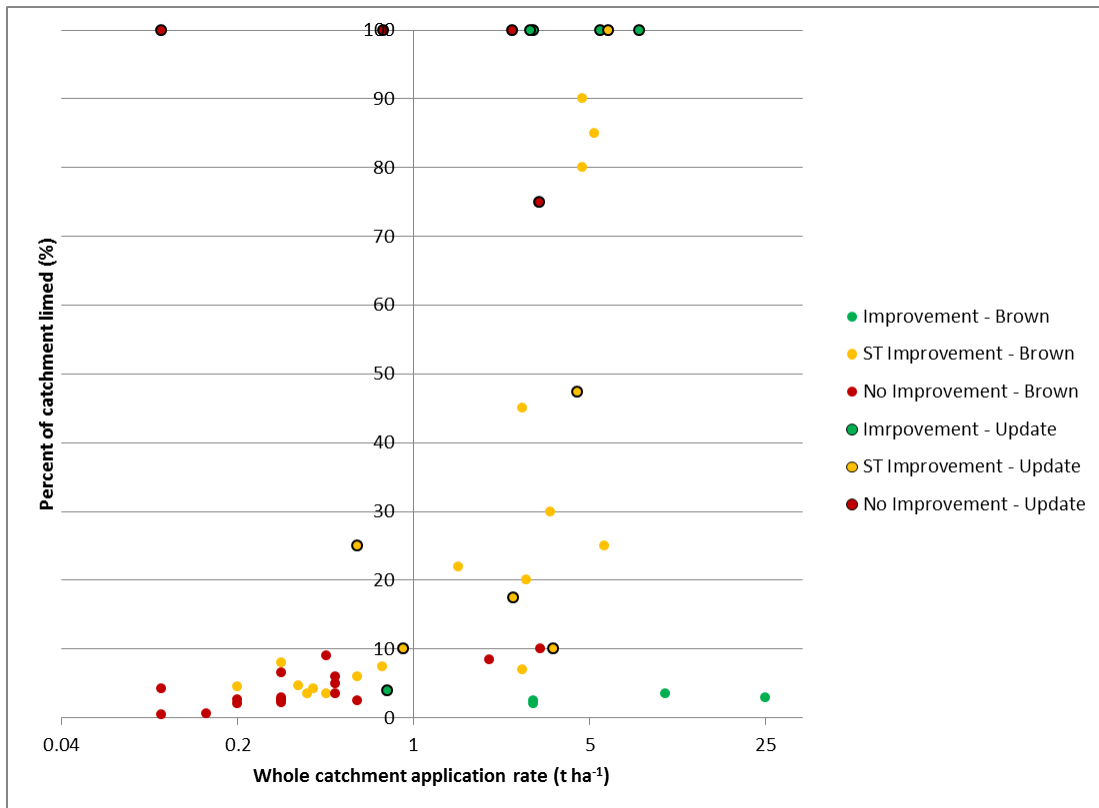


Figure 27. Percent of catchment limed vs. hole catchment liming application rates of terrestrial liming studies around the world [Updated from Brown, 1988] ST represents “short term” improvements.



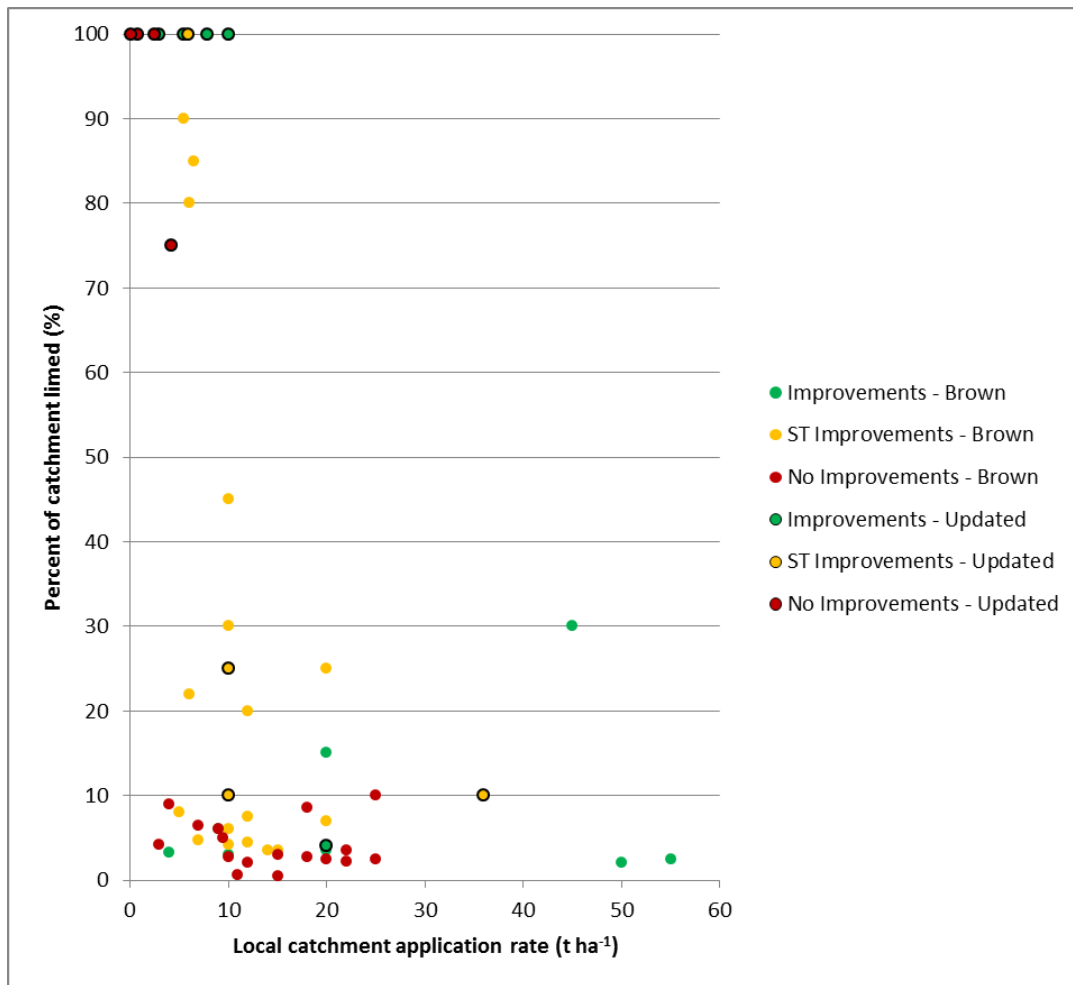


Figure 28. The percent of catchment limed vs. the local catchment application rate of terrestrial liming studies around the world [Updated from Brown, 1988]. ST represents “short term” improvements.

## 4.0 Discussion

### 4.1 Interpretation of Results

#### 4.1.1 Literature interpretation

Results from the streams corresponding to the Loch Fleet Project suggest that chances of success, “are greater if the application rate is in excess of 1 t ha<sup>-1</sup>”, and is more likely, “if either the local application rate is higher and/or high percentage of the catchment area is treated” (Brown, 1988). This

statement remains true when considering a dose for effective liming, and was taken into account during the decision process when choosing yearly application rates at Maria Brook, but especially during the decision for the appropriate application rates at Ted Creek.

#### 4.1.2 Maria Brook

Inclusion of all sites causes difficulty when determining pH trends; therefore the assumption is made that any improvements in water quality observed upstream at Site 5 should be mirrored downstream. Higher pH values in the grab samples are most likely due to slight changes in water chemistry due to storing and/or the delay in time between the sample drop-off date and the date of analysis. Major decreases in pH can be caused by chronic acid episodes, or seasonal increases in rainfall, like the decrease detected in October, 2012. Although the values of pH are higher in the grab samples than the in-situ pH data, similar trends in pH over time can be observed. An example of this is an abrupt decrease in pH in June, 2014 observed on both graphs, and another matching drop can be observed in October, 2014, with a steady increase afterwards. Although the trend line would suggest an overall decrease in pH through time (Figure 15), it can be observed that after an acid episode following liming, the pH increases rapidly, which suggests terrestrial liming is helping surface water quality rebound at a faster rate, and therefore terrestrial liming has been relatively effective at improving water quality at Maria Brook.

High amounts of DOC in surface water can lead to lower pH values, as it can act as an acidic input into surface waters. The trend line proposes a decrease in DOC throughout the study period, which suggests water quality has become less acidic over time (Figure 16).

As previously stated, at lower levels of pH, ionic Aluminum (Ali) is dissolved from clays present in soil where it becomes mobile in surface waters and is able to bind to the negatively charged gills sites of fish, particularly *Salmo salar*, which can lead to increased mortality rates. Measuring for total Al (Alt)

( $\mu\text{g/L}$ ) via grab sample analysis gives a rough approximation of the levels of ionic Al present in surface waters of the Maria Brook catchment throughout the study period. Abrupt spikes observed in total Al correspond to periods of low pH in Figure 17, which makes sense as these times relate to acid episodes or seasonal increases in rainfall.  $\text{Al}_t$  remains constant throughout the study, suggesting terrestrial liming had no effect on  $\text{Al}_t$ .

The addition of limestone to the system should increase Ca concentrations in the surface waters at Maria Brook. Therefore, Ca concentrations were analyzed along with pH, DOC, and  $\text{Al}_t$  to determine if levels were increasing throughout the duration of the study. This increasing Ca concentration trend was observed in Maria Brook throughout the total study (Figure 18), which suggests that vegetation and wildlife benefitted following terrestrial liming in Maria Brook.

#### *4.1.3 Ted Creek*

Similar analyses procedures to the ones conducted for the Before/After Control/Impact analysis at Maria Brook were completed for dose analysis at Ted Creek. In-situ transect pH was plotted against time to determine if surface water acidity would decrease throughout time following a mega-dosing liming strategy. The pour point of the Ted Creek catchment was chosen as the sites to be treated and analyzed for the study. Site 7 from Maria Brook was chosen as the control site for this study, as both catchments are part of the larger overall Gold River watershed. The trend for Ted Creek pH tends to decrease over time; however September to November is considered a 'rainy season', so naturally pH will decrease. In addition to this, DOC values increase during the Fall when leaves litter the ground and water, and decompose. This leads to an even higher increase in acidity, creating an extremely low pH in surface waters. Therefore, the June to September trend in pH will provide a better estimate of if pH has increased over time (Figure 15). The trend for these months shows a large increase in pH, suggesting effective terrestrial liming at Ted Creek.

There are three hydrograph positions that each have different effects on the pH of a stream; the rising limb, base flow and falling limb. It is natural for surface water pH to decrease during periods of rainfall due to the addition of SO<sub>2</sub> and NO<sub>2</sub> present in precipitation. Precipitation raises stage or water depth of the stream, this process is known as the rising limb of the hydrograph. Similarly, it is natural for surface water pH to increase as the stream returns to baseflow levels after periods of precipitation. During this time, after reaching peak flow the stage of the stream begins decrease as it returns to baseflow levels. This process is also known as the falling limb of the hydrograph. During periods of absent precipitation surface water pH will increase above standard baseflow values, which could be incorrectly recognized as an inclusive rise in baseflow pH. Therefore, a comprehensive analysis of baseflow pH response to terrestrial liming is critical to determine an overall dose-response relationship for Ted Creek. The trend line for the baseflow treatment vs. control pH suggests an increase in baseflow pH levels following terrestrial liming procedures.

Grab sample pH of treatment and control sites was plotted against time (Figure 17) in order to compare results to in-situ pH data of the two sites (Figure 14). The shaded portion of the graph represents the duration of the liming application. The trend line suggests that pH has decreased throughout time; however for the reasons previously mentioned in section 3.1.2, it is necessary to determine the overall trend in grab sample pH before the 'rainy season' to give an accurate analysis of pH response from terrestrial liming (Figure 22). The trend line from Figure 18 suggests that pH has actually increased over time, following terrestrial liming of the catchment. Similar trends in pH can be observed in the in-situ results (Figures 20 and 21). Therefore, this data would suggest that terrestrial liming was effective at improving water quality at Ted Creek.

Decreasing trends are observed in DOC (mg/L) between June and September 2015; however DOC (mg/L) significantly increases during September to October, 2015. This abrupt increase in DOC

levels would be due to the addition of litter fall as a result of seasonal changes in vegetation during this time of year; and should not be considered significant.

Spikes in the data generally corresponds to periods of lower grab sample pH values (Figure 22), which is expected as higher acidity would dissolve greater amounts of Al from the soils, causing a greater addition of Al to surface waters. Another detail worth noting is that treatment values for Al tend to be lower than those for the Control, proposing that terrestrial liming has lowered baseflow levels of total Al at Ted Creek.

The trend line for Ca concentrations suggests that levels are decreasing over time; however further analysis of the data before the 'rainy season' from June to September, 2015, indicates an increase in Ca concentrations (Figure 26). In addition to this, overall Ca concentrations at the treatment site are observed to be higher than those of the control site. The spikes in Ca concentrations correspond to periods of increased precipitation, and lower levels of pH, leading to dissolution of the powdered limestone. This solution in turn, infiltrates soils and eventually reaches groundwater where it is introduced to surface waters as recharge. Therefore, this data suggests that terrestrial liming at Ted Creek has increased Ca concentrations (mg/L), and provided a beneficial source of Ca to vegetation and wildlife in the local area.

#### *4.1.4 Range of doses for effective terrestrial liming*

Terrestrial liming in SWNS is a fairly new practice, therefore in order to move forward with larger water quality improvement projects, basic information about how a typical SWNS catchment (partial forest and wetland areas) responds to the addition of powdered limestone at different application rates is required. Figure 24 represents an updated graph originally produced by Brown (1988) of the dose relationship between the percent of catchment limed and the dose of limestone applied to the catchment, that have provided improvements in water quality following terrestrial liming

practices. Again, improvements” in water quality are defined as a baseflow pH of 6.0 maintained for at least one year or longer, where short-term (ST) improvements are defined as an increase in baseflow pH, or a baseflow pH of 6.0, that was maintained for less than one year (Brown, 1988). Data to update the graph was collected from liming studies that took place after the publication of Brown’s study, as well as the results determined from the two experimental liming studies summarized in this research, Maria Brook and Ted Creek. To reiterate for clarity, whole catchment liming considered the most effective method for terrestrial liming. Ted Creek terrestrial liming results fall within the “ST improvements” category, as analysis of this site only took place over a few months and further analysis is required to determine if improvements are long-term (Figure 27). Maria Brook terrestrial liming results also fall within the “ST improvements” category, as yearly application was required to maintain or raise pH above original baseflow levels.

#### *4.2 Applications of this research*

This research provides information for more effective terrestrial liming within Canada, particularly Southwest Nova Scotia, in which chronic acidification is a major issue. It outlines the first two experimental terrestrial liming studies to take place in Southwest Nova Scotia: a Before/After Control/Impact analysis, and a dose range analysis; where higher application rates during terrestrial liming procedures were used, as compared to the first study. Additional information regarding the relationships between water quality parameters (e.g. pH, DOC,  $Al_t$ , and Ca) is identified within this research, which aids in the necessarily understanding of how related variables behave within a catchment system. My research acts as a baseline for effective terrestrial liming within SWNS, and provides stakeholders with a detailed outline of reproducible methods required to complete an in-depth experimental terrestrial liming study. In addition to this, this research determines the first rough conversion of an in-stream liming dose to an equivalent terrestrial liming dose for a large study area.

This research builds upon previously determined relationships summarized by Brown (1988) between the percentage of the total catchment limed vs. the application rate of terrestrial liming methods in multiple catchments within Sweden and Norway. This update in the range of doses for effective terrestrial liming, included in this research, will act as a baseline for decision making regarding larger, future terrestrial liming projects in NS. This research also improves the global database of effective terrestrial liming studies completed, which inevitably provides valuable information on strategies for effective liming that can be replicated elsewhere in the world; especially in areas that have similar difficulties with chronic acidification. In addition to this, this research can help improve policy on mitigation procedures for surface water acidification in Nova Scotia and other parts of the world, through a better description of variables present within a catchment system and their relationships with each other. In addition to this, my research provides an updated definition of effective terrestrial liming targets for surface water parameters (e.g. pH of 6.0, Ca concentrations of 2.5 mg/L, and  $Al_t$  below 1.5  $\mu\text{g/L}$ ). This knowledge is essential for mitigation strategies for larger effective terrestrial liming projects within Nova Scotia with prospects to support Southern Upland Atlantic salmon populations.

#### *4.3 Limitations and recommendations for future work*

This research focusses on terrestrial liming methods within relatively small catchment areas in which manual spreading of limestone via bucket dispersal is feasible. However, there are additional terrestrial liming methods that have the potential to be more effective and have an influence on a greater spatial scale that are not outlined in this study, like helicopter liming application. This research provides valuable information on two experimental terrestrial liming studies within the Gold River watershed in SWNS; however, as previously stated in section 1.4, the amount of detail included, and scale of the projects (i.e. how large of a catchment was chosen for liming, and the percent of catchment limed for each study area) was limited to time and budget constraints, which also effects the type of

liming application methods used (e.g. manual bucket spreading of limestone vs. helicopter liming application).

Other important aspects of terrestrial liming that were outside the scope of my research include a detailed analysis of the relationship between pH and  $Al_i$ . In order to determine this relationship a conversion from  $Al_t$ , which is what is measured in a grab sample analysis of Aluminum, to  $Al_i$  is required. As previously stated in section 1.2.1, the species of  $Al_i$  are of interest in surface waters as  $Al^{3+}$  and  $Al^+$  bind to the negatively charged gill sites of aquatic species, like *Salmo salar*, causing increased stress and mortality rates. This source of information is crucial for an enhanced understanding and future practice of effective terrestrial liming in Southwest Nova Scotia.

The conversion from in-stream liming practices to reasonable terrestrial liming methods outlined in this research is a baseline, but should be improved upon by a more chemically accurate and variable encompassing analysis conversion, to better illustrate the true relationship between the two liming procedures. Furthermore, my research is limited to the standard calculations used in a first attempt to convert a current dose of powdered limestone used in-stream liming practices to an equivalent dose that could be used in terrestrial liming methods. Multiple variables are involved in both liming methods, which increase the difficulty to determine a precise conversion between an in-stream liming dose to a terrestrial liming dose. Therefore, an all-encompassing analysis is required to determine how variables, like Ca, behave in a catchment system, and to create a chemically-sound conversion of an in-stream liming dose to a terrestrial liming dose that can be used for effective liming within a catchment. This conversion is important to improve current or future liming practices by changing short-term mitigation into long-term improvements, in addition to improving surface water quality of Nova Scotian watersheds. Long-term mitigation strategies are the only approach to provide a stable and productive habitat for present and future *Salmo salar* populations.



An experimental terrestrial liming study using helicopter liming application would allow for a uniform distribution of limestone over the selected catchment treatment area, and allow for a greater portion of the watershed to be treated. This would lead to a closer representation of whole catchment liming, which is the most effective terrestrial liming method. Therefore, I recommend this type of liming application in order to enhance the understanding and information available for terrestrial liming practices in Nova Scotia, and to continue to improve upon a dose-response relationship for Southwest Nova Scotian catchments. This in turn, will allow for establishment of more effective mitigation strategies for *Salmo salar* populations.

Strong development and planning stages of an experimental liming study are needed to decrease the risk of complications during liming projects, and therefore should include the collaboration of multiple stakeholders, especially those with local knowledge (i.e. community groups, scientists, and governmental groups). Once a planning committee is formed it is recommended to follow a five step decision process (Appendix E) to determine an effective terrestrial liming strategy.

## 5.0 Conclusion

The objective of this research is to increase the effectiveness of terrestrial liming in Nova Scotia, with the overall goal to reduce the threat of extirpation to *Salmo salar* in SWNS. To meet this objective, I have outlined the first two experimental terrestrial liming projects completed in SWNS, and provided an updated range of doses for effective terrestrial liming practices in NS. I also have completed the first provisional in-stream liming to terrestrial liming conversion to act as a baseline for a more complete conversion between the two practices, to promote future liming practices that support long-term surface water quality improvements. I have also identified the information required for future studies and/or stakeholders to progress effective terrestrial liming practices within Nova Scotia, and ultimately

improve survival rates of *Salmo salar* populations in SWNS. Finally, this research represents a more informed decision making process regarding effective terrestrial liming methods in Nova Scotia.

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## 8.0 Appendices

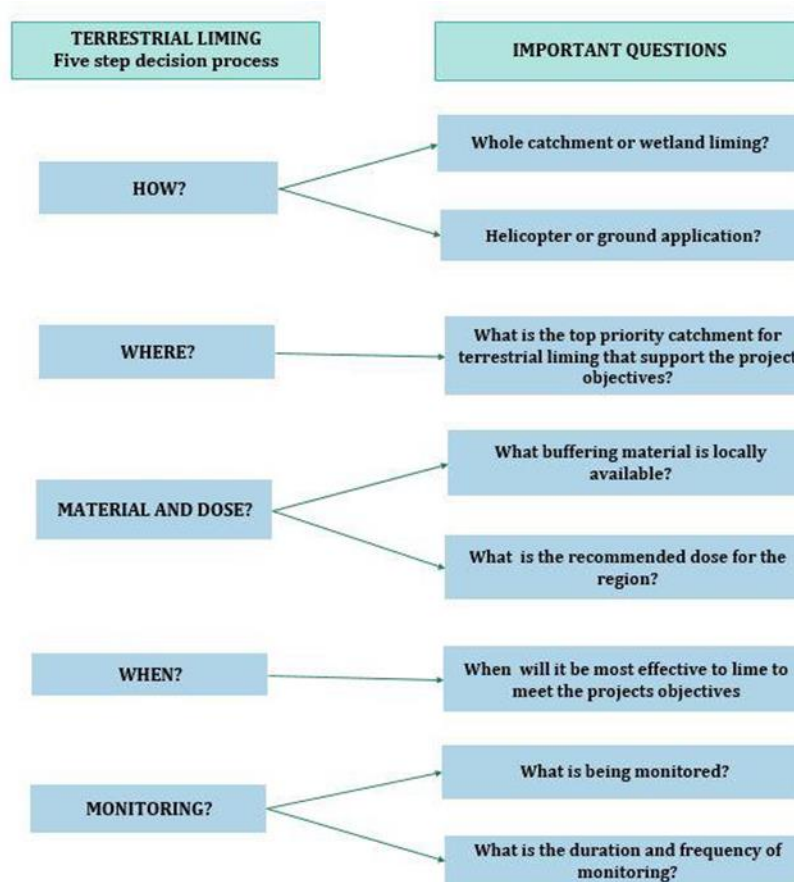
### 8.1 Appendix A

See attached data.

8.2 Appendix B  
See attached data.

8.3 Appendix C

Five step decision process for effective terrestrial liming practices [Geddes, 2015].



## 8.1 Appendix A

### *Maria Brook – In-situ Data (pH)*

Date	Site 1	Site 2	Site 3	Site 4	DMEMP	CMEMP	Site 7
21-Sep-11	5.98						
11-Oct-11	5.66	5.62	5.6	5.72			
28-Nov-11	5.22				5.49		
21-Dec-11						4.58	
24-Feb-12					4.82	4.79	
29-Mar-12		5.53	5.67		5.39	5.17	
17-Apr-12						5.58	
1-May-12						4.98	
8-May-12							
18-May-12					5.15	5.28	
25-May-12							
30-May-12					5.80	5.86	
4-Jun-12	5.93	5.78	5.49	6.02	5.65	5.40	
7-Jun-12	6.22	6.17	5.64	6.11	5.90	5.58	
12-Jun-12	6.18	6.22	6.01	6.16	5.90	5.69	
22-Jun-12	5.81	5.87	5.57	6.00	5.52	5.33	
27-Jun-12	4.61	4.84	5.14	5.14	4.24	4.48	
29-Jun-12	4.95	4.97	4.98	4.95	5.04	4.79	
19-Jul-12	5.89	5.97	5.48	6.14	5.63	5.46	
27-Jul-12	5.76	5.75	5.58	5.27	5.92	5.39	
3-Aug-12	5.74	5.78	5.66	5.80	5.66	5.38	
13-Aug-12	6.08	6.11	5.97	5.96	5.86	5.79	
23-Aug-12	6.04	6.33	6.26	6.39	5.98	6.32	
13-Sep-12					4.79	5.16	
26-Sep-12							
2-Oct-12					4.62	4.35	
19-Oct-12					4.74	5.29	
10-Nov-12					4.17	3.95	
22-Nov-12					4.47	4.46	
6-Dec-12					5.22	4.81	
9-Jan-13					4.17	4.20	
5-Feb-13					4.70	4.84	
27-Feb-13					4.46	4.22	
14-Mar-13					4.03	4.32	
19-Apr-13					4.67	4.96	
3-May-13	6.06	6.02	5.96	6.02	5.40	5.42	

29-May-13	5.89	5.88	5.87	5.94	5.86	5.46	
6-Jun-13					5.52	5.24	
5-Jul-13	6.00	5.98	6.18	6.14	5.54	5.41	
12-Jul-13	6.50	6.29	6.53	6.67	5.83	5.66	
13-Jul-13	6.68	6.68	6.50	6.77	5.88	5.58	
17-Jul-13	6.35	6.68	6.68	6.77	5.88	5.85	
23-Jul-13	6.57	6.34	6.60	6.66	5.99	5.72	
29-Aug-13	6.60	6.00	6.44	6.52	6.17	5.90	
6-Sep-13					5.35	5.24	
13-Sep-13	5.14				5.03	4.75	
29-Sep-13	6.41	6.33	6.12	6.34	5.51	5.63	
5-Oct-13					5.76	5.67	
20-Oct-13	6.13	5.97	6.15	6.25	5.62	5.53	
4-Nov-13					5.03	4.76	
11-Jan-14	5.65	5.63	5.68	5.69	5.22	5.06	
16-May-14					5.82	5.20	
23-May-14					5.86	5.61	5.55
30-May-14	6.81	6.66	6.72	6.98	6.45	5.93	5.95
6-Jun-14	6.21	6.18	6.44	6.66	5.60	5.67	5.51
13-Jun-14	6.74	6.17	6.03	6.64	5.93	5.84	5.64
20-Jun-14	5.68	5.48	5.54	5.55	5.37	5.28	5.15
27-Jun-14	4.56	5.31	4.89	4.97	4.62	4.68	4.52
7-Jul-14	4.47	4.81	4.66	4.55	4.40	4.84	5.83
18-Jul-14	4.69	5.01	5.04	4.74	4.41	4.41	4.42
25-Jul-14	5.88	5.52	5.55	7.14	4.85	5.18	5.51
1-Aug-14	4.40	4.73	4.63	4.53	4.55	4.53	4.66
19-Aug-14	5.56	5.83	5.86	5.75	5.67	5.66	5.55
21-Aug-14	6.32	5.82	5.96	5.97	5.85	5.65	5.63
06-Sep-14	6.58	6.07	5.88	6.42	6.07	6.05	5.98
13-Sep-14	6.17	6.22	6.18	5.75	6.25	6.20	5.91
26-Sep-14	5.30	5.53	5.74	5.74	5.32	5.21	5.08
10-Oct-14	5.50	5.79	5.94	5.12	5.47	5.48	5.26
24-Oct-14	4.17	5.33	4.96	4.64	4.63	4.41	4.26
14-Nov-14	5.22	5.88	6.15	5.36			
05-Dec-14	4.35	5.18	5.44	4.78	4.76	4.72	4.55
19-Jun-15					5.73	5.43	4.60
26-Jun-15					5.05	5.04	4.79
06-Jul-15	6.07	6.05	5.94	6.07	5.68	5.51	5.36
09-Jul-15					5.70	5.57	5.41
16-Jul-15					5.80	5.40	4.69
23-Jul-15					5.94	5.82	5.71
30-Jul-15					5.73	5.63	5.41



05-Aug-15					5.77	5.72	5.58
13-Aug-15					5.48	5.23	4.24
<b>average</b>					5.356901	5.249178	5.212963

*Maria Brook – Maxxam Data*

<b>pH Graph</b>	Sampling Date	Site 5	Site 6	Site 7	Threshold pH
	15-Dec-10				6.0
	7-Feb-11				6.0
	19-Mar-11				6.0
	5-Apr-11				6.0
	19-Apr-11				6.0
	3-May-11				6.0
	20-May-11				6.0
	20-Jun-11				6.0
	29-Jul-11				6.0
	16-Aug-11				6.0
	9-Sep-11				6.0
	20-Sep-11				6.0
	11-Oct-11				6.0
	26-Oct-11				6.0
	15-Nov-11				6.0
	13-Dec-11				6.0
	29-Mar-12				6.0
	8-May-12	6.11	6.19		6.0
	29-May-12	6.48	6.53		6.0
	8-Jun-12	6.61	6.64		6.0
	19-Jun-12	6.79	6.72		6.0
	16-Jul-12	6.66	6.40		6.0
	30-Jul-12	6.21	6.29		6.0
	13-Aug-12	6.55	6.66		6.0
	29-Aug-12	6.52	6.60		6.0
	14-Sep-12	5.32	5.37		6.0
	1-Oct-12	4.49	4.55		6.0
	11-Oct-12	4.97	5.07		6.0
	7-Nov-12				6.0
	3-Dec-12	5.23	5.28		6.0
	8-Jan-13	6.03	6.01		6.0

	6-Feb-13	5.93	6.01		6.0
	5-Mar-13	5.99	6.05		6.0
	3-Apr-13	5.26	5.40		6.0
	17-Apr-13	5.44	5.51		6.0
	12-Jul-13				6.0
	23-Jul-13				6.0
	7-Aug-13				6.0
	29-Aug-13				6.0
	29-Sep-13				6.0
	20-Oct-13	5.48	5.49		6.0
	16-May-14	6.03	5.96		6.0
	23-May-14	5.94	5.87	5.83	6.0
	30-May-14	5.98	6.02	5.98	6.0
	6-Jun-14	5.74	5.73	5.61	6.0
	13-Jun-14	5.96	6.09	5.95	6.0
	20-Jun-14	5.80	5.61	5.51	6.0
	27-Jun-14	4.75	4.83	4.77	6.0
	7-Jul-14	5.80	5.78	5.67	6.0
	18-Jul-14	5.79	5.86	5.60	6.0
	25-Jul-14	6.15	6.15	6.02	6.0
	1-Aug-14	6.32	6.24	6.22	6.0
	19-Aug-14	5.95	6.00	5.92	6.0
	5-Sep-14	6.47	6.42	6.29	6.0
	12-Sep-14	6.45	6.53	6.42	6.0
	26-Sep-14	5.79	5.57	5.46	6.0
	10-Oct-14	5.70	5.10	5.69	6.0
	24-Oct-14	4.63	4.58	4.61	6.0
	14-Nov-14	5.46	5.32	5.29	6.0
	5-Dec-14	4.87	4.74	4.89	6.0
	19-Jun-15	5.90	5.93	6.01	6.0
	26-Jun-15	5.37	5.35	5.74	6.0
	6-Jul-15	5.99	5.93	5.74	6.0
	9-Jul-15	5.94	5.89	5.74	6.0
	16-Jul-15	6.14	6.14	6.10	6.0
	<b>average pH</b>	5.83	5.82	5.70	

DOC Graph	Sampling Date	Site 5	Site 6	Site 7
	15-Dec-10			
	7-Feb-11			

	19-Mar-11			
	5-Apr-11			
	19-Apr-11			
	3-May-11			
	20-May-11			
	20-Jun-11			
	29-Jul-11			
	16-Aug-11			
	9-Sep-11			
	20-Sep-11			
	11-Oct-11			
	26-Oct-11			
	15-Nov-11			
	13-Dec-11			
	29-Mar-12			
	8-May-12			
	29-May-12			
	8-Jun-12			
	19-Jun-12			
	16-Jul-12			
	30-Jul-12			
	13-Aug-12			
	29-Aug-12			
	14-Sep-12			
	1-Oct-12			
	11-Oct-12			
	7-Nov-12			
	3-Dec-12			
	8-Jan-13			
	6-Feb-13			
	5-Mar-13			
	3-Apr-13			
	17-Apr-13			
	12-Jul-13			
	23-Jul-13			
	7-Aug-13			
	29-Aug-13			
	29-Sep-13	12.0	11.0	
	20-Oct-13	18.0	17.0	
	16-May-14	6.3	6.4	
	23-May-14	6.8	6.2	6.1
	30-May-14	8.1	6.1	5.7

	6-Jun-14	11.0	11.0	10.0
	13-Jun-14	8.1	7.3	7.0
	20-Jun-14	15.0	16.0	16.0
	27-Jun-14	18.0	16.0	20.0
	7-Jul-14	13.0	12.0	12.0
	18-Jul-14	16.0	14.0	15.0
	25-Jul-14	7.0	7.0	8.0
	1-Aug-14	9.0	9.4	9.3
	19-Aug-14	18.0	17.0	17.0
	5-Sep-14	8.0	9.2	8.5
	12-Sep-14	9.0	8.5	8.1
	26-Sep-14	16.0	18.0	16.5
	10-Oct-14	19.0	17.0	16.0
	24-Oct-14	17.0	18.0	19.0
	14-Nov-14	10.0	10.0	10.0
	5-Dec-14	10.0	11.0	12.0
	19-Jun-15	11.0	11.0	8.8
	26-Jun-15	15.0	11.0	15.0
	6-Jul-15	10.0	9.1	8.2
	9-Jul-15	9.1	8.8	8.4
	16-Jul-15	9.8	8.7	8.8
	<b>average</b>	11.9	11.4	11.5

<b>Al Graph</b>	Sampling Date	Site 5	Site 6	Site 7	Threshold Total Al (µg/L)
	15-Dec-10				50
	7-Feb-11				50
	19-Mar-11				50
	5-Apr-11				50
	19-Apr-11				50
	3-May-11				50
	20-May-11				50
	20-Jun-11				50
	29-Jul-11				50
	16-Aug-11				50
	9-Sep-11				50
	20-Sep-11				50
	11-Oct-11				50
	26-Oct-11				50
	15-Nov-11				50

	13-Dec-11				50
	29-Mar-12				50
	8-May-12	221.8	235.9		50
	29-May-12	308.5	302.0		50
	8-Jun-12	327.0	306.0		50
	19-Jun-12	336.9	308.9		50
	16-Jul-12	1418.0	496.6		50
	30-Jul-12	361.1	381.9		50
	13-Aug-12	359.9	348.1		50
	29-Aug-12	284.0	325.8		50
	14-Sep-12	502.1	479.0		50
	1-Oct-12	413.0	454.4		50
	11-Oct-12	524.0	509.5		50
	7-Nov-12				50
	3-Dec-12	342.2	334.6		50
	8-Jan-13	209.0	211.5		50
	6-Feb-13	195.3	203.9		50
	5-Mar-13	182.9	191.1		50
	3-Apr-13	214.0	226.6		50
	17-Apr-13	388.8	474.8		50
	12-Jul-13	985.0	410.0		50
	23-Jul-13	423.0	441.0		50
	7-Aug-13	360.0	373.0		50
	29-Aug-13	352.0	315.0		50
	29-Sep-13	1500.0	440.0		50
	20-Oct-13	920.0	440.0		50
	16-May-14	230.0	250.0		50
	23-May-14				50
	30-May-14	700.0	260.0	340.0	50
	6-Jun-14	370.0	360.0	410.0	50
	13-Jun-14	390.0	350.0	700.0	50
	20-Jun-14	570.0	540.0	830.0	50
	27-Jun-14	490.0	530.0	610.0	50
	7-Jul-14	580.0	460.0	630.0	50
	18-Jul-14	430.0	430.0	450.0	50
	25-Jul-14	430.0	400.0	450.0	50
	1-Aug-14	380.0	410.0	420.0	50
	19-Aug-14	750.0	490.0	500.0	50
	5-Sep-14	380.0	310.0	330.0	50
	12-Sep-14	450.0	400.0	320.0	50
	26-Sep-14	560.0	560.0	570.0	50
	10-Oct-14	530.0	430.0	430.0	50

	24-Oct-14	470.0	530.0	600.0	50
	14-Nov-14	330.0	330.0	740.0	50
	5-Dec-14	300.0	320.0	1300.0	50
	19-Jun-15	350.0	380.0	1000.0	50
	26-Jun-15	430.0	400.0	450.0	50
	6-Jul-15	340.0	330.0	320.0	50
	9-Jul-15	410.0	380.0	450.0	50
	16-Jul-15	410.0	340.0	330.0	50
	<b>average</b>	465.4	378.3	553.6	

<b>Ca Graph</b>	Sampling Date	Site 5	Site 6	Site 7	Threshold Ca (mg/L)
	15-Dec-10				2.5
	7-Feb-11				2.5
	19-Mar-11				2.5
	5-Apr-11				2.5
	19-Apr-11				2.5
	3-May-11				2.5
	20-May-11				2.5
	20-Jun-11				2.5
	29-Jul-11				2.5
	16-Aug-11				2.5
	9-Sep-11				2.5
	20-Sep-11				2.5
	11-Oct-11				2.5
	26-Oct-11				2.5
	15-Nov-11				2.5
	13-Dec-11				2.5
	29-Mar-12				2.5
	8-May-12	1.06	0.98		2.5
	29-May-12	1.42	1.30		2.5
	8-Jun-12	1.61	1.45		2.5
	19-Jun-12	1.70	1.36		2.5
	16-Jul-12	1.90	1.43		2.5
	30-Jul-12	2.19	2.17		2.5
	13-Aug-12	1.66	1.54		2.5
	29-Aug-12	1.30	1.48		2.5
	14-Sep-12	1.86	1.66		2.5
	1-Oct-12	1.32	1.33		2.5
	11-Oct-12	1.66	1.61		2.5

	7-Nov-12				2.5
	3-Dec-12	1.49	1.46		2.5
	8-Jan-13	1.10	0.97		2.5
	6-Feb-13	1.10	1.03		2.5
	5-Mar-13	1.09	1.08		2.5
	3-Apr-13	0.87	0.85		2.5
	17-Apr-13	0.90	0.92		2.5
	12-Jul-13	2.39	1.44		2.5
	23-Jul-13	1.60	1.45		2.5
	7-Aug-13	1.42	1.28		2.5
	29-Aug-13	1.70	1.30		2.5
	29-Sep-13	2.90	1.60		2.5
	20-Oct-13	2.30	1.70		2.5
	16-May-14	1.40	1.10		2.5
	23-May-14				2.5
	30-May-14	1.70	1.20	1.20	2.5
	6-Jun-14	1.50	1.50	1.30	2.5
	13-Jun-14	1.70	1.50	1.50	2.5
	20-Jun-14	1.70	1.50	1.40	2.5
	27-Jun-14	1.50	1.40	1.40	2.5
	7-Jul-14	1.80	1.40	1.40	2.5
	18-Jul-14	2.00	1.80	1.50	2.5
	25-Jul-14	2.00	1.60	1.40	2.5
	1-Aug-14	1.90	1.80	1.70	2.5
	19-Aug-14	2.50	2.00	1.70	2.5
	5-Sep-14	2.10	1.70	2.00	2.5
	12-Sep-14	2.20	2.10	1.70	2.5
	26-Sep-14	2.10	1.90	1.50	2.5
	10-Oct-14	2.50	2.00	1.50	2.5
	24-Oct-14	1.60	1.40	1.40	2.5
	14-Nov-14	1.30	1.20	1.20	2.5
	5-Dec-14	1.10	0.99	1.30	2.5
	19-Jun-15	1.50	1.50	1.30	2.5
	26-Jun-15	1.20	1.10	1.00	2.5
	6-Jul-15	1.30	1.10	0.98	2.5
	9-Jul-15	1.60	1.20	1.10	2.5
	16-Jul-15	1.40	1.10	1.10	2.5
	<b>average</b>	1.66	1.42	1.39	





post	23-Oct-15	falling limb	3.82	4.39	4.35	5.63	4.81	6.20	6.00	26.80	12.20	328	341	1.400	1.400
post	30-Oct-15	falling limb	3.67	3.61	3.88	4.31	4.34	5.37	6.00	33.90	24.10	299	632	1.550	1.860
post	06-Nov-15	baseflow	3.65	4.37	3.90	4.80	4.63	5.95	6.00	24.30	10.90	285	364	1.220	1.170
post	13-Nov-15	rising limb	3.65	4.63	3.85	4.90	5.28	5.49	6.00	19.90	12.80	300	411	1.250	1.370
post	20-Nov-15	baseflow	3.49	4.14	3.76	5.16	5.29	6.56	6.00	21.00	8.66	263	292	1.240	1.230
post	27-Nov-15	falling limb	3.55	3.81	4.17	4.44	4.76	5.48	6.00	15.80	12.70	168	404	0.883	1.170
		<b>average</b>	5.17	5.12	5.52	5.67	5.67	6.05	6.00	15.22	10.28	282.02	453.53	2.96	1.37