Characterizing acid episode frequency, duration, and severity in Nova Scotia's acidified streams

Honours Thesis by:

Maria Armstrong, BSc. Honours Environmental Science, Dalhousie University (2014)

Project Supervisor, Dr. Shannon Sterling,
Associate Professor of Earth Science and Environmental Science
Principal Investigator of Dalhousie's Hydrologic Research Group

Contents

Abstract

Acid episodes are a key factor in determining the state of freshwater ecosystems that have been chronically acidified by acid precipitation. An acid episode can be defined as a rapid drop in freshwater pH to well below thresholds for biological impact (around pH 5.5) that occur during run-off events in acidified catchments. There has been a general trend of recovery from acidification in North America and Europe following policies enforcing a decrease in emissions that cause acid precipitation. South Western Nova Scotia (SWNS) is an exception to this trend with pH levels not showing signs recovery despite decreased acid deposition. Acid episodes can be a barrier to biological recovery even if annual mean pH levels are increasing and have been identified as a threat to aquatic biota in Nova Scotia, in particular local Atlantic Salmon populations. However, there have been no recent studies on episodic acidification in the streams of this highly acid sensitive region.

This study uses high frequency measurements of stream pH and water level to determine the annual and seasonal frequency, duration, and severity of acid episodes in four SWNS streams. The aim is to determine what catchment characteristics may impact acid episode behavior and find seasonal episode trends. Episode frequency was found to be greater than in previous studies in SWNS, and in other regions, with up to 15 episodes below pH 5.5 for greater than 24 hours occurring per year. Seasonally, summer episodes in the streams are frequent but short whereas spring episodes are less frequent but both spring and winter episodes have longer durations. This seasonal trend has implications for salmon health due to the spring life stage of salmon being most acid sensitive. Results show that smaller catchments may have a stronger relationship between stage and episode pH response during run-off as well more frequent episodes with more severe drops in pH. Further studies with a larger spatial sampling are needed to determine the impact of other catchment characteristics on episodic acidification.

1.0 Introduction

Acid episodes are a key factor in the determining the health of a freshwater ecosystem that has been chronically acidified by acid precipitation (Weatherly and Omerod, 1991; Wright, 2008). Episodes occur during large run-off events in an acidified catchment causing a drop in freshwater pH to well below the systems chronic level and have been identified as a barrier to expected biological recovery even in streams where annual mean pH is increasing (Kowalik et al., 2007; Mant el. al., 2013). A key species impacted by acidic episodes is *Salmo salar* (Atlantic Salmon), with freshwater populations critically declining in Norway and Atlantic Canada due to acidification, and it is therefore important to quantify the frequency, duration, and severity of acid episodes to aid *Salmo salar* restoration efforts (Sandøy and Langåker, 2001; Gibson et al., 2011).

Since the 1970s many locations in North-Eastern North America and Northern Europe have undergone acidification of freshwater systems due to acid precipitation and the low buffering capacity of the geology in these regions. There has been a general trend of recovery from chronic acidification in most of these locations following reductions in emissions of sulphur dioxide and nitrogen oxides that result in acid deposition (Skjelkvale et al., 2005; Stoddard et al., 1999). South West Nova Scotia (SWNS) is the exception to this trend where the lake record shows no significant increases in pH or acid neutralizing capacity (ANC) in recent decades (Whitfield et al., 2007).

An acid episode can be broadly defined as a rapid drop in pH to below base-flow values which occurs during large run-off events. These episodes can occur naturally but the frequency, severity, and duration is thought to be worsened for chronically acidified streams (e.g. pH < 6 or ANC < 0 mg/L) due to the increase of acid inputs and eventual depletion of acid neutralizing capacity (ANC) in the watershed system (Laudon et al. 2000). There are various hydrochemical triggers for acid episodes during storms or snow-melt including acid deposition, leaching of sulphur stored in soils (Alewell et al., 2000), flushing of organic acids from wetlands (Kerekes and Freedman, 1989), sea-salt deposition (Heath et al., 1992), or base cation dilution (Davies et al., 1992).

Acid episodes have been identified as a threat to aquatic biota in Nova Scotia, in particular local *Salmo salar* populations (Bowlby et al., 2013) but there have been no recent studies on the occurrence of episodes in the streams of this highly acid sensitive region. This study uses sub-daily pH measurements to examine the frequency, duration, and severity of acid episodes in four acidified streams in Nova Scotia including seasonal and spatial episode trends.

1.1 Research Base and Knowledge Gaps

Biological studies on the impact of acidification have suggested a threshold for freshwater pH of approximately 5.5 below which conditions become toxic for most aquatic life (Kroglund et al., 2007; Lacoul et al., 2011). Chronically acidified streams are those which have persistently low pH levels near or below the pH 5.5 threshold. Both chronically acidified streams and streams with average conditions above pH 5.5 can experience episodic acidification resulting in drops in pH to below toxic levels. Moreover, acid episodes have been shown to slow biological recovery in an acidified system even if annual average pH levels have increased (Kowalik et al., 2007; Mant el. al., 2013). When base cations (i.e. calcium, magnesium, sodium, and potassium) have been depleted from the soil by hydrogen ion exchange due to acidification, ionic aluminum (Al_i) can be leached out during run-off adding to the toxicity of acid episodes (Driscoll et al. 1982).

During episodes a decrease of pH and base cations coupled with an increase in toxic Al_i causes considerable stress to the freshwater biota. A number of studies have documented the toxicity of these episodes for macro-invertebrates and acid-sensitive fish populations (Lepori and Ormerod, 2005; Monette and McCormick, 2008). The effect of acid episodes on *Salmo salar* has been well researched due to their economic and cultural importance. Recent tests have shown that it can take more than two weeks for *Salmo salar* to recover from acute exposure to acidic water and high aluminum concentrations (Nilsen el al., 2013). This demonstrates the need to determine frequency of acid episodes in order to understand the impacts to salmonids. Seasonal timing of episodes is also an important factor with spring snow melt acid episodes being more detrimental due to the coincidence with the sensitive smoltification life stage of salmon (Staurnes et al., 1995). Overall, acid episodes can significantly reduce the survival rate of *Salmo salar* within streams and on returning to the marine environment (Magee et. al. 2003).

Despite numerous regional studies on triggers, effects, and models of acid episodes (Davies et al. 1992; Heath et al. 1992; Wellington and Driscoll, 2004; Laudon, 1999) there have been few studies on the long-term trends of episodic acidification across Europe and North America due to data availability (Laudon, 2007). In general, there has been a greater focus on determining long-term recovery of average pH and ANC values. Research in Swedish streams has shown that episodic acidification has improved in recent decades although recovery has been limited in areas with greater occurrence of sea-salt deposition and drought demonstrating a shift in acid episode drivers from acid deposition related to weather related (Laudon, 2007). This shift highlights the possibility for increases in weather extremes due to climate change to become a barrier to acidification recovery and therefore the importance of continuing to monitor acid episode behaviour.

Episodic acidification trends have been studied in a limited capacity for Nova Scotia using weekly data frequency but have not been studied for the recent decade (Laudon et. al., 2002; Clair et. al., 2001; Lacroix and Knox, 2005).There have also been few studies to accurately capture episode frequency, duration, and severity by using high-frequency water chemistry. Acid episode studies using high-frequency measurements have been done in the Southern Appalachians but no similar studies have been done in low-lying or coastal areas (Robinson & Roby, 2006; Deyton et al., 2009; Mauney, 2009; Neff et al. 2012).

In summary, there is a need for more accurate characterization of acid episode behavior with sub-daily measurements in order to determine the timing and levels of exposure of acidity to *Salmo Salar*. This includes a need to determine seasonal trends of acid episodes due to the sensitivity of salmon to spring episodes. In order to plan appropriate mitigation there also is a need for more information on how episodic acidification varies spatially so that the most impacted streams can be targeted for restoration.

1.2 Acidification and Mitigation in Nova Scotia

In South Western Nova Scotia (SWNS) acidified freshwater systems have some of the lowest pH levels in North America and have not recovered in synchrony with a reduction in acid deposition from industrial emissions (Clair, 2011; Watt et. al., 2000). This lack of recovery can be attributed to physical characteristics of SWNS that makes the region sensitive to acidification including the low buffering capacity of the region's geology (Watt et al., 2000), low acid neutralizing capacity (ANC), organic sources of acidity from extensive wetlands, and sea-salt deposition due to proximity to the ocean (Clair, 2007).

The acidification problem in SWNS has been a direct threat to local *Salmo salar* (*Salmo Salar*) which have been extirpated from various streams in the area and local populations have recently been given "Endangered" status by the Committee on the Status of Endangered Wildlife in Canada (COSEWIC) (Bowlby et al., 2013). Many streams in SWNS are below the biological threshold of pH 5.5 during a large portion of the year and acid episodes have been recorded as occurring throughout the year with minimums as low as pH 4.0 (Clair et al., 2001; Clair et al., 2007). Furthermore, a recent study has identified several rivers in SWNS where Al_i concentrations were above toxic levels for salmon (Dennis and Clair, 2012). Watersheds in this region are not predicted to recover from acidification to pre-industrial levels of pH and ANC in this century based on policy decreases in emissions (Whitfield et al., 2007). The current recovery potential assessment for Southern Upland *Salmo salar* uses only chronic pH as an index of acidification which may not be a sufficient indicator for stream health if severe acid episodes are continuing (Bowlby et al., 2013). Therefore, determining the extent of episodic acidification in SWNS is important for planning effective mitigation for the survival of Southern Upland *Salmo salar* populations.

Mitigation of acidification involves the application of limestone (calcium carbonate or other buffering compounds) directly to water (in-situ) or over the whole catchment in order to buffer acidity and replenish essential base cations. There have been a few liming application studies in Nova Scotia; to-date no regional mitigation plan has been developed. An in-situ liming doser was installed in the West River from 2005 to 2013 resulting in successful increases of salmon productivity but is likely to shut down in the near future due to lack of resources for the private group running the program. Preliminary research for catchment liming of a small acidified catchment in New Russell, Nova Scotia is currently being done by Dalhousie Universities' Hydrologic Research Group (HRG) in collaboration with the Bluenose Coastal Action Foundation (BCAF) (Angelidis, et al., 2013). For the purposes of implementing a liming program it is important to know what the current risk of episodic acidification is for stream fauna, which streams are most are vulnerable to acid episodes, and which season should be targeted to reduce episodes.

1.3 Study Approach

This study focuses on characterization of episodic stream acidification in Nova Scotia using high frequency data (hourly and 15-minute) collected from four streams in recent years. The main research objective is characterizing the extent of episodic acidification in streams in SWNS and to provide baseline data on acid episodes for the province. The research question is the following:

What is the frequency, duration, and severity of acid episodes in four SWNS streams?

A. Is there a difference in frequency, duration, and severity of acid episodes between watershed types?

B. Is the frequency, duration, and severity explained by meteorological or hydrological conditions?

C. How does this frequency and/or severity change with seasons and inter-annual weather variations?

These questions are studied using high frequency (hourly and 15-minute) pH and water level data collected for four acidified streams by Nova Scotia Environment (NSE) and Dalhousie's HRG and supplemented with an atlas of Nova Scotia's water catchment characteristics form the Nova Scotia Watershed Assessment Program (NSWAP). The water quality data sets are limited by relatively shorter monitoring durations of eight years or less starting in 2002 but adequately capture acid episode parameters due to frequent measurements. Due to the small sampling size of streams with available data the spatial analyses between watersheds is limited to a baseline study of possible watershed traits contributing to the risk of episodic acidification in SWNS.

Analysis of these research questions contributes much needed information on episodic acidification to aid the planning of mitigation for recovery of acidified streams in SWNS. Outside of the regional applications this study adds information to continued acidification research including the improvement of acid episode modeling. Due to there being few studies that have applied high-frequency in-situ pH measurements to analysis of acid episodes this study could provide validation for the use of this method in future research.

2.0 Literature Review

There is a large body of research on acidification starting as early as the 1960s when acidification became an apparent threat to freshwater ecosystems in Europe and North America. This literature review will focus on studies in the past few decades which have aimed to determine the causes, biological implications, and trends of stream episodic acidification.

2.1 Episode Drivers

Numerous studies have analyzed acid episodes alongside meteorological, soil chemistry, and water chemistry data to determine the chemical and hydrological triggers of acid episodes and the seasonality of these triggers. This has been important for understanding anthropogenic contributions to naturally occurring freshwater pH fluctuations. Davies et al. (1992) reported base-cation or ANC dilution to be the most common driver of acid episodes in Europe. During high runoff, from spring snowmelt or heavy rains, ANC can be diluted causing a drop in pH. High runoff can also flush out organic acids from wetlands further depressing pH (Laudon et al., 1999; Wellington and Driscoll, 2004). These two natural drivers have been shown to cause acid episodes even in locations with low anthropogenic acid deposition but are critical for streams with already low baseflow pH (Laudon et al., 2000). In coastal areas, marine storms can also cause acid episodes due to deposition of sea-salts and this effect has been shown to be more significant in areas where there is depleted or low base cations in soil due to acidification (Heath et al. 1992). During the summer, droughts can expose sulphur stored in wetlands causing sulphur to be oxidized to sulphate which can then be transported to streams during the next high run-off event potentially causing an acid episode (Huntington et al., 1994). Kerr et al. (2002) showed that this drought effect is an important mechanism in catchments in Eastern North America, especially those which have more wetland coverage. This mechanism contributes to episodic acidification in the freshwater systems of Eastern North America and helps to explain a higher sulphate export in catchments than is expected under reduced sulphate deposition.

2.2 Long Term Trends

Acid deposition has been significantly decreased due to successful emission reductions and has resulted in recovery of many streams in Europe and North America from chronic acidification (Stoddard et al., 1999). The exception to this trend is SWNS where freshwater acidity continues to be the lowest in North America and is not expected to recover in the next century (Clair et al. 2011). In areas where recovery is occurring studies have found that episodic acidification may continue to be widespread due to acid depletion of soil buffering capacity (Lawrence, 2001). A study of a thirty year record of stream water chemistry in Birkenes, Norway has shown that the reduction in chronic acidification has been coupled with a positive trend in recovery from episodic acidification (Wright, 2008). In other regions of Europe and North America there are few similar long term analyses on trends of acid episode occurrence. However, multiple studies in Europe have shown an apparent shift in episodic acidification from primarily acid deposition triggered to being triggered by weather extremes, such as drought and frequent storms, in the past decade (Laudon, 2007; Wright, 2008; Erlandsson et al., 2010; Feeley et al., 2013). This shift is thought to be due to reductions in acid deposition but slow recovery of buffering capacity in soils (Aherne et al., 2003 and Beier et al., 2003) leaving freshwater systems more vulnerable to weather extremes (Evans, 2005).

Sea-salt deposition from marine storms and sulphate exports from drought may become more important triggers of acid episodes in acidified catchments weather extremes increase as may be associated with climate change (Christensen et al., 2013). Indeed, Laudon (2007) has shown that an increase in droughts and marine storms has limited recovery from episodic acidification following declines in anthropogenic acid deposition. This study highlights the importance of continuing long term surface water monitoring programs in catchments previously exposed to acid deposition in order to capture potential interactions between climate change and episodic acidification.

2.3 Episode Impacts on Biota

Focusing stream health assessment on average pH over seasons or years may be misleading for predicting biological recovery in acidified catchments. In streams that are recovering from chronic acidification continued acid episodes have been shown to prevent recolonization of macroinvertabrates, which can be important bioindicators of stream health (Kowalik et al. 2007). Acid episodes are often coupled with spikes in toxic aluminum cations, mobilized from catchment soils, which bind to negatively charged sites on gills of *Salmo salar* and other salmonids resulting in impaired ion regulation and respiration (Lacroix et al., 1993; Wilkinson and Campbell, 1993). A study by Nilsen et al. (2013) found that even short acid and aluminum exposure of *Salmo salar* smolts (2 to 7 days) resulted in physiological impacts that could take more than two weeks to recover from. The result of smolt acid episode exposure is a lower survival rate on returning to sea, due to a lowered tolerance for secondary stressors in the marine environment, resulting in negative population effects (Kroglund et al., 2007). It is therefore important to quantify the frequency, duration, and severity of acid episodes for the restoration of *Salmo salar* which are already critically declining in Norway and Atlantic Canada in part due to the impacts of acidification (Sandøy and Langåker, 2001; Gibson et al., 2011).

2.4 Seasonal Variations

Monette & McCormick (2008) found that the spring smolt life stage of *Salmo salar* are most vulnerable to acidification likely due to gill transformations during the transition from parr-smolt (smoltification) in preparation for migration to seawater. This life stage coincides with spring snowmelt when episodes are thought to be severe and it is therefore important to determine the seasonality of acid episode behavior. In Nova Scotia, due to the mild winter, snowmelt and rainfall run-off occur often while soils are frozen or partially frozen which means there is little sub-surface flow and hence little opportunity for soils to buffer precipitation resulting in a period of low pH and high episodic acidification during late winter and early spring (Laudon, 2002). Laudon et al. (2002) noted that in Nova Scotia winter high-run off events are preceded by rainfall and result in a period of winter episodes lasting for several months and are longer than the spring flood episodes seen in Sweden which are preceded by four to six months of thick snow pack. Lacroix and Korman (1995) modelled *Salmo salar* populations in the Westfield River and found a greater impact on populations when fall (September to December) episodic acidification occurred earlier and when spring (February to May) recovery of pH was delayed.

2.5 Methods for Measuring Acid Episodes

Episodic acidification became an apparent biological threat in the 1980s (Watt, 1987) and since then there have been continued advances in measurement and modeling technology leading to more accurate determination of acid episodes. During the history of water quality studies there has generally been a divide in measurement frequency between hydrometric parameters (water level, flow, discharge, etc.), for which sub-daily measurements are available, and water chemistry parameters, which have been limited to weekly or monthly sampling (Kirchner, 2004). This divide is due to a previously wider availability of robust in-situ instruments for continuously monitoring hydrometric parameters than in-situ instruments that measure water chemistry (Kirchner, 2004). The exception to the generally lower frequency of water chemistry measurements is studies of acid episodes using sub-daily measurements taken in specific storm events and triggered by increases in water level or discharge (e.g. Lawrence, 2002). Consistently monitoring stream chemistry with automatic grab samples or by hand with pH meters on a sub-weekly level is resource (e.g. laboratory grab sample analysis costs) and time intensive and there are also potential chemical stability issues in the transport of samples. However, since the 1990s instruments for automated high-frequency in-situ measurements of water chemistry have become available. Incorporation of these instruments in water quality programs has resulted in an improved understanding of nutrient dynamics (Wade et al., 2012), storm flow geochemistry, and biologically induced diurnal water chemistry variations (Jarvie et al., 2001). For example, Jarvie et al. (2001) found that during baseflow conditions in the summer, when rates of biological activity are high, there is a diurnal variation in pH of up to 1 pH unit due to changes in the concentration of carbonic acid in stream water mediated by aquatic plant photosynthesis. This demonstrates the ability of these instruments to capture high-resolution changes in stream pH.

2.6 Episode Frequency

Despite the growing availability of automated water-chemistry instruments there have been only a few studies have used high-frequency data for acid episode analysis. Most of these studies have been conducted in Great Smokey Mountain National Park (GRSM) in the Southern Appalachians (Robinson & Roby, 2006; Deyton et al., 2009; Mauney, 2009; Neff et al. 2012). Deyton et al. (2009) contributed to an understanding of storm flow chemical triggers in GRSM and Neff et al. (2012) related storm flow chemistry to catchment soil and vegetation types. However, in both studies use of the continuous monitoring data was not the main focus of the analyses. In the case of Deyton et al. (2009) continuous monitoring was used to determine stormflow pH response, defined as the difference in pH between the minimum during stormflow and the antecedent value during baseflow, in order to relate pH response to stream discharge and number of dry days leading up to a precipitation event.

In contrast, the studies by Robinson and Roby (2006) and Mauney (2009) in GRSM highlights the use of continuous monitoring in characterization of acid episode duration and frequency. Robinson and Roby (2006) developed methodology for the characterization acid episode behavior (i.e. frequency, duration, severity) with concentration-duration-frequency (CDF) curves which could allow further comparisons of acid episode data. Mauney (2009) used the CDF methods to relate acid episode behavior to catchment characteristics. Results from the temporal analysis of one site with 4 years of 15-minute data suggested that continuous monitoring from one year could be sufficient for modeling acid episode frequency and duration for a particular catchment. However, the site used for the temporal analysis was a small headwater stream and Mauney (2009) found that it was more difficult to model acid episode behavior for larger catchments.

Outside of North America, a study of acid episodes was conducted in the Allt a'Mahrcaidh catchment of Scotland by Bonjean et al. (2007), using 15-minute monitoring, found that precipitation sea-salt conductivity, acid episode peak flow rate, and antecedent run-off conditions in the three weeks leading up to an episode were strong explanatory variables of episode severity (maximum hydrogen ion concentration) and duration (hours below a pH threshold of 5.5) with sea-salt conductivity being the strongest predictor even in inland areas. However, this study focused on determining episode triggers and therefore did not summarize the data collected on episode severity and duration.

In each of these studies the authors highlight the importance of sub-hourly monitoring for developing a detailed understanding of acid episode processes. Episodes occurred during periods that were hours to weeks long which means monitoring on a weekly basis, or less frequent, would inherently be unable to capture every episode and as seen in Nilsen et al. (2013) even short episodes can have significant biological impacts.

Results from Clair et al. (2001) identified acid episodes in SWNS as a seasonal phenomenon with a predicted two to four episodes per year with two triggers: heavy rainfall in late autumn and snowmelt processes during late winter/spring. The most recent findings on acid episode occurrence in Nova Scotia are from a preliminary catchment liming study at Maria Brook, a small acidified catchment in New Russell, Nova Scotia (Angelidis et al., 2013). This study has found that, contrary to Clair et al. 2001, acid episodes is SWNS are a meteorological phenomenon occurring throughout the year with almost every rainfall greater than 10 mm independent of the season. A greater number of episodes were recorded from this study than in Clair et al. (2001) which is likely due to much higher sampling frequency with 15-minute continuous monitoring although the small size of the Maria Brook catchment may also contribute to the frequent episodes in response to precipitation (Mauney, 2009).

2.7 Impact of Catchment Characteristics on Episodic Acidification

Although a number of studies have related catchment characteristics to acidification vulnerability (Sullivan, 2007; Clair et al., 2007) there have been fewer studies to draw that link to acid episode frequency or severity. Research on acidified catchments in the Southern Appalachians have found smaller streams at higher elevations and greater slope to be more vulnerable to acid episode due in part to more limited interactions of run-off with soils giving less opportunity for neutralization of acid inputs to streams (Deviney et al., 2006; Mauney, 2009; Table 1). Deviney et al. (2006) found that consistent with prior studies acidification vulnerability in the Southern Appalachians (Herlihy, 1993), bedrock geology was also important in episodic acidification with less basaltic or carbonate bedrock giving rise to higher risk of experiencing acid episodes due to low buffering capacity of soils overlaying this geology type (Table 1). There have been no similar studies of episodic acidification in streams in low-lying coastal areas which may have different relationships between acid episode behavior and catchment characteristics due to less heterogeneity in slope and the greater potential for water chemistry to be influenced by wetlands, lakes, and marine proximity. A study in a lower altitude region of a Northern Sweden stream network found that spring flood pH was lowest in small, higher altitude, wetland-dominated catchments and catchments with a greater presence of lakes were associated with a smaller pH drop during spring flood due to lakes capacity to buffer changes in water chemistry (Buffam et al., 2008; Table 1). However, the study in northern Sweden is focused on a single spring flood sampling event for each site and therefore did not capture acid episode frequency and duration relation to catchment characteristics.

Table 1. Catchment characteristic impact on episodic acidification as identified in multiple regional studies.

Study and Location	**Dependent Variable(s)**	**Catchment Characteristics (Independent Variables)**	
		Increase episodic acidification	**Decrease episodic acidification**
Deviney et al. (2006) **Southern Appalachians**	Recurrence intervals of minimum ANC	-Smaller catchment size -Granitic or siliclastic bedrock	-Larger catchment size -Basaltic or carbonate bedrock
Mauney et al. (2008) **Southern Appalachians**	Duration slope (from CDF curve equation)	-Smaller catchment size -Higher absolute elevation -Siliclastic sulphic slate bedrock -Steeper slope	-Larger catchment size -Lower elevation -Shallower slope
Buffam et al. (2008) **Northern Sweden**	Spring-flood pH minimum and magnitude of drop	-Smaller catchment size -Higher elevation -Headwater streams -Higher proportion of wetlands -High coniferous forest density	-Larger catchment size -Lower elevation -Presence of lakes -Fine sorted surficial sediments

2.8 Acidification Research in SWNS

South Western Nova Scotia is uniquely sensitive to acidification and therefore has not seen the recovery with decreased acid deposition that is the trend for most other locations in Europe and North America (Dennis and Clair, 2011). Concentrations of sulphate in headwater lakes in SWNS have significantly decreased since the 1980s but pH and ANC remain low throughout the region and are not predicted to recover to pre-industrial levels in the next century under proposed emission reductions (Whitfield, 2006; Whitfield, 2007). Clair et al. (2007) provides a comprehensive review of acidification research in Atlantic Canada with studies addressing concern for impacts on aquatic ecosystems starting in the mid-to-late 1970s. SWNS was found to have the most acid waters in the Atlantic region.

The ecological impact of decades of acid depostion in Nova Scotia has been most apparent in the large declines in *Salmo salar* populations of 83 to 99% since the 1980s (Gibson et al., 2011). Although other factors have contributed to this decline, acidification has been identified by multiple studies as a significant threat (Watt, 1987; Lacroix, 1989). Recently a study has determined that Al_i is playing a larger role in the toxic effects of acidification in Nova Scotia than previously thought and connected the greatest loss of salmon populations in SWNS to high levels of biologically accessible Al_i which can be increased during low pH events (Dennis and Clair, 2012).

Few acid episode studies have been done in Nova Scotia and have mainly used weekly data from monitoring stations in Kejimkujik National Park (KNP). Clair et al. (2001) used measurements from 1987 to 1995 for Mersey River, Moose Pit Brook, and Pine Marten Brook to determine the seasonal variation of low pH and determine if daily discharge could be used to create a statistical relationship to predict pH extremes. They found that a statistical approximation of pH using discharge was unable to model measured drops in pH in order to increase data frequency and therefore only the measured weekly pH data was used for analysis which could ultimately result in missing some episodes.

Laudon et al. (2002) used the same weekly pH measurements from 1983 to 1998 as did Clair et al. (2001) for Mersey River and Moose Pit Brook in KNP to evaluate winter episode response to decreases in acid deposition. The study focused on the cause of ANC depression during episodes and did not examine changes in episode frequency or duration. The main findings were a decreasing trend in ANC depressions caused by sulphate deposition but limited recovery in the average peak flow pH and base cation concentrations over the study period. This study contributed to a better understanding of winter episode dynamics in Nova Scotia but is still limited by data collection frequency and lacks spatial scope.

2.9 Knowledge Gaps

The body of literature on acid episodes is large but historically studies been focused on grab sample chemistry and few have captured acid episode frequency using high-resolution water quality data. There is also a lack of studies in low-lying areas on acid episode frequency, duration, and severity in relation to catchment characteristics. In Nova Scotia, there have been few acid episode studies and those have been limited to Kejimkujik National Park with a long term set of weekly monitoring. Moreover, there have been no acid episode studies in Nova Scotia in the recent decade during which sulphate deposition has continued to decrease and other regions have seen an increasing interaction between extreme weather events and episodic acidification. In summary, a better characterization acid episode frequency, duration, and severity as well as long-term trends of episodic acidification in Nova Scotia's streams is needed for effective future planning of restoration.

3.0 Methods

3.1 Overview

Acid episodes were characterized using two main tools applied to stream pH and hydrometric data collected in seven acidified streams in Nova Scotia. The first tool is annual and seasonal summary tables and graphs of acid episode frequency, duration, and severity categorized by multiple pH thresholds for each site (Mauney, 2009). The second tool is a relation of pH response during run-off events to stage or discharge increase and the time since the last episode as a proxy for the number of "dry days" leading up to an episode (eg. Deyton et al., 2009). The resulting acid episode characterization using these two methods is used to relate seasonal variations within streams to changes in weather and discuss the impact of catchment characteristics on acid episode behavior. The analysis will largely be retrospective and descriptive with an analytical component for determining pH response to storm flow.

3.2 Study Area Description

The stream sites were chosen from the available water quality monitoring programs in Nova Scotia (Figure 1.) with only streams in low ANC watersheds being used in this analysis due to the importance of acid episodes for determining the health acidified stream (Weatherly and Omerod, 2001). The water quality data comes from three organizations with stream monitoring programs: Nova Scotia Environment (NSE), Environment Canada (EC), and Dalhousie University Hydrologic Research Group (HRG) (Fig. 1). However, due to time restraints the long-term weekly data from Environment Canada was not used in the final analysis.

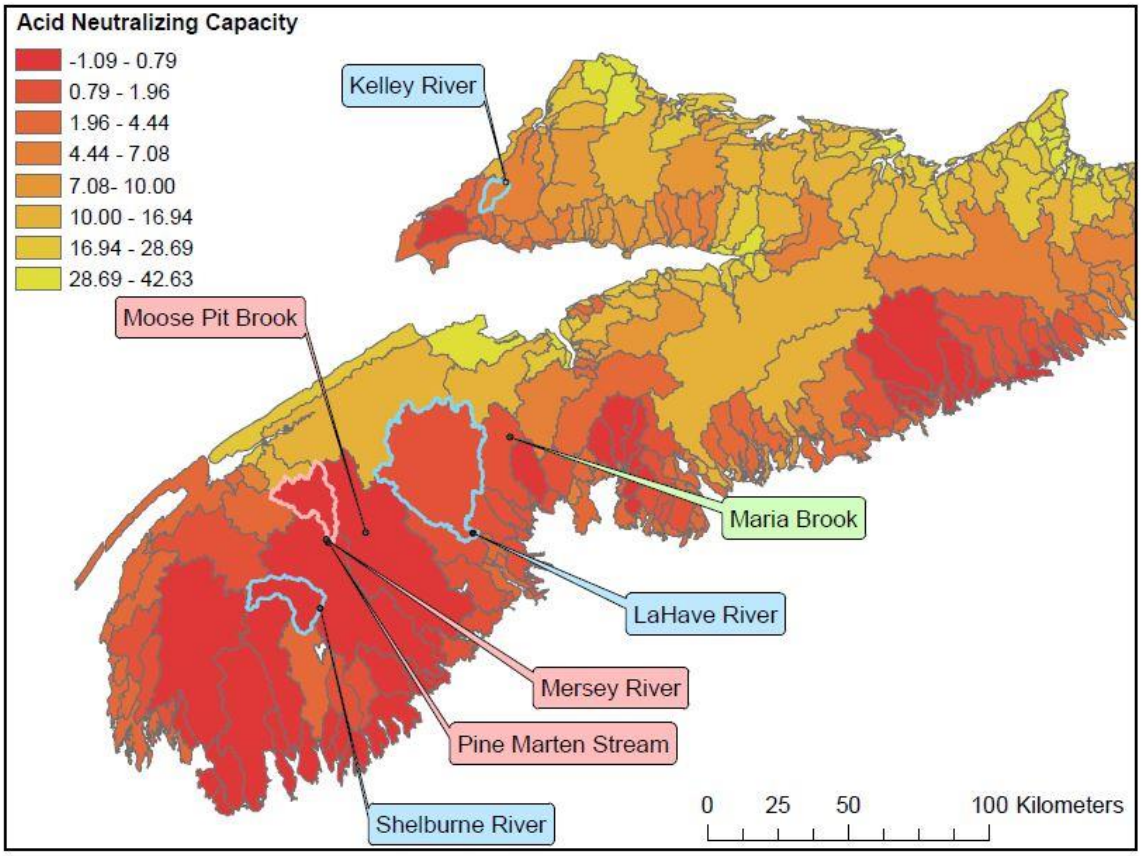

Figure 1. Map of stream water quality monitoring sites in relation to the ANC of watersheds in Nova Scotia (NSWAP). Blue sites are monitored by NSE, red sites are monitored by EC within KNP, and green sites are monitored by Dalhousie HRG and BCAF.

3.2.1 NSE site description

Nova Scotia Environment has a network of automated water quality monitoring stations and from this data set three streams were selected; Kelley River (KR), LaHave River (LHR), and Shelburne River (SR). Each monitoring site is located on the main-stem of the stream. Kelly River is a 64.5 km^2 catchment located in the northwest part of Nova Scotia and drains into the Cumberland Basin in the Bay of Fundy (NSE, 2010; Table 2). Bedrock geology in the Kelley River watershed is dominated by sandstones, conglomerates, and shales (NSE, 2010). Although this stream is outside of the SWNS region it is be included in this study because it has low ANC and includes *Salmo salar* habitat (NSE, 2010). LaHave River (1260 km^2) and Shelburne River (277 km^2) are both in SWNS and drain into the Atlantic Ocean. Both catchments are underlain primarily by granitic bedrock with some shale (NSE, 2010). Shelburne is the most poorly drained of the three sites and contains a large number of peat bogs in the landscape with 18% wetland or water coverage and this may contribute to the very low average pH of 4.4 (NSE, 2010; Table 2).

3.2.2 HRG's Maria Brook site description

Maria Brook (MB) is a small 0.47 km^2 headwater catchment that is a sub-basin of the Gold River watershed located in SWNS (Angelidis et al., 2013). Maria Brook was selected in October 2010 by HRG in cooperation with the community group Bluenose Coastal Action Foundation (BCAF) as a site to study catchment liming on a small scale (Angelidis et al., 2013) The site was chosen because the granitic bedrock and conifer-dominated forest is typical to SWNS, there is no urban development within the catchment, the hypsometry is well-defined with a standard tear-shaped morphology, and there is easy access to site with the provision of supportive private land owners. The Gold River watershed also supports important *Salmo salar* habitat (Angelidis et al., 2013).

Table 2. Stream water quality monitoring site locations and catchment characteristics. The mean pH for each NSE site and Maria Brook was calculated by averaging all the pH data points over the collection period. The mean pH for the EC sites was determined by Clair et al. (2008).

Stream	Coordinates	Catchment Area (km^2)	Stream Order	Land Cover	Mean pH
Kelley River (KR)	45° 35'10"N 64° 27'05"W	64.5	4	Forest 80.3% Wetland/Water 11.5% Clearcut 6.7% Urban 1.2%	5.5
LaHave River (LR)	44° 26'50"N 64° 35'28"W	1260	4	Forest 86.3% Wetland/Water 10.1% Agriculture 2.1% Urban 1.4%	5.5
Shelburne River (SR)	44*12'59"N 65*14'32"W	277.4	4	75% Forest 18% Wetland/Water 0.5% Urban 5.9% Barren	4.4
Maria Brook (MB)	44°46'40"N 64°24'52"W	0.47	1		5.2

3.3 Maria Brook Catchment Liming Design

In May 2012, 27 tonnes of powdered limestone was applied to the presumed hydraulic source area of the catchment and in June 2013 another 60 tonnes was added. The limestone was applied by hand to a total of 2.04 ha of the catchment in 20 x 20 meter quadrats. There are two continuous monitoring stations in the Maria Brook, a control site immediately above of the limestone application area and treatment site, 300 m downstream of the limestone application (Angelidis et al., 2013). This continuous monitoring allows for a comparison of episodic acidification between the control and treatment site to determine if the limestone is having an impact on episode behavior.

3.4 Meteorological and Precipitation Chemistry Data Collection

Meteorological data for each site is available from nearby EC weather stations (state locations) and the Maria Brook site includes temperature and rainfall measurement collection. For SR and MB the closest weather station is in KNP. Average yearly total precipitation for this station is 1,352 mm, occurring largely between November and April, and an equivalent 18% of that precipitation is snow (Clair et al., 2008). Nappan is the closest EC weather station for KR and average yearly total precipitation (from 1981 to 2005) amounts to 1,155 mm. The closest EC weather station to LR is in Bridgewater and average yearly total precipitation (from 1981 to 2005) is 1,536 mm.

3.5 Water Quality Data Collection

The NSE stream sites have been monitored with multi-parameter sondes at an hourly frequency starting in 2002 (SR) with the longest data sets spanning about 8 years for KR and SR and the shortest spanning 4 years for LHR (Table 3). Water level (stage) at all NSE sites is also monitored at an hourly frequency. There are two Mobile Environmental Monitoring Platforms (MEMPs) at Maria Brook located at the control and treatment sites. The MEMPs are equipped with YSI-6600 multi-parameters sondes, which collect pH, conductivity, and stream temperature at 15-minute intervals. The MEMPs each have an OTT water bubbler, which measures stage height, and meteorological equipment that measures precipitation amounts and air temperature all with 15-minute frequency (Table 3). Reliable continuous water quality data begins in May 2012 just prior to the application of limestone. Grab sample measurements and transect measurement are also done on a bi-weekly frequency starting in Fall 2010 and are used for any corrections or calibrations of the continuous sonde data.

Table 3. Frequency and availability of stream chemistry and hydrometric data sets for each stream monitoring site.

Source	Data Type	Location	Sampling Frequency	Date Start	Date End
Environment Canada CAPmON	Precipitation chemistry	Kejimkujik National Park	monthly	1-Jul-1983	1-Dec-2011
Environment Canada (EC)	Grab sample stream chemistry & discharge	Mersey River	weekly (chem.) & daily (discharge)	27-Jan-1980	18-Jul-2011
		Moose Pit Brook	weekly (chem.) & daily (discarge)	3-May-1983	26-Jul-2011
		Pine Marten Stream	weekly (chem.) & daily (discharge)	21-Dec-1990	26-Jul-2011
Nova Scotia Environment (NSE)	In-situ stream chemistry & water level	Kelley River	hourly	17-Dec-2004	22-Nov-2012
		La Have River	hourly	30-Oct-2008	11-Mar-2013
		Shelburne River	hourly	16-Aug-2002	2-Nov-2010
Dalhousie Univeristy Hydrologic Research Group (HRG)	In-situ stream chemistry & water level	Maria Brook CMEMP	15-Minute	2-May-2012	4-Nov-2013
		Maria Brook DMEMP	15-minute	12-Jun-2012	22-Nov-2013

3.6 Acid Episode Thresholds

For this study acid episodes are defined using multiple thresholds at pH levels ranging from pH 4.0 to 6.0 with 0.5 pH unit intervals. Using a multi-threshold approach for determining acid episode severity, frequency, and duration (Robinson and Roby, 2006; Mauney, 2009) an episode is considered for each threshold as the time between when the stream pH dips below the threshold (downcross) to when it returns to pH levels above the threshold (upcross) (Fig. 2). This method is applied to the data set using a program developed in R (Appendix 1). Previous studies have often defined an acid episode as occurring when stream pH dips below a particular threshold that is based on biological studies of toxicity. The focus of acidification mitigation in Nova Scotia is largely on the recovery of *Salmo salar* populations and therefore thresholds for toxicity to salmon are considered in this analysis. Below a threshold of pH 5.5, in the "Al_i toxic zone" (pH 4.8 to 5.5), there is an increased risk of aluminum toxicity for *Salmo salar* and below a threshold of pH 4.8, in the "acidity toxic zone", toxicity to salmon is dominated by low pH (Lacouel et al., 2011). By using multiple thresholds of pH the analysis is better able to compare the inter-seasonal and catchment-to-catchment variations in baseflow pH when determining acid episode frequency. For example, the Shelburne River is acidic year round with an average baseflow pH of 4.4 and therefore if a biological threshold of 5.5 or 4.8 was applied for determining episodic acidification the variability of pH extremes would not be captured. This method also allows for comparison of the results to biological studies of acid tolerances for a variety of aquatic species.

3.7 Procedures and Reasearch Tools

For each crossing of a pH threshold the following information is collected using the R program (Appendix 1) and by hand from the pH and hydrometric (Fig. 2), and meteorological data:

1. The minimum pH reached after the threshold;
2. The maximum pH before the threshold is crossed (the first maximum working backwards from the threshold);
3. The duration spent below the threshold (the time from the threshold downcross to upcross);
4. The change in stage or discharge from minimum stage before the episode to maximum stage during the episode;
5. The maximum stage or discharge during the episode;

6. And the amount of time since the last episode which includes the time between the last threshold up cross to the next episode downcross.

This information is used to characterize acid episode behavior in terms of duration and frequency of events below pH thresholds and pH response to increased run-off.

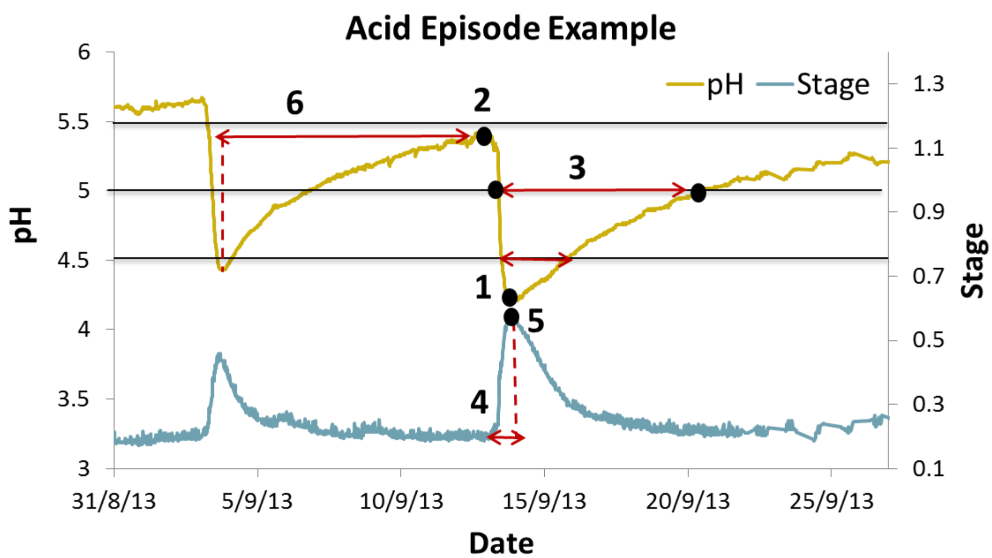

Figure 2. Example data collected on pH and water level (m) for an acid episode which crosses the 5.0 and 4.5 thresholds. Data is from the Maria Brook control site.

For the characterization of episode frequency, duration, and severity the data collection is inclusive, meaning that every crossing of a pH threshold is used in order to determine the total duration the stream water at each site spent below each pH threshold. However, for the hourly and 15-minute data sets episodes with durations of less than 1 hour will not be included in order to account for the differences in measurement frequency between the Maria Brook and NSE data sets.

To characterize storm-flow pH response the pH change, ΔpH, from the maximum during baseflow conditions to the minimum during an episode is related using standard least squares linear regression analysis to the maximum stage during the episode, the change in stage during the episode, and the time since last the episode (Deyton et al., 2009). This method will only be used for the high-frequency data from NSE and HRG.

3.8 Analysis

3.8.1 Annual and seasonal within stream variation

For the NSE and Maria Brook Sites with high-frequency data a descriptive analysis of seasonal and annual patterns within each stream is done with the aid of the previously metioned summary tables and graphs and regression analysis of pH response. Episodes are classified by threshold crossed and categories of duration below each threshold (e.g. < 24 hours, < 1 week ≥ 24 hours). This allows for identification of the frequency of episodes with the greatest severity and longest duration and hence the greatest potential for impacting aquatic biota.

3.8.2 Impact of catchment characteristics on acid episode behaviour

The analysis of the impact of catchment charactertics on acid episode duration, frequency, and severity is limited to a discussion comparing the results for each stream because the sample size of seven streams is too small for statistical analysis. This discussion is based on the traits previous studies (Table 1) have found to increase the vulnerability of a stream to acid episodes such as catchment area, elevation, and slope (Deviney et al., 2006; Mauney, 2009) or presence of wetlands and lakes (Buffam et al., 2008).

3.8.3 Liming impact on acid episode behaviour

An analysis of the impact that liming has had in Maria Brook on episodic acidification is done by using a paired t-test to determine if there is a significant difference between upstream of the liming and downstream of the liming. This analysis is partially limited due to their being few reliable high-frequency of measurements prior to the limestone application for comparing pre-liming and post-liming data to ensure differences in episodic acidification is not due to other variables that differ between the upstream and downstream sites. However, grab-samples from pre-liming are available and have shown that there was no significant difference in pH from Site 5 to Site 6 (Angeledis et al., 2013).

3.9 Limitations and Delimitations

The spatial scope of this is study delimited to a few sites in South West Nova Scotia. Hence, the sample is not representative of Atlantic Canada but purposively captures the regions where impacts of acidification are greatest. Another delimitation is that no causal anlysis of meteorological and chemical episode triggers is done. This is partially because of the lack of consistant full chemical grab sample analysis on stream water during storm flow events but also due to the complexity involved in developing causal relationships. Also, the stochastic nature of acid episodes makes it difficult to relate episode behavior to average meteorological conditions.This study instead focuses on characterizing stream health in terms of episodic acidification as baseline information for developing hypotheses about how catchment characteristics might impact stream vulnerability to epsiodes.

The number of sites and measurement frequency is limited by the availability of secondary water quality data since the timespan and budget for this project does not allow for collection of primary data. For this reason a statistical analysis of the impact of catchment characteristics on episodic acidification across watersheds is not possible due to the small spatial sampling size. Long-term analysis using EC data was an objective at the beginning of the study but the study has since been limited to the analysis of NSE data due to time restraints and issues with applying the original proposed methodology to the long-term data sets.

4.0 Results and Discussion

4.1 Catchment Variations in Episode Frequency, Duration, and Severity

The results for annual and seasonal means of episode frequency, duration, and severity generally have large standard deviations (Table 4) due to the stochastic nature of acid episodes (Bobba et al., 1990). However, the averages of these acid episode parameters can provide a baseline for the understanding of acid episode frequency, duration, and severity trends in the streams of SWNS. Overall, episode frequencies increase with decreasing episode duration and severity (Table 4).

The MB sites have the most frequent episodes occurring below pH 5.5 (including pH 5.0 and 4.5 thresholds) with frequencies of 14.0 ± 5 and 15.3 ± 5 episodes per year for the control and treatment site respectively for episode durations longer than 24 hours below the pH 5.0 threshold (Table 4). For SR average annual frequencies of episodes with durations longer than 24 hours below the 4.5 threshold are similar to that of the MB control site, 7.7 ± 2 episodes for SR and 9.3 ± 3 episodes for MB, but overall episodes would be seen less frequently throughout the year due to the consistently low pH in the SR (Table 4). Shelburne River was the only stream to have an episode under the 4.0 threshold with one six hour episode occurring over the eight year collection period (Table 4). For MB and KR, acid episodes are most frequent at the pH 5 threshold and less so for higher and lower pH thresholds (Fig. 3). LaHave River experiences high annual episode frequency for the pH 6 threshold due to its relatively higher baseflow pH (Fig. 3). In general, episodes tend to be most frequent at the threshold that is close to the streams baseflow pH since this threshold would be crossed for even small run-off events.

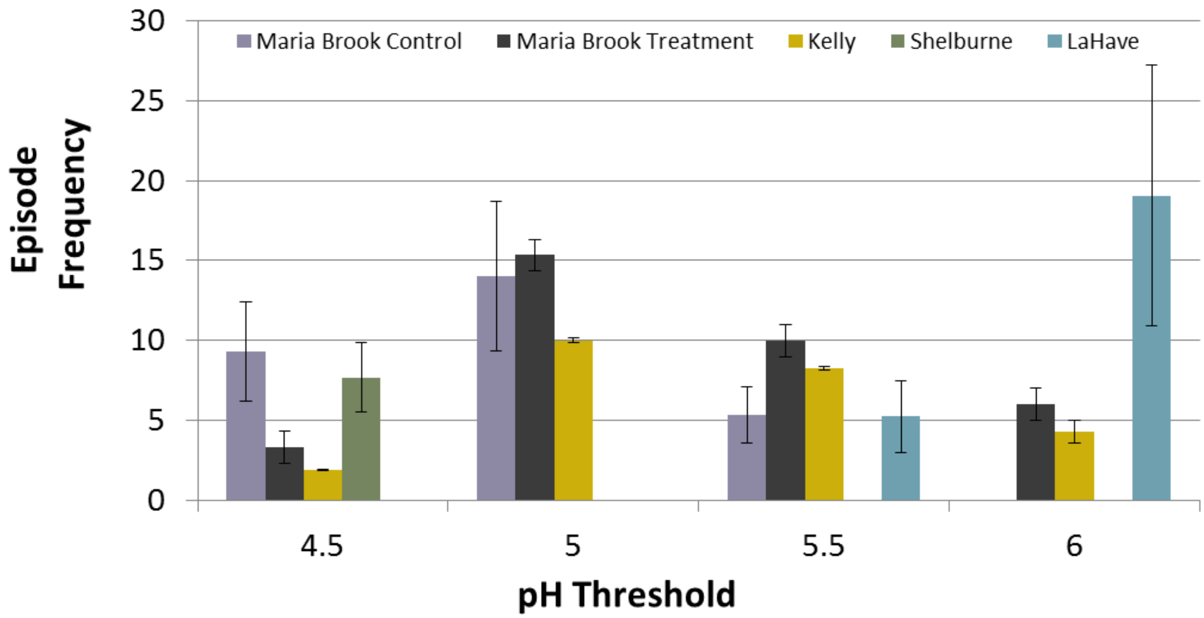

Figure 3. The annual average episode frequency for each episode lasting longer than 24 hours below the threshold. Error bars represent standard error.

Table 4. Summary table of annual average acid episode frequency and duration. Episode duration categories are divided as follows: < 24 hours , < 1 week ≥ 24 hours, < 4 weeks ≥ 1 week, > 4 weeks, and total episodes > 24 hours.

			Annual Mean Time Below Threshold		Annual Mean Number of AE					Stand. Dev. of Total AE > 24 hours
Site	**Years**	**Thres -hold**	**Total Hours**	**Propor-tion of Year**	**< 24 hours**	**< 1 week**	**< 4 weeks**	**> 4 weeks**	**Total AE > 24 hours**	
Kelley River	7.9	4.5	182	0.02	4.7	1.9	0.0	0.0	1.9	0.07
		5	2153	0.25	11.5	6.2	3.4	0.4	10.0	0.36
		5.5	4979	0.57	11.0	3.2	3.4	1.6	8.2	0.29
		6	5521	0.63	10.9	1.8	1.3	1.5	4.3	1.98
LaHave River	4.2	5	33	0.00	0.0	0.0	0.0	0.0	0.0	0.00
		5.5	816	0.09	14.8	4.3	1.0	0.2	5.2	4.60
		6	6842	0.78	41.0	11.2	6.4	1.7	19.0	16.73
Shelburne River	8.2	4	6	0.00	0.6	0.1	0.0	0.0	0.0	0.00
		4.5	9549	1.09	5.1	3.3	2.6	3.4	**7.7**	6.21
Maria Brook Treatment	1.5	4.5	225	0.03	4.7	3.3	0.0	0.0	3.3	3.81
		5	1514	0.17	13.3	15.3	0.7	0.0	**15.3**	5.72
		5.5	4676	0.53	24.7	4.0	4.7	2.0	10.0	2.18
		6	2319	0.26	10.0	3.3	2.0	0.7	6.0	1.36
Maria Brook Control	1.5	4.5	667	0.08	4.7	11.3	0.0	0.0	**9.3**	6.26
		5	3273	0.37	5.3	9.3	3.3	1.3	**14.0**	4.08
		5.5	6542	0.75	24.7	2.7	1.3	2.0	5.3	2.45
Average		4.5	2656	0.30	4.8	5.0	0.6	0.9	5.6	
		5	1743	0.20	7.5	7.7	1.9	0.4	9.8	
		5.5	4253	0.49	18.8	3.5	2.6	1.5	7.2	
		6	4894	0.56	20.6	5.4	3.2	1.3	9.8	

On average the longest episodes occur in the SR and have a mean duration of 21.5 ± 7 days spent below the pH 4.5. The LR is relatively less acidified and therefore as expected has shorter, less severe, episodes which are on average 1.7 ± 5 days for the duration spent below pH 5.5 (Fig. 4). For MB and KR episode durations become longer for higher pH thresholds (Fig. 4). The differences in episode durations for MB and KR are statistically significant for episodes below the pH 4.5 threshold but not for the pH 5.0 and pH 5.5 thresholds (significance level of α=0.05). Episodes below the pH 4.5 threshold in KR, although less frequent than for MB, are on average 2 days longer than the MB episodes whereas episodes below the pH 5.5 threshold for KR were on average 1.9 days shorter than the MB episodes.

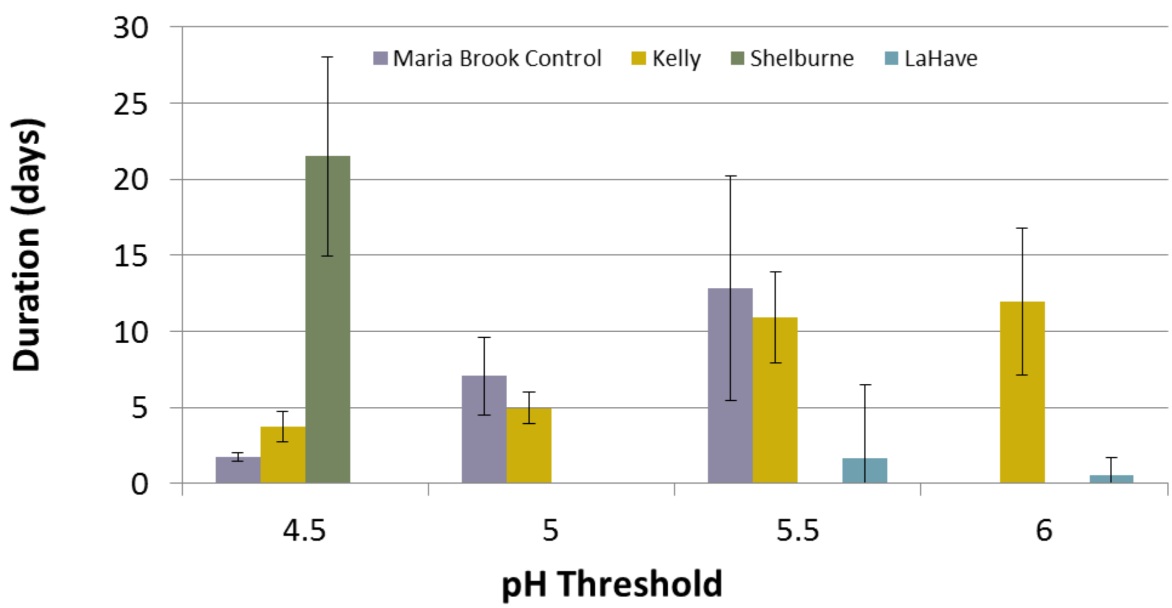

Figure 4. The average annual episode duration from the pH threshold downcross to the pH threshold upcross. Error bars represent standard error.

The episode severity in terms of the length of time the stream is below low pH thresholds is greatest for SR which is consistently below the pH 4.5 threshold (Fig. 5). The least severe episodic acidification by this definition is the LR which is always above the pH 5 threshold and only remains below the pH 5.5 threshold for about 1% of the year on average (Fig. 5). The MB control site is below all of the thresholds for a longer proportion of the year than KR, although the difference is only statistically significant for the pH 6.0 threshold which MB is consistently below (Fig. 5).

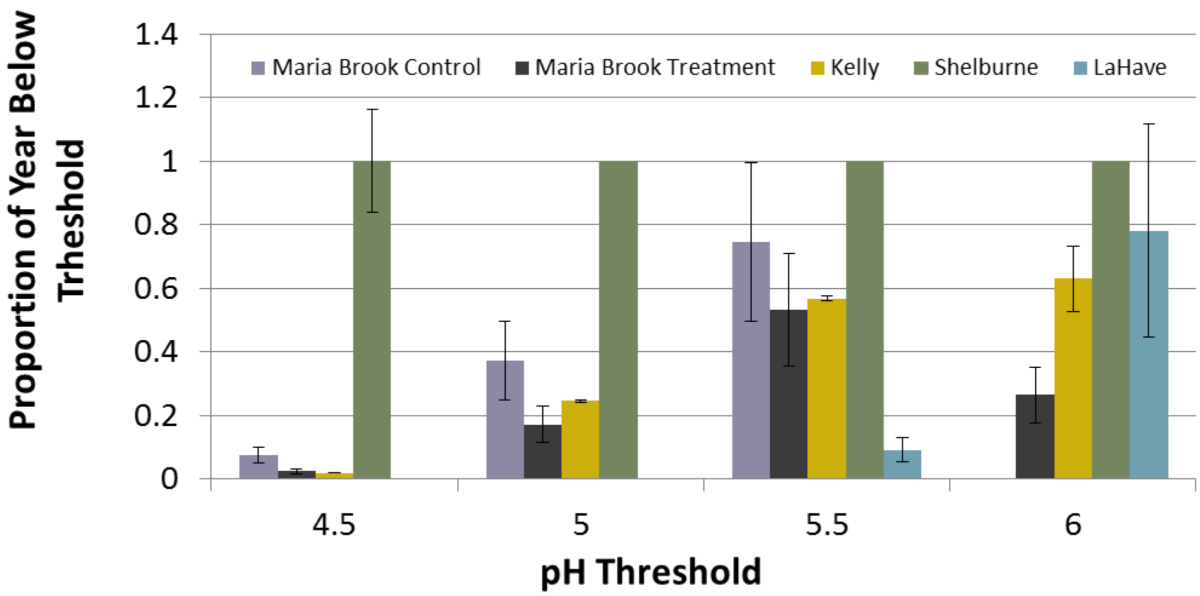

Figure 5. The annual average proportion of the year for which the stream pH is below each threshold.

The episode severity in terms of the magnitude of pH drop is greatest for MB and KR with an average drop of 39.2 and 34.2 μeq H+/L respectively for episodes crossing the pH 4.5 threshold (Fig. 6). The difference between the magnitude of pH drop for MB and KR is statistically significant at the pH 5.0 threshold but not the pH 4.5 and 5.5 thresholds. For SR the annual average magnitude of pH drop for episodes crossing the pH 4.5 threshold is 18.8 μeq H+/L. The magnitude of pH drop is much smaller for LR with an average drop of 2.1 ueq of H+/L for episodes crossing the pH 5.5 threshold (Fig. 6).

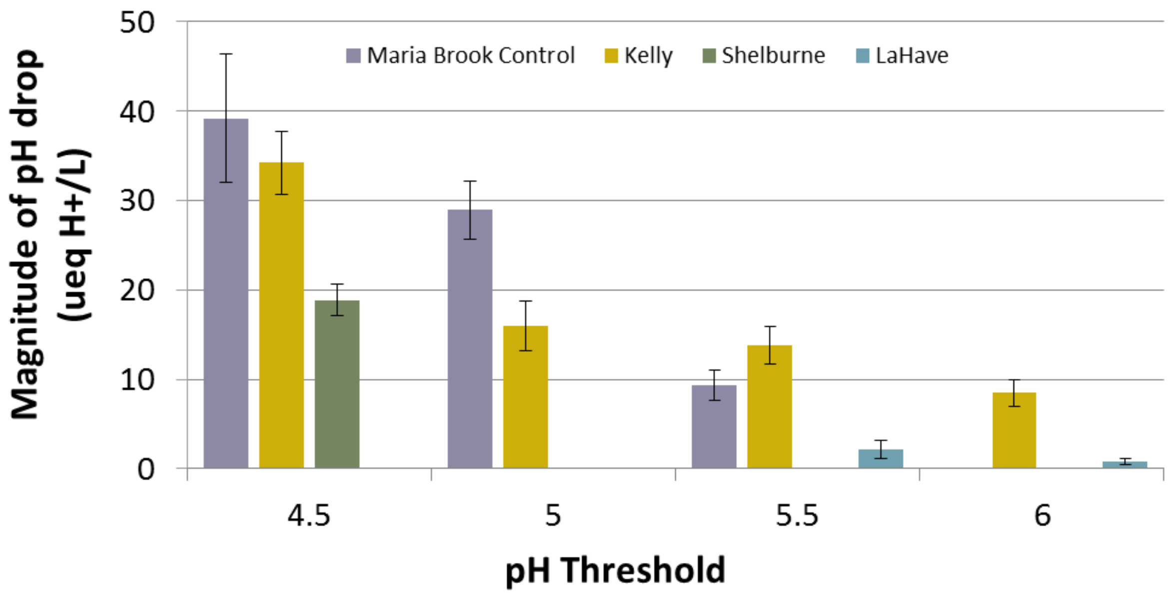

Figure 6. The average change in hydrogen ion concentrations during an AE. Error bars represent standard error.

Episode frequencies found in this study were much higher in comparison to the previous acid episode study in Nova Scotia using weekly data in KNP streams by Clair et al. (2001) which predicted probabilities of 4 significant pH events per year. This difference in episode frequency is likely a function of having higher frequency data collection for this study as well as a more inclusive definition of acid episodes.

In comparison to the study by Mauney (2009) in the Southern Appalachians, Maria Brook and Kelly River experienced longer episodes on average and more frequent episodes occurring below the pH 5.0 threshold. Mauney (2009) found that for a small first order catchments episodes duration ranged from 0.2 to 6.55 days with 17 episodes below pH 5.5 for greater than 24 hours but only 4 episodes occurring below pH 5.0 for greater than 24 hours. This higher episode frequency, duration, and severity compared to the findings of Mauney (2009) is likely due to the very low ANC in all of the catchments in this study with ANC values less than 7 µeq/L (Fig. 1) and the streams in GSMR streams having ANC values of approximately 50 to 200 µeq/L.

The difference in episode frequency, duration, and severity seen between streams is mainly a function of the acidification of the streams as measured by mean pH. This trend suggests that mean pH could be sufficient for determining stream health. Although, in KR annual pH is 5.5 but frequent episodes still occur and are similar to that of MB with a mean annual pH of 5.2. A larger sample size of streams would be needed to determine the impacts of catchment characteristics on acid episode behavior of similarly acidified catchments.

4.2 Episode Response to Meteorological Conditions

For all sites, stage increase is a strong predictor of pH response during an acid episode with R-squared values of 50.4 % (LR) to 81.1% (MB) (Table 5). However, the residuals for these relationships are non-parametric and therefore the relations may not be as strong as predicted by standard linear regression. Maximum stage is a weaker predictor of pH response during an acid episode with R-squared values of 20.6% (KR) to 65.6% (MB) (Table 5). Although weak, a positive relationship is seen between the time since the last episode occurred and how severe the episode is in terms of pH change with R-squared values of 6.4% (SR) to 45.9% (MB) (Table 5).

Table 5. Standard linear regression analysis of acid episode pH response for the predictors of episode stage increase (m), maximum stage during the episode (m), and the time since the last episode (TSLE) in hours. Maria Brook was analyzed using the control site due to the treatment site not having a complete set of stage data.

Site	Predictor	N	SLR Equation	R-squared
Kelly River	Stage increase (m)	431	pH change = 0.229 + 1.28 Stage increase	51.2%
	Maximum stage (m)	459	pH change = - 0.429 + 0.802 Max stage	20.6%
	Time since last episode (hours)	425	pH change = 0.404 + 0.000421 TSLE	38.8%
LaHave River	Stage increase (m)	235	pH change = 0.168 + 0.444 Stage increase	50.4%
	Maximum stage (m)	237	pH change = - 0.331 + 0.254 Max Stage	29.1%
	Time since last episode (hours)	339	pH change = 0.233 + 0.000174 TSLE	28.2%
Shelburne River	Stage increase (m)	88	pH change = 0.0767 + 0.397 Stage increase	65.6%
	Maximum stage (m)	88	pH change = - 0.125 + 0.363 Max stage	61.8%
	Time since last episode (hours)	84	pH change = 0.165 + 0.000086 TSLE	6.4%
Maria Brook (Control)	Stage increase (m)	99	pH change = 0.0755 + 2.76 Stage increase	81.1%
	Maximum stage (m)	99	pH change = - 0.409 + 2.41 Max stage	65.6%
	Time since last episode (hours)	90	pH change = 0.292 + 0.000964 TSLE	45.9%

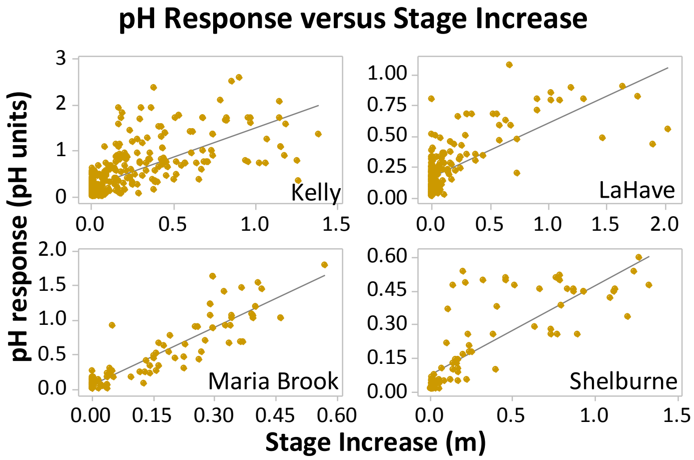

Figure 7. Linear regression fit of acid episode pH response (pH units) plotted against episode stage increase (meters) for each of the streams with high-frequency measurements.

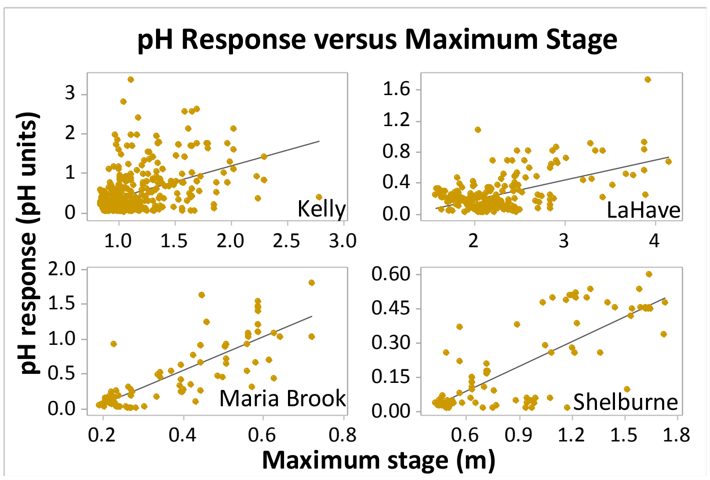

Figure 8. Linear regression fit of acid episode pH response (pH units) plotted against maximum stage during the episode (meters) for each of the streams with high-frequency measurements.

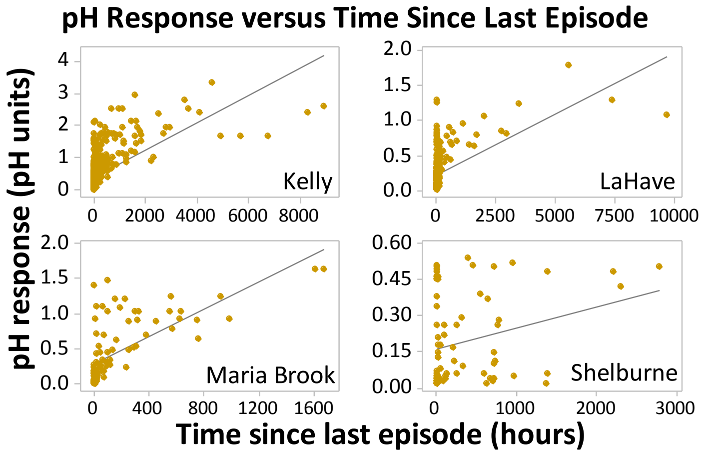

Figure 9. Linear regression fit of acid episode pH response (pH units) plotted against the time since the last episode (hours) for each of the streams with high-frequency measurements.

The results of these regression analyses of pH response are comparable to the results from the analysis done by Deyton et al. (2009) in GSMR which found strong positive relations between the magnitude of pH episode drops and maximum episode discharge as well as the number of "dry days". The parameter "dry days" was measured as the baseflow period between storm hydrographs whereas this study used the time between episodes crossing the pH threshold as a proxy for "dry days". In the study by Deyton et al. (2009), a stronger relationship was found for episode pH response and the number of "dry days" than for this study. The hypothesis to explain the relationship between preceding dry days and episode pH response given by Deyton et al. (2009) is that during long dry periods, dry deposition of sulphate and nitrate builds up giving rise to a large flush out of acids from the soil and forest canopy during the next storm event. The much weaker relationship seen in this study may be attributed to a lesser amount of dry acid deposition between storm events as well as an on average shorter period between episodes due to frequent precipitation.

The difference in the strength of the pH response relationship to stage change between the streams may be attributed to catchment size. The smallest catchment, MB, had the strongest relationship between pH response and stage change (R-squared of 81.1%) whereas the largest catchment, SR, had the weakest pH-stage relationship (R-squared of 51.4%). A study of three basins in KNP by Clair et al. (2001) found the opposite phenomenon with the largest catchment, Mersey River, had a more predictable pH to discharge relationship and the weakest correlation was found for the smallest catchment, Pine Marten Brook. Clair et al. (2001) hypothesized that this difference could be attributed to a smoothing effect due to the multiple basins flowing into the Mersey River. Based on the results in this study, I hypothesize that the multiplicity of basins flowing into the larger streams may make pH response to meteorological conditions more variable due to biogeochemical reactions in each tributary affecting the larger stream chemistry. The stronger relationship between stage and episode pH response for small catchment may also be due to less time for run-off interaction with soils in smaller catchments resulting in acid response being more directly related to stream discharge increases (Mauney 2008). These hypothesis fits with the results by Mauney (2009) which found it was easier to predict acid episode duration and frequency for smaller streams. Although, given these two opposing hypothesis it may be possible that depending on the characteristics of the basins flowing into a stream, a higher order stream may experience increased or decreased variability in pH in relation to stream flow. More research is needed to determine the effect of catchment size, as well as other factors such as slope, soils, presence of wetlands and lakes, and geology, on episode variability with stream discharge increase.

4.3 Impact of Catchment Liming

Despite an increase in limestone application from 27 tonnes applied in May 2012 to 60 tonnes applied in July 2013, acid episodes following the 2013 application exhibited less of difference in pH drop between the upstream control site and downstream treatment site than following the 2012 application (Fig. 10). However, analyzing all acid episodes from 2012 to 2013 (at a significance level of $\alpha = 0.05$) reveals that there is a significant difference between the control and treatment site for the minimum pH reached during an episode (p-value <0.001), the magnitude of the pH drop from maximum to minimum in μ equivalents of H^+ per liter (p-value 0.007), and a weakly significant difference for the duration in hours spent below each threshold (4.5 or 5) during an episode (p-value 0.060) (Table 5). On average, the episode minimum pH at the treatment site is 0.18 pH units higher than at the control site and the episode magnitude of pH drop is lower by 9.77 μeq H^+/L (Table 5). The mean difference in episode duration at between the treatment and control is 77.2 hours (3.2 days) which for *Salmo Salar* could be considered a significant reduction in acidity exposure time (Table 5; Nilsen et al., 2013).

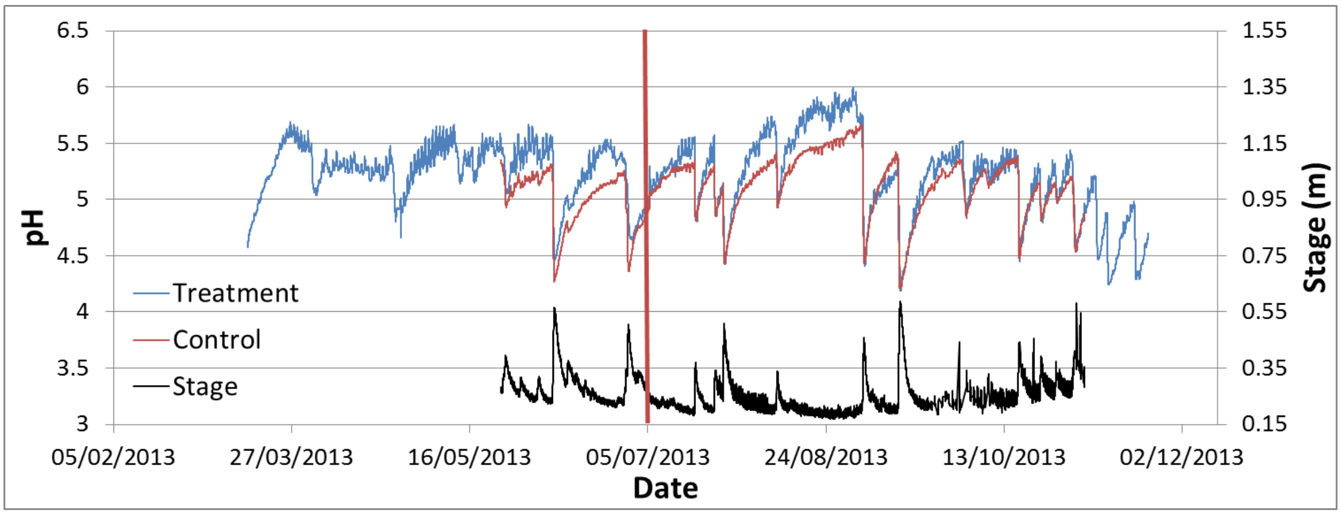

Figure 10. Time series of Maria Brook pH levels for March 2013 to November 2013. The treatment site series is in blue and the control site series is in red. The red line indicates the second liming application in July 2013.

Table 5. A paired t-test of acid episode parameters to compare the control site and treatment site). The parameters include: the duration in hours spent below each threshold (4.5 or 5) during an episode, the minimum pH reached during and episode, and the magnitude of the pH drop from maximum to minimum (μeq H^+/L**).**

Parameter	N	P-value	Mean Difference	Site	Mean	Standard Error
Episode duration (hours) below threshold	18	0.060	77.2	CMEMP	133.8	45.8
				DMEMP	56.6	11.4
Minimum pH	27	<0.001	-0.18	CMEMP	4.4841	0.0520
				DMEMP	4.6678	0.0435
Magnitude of pH drop (μeq H^+/L)	27	0.007	9.77	CMEMP	29.24	3.84
				DMEMP	19.47	2.56

4.4 Annual and Seasonal Variation

For all sites, acid episodes occurred throughout the year and were not exclusive to particular seasons. In general, episode frequency tended to be greatest in the winter and the summer and interestingly the spring episodes tended to be least frequent despite this being rainy season with snowmelt episodes. At MB episodes occurred most frequently in the Fall and Summer with an average of 5.0 ± 1 episode per year and 8.0 ± 2 episodes per season in occurring in the Fall season below for the pH 5.0 threshold at the MB treatment and control site respectively (Fig. 11). However it should be noted that there is incomplete data for the spring and winter seasons for MB which means some episodes were likely missed for these seasons (Appendix 2). In LR episodes were most frequent during the winter season, with an average of 5.9 ± 1 episodes per season, and summer season, with an average of 3.8 ± 2 episodes per season for episodes below the pH 6 threshold (Fig. 11). In SR episodes were most frequent during the summer with an average of 2.8 ± 1 episodes per season (Fig. 11). For KR episodes for the pH

5.5 and 6 thresholds are most frequent in the summer with frequencies of 1.7 ± 0 and 2.7 ± 1 episode per season respectively. Episodes below the pH 5 thresholds for KR are most frequent in the winter with 3.6 ± 1 episodes per season, and episodes below the pH 4.5 threshold are most frequent in the fall with 1.0 ± 1 episodes per season (Fig. 11).

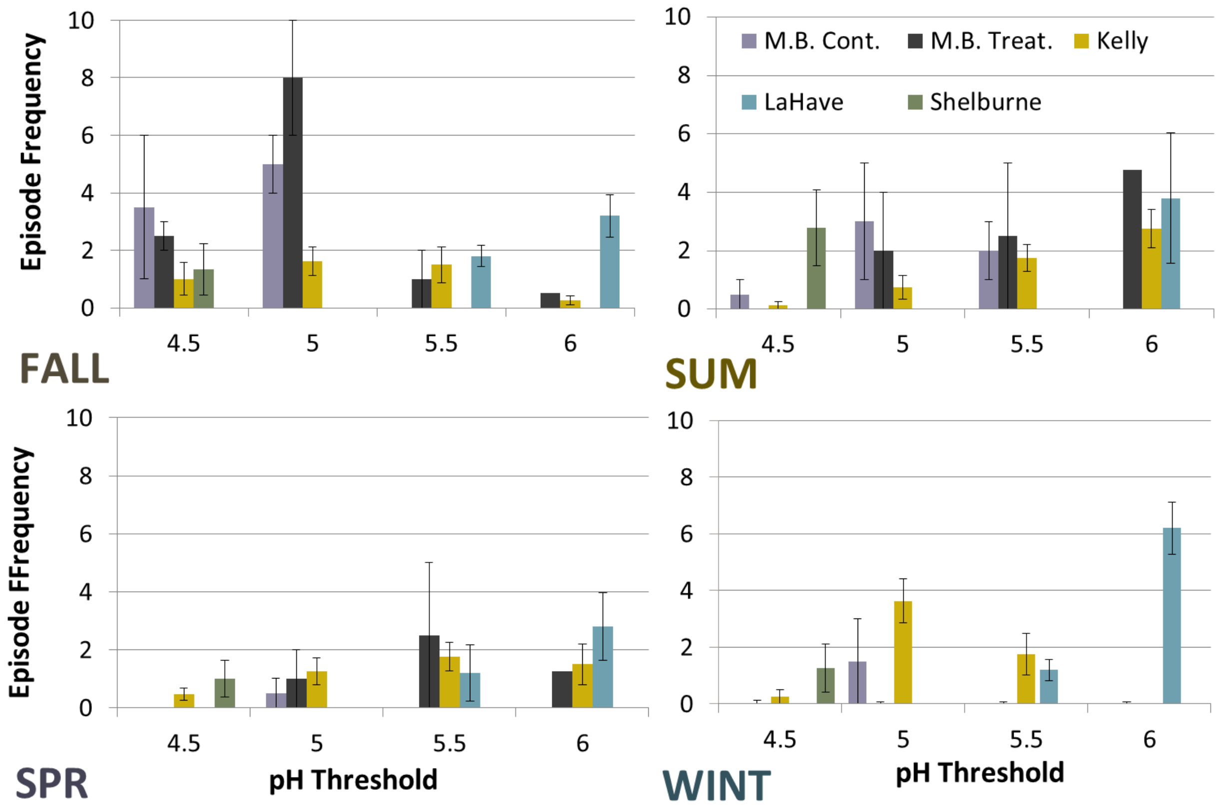

Figure 11. The seasonal average frequency of episodes longer than 24 hours for each stream and pH threshold. Error bars represent standard error.

The proportion of a season spent below each threshold is highly variable from year-to-year however in general the spring, winter, and fall seasons have the greatest proportion of the year below each threshold (Fig. 12). This is consistent with the higher precipitation in Nova Scotia during these seasons. Some error is introduced into this analysis for long episodes below the higher pH thresholds which can span multiple seasons. Episodes were categorized into seasons based on the date of the episode upcross above the threshold (or the end of the episode). Therefore, the higher proportion of the summer season below the 5.5 and 6.0 thresholds seen for MB and KR is due to episodes beginning in the spring, during snowmelt and high precipitation, and ending in the summer as the pH recovers (Fig. 12). This error influences the proportion of the winter season below the pH 6 threshold in KR which is low because some episodes beginning winter are not recovering to above the pH 6 threshold until the spring. Maria Brook also has uncharacteristically low spring episode proportions due to data gaps during the spring (Fig. 11; Appendix 2). The results of the analysis for the proportion of the season below each threshold shows that although spring episodes are less frequent they tend to have longer durations.

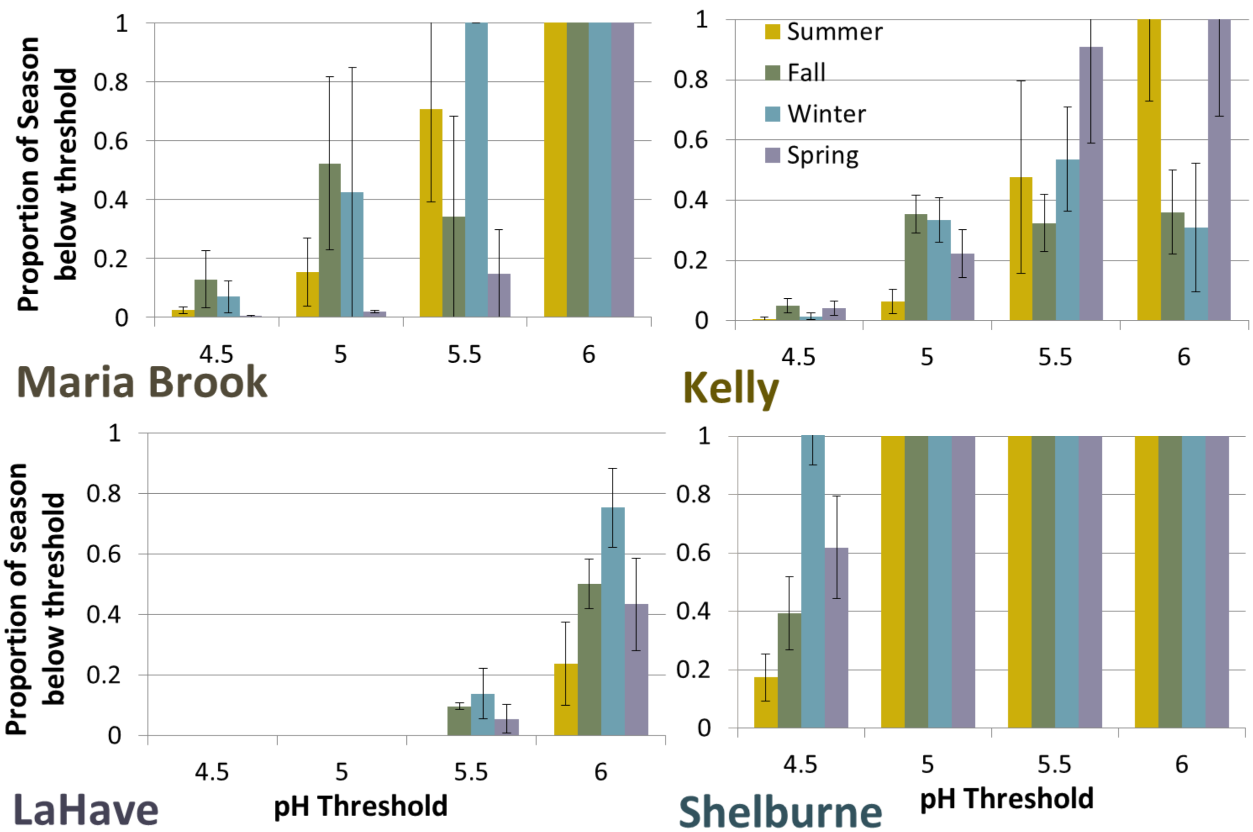

Figure 13. The proportion of each season for which the stream pH was below the threshold. Error bars represent standard error.

Overall, these results are similar to those found by Clair et al. (2001) in KNP with seasonal episode frequency varying from year-to-year and stream-to-stream but generally with longer episodes in the winter and spring and with frequent but short episodes in the summer. The shorter but more frequent summer episodes may be due to high baseflow pH in the summer resulting in shorter recovery times for episodes where as in the spring stream pH is consistently low due to snowmelt and frequent precipitation leaving little time for pH recovery between episodes. The implications for the health of *Salmo Salar* are that severe episodes are long lasting during the acid sensitive spring smoltification period with 90.8 ± 32 % of the spring season in KR being below the biological threshold of pH 5.5 despite higher pH levels during the rest of the year.

5.0 Conclusion and Recommendations

Using a novel method for characterizing acid episode behavior episodes below the biological toxicity threshold of pH 5.5 were found to be more frequent and occurring at longer durations than previous studies in NS and in other locations have found. Although the results suggest that mean pH may be a predictor of the extent of episodic acidification there is still a lot to be learned from analyzing high-frequency data for acid episodes including a better understanding of stream biota exposure to acidity levels on an annual and seasonal basis. Using average annual pH as an indicator stream health can be misleading because streams with pH levels at or above the limit for toxicity, such as Kelly River, still exhibit severe acid episodes and acidity exposure can be high in the spring during the most sensitive life stage of *Salmo Salar*. However, further studies are needed to determine whether a metric either than average annual pH, which captures seasonal and year-to-year pH variations, should be used as an indicator of stream health and impacts to *Salmo Salar* for developing appropriate mitigation plans.

The baseline characterization of frequency, duration, and severity of acid episodes in this study can be connected to bioassay studies of acid exposure to *Salmo Salar* in order to more accurately determine episode impacts on salmon health. Further analysis should be done to determine Al_i exposure during acid episodes of varying severity and duration. For Maria Brook and Kelly River, the greatest proportion of the year is spent below the pH 5.5 threshold which may suggest that Al_i rather than acidity the main cause of episode toxicity in these streams, given that Al_i toxicity dominates in the pH 4.8 to 5.5 range, but more research based on Al_i concentrations during episodes would be needed.

From the results, a few hypotheses were developed to explain the differences in acid episode behavior between catchments:

1. Smaller catchments have stronger relationships between stage and episode pH response and this may be attributed to less time for soil interaction during run-off events as well as the multiplicity of basins flowing into larger streams resulting in more variation in pH response due to biogeochemical reactions effecting pH occurring in each tributary of the stream;
2. Smaller catchments have more frequent episodes with more severe pH drops which may be, again, attributed to less soil interaction during run-off resulting in less buffering of run-off acidity.

Catchment liming in Maria Brook was found to reduce the length of acid episodes although continued research will be needed to determine the whether catchment liming can reduce episodic acidification over the long-term. The methodology developed in this study can be expanded to a greater spatial range of streams in order to explore these hypotheses further and compare the impact of other catchment characteristics and catchment liming on acid episode behaviour.

The difficulties encountered throughout this research project in analyzing large volumes high-frequency data highlights the importance of continuing to develop methodology for extracting meaningful analysis of episodic acidification from valuable continuous stream monitoring. The R-programming used in this project can be further developed in order to make it more user-friendly as a tool for researchers and decision makers involved in monitoring stream acidification.

Future research should include a long-term analysis of acid episode behavior in streams to determine whether there are any trends and relate changes in acid episode behavior to changes in weather patterns and acid deposition. It is important to continue long-term monitoring of acid episodes at sites which continue to be acidified and those which are recovering due to the potential interaction between episodic acidification and climate change (Laudon, 2007).

6.0 Acknowledgements

I would like to thank my supervisor, Dr. Shannon Sterling, for all the assistance and valuable feedback throughout this project. I would also like to thank Dr. Tarah Wright who helped with developing my thesis proposal as the undergraduate honours course coordinator.

Special thanks to Sarah Ambrose, who wrote and helped with the R-programming, and to everyone else in the Hydrologic Research Group at Dalhousie University for collecting and managing the Maria Brook continuous data and for the occasional help locating information for my project.

Finally, thanks to Nova Scotia Environment for sharing the data used in this project as well as Kevin Garroway who was my main contact at NSE and provided valuable feedback on the final thesis and presentation.

7.0 References

Aherne, J., Dillon, P., & Cosby, B. (2003). Acidification and recovery of aquatic ecosystems in south central ontario, canada: Regional application of the MAGIC model. *Hydrology and Earth System Sciences Discussions, 7*(4), 561-573.

Alewell, C., Manderscheid, B., Meesenburg, H., & Bittersohl, J. (2000). Environmental chemistry: Is acidification still an ecological threat? *Nature, 407*(6806), 856-857.

Angelidis, C., Armstrong, Biagi, K. M., M., Sterling, S., Clair, T. A., and Breen, A. (2012). Catchment liming to protect Atlantic Salmon in Nova Scotia – approaches needed and knowledge gained. *Hydrology and Earth System Sciences. In Progress.*

Automated surface water quality monitoring program | surface water | Nova Scotia environment Retrieved 11/25/2013, 2013, from http://www.novascotia.ca/nse/surface.water/automatedqualitymonitoring.asp

Beier, C., Moldan, F., & Wright, R. F. (2003). Terrestrial ecosystem recovery-modelling the effects of reduced acidic inputs and increased inputs of sea-salts induced by global change. *AMBIO: A Journal of the Human Environment, 32*(4), 275-282.

Bonjean, M. C., Hutchins, M., & Neal, C. (2007). Acid episodes in the Allt A'mharcaidh, Scotland: An investigation based on sub-hourly monitoring data and climatic patterns. *Hydrology and Earth System Sciences Discussions, 11*(1), 340-355.

Bowlby, H., Gibson, A., & Levy, A. (2013). Recovery potential assessment for southern upland Atlantic Salmon: Status, past and present abundance, life history and trends. *Fisheries and Oceans Canada. Canadian Science Advisory Secretariat Research Document, 5*

Clair, T. A., Bobba, A. G., & Miller, K. (2001). Yearly changes in the seasonal frequency and duration of short-term acid pulses in some nova scotia, Canada streams. *Environmental Geology, 40*(4-5), 582-591.

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

Clair, T. A., Dennis, I. F., Vet, R., & Weyhenmeyer, G. (2011). Water chemistry and dissolved organic carbon trends in lakes from Canada's Atlantic provinces: No recovery from acidification measured after 25 years of lake monitoring. *Canadian Journal of Fisheries and Aquatic Sciences, 68*(4), 663-674.

Christensen, J.H., Krishna Kumar, K., Aldrian, E., An, S. I., Cavalcanti, I.F.A., … Zhou, T. (2013). Climate Phenomena and their Relevance for Future Regional Climate Change. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Davies, T.D., Tranter, M., Wigington, P.J. and Eshleman, K. (1992).Acidic episodes in surface waters in Europe. *Journal of Hydrology, 132, 25-69.*

Dennis, I. F., Clair, T. A., & Kidd, K. (2012). The distribution of dissolved aluminum in Atlantic Salmon (Salmo salar) rivers of Atlantic Canada and its potential effect on aquatic populations. *Canadian Journal of Fisheries and Aquatic Sciences, 69*(7), 1174-1183.

Deviney, F. A., Rice, K. C., & Hornberger, G. M. (2006). Time series and recurrence interval models to predict the vulnerability of streams to episodic acidification in Shenandoah National Park, Virginia. American Geophysical Union, 2000 Florida Ave., N.W. Washington DC 20009 USA, Retrieved from http://search.proquest.com/docview/20994565?accountid=10406

Deyton, E. B., Schwartz, J. S., Robinson, R. B., Neff, K. J., Moore, S. E., & Kulp, M. A. (2009). Characterizing episodic stream acidity during stormflows in the Great Smoky Mountains national park. *Water, Air, and Soil Pollution, 196*(1-4), 3-18.

Driscoll, C., & Likens, G. (1982). Hydrogen ion budget of an aggrading forested ecosystem. *Tellus, 34*(3), 283-292.

Erlandsson, M., Laudon, H., & Fölster, J. (2010). Spatiotemporal patterns of drivers of episodic acidification in Swedish streams and their relationships to hydrometeorological factors. *Science of the Total Environment, 408*(20), 4633-4643.

Feeley, H. B., Bruen, M., Blacklocke, S., & Kelly-Quinn, M. (2013). A regional examination of episodic acidification response to reduced acidic deposition and the influence of plantation forests in Irish headwater streams. *Science of the Total Environment*, *443*, 173-183.

Gibson, A. J. F., Bowlby, H. D., Hardie, D. C., & O'Reilly, P. T. (2011). Populations on the brink: Low abundance of southern upland Atlantic Salmon in Nova Scotia, Canada. *North American Journal of Fisheries Management*, *31*(4), 733-741.

Heath, R. H., Kahl, J. S., Norton, S. A., & Fernandez, I. J. (1992). Episodic stream acidification caused by atmospheric deposition of sea salts at Acadia National Park, Maine, united states. *Water Resources Research*, *28*(4), 1081-1088.

Huntington, T., Hooper, R., & Aulenbach, B. (1994). Hydrologic processes controlling sulphate mobility in a small forested watershed. *Water Resources Research*, *30*(2), 283-295.

Jarvie, H. e. P., Neal, C. o., Smart, R. i., Owen, R. o., Fraser, D. e., Forbes, I. a., & Wade, A. n. (2001). Use of continuous water quality records for hydrograph separation and to assess short-term variability and extremes in acidity and dissolved carbon dioxide for the River Dee, Scotland. *Science of the Total Environment, the, 265*(1-3), 85-97.

Kerekes, J., Freedman, B. (1989). Seasonal variations of water chemistry in oligotrophic streams and rivers in Kejimkujik National Park. Nova Scotia. *Wat. Air Soil Pollut*. 46: 131-144

Kerr, J., Eimers, M., Creed, I., Adams, M., Beall, F., Burns, D., . . . Courchesne, F. (2012). The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern USA. *Biogeochemistry, 111*(1-3), 393-409.

Kirchner, J. W., Feng, X., Neal, C., & Robson, A. J. (2004). The fine structure of water-quality dynamics: The (high-frequency) wave of the future. *Hydrological Processes, 18*(7), 1353-1359.

Kowalik, R. A., Cooper, D. M., Evans, C. D., & Ormerod, S. J. (2007). Acidic episodes retard the biological recovery of upland British streams from chronic acidification. *Global Change Biology, 13*(11), 2439-2452.

Kroglund, F., Finstad, B., Stefansson, S., Nilsen, T., Kristensen, T., Rosseland, B., . . . Salbu, B. (2007). Exposure to moderate acid water and aluminum reduces Atlantic Salmon post-smolt survival. *Aquaculture, 273*(2), 360-373.

Lacoul, P., Freedman, B. and Clair, T.: Effects of acidification on aquatic biota in Atlantic Canada, *Environmental Reviews*, 19: 429-460, 2011.

Lacroix, G. L. (1989). Ecological and physiological responses of Atlantic Salmon in acidic organic rivers of nova scotia, Canada. *Water, Air, and Soil Pollution, 46*(1-4), 375-386.

Lacroix, G. L., Peterson, R. H., Susan Belfry, C., & Martin-Robichaud, D. (1993). Aluminum dynamics on gills of Atlantic Salmon fry in the presence of citrate and effects on integrity of gill structures. *Aquatic Toxicology, 27*(3), 373-401.

Lacroix, G. L., & Knox, D. (2005). Acidification status of rivers in several regions of Nova Scotia and potential impacts on Atlantic Salmon. Fisheries & Oceans Canada, Science Branch, Biological Station. Retrieved from http://search.proquest.com/docview/189489581?accountid=10406

Laudon, H., & Bishop, K. (1999). Quantifying sources of acid neutralisation capacity depression during spring flood episodes in northern Sweden. *Environmental Pollution, 105*(3), 427-435.

Laudon, H. (2007). Recovery from episodic acidification delayed by drought and high sea salt deposition. *Hydrology and Earth System Sciences Discussions, 4*(5), 2975-2996.

Laudon, H., Clair, T. A., & Hemond, H. F. (2002). Long-term response in episodic acidification to declining SO< sub> 4</sub>< sup> 2</sup> deposition in two streams in Nova Scotia. *Hydrology and Earth System Sciences Discussions, 6*(4), 773-781.

Laudon, H., Westling, O., & Bishop, K. (2000). Cause of pH decline in stream water during spring melt runoff in northern Sweden. *Canadian Journal of Fisheries and Aquatic Sciences, 57*(9), 1888-1900.

Lawrence, G. (2002). Persistent episodic acidification of streams linked to acid rain effects on soil. *Atmospheric Environment, 36*(10), 1589-1598.

Magee, J. A., Obedzinski, M., McCormick, S. D., & Kocik, J. F. (2003). Effects of episodic acidification on Atlantic Salmon (Salmo salar) smolts. *Canadian Journal of Fisheries and Aquatic Sciences, 60*(2), 214-221. Retrieved from http://search.proquest.com/docview/219284009?accountid=10406

Mant, R. C., Jones, D. L., Reynolds, B., Ormerod, S. J., & Pullin, A. S. (2013). A systematic review of the effectiveness of liming to mitigate impacts of river acidification on fish and macro-invertebrates. *Environmental Pollution, 179*, 285-293.

Mauney III, J. L. (2009). Characterizing episodic stream acidification using a concentration-duration-frequency methodology in watersheds of the Great Smoky Mountains national park. *Masters Theses, University of Tennessee*. Retrieved from: http://trace.tennessee.edu/utk_gradthes/544

Monette, M. Y., & McCormick, S. D. (2008). Impacts of short-term acid and aluminum exposure on Atlantic Salmon (Salmo salar) physiology: A direct comparison of parr and smolts. *Aquatic Toxicology, 86*(2), 216-226.

Nilsen, T. O., Ebbesson, L. O. E., Handeland, S. O., Kroglund, F., Finstad, B., Angotzi, A. R., & Stefansson, S. O. (2013). Atlantic Salmon(Salmo salar L.) smolts require more than two weeks to recover from acidic water and aluminum exposure. *Aquatic Toxicology, 142–143*(0), 33-44. doi:http://dx.doi.org/10.1016/j.aquatox.2013.07.016

Neff, K. J., Schwartz, J. S., Moore, S. E., & Kulp, M. A. (2012). Influence of basin characteristics on baseflow and stormflow chemistry in the Great Smoky Mountains national park, USA. *Hydrological Processes, 27*(14), 2061-2074.

Robinson, R. B., & Roby, J. C. (2006). Concentration–Duration–Frequency curves for pH in a stream in the Great Smoky Mountains. *Journal of Environmental Engineering, 132*(12), 1600-1605.

Sandøy, S., & Langåker, R. (2001). Atlantic Salmon and acidification in southern Norway: A disaster in the 20th century, but a hope for the future? *Water, Air, and Soil Pollution, 130*(1-4), 1343-1348.

Skjelkvåle, B., Stoddard, J., Jeffries, D., Tørseth, K., Høgåsen, T., Bowman, J., . . . Rogora, M. (2005). Regional scale evidence for improvements in surface water chemistry 1990–2001. *Environmental Pollution, 137*(1), 165-176.

Staurnes, M., Kroglund, F., & Rosseland, B. (1995). Water quality requirement of Atlantic Salmon (Salmo salar) in water undergoing acidification or liming in Norway. *Water, Air, and Soil Pollution, 85*(2), 347-352.

Stoddard, J. L., Jeffries, D., Lükewille, A., Clair, T., Dillon, P., Driscoll, C., . . . Kellogg, J. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature, 401*(6753), 575-578.

Watt, W. (1987). A summary of the impact of acid rain on Atlantic Salmon (Salmo salar) in Canada. *Water, Air, and Soil Pollution, 35*(1-2), 27-35.

Watt, W., Scott, C., Zamora, P., & White, W. (2000). Acid toxicity levels in Nova Scotian rivers have not declined in synchrony with the decline in sulphate levels. *Water, Air, and Soil Pollution, 118*(3-4), 203-229.

Weatherley, N., & Ormerod, S. (1991). The importance of acid episodes in determining faunal distributions in welsh streams. *Freshwater Biology, 25*(1), 71-84.

Wellington, B. I., & Driscoll, C. T. (2004). The episodic acidification of a stream with elevated concentrations of dissolved organic carbon. *Hydrological Processes, 18*(14), 2663-2680.

Whitfield, C. J., Aherne, J., Watmough, S. A., Dillon, P. J., & Clair, T. A. (2006). Recovery from acidification in Nova Scotia: Temporal trends and critical loads for 20 headwater lakes. *Canadian Journal of Fisheries and Aquatic Sciences, 63*(7), 1504-1514. Retrieved from http://search.proquest.com/docview/219345620?accountid=10406

Whitfield, C. J., Aherne, J., Dillon, P. J. and Watmough, S. A. (2007). Modelling acidification, recovery and target loads for headwater catchments in Nova Scotia, Canada. *Hydrology and Earth System Sciences, 11(2), 951-963.*

Wilkinson, K. J., & Campbell, P. G. (1993). Aluminum bioconcentration at the gill surface of juvenile Atlantic Salmon in acidic media. *Environmental Toxicology and Chemistry, 12*(11), 2083-2095.

Wright, R. (2008). The decreasing importance of acidification episodes with recovery from acidification: An analysis of the 30-year record from Birkenes, Norway. *Hydrology and Earth System Sciences, 12*(2), 353-362.

8.0 Appendix 1: R Program to Collect Acid Episode Parameters

```
#Acid Episode Frequency Program
#January 28, 2014
#Created by Sarah Ambrose
#Edited by Maria Armstrong

# How to run this:
#1. Save the excel data as a csv file
#2. Change the working directory (where the data is stored) - this is line 17-20 (just select
one.make up your own)
#3. Change the name of the data you are reading (data1 = ....) line 24
#4. Change the output name of the results (line 259)

#This sets where the file you are reading is
#change this to where data is stored
#*********************************
setwd("C:\\Users\\Maria\\Desktop\\Thesis\\CSV data for program")

#Change the name to whatever file you need
#*****************************************

data1 = read.csv("KelleyRiverHourly.2008.csv", head = TRUE)
data1 = data1[-1,]

#Prints the first few lines of the data to check that it is being read correctly
head(data1)

data1 = as.data.frame(data1)

#This is for formatting columns

data1$pH = as.numeric(as.character(data1$pH))
data1$Stage = as.numeric(as.character(data1$Stage))
data1$Flow = as.numeric(as.character(data1$Flow))
data1$Date = as.character(data1$Date)
x = data1$Date
x_new = strptime(x, "%d/%m/%Y %k:%M")
x_new = format(x_new, "%Y-%m-%d %H:%M")
dont = TRUE
r = 0
i_down = c()
i_up = c()

#Below are the numbers used to represent each pH threshold
#6 = 1
#5.5 = 2
#5 = 3
#4.5 = 4
#4 = 5

#This declares the lists and vectors that are going to be used
o6 = c(NA,NA,NA,NA)
o5.5 = c(NA,NA,NA,NA)
o5 = c(NA,NA,NA,NA)
o4.5 = c(NA,NA,NA,NA)
o4 = c(NA,NA,NA,NA)
Down = c()
Up = c()
Min = c()
Max= c()
```

```
Min_time=  c()
Min_stage = c()
Min_stage_time = c()
Max_time = c()
Max_stage = c()
Max_stage_time = c()
Cross = c()
thresh = list()
old = c(1,1,1,1,1)
NA_down = c()
NA_up = c()

#This loops through each line of the data frame/row in excel
#dim(data1) gives the dimensions of the data frame, [1] gives the rows

for(i in 1:dim(data1)[1]){

  if(i==1){
  go = TRUE
             if(data1$pH[i]<=6  )  {
                    o6[1]  =  i
                    o6[3] = -1}
             if(data1$pH[i]<=5.5){
                    o5.5[1]=   i
                    o5.5[3] = -1}
             if(data1$pH[i]<=5 )   {
                    o5[1]  =   i
                    o5[3] = -1}
             if(data1$pH[i]<=4.5 ) {
                    o4.5[1]=   i
                    o4.5[3] = -1}
             if(data1$pH[i]<=4 )  {
                    o4[1]  =   i
                    o4[3] = -1}
             old = c(i,i,i,i,i)
             }
  #if the current value and previous value are not NA
  else if(is.na(data1$pH[i])==FALSE & is.na(data1$pH[i-1])==FALSE){

  go = TRUE
 # print("yes")
  #checks if it is above all thresholds
  #close out the 6 if above
  if(data1$pH[i]>6){
    if(data1$pH[i-1]<=6 & is.na(o6[2])==TRUE & is.na(o6[1])==FALSE){
      o6[2] = i
         o6[4] = 0
      }}

  if(data1$pH[i]<6 & data1$pH[i]>5.5){
    if(data1$pH[i-1]>=6 & is.na(o6[1])==TRUE & is.na(o6[1])==TRUE){
             o6[1] = i
             o6[3] = 0}
    else if(data1$pH[i-1]<=5.5 & is.na(o5.5[2])==TRUE & is.na(o5.5[1])==FALSE){
             o5.5[2] = i
             o5.5[4] = 0}}

    if(data1$pH[i]<5.5 & data1$pH[i]>5){
       print("ya")
      if(data1$pH[i-1]>=5.5 & is.na(o5.5[1])==TRUE & is.na(o5.5[2])==TRUE){
             o5.5[1] = i
             o5.5[3] = 0}
```

```
     else if(data1$pH[i-1]<=5 & is.na(o5[2])==TRUE & is.na(o5[1])==FALSE){
          o5[2] = i
          o5[4] = 0}}

   if(data1$pH[i]<5& data1$pH[i]>4.5){
     if(data1$pH[i-1]>=5 & is.na(o5[1])==TRUE & is.na(o5[2])==TRUE){
                o5[1] = i
                o5[3] = 0}
     else if(data1$pH[i-1]<=4.5 & is.na(o4.5[2])==TRUE  & is.na(o4.5[1])==FALSE){
                o4.5[2] = i
                o4.5[4] = 0} }

     if(data1$pH[i]<4.5 & data1$pH[i]>4){
       if(data1$pH[i-1]>=4.5 & is.na(o4.5[1])==TRUE & is.na(o4.5[2])==TRUE){
                o4.5[1] = i
                o4.5[3] = 0}
       else if(data1$pH[i-1]<=5 & is.na(o4[2])==TRUE  & is.na(o4[1])==FALSE){
                o4[2] = i
                o4[4] = 0} }

       if(data1$pH[i]<4 & is.na(data1$pH[i]) == FALSE){
         if(data1$pH[i-1]>=4 & is.na(o4[1])==TRUE){
                        o4[1] = i
                        o4[3] = 0} }
                #Checks if this is the last values - then closes out loops
          if(i == dim(data1)[1]){
                if(data1$pH[i]<=6){
                        o6[2] = i
                        o6[4] = 1
                        if(data1$pH[i]<=5.5 ){
                                o5.5[2] = i
                                o5.5[4] = 1
                                if(data1$pH[i]<=5){
                                        o5[2] = i
                                        o5[4] = 1
                                        if(data1$pH[i]<=4.5){
                                                o4.5[2] = i
                                                o4.5[4] = 1
                                                if(data1$pH[i]<=4 ){
                                                        o4[2] = i
                                                        o4[4] = 1
          }}}}}}
      }

#Previous value NA, current value is NOT NA
else if(is.na(data1$pH[i])==FALSE & is.na(data1$pH[i-1])==TRUE) {
   go = TRUE
          if(data1$pH[i]<6 )  {
                o6[1]  =  i
                o6[3] = -1}
          if(data1$pH[i]<5.5 ){
                o5.5[1]=   i
                o5.5[3] = -1}
          if(data1$pH[i]<5)   {
                o5[1]  =   i
                o5[3] = -1}
          if(data1$pH[i]<4.5) {
                o4.5[1]=   i
                o4.5[3] = -1}
          if(data1$pH[i]<4 )  {
                o4[1]  =   i
                o4[3] = -1}
          old = c(i,i,i,i,i)
```

```
          }

    #This is where the value is NA
    #closes out the values if the previous value was NOT NA, current value IS NA
      else if(is.na(data1$pH[i-1])==FALSE & is.na(data1$pH[i])==TRUE){
      go = TRUE
    #has to close out any open intervals
            #print("Here")
        if(data1$pH[i-1]<=6){
         o6[2] = i-1
             o6[4] = 1
         if(data1$pH[i-1]<=5.5 ){
           o5.5[2] = i-1
                 o5.5[4] = 1
           if(data1$pH[i-1]<=5){
             o5[2] = i-1
                   o5[4] = 1
             if(data1$pH[i-1]<=4.5){
               o4.5[2] = i-1
                       o4.5[4] = 1
               if(data1$pH[i-1]<=4 ){
                 o4[2] = i-1
                         o4[4] = 1
         }}}}}
     }
      else{
          go = FALSE}

if(go == TRUE){
  thresh[[1]] = o6
  thresh[[2]] = o5.5
  thresh[[3]] = o5
  thresh[[4]] = o4.5
  thresh[[5]] = o4
  thresh[[6]] = c(1,2,3,4)

  for(k in 1:5){

  if(length(thresh[[k]]) ==4){
    if (is.na(thresh[[k]][1]) == FALSE & is.na(thresh[[k]][2]) == FALSE &
is.na(thresh[[k]][3]) == FALSE & is.na(thresh[[k]][4]) == FALSE) {
             print(k)
             #print(thresh[[k]])
             r = r+1
      # get the first and last time
      dp = thresh[[k]][1]
      up = thresh[[k]][2]


      Down[r] = x_new[dp]
           Up[r] = x_new[up]

      min_df = data1[dp:up,]
      max_df = data1[old[k]:dp,]

      #Determines min and max pH for each episode
      min_vals = min_df[min_df$pH == min(min_df$pH),]
      max_vals = max_df[max_df$pH == max(max_df$pH),]

      #Determines min and max stage or flow for each episode
      min_stage = max_df[max_df$Stage == min(max_df$Stage),]
      max_stage = min_df[min_df$Stage == max(min_df$Stage),]
```

```
      Min[r] = min_vals[1,]$pH
      Max[r] = max_vals[1,]$pH
      Min_stage[r] = min_stage[1,]$Stage
      Max_stage[r] = max_stage[1,]$Stage

# Can be uncommented to use for flow
#      min_stage = max_df[max_df$Flow == min(max_df$Flow),]
#      max_stage = min_df[min_df$Flow == max(min_df$Flow),]
#
#      Min[r] = min_vals[1,]$pH
#      Max[r] = max_vals[1,]$pH
#      Min_stage[r] = min_stage[1,]$Flow
#      Max_stage[r] = max_stage[1,]$Flow

       #Determines the time at which the min/max occured

      Min_time[r] = x_new[as.numeric(rownames(min_vals[1,]))-1]

      Min_stage_time[r] = x_new[as.numeric(rownames(min_stage[1,]))-1]

      Max_time[r] =  x_new[as.numeric(rownames(max_vals[1,]))-1]

      Max_stage_time[r] = x_new[as.numeric(rownames(max_stage[1,]))-1]

         i_down[r] = dp
         i_up[r] = up
      Cross[r] = k
         NA_down[r] = thresh[[k]][3]
      NA_up[r] = thresh[[k]][4]
         #place the up value as old
         old[k] = up

      if (k ==1){
        o6 = c(NA,NA,NA,NA)}
        else if(k ==2){
        o5.5 = c(NA,NA,NA,NA)}
        else if(k ==3){
        o5 = c(NA,NA,NA,NA)}
        else if(k ==4){
        o4.5 = c(NA,NA,NA,NA)}
        else{
        o4 = c(NA,NA,NA,NA)}
             }

             }}

         }}

X = data.frame(Cross =Cross,Down = Down, Up = Up, Min = Min, Max = Max, Min_time = Min_time,
Max_time = Max_time,
  Min_stage = Min_stage, Min_stage_time = Min_stage_time, Max_stage =Max_stage,
Max_stage_time = Max_stage_time, NAs_down = NA_down, NA_up = NA_up)

#The file will save to the same place it is read from
write.csv(X, file = "KelleyRiverHourly.2008.R_Workup.csv")

#The last two columns indicate if NA values were used for starting or ending this acidic
episode
# The column NAs_down indicates if an NA was used to open the interval. -1 means yes,0 means
no, start means the start of the program
#The column NA_up indicated is an NA was used to close and episode. 1 means yes, and NA
values closed the episode, and 0 means no.
```

9.0 Appendix 2: Data Gaps

Site	Parameter	Start of Data Gap	End of Data Gap	Total Days
Kelly River	pH	18/03/2005 0:00	04/05/2005 23:00	48.0
		08/03/2007 3:00	20/03/2007 14:00	12.5
		26/01/2009 15:00	28/01/2009 17:00	2.1
		02/03/2009 18:00	06/03/2009 23:00	4.2
		18/04/2009 15:00	24/04/2009 11:00	5.8
		06/12/2008 3:00	07/12/2008 8:00	1.2
		12/02/2011 11:00	01/03/2011 10:00	17.0
		03/01/2009 12:00	05/01/2009 0:00	1.5
LaHave River	pH	22/09/2009 11:00	22/09/2009 23:00	0.5
		15/02/2011 3:00	15/02/2011 16:00	0.5
		19/02/2011 0:00	27/02/2011 0:00	8.0
		01/03/2011 0:00	01/03/2011 23:00	1.0
		02/03/2011 15:00	04/03/2011 20:00	2.2
		05/03/2011 10:00	04/04/2011 9:00	30.0
		07/04/2011 21:00	11/04/2011 21:00	4.0
		12/04/2011 10:00	13/04/2011 11:00	1.0
		13/04/2011 16:00	14/04/2011 0:00	0.3
		30/04/2011 10:00	12/05/2011 15:00	12.2
		19/05/2011 22:00	26/05/2011 11:00	6.5
		15/11/2011 13:00	02/12/2011 13:00	17.0
		27/11/2002 14:00	10/07/2003 13:00	225.0
		22/06/2004 11:00	07/03/2005 3:00	257.7
Shelburne River	pH	25/12/2005 5:00	26/12/2005 8:00	1.1
		07/09/2006 12:00	11/09/2006 23:00	4.5
		16/11/2006 1:00	20/11/2006 16:00	4.6
		01/09/2007 21:00	07/09/2007 9:00	5.5
		02/12/2007 10:00	06/12/2007 14:00	4.2
		13/01/2009 9:00	15/01/2009 12:00	2.1
		19/01/2009 14:00	26/01/2009 13:00	7.0
Maria Brook Control	pH, Stage	17/04/2012	02/05/2012	15.0
		14/03/2013	24/05/2013	71.0
		30/09/2013	02/10/2013	2.0
Maria Brook Treatment	pH	27/11/2012	14/03/2013	107.0

10.0 Appendix 3: Annual Episode Duration and Frequency

Stream	Year	Cross	Total Duration Below Threshold	Proportion of Year Below Threshold	< 24	< 1 week	< 4 weeks	> 4 weeks	> 24
MB Control	2012	4.5	794	0.09	2	13	0	0	12
MB Control	2013	4.5	207	0.02	5	4	0	0	2
MB Control	2012	5	1908	0.22	4	3	2	1	6
MB Control	2013	5	3001	0.34	4	11	3	1	15
MB Control	2012	5.5	1513	0.17	32	4	2	0	5
MB Control	2013	5.5	8299.5	0.95	5	0	0	3	3
MB Treatment	2012	4.5	109	0.01	2	2	0	0	2
MB Treatment	2013	4.5	228	0.03	5	3	0	0	3
MB Treatment	2012	5	907	0.10	3	11	0	0	11
MB Treatment	2013	5	1364	0.16	17	12	1	0	12
MB Treatment	2012	5.5	2045	0.23	3	1	1	1	3
MB Treatment	2013	5.5	4968	0.57	34	5	6	2	12
MB Treatment	2012	6	3478	0.40	15	5	3	1	9
MB Treatment	2013	6	0	0.00	0	0	0	0	0
Kelly	2005	4.5	105	0.01	1	1	0	0	1
Kelly	2006	4.5	0	0.00	0	0	0	0	0
Kelly	2007	4.5	0	0.00	0	0	0	0	0
Kelly	2008	4.5	202	0.02	4	2	0	0	2
Kelly	2009	4.5	611	0.07	15	6	0	0	6
Kelly	2010	4.5	20	0.00	0	0	0	0	0
Kelly	2011	4.5	101	0.01	1	2	0	0	2
Kelly	2012	4.5	399	0.05	16	4	0	0	4
Kelly	2005	5	1534	0.18	1	7	3	0	10
Kelly	2006	5	1348	0.15	5	6	4	0	10
Kelly	2007	5	819	0.09	1	4	1	0	5
Kelly	2008	5	1848	0.21	21	7	4	0	11

Kelly	2009	5	4551	0.52	24	5	4	3	12
Kelly	2010	5	1242	0.14	15	7	1	0	8
Kelly	2011	5	2861	0.33	10	9	5	0	14
Kelly	2012	5	2809	0.32	14	4	5	0	9
Kelly	2005	5.5	5261	0.60	8	3	5	3	11
Kelly	2006	5.5	4787	0.55	9	8	5	2	15
Kelly	2007	5.5	1840	0.21	14	1	3	1	5
Kelly	2008	5.5	4477	0.51	12	4	5	1	10
Kelly	2009	5.5	8415	0.96	22	1	1	3	5
Kelly	2010	5.5	2809	0.32	13	2	7	0	9
Kelly	2011	5.5	5269	0.60	1	3	0	1	4
Kelly	2012	5.5	6480	0.74	8	3	1	2	6
Kelly	2005	6	6763	0.77	20	3	1	2	6
Kelly	2006	6	5378	0.61	26	3	3	3	9
Kelly	2007	6	3813	0.44	0	0	1	1	0
Kelly	2008	6	6330	0.72	16	2	1	2	5
Kelly	2009	6	7884	0.90	5	0	1	2	3
Kelly	2010	6	6567	0.75	16	2	2	1	5
Kelly	2011	6	6881	0.79	3	4	1	1	6
Kelly	2012	6	7607	0.87	25	3	2	2	6
LaHave	2010	5	7	0.00	0	0	0	0	0
LaHave	2012	5	133	0.02	0	0	0	0	0
LaHave	2008	5.5	440	0.05	16	2	1	0	3
LaHave	2009	5.5	907	0.10	21	8	1	0	9
LaHave	2010	5.5	1308	0.15	4	4	0	1	4
LaHave	2011	5.5	148	0.02	1	2	0	0	2
LaHave	2012	5.5	402	0.05	6	2	1	0	3
LaHave	2013	5.5	224	0.03	14	0	1	0	1
LaHave	2008	6	1257	0.14	3	3	3	0	6
LaHave	2009	6	6981	0.80	64	17	10	2	29
LaHave	2010	6	5333	0.61	66	7	5	2	14

LaHave	2011	6	3823	0.44	27	14	5	1	20
LaHave	2012	6	3752	0.43	12	6	4	2	11
LaHave	2013	6	7589	0.87	0	0	0	0	0
Shelburne	2002	4	0	0.00	0	0	0	0	0
Shelburne	2003	4	0	0.00	0	0	0	0	0
Shelburne	2004	4	0	0.00	0	0	0	0	0
Shelburne	2005	4	0	0.00	0	0	0	0	0
Shelburne	2006	4	0	0.00	0	0	0	0	0
Shelburne	2007	4	53	0.01	5	1	0	0	0
Shelburne	2008	4	0	0.00	0	0	0	0	0
Shelburne	2009	4	0	0.00	0	0	0	0	0
Shelburne	2010	4	0	0.00	0	0	0	0	0
Shelburne	2002	4.5	177	0.02	0	0	0	0	0
Shelburne	2003	4.5	7004	0.80	4	0	0	1	1
Shelburne	2004	4.5	7998	0.91	2	1	1	1	3
Shelburne	2005	4.5	7952	0.91	6	0	1	2	3
Shelburne	2006	4.5	15567	1.78	15	9	10	4	23
Shelburne	2007	4.5	5495	0.63	0	1	1	6	0
Shelburne	2008	4.5	10991	1.25	4	1	0	5	6
Shelburne	2009	4.5	16249	1.85	2	0	1	6	7
Shelburne	2010	4.5	6871	0.78	9	15	7	3	20

11.0 Appendix 4: HRG Maria Brook Data Management

HRG MEMP DATA MANAGEMENT SYSTEM

Document prepared by Maria Armstrong
Mar 8, 2013

A. WEEKLY Download and Backup of Data

1. Download MEMP data weekly to:
   C:\Users\HSG\Desktop\MEMP_Raw_Data_Automatic_Remote_Upload
   CMEMP_ECSample.dat
   CMEMP_FifteenMin.dat
   CMEMP_TrbleSht.dat

2. Save a copy of the raw data (using the same naming system as above) in:
   S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Figure 4 MEMP 15 min data\CMEMP Data\Downloaded Raw Data
   Or in:
   S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Figure 4 MEMP 15 min data\DMEMP Data\Downloaded Raw Data

   This will provide a backup of all the raw data downloaded without overwriting any saved files.
   DMEMP_ECSample_12 Feb 2013_MA.dat
   DMEMP_FifteenMin_12 Feb 2013_MA.dat
   DMEMP_TrblSht_12 Feb 2013_MA.dat

3. Open the raw data in MS Excel and save this file as a backup in:
   S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Figure 4 MEMP 15 min data\CMEMP Data\Formatted Data
   Files organized by site (CMEMP or DMEMP), type of data, and month/year
   Label the files as following (using the date of download and the appropriate MEMP):
   DMEMP_ECSample_12 Feb 2013_MA.xlsx
   DMEMP_FifteenMin_12 Feb 2013_MA.xlsx
   DMEMP_TrblSht_12 Feb 2013_MA.xlsx

   This will provide a copy of all the downloaded data without overwriting any of the saved files.

B. Error Checking (Short)

4. Briefly check over newly saved data for any errors and note what might need troubleshooting e.g. checking MEMP in the field. Let Shannon know of any gaps or outliers in data.

C. Error Checking (Long)

5. Add newest downloaded data to the following excel spread sheet (copy/paste).

S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Figure 4 MEMP 15 min data\Error checked data\All MEMP Data Error Checked 19 Feb 2013 MA

6. Update **All Dates** graphs by editing the end range value in **Select Data** (may also need to change x-axis range to see all dates).
   a. Look for anomalies in the graph that may indicate errors or missing data
   b. Go to these errors in the dataset to determine which dates/times are potentially erroneous.

7. For each site, data source, and parameter:
   Record the dates by data quality (good, bad, unsure) in:
   S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Inventory of Data Quality Feb 4 2013 MA
   a. For errors record why the dates should not be used in analysis.
   b. Record as much information as possible about the errors.
   c. Look at field notes, troubleshoot, etc. to find potential cause of the error and record this.

8. After the inventory of data quality is updated:
   Highlight erroneous data (red-bad, yellow-missing) and **clear contents** in:
   S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Figure 4 MEMP 15 min data\Error checked data\All MEMP Data Error Checked 19 Feb 2013 MA

   *DO NOT **delete** whole rows. Leave blanks in place of bad or missing data and if necessary include comments.

   Highlight the column header green if it has been thoroughly error checked.

   Save file with correct date and signature.

Bi-Monthly Time Series

9. In:
   S:\HRG\104 - Maria Brook Liming Project\Data and Analyses\Inventory of Data Quality Feb 4 2013 MA
   a. Create a copy of the **All Dates** tab.
   b. Rename tab to current months.
   c. Change the range of the x-axis to only include those two months .
10. Print graphs
   *Make sure legend does not overlap lines on graph.

11. Mark on printed graphs field dates, meteorological events (e.g Hurricanes), potential snow melt events, etc.