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Discussions

Terrestrial liming to promote Atlantic Salmon recovery in Nova Scotia – approaches needed and knowledge gained after a trial application

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Abstract

Populations of Atlantic salmon (*Salmo salar*) in Southwest Nova Scotia (SWNS) have plummeted since the 1980s. Acidification is considered a main threat to this population. The lakes and streams of SWNS were among the most heavily acidified in North America during the last century and calcium levels are predicted to continue to fall in coming decades. One of the most promising mitigation options to reduce the risk of extirpation of the SWNS *Salmo salar* is terrestrial liming; however, both the chemistry of SWNS rivers, and effective strategies for terrestrial liming in SWNS are poorly understood. Here we have launched the first terrestrial liming study in Nova Scotia, employing a test hydrologic source area liming strategy in a 5 ha experimental catchment in SWNS, Maria Brook; we apply an average local application rate of 13 t ha^{-1} to 10 % of the 47 ha catchment. We employ high frequency stream monitoring to complement grab sampling to identify which constituents pose a threat to *Salmo salar* and to identify strategies for larger scale terrestrial liming that would fit the local conditions. Results indicate that the water chemistry conditions are currently at toxic levels for *Salmo salar* throughout the year, with levels of ionic aluminium exceeding toxic thresholds almost 100 % of the time. The stream chemistry in Maria Brook is remarkably similar to pre-recovery conditions in other heavily acidified watersheds, such as Birkenes in Norway. Our results support the hypothesis that there has been no recovery from acidification in SWNS. Results from the first year of post-liming do not show an improvement in stream chemistry levels, and further lime application is needed to improve the water chemistry conditions to needed levels for the recovery of *Salmo salar*.

1 Introduction

Following reductions in anthropogenic sulphur and nitrogen emissions in North America and Europe in the past decades it is expected that surface waters would show signs of recovery from acidificiation. Indeed, surface waters in Europe and North America have shown a steady improvement in annual average stream chemistry (Skjelkvale et al., 2005; Stoddard et al., 1999). However, recent analyses of lake chemistry data from Southwest Nova Scotia (SWNS) (Fig. 1) suggest that this region might be an exception as the record shows no increase in pH in recent decades, and calcium (Ca^{2+}) concentrations remain low compared to elsewhere in the world (Clair et al., 2011).

Despite being located well downwind of sulphur emissions, SWNS was strongly affected by acid precipitation (Hindar, 2001) due to bedrock types, thin soils with low acid neutralizing capacity, extensive wetlands, and episodic sea salt inputs (Freedman and Clair, 1987; Wright, 2008; Clair et al., 2011; Watt et al., 2000; Whitfield et al., 2007).

During the 1980s and 1990s, when the awareness of this issue was at its zenith, acidification was identified as a main cause of the extirpation of native Atlantic salmon populations in many rivers in Scandanavia and the eastern USA (Parrish et al., 1998; Hesthagen and Hansen, 1991) as well as in SWNS (Watt, 1987).

Recently, the resident SWNS (Southern Upland) population has further declined. For example, in two SWNS rivers, Atlantic salmon (*Salmo salar*) populations have declined by 88 to 99 % from the observed abundance in the 1980s (Gibson et al., 2011; DFO, 2013). In 2010, the Southern Upland population was evaluated as “Endangered” by the Committee on the Status of Endangered Wildlife in Canada (COSEWIC) and is currently under review to be listed under the Canadian Species at Risk Act (DFO, 2013). Among possible threats, acidification has been identified a main threat to these populations (DFO, 2013), but much remains unknown on the current level of acidification in the region and how it might be ameliorated.

While population modelling for two of the larger *Salmo salar* populations in the region indicate a high probability of extirpation (87 and 73 %) within 50 years in the absence of human intervention (DFO, 2013), more encouragingly, the models also indicate that relatively small increases in either freshwater productivity or at-sea survival are expected to reduce this risk (DFO, 2013). For example, it is projected that a 20 % increase in the productivity of the *Salmo salar* population in the LaHave River in SWNS would reduce the probability of extirpation within 50 years from 87 to 21 % (DFO, 2013). Apart from

source reduction, the application of a neutralizing agent to the waters or soils (liming) is the only mitigation option known to reverse the effects of acidification. However, no acidification mitigation program currently exists in Nova Scotia.

There are three main methods of large-scale liming: lake liming, direct addition of limestone to streams, and terrestrial liming (Clair and Hindar, 2005). The first two types of liming mitigation measures have been tested in SWNS. From 2000–2004 limestone was added to Big LaHave Lake, but was not effective in increasing lake pH, due to short mean residence time of water in the lake, typical of lakes in SWNS (Clair, 2012). Second, from 2005 to 2013 a doser deposited lime directly into the West River, NS at rates which were a function of stream discharge and pH. Initial results indicate that the lime dosing method has been successful in increasing salmon productivity; smolt production has risen dramatically in those five years. However, the private group which has run this facility has exhausted its resources and the West River lime doser is likely to close in the near future.

A third option, terrestrial liming, applies a neutralizing agent directly to soils (Ivahnenko et al., 1988; Bradley and Ormerod, 2002; Clair and Hindar, 2005), usually limestone or dolomite. Terrestrial liming increases the amount of Ca^{2+} and other base cations available to exchange with the incoming hydrogen ions (H^+), thus increasing total alkalinity and reducing the release of aluminium ions from soils (Dennis and Clair, 2012). Terrestrial liming is therefore expected to lower H^+ and ionic aluminium (Al_i) and increase Ca^{2+} concentrations in surface waters (Clair and Hindar, 2005; Westling and Zetterberg, 2007). Terrestrial liming has been shown to be effective in restoring fisheries and aquatic communities in chronically acidified streams with low acid-neutralizing capacity, particularly in Scandanavia and the UK (Mant et al., 2013; Eriksson et al., 1983; Bradley and Ormerod, 2002; Hesthagen et al., 2011; Hindar et al., 1996), but also in the Allegheny Plateau in the USA (McClurg et al., 2007). In some cases liming has been effective for over 15 years after application (Clair and Hindar, 2005). Terrestrial liming can be done further divided into forest liming with the primary goal of improving forest soils, whole-catchment liming for aquatic effects, and wetland or hydrologic source area liming (Hindar et al., 1996; Jenkins et al., 1991).

While there is a rich body of knowledge on the effectiveness of terrestrial liming in Europe and the UK (Clair and Hindar, 2005; Rizvi et al., 2012; Mant et al., 2013; Olem, 1991; Olem et al., 1991; Hindar et al., 2003; Hindar, 2005), there are few available studies on the effectiveness of terrestrial liming in North America (Smallidge and Leopold, 1997). Further, no terrestrial liming studies have been completed in Nova Scotia and there is little available local information to guide liming efforts.

For terrestrial liming to be effective, the correct dose and type of buffering agent needs to be placed in the right location and it needs to be active at the right time (Dickson and Brodin, 1995); its effectiveness is also dependent upon the morphometry and hydrology of the catchment (Waters et al., 1991). Thus the buffering agent should be placed on the critical source areas (CSAs) for identified target parameters that are closely tied to salmonid health status, such as aluminium (Bradley and Ormerod, 2002; Jenkins et al., 1994; Waters et al., 1991), and the annual pattern of its chemical activity should correspond to the annual pattern of the targeted parameters, as well as being active when the target (biological) species are particulalry sensitive to effects of exposure, such as during smoltification.

Acidification is known to reduce terrestrial and aquatic productivity (Bradley and Ormerod, 2002) and observed declines in fish populations and decreases in terrestrial and aquatic ecosystem productivity are attributed specifically to the combined effects of elevated H^+ and Al_i and low Ca^{2+} concentrations (Rosseland and Staurnes, 1994). These three parameters have yet to be examined in recent years in SWNS, particularly in the context of possible terrestrial liming.

pH is a common target parameter for acidification mitigation for salmon populations. Annual average pH is a commonly used metric of stream health, currently used for recovery planning (DFO, 2013). However, some of the most biologically damaging effects of acidification occur during acid shock pulses, or acid episodes, in streams – events characterized by pH plummeting below chronic values for a short period (hours

to days) (Weatherly and Ormerod, 1991; Wright, 2008; Monette and McCormick, 2008; Borg and Sundbom, 2014). These episodes are generally precipitation-triggered but can be the result of acid inputs via mobilization of stored sulfur in the soils (Alewell et al., 2000), spring snowmelt, or sea salt deposition (Clair et al., 2001). Acid episodes have been identified as a key variable in recognizing and understanding the health of an ecosystem (Weatherly and Ormerod, 1991; Wright, 2008). In the most comprehensive study on acid episodes in SWNS, Clair et al. (2001) examined acid episodes in three rivers using daily, weekly, and hourly data from 1990 to 1995, and found that in each river two to four significant pH events occured over a year. However, information on current frequency and severity of acid episodes in SWNS is needed.

Al_i is accepted as a key factor responsible for the demise of biotic communities in acidified environments (Cronan and Schofield, 1979; Gensemer and Playle, 1999). Yet Al_i has not been considered to be an important threat to *Salmo salar* populations in SWNS; studies from the 1980s concluded that Al_i was not a significant threat to Atlantic salmon populations in SWNS because the presence of dissolved organic carbon (DOC) which can render Al_i biologically inaccessible (e.g., Lacroix and Kan, 1986; Lacroix and Townsend, 1987; Watt et al., 2000; Lacroix et al., 1990). However, a recent study has provided new data that challenge this view; Dennis and Clair (2012) measured Al_i in 11 rivers in SWNS in the fall of 2006 and showed that in seven of these there is insufficient DOC to render Al_i biologically inaccessible, and the Al_i concentrations exceeded values identified as toxic to aquatic life.

Chronic acid inputs to the land surface cause aluminium to leach out from the soils (Bache, 1986; Clair et al., 2004). The toxicity of aluminium is governed by pH, and the most toxic range of pH (referred to here as the "Al_i toxic zone") is approximately 4.8 to 5.8; in this range, the species of $AlOH^{2+}$ and $Al(OH)_2{}^+$ are at their highest proportions of total aluminium (Gensemer and Playle, 1999), the most toxic forms of aluminium for fish and other aquatic species (Kure et al., 2013). In this pH range concentrations of Al_i around 10 to 15 $\mu g\,L^{-1}$ have been noted to impair the sea-water tolerance of salmon smolts (Staurnes et al., 1995; Howells et al., 1990; Dennis and Clair, 2012), and a number of other aquatic species groups such as macroinvertebrates are also affected at these aluminium levels (Lacoul et al., 2011). Below pH levels of 4.8 (referred to here as the "acidity toxic zone") the toxicity to Atlantic salmon is dominated by the low pH itself (Lacoul et al., 2011). Apart from the Dennis and Clair (2012) study, little is known about the current prevalence of Al_i in SWNS rivers.

Reduced Ca^{2+} concentration in surface water is another key component of acidification stress (Jeziorski et al., 2008). Ca^{2+} is the most important base cation for neutralization of acid precipitation (Clair et al., 2011), and is also an essential nutrient for all organisms (Jeziorski et al., 2008); for example, Ca^{2+} ions are a necessary component of plant cell walls and membranes. Reduced levels of available Ca^{2+} also play a role in increasing the toxicity of Al_i for *Salmo salar* (Howells et al., 1983). In SWNS, dissolved Ca^{2+} levels are low and model simulations predict that, due to continued acid deposition and low rates of Ca^{2+} release from the surrounding bedrock, concentrations in SWNS rivers will continue to decrease by 5 to 15 % over the next 40 to 50 years, and will not begin to recover for 90 years if acid emission reductions continue at present rates (Clair et al., 2004). However, Ca^{2+} concentrations in SWNS rivers have not been published.

The goal of this study is to inform future mitigation and recovery strategies for *Salmo salar* in SWNS by conducting a test wetland liming experiment in a small headwater catchment, and to ask the following questions:

1. Does the headwater catchment in SWNS show signs of acidification? What is the current state of target parameters, pH, Ca^{2+}, and Al_i, in a small catchment? Which of these chemical parameters are beyond threshold levels for aquatic health? At what time of year are these parameters of concern? Are acid episodes present and of sufficient frequency to be of concern for salmonids?

2. Is there any change to the target parameters and acid episodes following a test hydrologic source area liming?

A more applied goal, driven by the urgent need to reverse the declines of *Salmo salar* in SWNS, is to inform terrestrial liming strategies and monitoring in SWNS by learning which parameters are of concern in SWNS streams and at which time of year their levels are of most concern.

2 Materials and methods

2.1 Study background and site description

In October 2010 we selected an experimental catchment for liming, the 47 ha Maria Brook located in the Mill Brook sub-basin of the Gold River watershed in SWNS (Fig. 1). The Maria Brook catchment was selected for several reasons. It is a typical watershed of the region, with gentle slopes and a forest cover dominated by Red Spruce (*Picea rubens*), Balsam Fir (*Abies balsamea*) and White Spruce (*Picea glauca*). It is well-connected to important *Salmo salar* habitat in the Gold River Watershed. And it has supportive private land owners who allow access for manual liming application and monitoring. The study catchment is without roads or development and has a well-defined hypsometry with a classic tear-shaped morphology. A 5 ha circular low-gradient area exists in the middle of the catchment, which we estimate as the hydrologic source area or dynamic contributing area (following Dunne and Black, 1970) as we have observed saturation of the upper soil layers during storms. We dug soil pits in the upslope and toe-slope areas of this zone. The upslope areas have well-drained deep (80 cm) sandy-loam soils. The toe-slope areas have imperfectly to poorly drained stony soils where the rooting zone is restricted to a 10 to 20 cm deep organic layer and water flow is concentrated above 25 cm depth. In the riparian area, an auger core showed a 65 cm deep organic mesic/hydric soil. In the soil pits we observe post-rainfall flow over the compacted subsoil, and on the surface in the 5 ha hydrologic source area we observe post-rainfall surface flow, following topographic gradients. In SWNS, it has been noted that seepage into the underlying subsoils and rocks is often low because of the generally impervious nature of the compacted subsoil and the underlying bedrock (Yanni et al., 2000).

The catchment is 24 km from the south-western coast of Nova Scotia and is underlain by granitic bedrock (Table 2) comprising less than 1 % CaO equivalent (Charest, 1976; MacDonald, 2001; Farley, 1978). The region has mean annual precipitation in the range 1150 to 1500 mm and a mean annual average temperature of 7.0 ± 1.4 °C. Temperatures are warmest in July (with a 1981 to 2010 monthly normal of 19.0 ± 1.2 °C) and coolest in January (−5.7 ± 2.2 °C) (Environment Canada, 2014). In general in SWNS, precipitation rates rise in the autumn, peak in December and are lowest during summer (Yanni et al., 2000).

2.2 Experimental design and data collection

We monitor water chemistry at six sites, three sites since 2010 and three sites since 2012 (Table 1, Fig. 1). Data are collected by three methods: stream grab samples collected semi-monthly at Sites 1 to 6, in situ continuous monitoring at Sites 5 and 6 via mobile environmental monitoring platforms (MEMPs), and semi-monthly measurements along a stream transect between Sites 5 and 6 (Table 1).

Grab samples were collected approximately every two weeks since 2010 and refrigerated until analysis at Environment Canada's Atlantic Laboratory for Environmental Testing (ALET) for major ions and metals, including total aluminium (Al_t), using ICP-MS and Ion Chromatography; physical parameters and total organic carbon (TOC) were measured with standard Environment Canada operating protocols.

The MEMPs measure meteorology, water levels, and water chemistry every 15 min. Water level is measured with an OTT Hydromet compact bubbler sensor. Rainfall data is collected at Site 5. Data collected by the MEMP sensors are recorded by a Campbell Scientific data logger (CR1000). The MEMPs became available to the project one month prior to the Phase 2 liming treatment, so Phase 1 high frequency data are limited.

Acid episodes (which we define as a drop of at least 0.2 pH units within 24 h of a rainfall event, with a pH minimum is below 5.5), are monitored using 15 min-interval measurements made by two YSI 6600 sondes, one at each of Sites 5 and 6 (with a specified accuracy of ±0.2 pH units when properly calibrated). Calibrations took place approximately every 2–4 months; during this time interval very little fouling on the sensors was evident. In the analysis of acid episodes we employ the United States Geological Survey (USGS) protocols (Wagner et al., 2000) to determine whether to accept or reject a pH measurement, and if the measurements collected by either of the YSI 6600s have consistently drifted above or below the transect measurements a correction is applied (following Wagner et al., 2006).

In the transect, pH, conductivity, and stream temperature are measured every 50 m along a 300 m section of the brook linking Site 6 to Site 5 through the liming zone. For waters with low ionic strength, such as in Maria Brook, pH is difficult to measure accurately (Galloway et al., 1979), and therefore our study design employs replicate measurements of pH with different sensors; when conducting transects, we measure pH using both a YSI 600 sonde (with a specified accuracy of ± 0.2 pH units when properly calibrated) and a YSI EcoSense pH 10 pen probe (with a specified accuracy when properly calibrated of ± 0.1 pH units when calibrated within 10 °C of sample temperature (typical), otherwise ± 0.2 pH units). A two-point calibration of pH (pH 4 and pH 7), is conducted for the YSI 600 and the YSI EcoSense pH10 pen before each field visit; a one-point calibration for conductivity (12 880 $\mu S\,cm^{-1}$) is conducted semi-monthly for the YSI 600 sondes.

To estimate Al_i, we use a multiple regression model ($R^2 = 0.68$) developed by Denis and Clair (2012) using samples from 92 sites across Atlantic Canada:

$$Al_i = -166.5 + 0.5 \times Al_t - 5.06 \times TOC + 23.5 \times pH \quad (1)$$

To avoid extreme extrapolation we only estimate Al_i for samples in which Al_t, TOC, and pH are within 10% of the range of the data used to develop the model, and any negative estimates of Al_i are set to zero.

2.2.1 Study phases

The study consists of three phases. Phase 1 is the pre-treatment monitoring phase (December 2010 to May 2012). Phase 2 is a test-treatment and monitoring phase (June 2012 to May 2013), during which a low dose of powdered limestone ($CaCO_3$) was applied to the soils in part of the catchment to assess the feasibility and logistics of limestone application and the ability of the sensors to detect a change in water chemistry due to the limestone. Phase 3 is planned as the main liming phase during which there will be a larger-scale application of the powdered limestone.

2.2.2 Study sites

Site 3 and Site 6 are control sites and the four treatment sites are 1, 2, 4, and 5 (Fig. 1), and the transect stations are between Site 6 and Site 5. Site 6 is located immediately above the liming zone in Maria Brook and Site 3 is located on Mill Creek, just upstream of the junction with Maria Brook. Mill Creek thus serves as an unlimed comparison watershed; however, the Mill Creek catchment (like the other surrounding watersheds) differs from the Maria Brook catchment as it contains a lake and residential development. The four treatment sampling sites are downstream from the liming zone: Site 5 is located immediately below the limestone application area; Site 1 is located on Maria Brook 200 m downstream of Site 5, and upstream of the road crossing; Site 2 is located on Mill Brook, downstream of the junction of Maria Brook, and Site 4 is located 1020 m farther downstream from Site 2 along Mill Brook.

2.3 Phase 2 test limestone application

The liming approach for this study follows recommendation by several researchers (Nisbet, 1993; Waters et al., 1991; Jenkins et al., 1994; Hindar et al., 1996) of targeting liming in the hydrological source area with a readily available form of powdered limestone, or otherwise known as wetland liming. We divided the presumed hydraulic

source area in Maria Brook into 20 m × 20 m quadrats. The first test application of powdered limestone was conducted in May and June 2012. Highschool students and community groups applied almost 28 tonnes of powdered (< 2.0 mm) limestone by hand to 51 quadrats (2.04 ha, or 4.3 % of the catchment) (Fig. 1); however, of this only about 23.5 tonnes fell within the area draining into Site 5. The average local rate of application was 13 t ha^{-1} with a range of 1 to 48 t ha^{-1} applied in each quadrat (Fig. 1). Limestone was not placed within 1 m of the stream. The test limestone application is concentrated near the bottom of the transect (Fig. 1). This application rate is in line with that of other studies, such as reported by Hindar et al. (1996) in which 4.0 % of a catchment was limed at 20 t ha^{-1}.

We chose to apply the limestone in late spring/early summer (May/June) at the beginning of the drier season because of reduced overland flow during this time, thus providing more opportunity for uptake of the limestone into the soils and plants before heavy rainfall. We chose not to lime in the autumn after the major litter fall because of the reduced contact the limestone would have with the soil.

2.4 Water chemistry target values

For the purposes of this paper we identify target values for stream chemistry parameters important for *Salmo salar* survival.

We set the pH target to be above 5.8, and the Al_i target to be less than 15 µg L^{-1}. For Ca^{2+} we set the target to be above 1.5 mg L^{-1}, the threshold value identified for the survival of *Daphnia pulex*, a common aquatic invertebrate species and an important organism in the aquatic food chain (Jeziorski et al., 2008). The Al_i target represents levels recommended for waters with low Ca^{2+} concentrations (< 2 mg L^{-1}) (Howells et al., 1990), although in waters with high levels of dissolved organiz carbon, as in SWNS, high Al_i concentrations could be accepted; more study is needed to better refine the targets; this is a complex relation that is also affected by temperature of surface waters (Lydersen, 1990).

3 Results

The total precipitation for the Phase 1 and 2 was 970 mm, of which 800 mm occurred during 2012. The summer of 2012 was relatively dry, with 162 mm of rain falling from 1 June through 31 August. A total of 19 storm events including two hurricane events were sampled over 15 months from December 2011 to March 2013, with 72 h period rainfall ranging from 7 to 80 mm.

3.1 Assessment of acidification status

3.1.1 pH

pH measurements during laboratory analysis of water samples at ALET (ex situ) were consistently higher than measurements of pH made with YSI 6600 and YSI 600 sondes and YSI Ecosense pH10 pen probes (in situ); i.e., consistently, sample pH levels rose after collection. Because we are concerned with toxic in situ river chemistry for *Salmo salar*, our evaluation of pH levels relative to toxic thresholds focuses on the in situ measurements.

In situ pH values were within the $\mathrm{Al_i}$ toxic zone (Site 6) or just above the $\mathrm{Al_i}$ toxic zone (Site 5) during the dry base flow periods in the summer of 2012 (Fig. 2a). During a series of rainfall events in the fall and winter of 2012/13, pH remained below target values; immediately after rainstorms, pH dropped into the acidity toxic zone, and then rose into the Al_i toxic zone until the next rain event. This pattern continued into the smolitifcation period in late spring 2013. The running two week mean pH stayed below 5.0 between 12 September and 26 February 2013 (Fig. 2a).

Ex situ pH values in the previous year (i.e. before commencement of in situ measurements) follow a similar seasonal pattern: pH was in or near to the $\mathrm{Al_i}$ toxic zone during the winter 2010 and 2011, and rose in the spring/summer months of 2011 and 2012.

Continuous monitoring recorded 19 acid episodes in a nine-month period between July 2012 and March 2013 (Table 3). An acid episode occurred for every rainfall event greater than 10 mm in 72 h. The acid episodes lasted between just over 12 h to 1.5 days (e.g., Fig. 3), and the stream pH dropped on average 34.7 $\mu\mathrm{Eq\,L^{-1}}$ at the control site (Site 6) and 16.5 $\mu\mathrm{Eq\,L^{-1}}$ at the treatment site (Site 5). The average minimum pH during the episodes was 4.36 (control), and 4.69 (treatment) (Site 6 and Site 5, respectively).

The largest drop in pH (78 $\mu\mathrm{Eq\,L^{-1}\,H^+}$) and the lowest minimum pH (4.07) occurred at the control site (Site 6) on 10 September 2012 coincident with a 52 mm rainfall event at the end of a dry summer – the first major rainstorm in 75 days – during the passing of Hurricane Leslie (Fig. 3b, Table 3). The pH minimum occurred 29 h after the peak rainfall intensity. There was no increase in conductivity associated with this storm, as may be expected with an assumed influx of ions from a sea-based storm (Fig. 3b).

The second record low pH value in Maria Brook (also 4.07, Site 6) occurred after a 79.9 mm rainfall event that occurred with the passing of Hurricane Sandy on 31 October 2012, which also caused the second largest magnitude of pH drop of 72 $\mu\mathrm{Eq\,L^{-1}}$ (at Site 6) (Fig. 3c).

3.1.2 Aluminium

During the study period (Table 1) grab sample results from the six sites reveal a range of $\mathrm{Al_t}$ concentrations from 52 $\mu\mathrm{g\,L^{-1}}$ (Site 3) to 1420 $\mu\mathrm{g\,L^{-1}}$ (Site 5) with a mean of $250 \pm 15\,\mu\mathrm{g\,L^{-1}}$ (Fig. 2e). In the first year of study, the annual pattern for $\mathrm{Al_t}$ ranges from a low of 100 to 250 $\mu\mathrm{g\,L^{-1}}$ between December 2010 and April 2011 to a high of 400 to 610 $\mu\mathrm{g\,L^{-1}}$ between July and October 2011. In the second year of study, $\mathrm{Al_t}$ rises in the spring from April 2012 to peak values in July of 500 to 1420 $\mu\mathrm{g\,L^{-1}}$. Levels of $\mathrm{Al_t}$ are highest at Sites 5 and 6, although at these sites, data are only available for the second year of observation.

$\mathrm{Al_t}$ concentration correlates with TOC at each site (Fig. 5); this relationship is strongest at Site 4 and Site 1 ($R^2 = 0.84$, 0.81, respectively). The relationship is weakest at Site 3 ($R^2 = 0.52$), the site that is located most closely downstream from a lake. Sites 1, 5, and 6 generally have higher concentrations of $\mathrm{Al_t}$ with lower TOC concentrations; in contrast, $\mathrm{Al_t}$ at Sites 2, 3, and 4 falls more quickly with a reduction in TOC. The highest TOC values are found at the three sites in Maria Brook (1, 5, and 6).

Equation (1) gives a range of $\mathrm{Al_i}$ at Maria Brook from $0.0\,\mu\mathrm{g\,L^{-1}}$ to $160\,\mu\mathrm{g\,L^{-1}}$ at the six sites between December 2010 to November 2012 (Fig. 2b), although $\mathrm{Al_i}$ values as low as $-15\,\mu\mathrm{g\,L^{-1}}$ (set to zero along with three other values) and as high as $612\,\mu\mathrm{g\,L^{-1}}$ (rejected (see Section 2.2) along with four other values out of the total of 146) were calculated. For $\mathrm{Al_i}$, the highest calculated concentrations occur during the low flows in the summer months of 2011 and 2012 at Sites 1, 2, 5, and 6, which are within or immediately downstream from the Maria Brook catchment. At all sites, 89 % of the samples have $\mathrm{Al_i}$ levels above, and up to 10 times, the recommended target value of $15\,\mu\mathrm{g\,L^{-1}}$ (Fig. 2b). $\mathrm{Al_i}$ levels exceed the $15\,\mu\mathrm{g\,L^{-1}}$ water quality threshold 100 % of the time (both pre- and post-liming) at the sites in Maria Brook (Sites 1 and 5 (treatment) and 6 (control)). Pre treatment (Phase 1), 95 % of all samples from Sites 1, 2, 4, and 5, and 88 % of the samples taken from the control sites (Sites 3 and 6) were outside of the target range. Following the limestone application (Phase 2), 90 % of samples from the treatment sites and 75 % of the samples from the control sites remained outside of the target zone.

3.1.3 Calcium

The $\mathrm{Ca^{2+}}$ concentration in grab samples from all sites varied from a minimum of $0.77\,\mathrm{mg\,L^{-1}}$ in March 2011 to a maximum of $3.95\,\mathrm{mg\,L^{-1}}$ during the summer months of 2012 (Fig. 2c). A seasonal pattern is evident in both 2011 and 2012. $\mathrm{Ca^{2+}}$ concentrations are below water quality threshold of $1.5\,\mathrm{mg\,L^{-1}}$ for all sites for extended periods during the winter and spring, for example from December 2010 to July 2011 and from November 2011 to May 2012. Between December 2010 and September 2012 $\mathrm{Ca^{2+}}$ concentrations were below the target levels for 51.2 % of the samples.

To gain higher temporal resolution of $\mathrm{Ca^{2+}}$ levels at Maria Brook we develop a parametric linear regression relation between $\mathrm{Ca^{2+}}$ and specific conductance to estimate continuous $\mathrm{Ca^{2+}}$ concentrations from the continuous conductivity measurements at Sites 5 and 6 (Supplement).

3.2 Response to Phase 2 test-liming

Results from the pre-liming period (Phase 1) show that the pH is not significantly different between the control site Site 6 and treatment site Site 5 (Table 4, Fig. 4a). Moving from the pre-liming (Phase 1) to the post-liming (Phase 2) period, the longitudinal transects data show that post-liming, pH at Site 5 became higher relative to Site 6 (Fig. 4a) but that the change is not significant.

In December 2012 there was a cold snap with no snow cover, and between December 2012 and March 2013 the soils may have been frozen for part or all of this period. During this period, “possibly frozen, post-liming”, pH at Site 5 was not clearly different from pH at Site 6 (Fig. 4a). It may be that the frozen soil reduces the interaction of surface water with the limestone in the soil, but more study is required.

Results show a difference in slope of pH drop between the control and the treatment sites, coincident with the rising limb of the hydrograph during the beginning of the episodes (Fig. 3), suggesting that acid neutralization by the applied powdered limestone is particularly effective during the rising hydrograph limb of the storm event as the water table rises and comes closer into contact with the powdered limestone that is presumably in the upper horizons of the soil profile. No significant rainfall occurred in the last month of Phase 1 when the MEMPs became available, so comparison of acid episodes between Sites 5 and 6 is limited to post-liming (Phase 2).

4 Discussion

The observations at Maria Brook are consistent with observations from the lake record that there has been no recovery in SWNS from acidification (Clair et al., 2011). The chronic levels of pH and Al_i observed are toxic to aquatic systems, and the levels of Ca^{2+} observed are below threshold needed for aquatic productivity. Acid episodes, occurring with storm events, lowerered pH and Ca^{2+} levels even further than the chronic levels. Other regions, such as in Wales and Norway, have reported high aluminium concentrations linked with acid episodes (Soulsby, 1995; Soulsby and Reynolds, 1993; Sullivan et al., 1986). However, at Maria Brook the highest Al_i values were observed during low flows (Fig. 2); this might be because Maria Brook is chronically acidified rather than episodically acidified, but more investigation is needed.

The seasonal or wet/dry cycles of pH at Maria Brook are similar to those observed by Clair et al. (2001) at Pine Marten Brook in Kejimkujik Park in Nova Scotia from 1992 to 1995 where winter pH ranges between 4.5 and 5.0 (acidic zone), dropping to close to 4.0 following rainfall events, and then rising higher, to almost 5.0 to 5.5 (Al_i toxic zone) in the wet/dry shoulder seasons, and then up above 5.5 during the drier periods in summer.

The Maria Brook pH observed is also similar to the Surface Waters Acidification Program (SWAP) Birkenes site in southernmost Norway during the 1980s (Table 2). The current annual pattern and values of Ca^{2+} in Maria Brook are also similar to Birkenes catchment from 1972 to 1988 (Christophersen et al., 1982). Further, the Ca^{2+} values detected are in line with those projected by (Clair et al., 2004) in a modelling study for the year 2000 for 40 rivers in SWNS, predicting an average Ca^{2+} concentration of $1.26 \pm 1.23\,\mathrm{mg\,L^{-1}}$ ($62.7 \pm 61.6\,\mathrm{\mu Eq\,L^{-1}}$).

Like pH and Ca^{2+}, the maximum Al_i levels at Maria Brook ($610\,\mathrm{\mu g\,L^{-1}}$) are comparable to the maximum Al_i levels recorded in Birkenes ($540\,\mathrm{\mu g\,L^{-1}}$) pre-recovery phase, and are higher than the Al_i at other sites in Scandanavia, such as Atna, Hoylandet and Svartberget during the 1980s (Seip et al., 1991). Further, the Al_i measured at Maria

Brook are also higher than estimates in a recent autumn survey of Al_i (Dennis and Clair, 2012); for the 11 rivers that they surveyed in SWNS for which pH was below 6, the maximum Al_i concentration observed was $55.93\,\mathrm{\mu g\,L^{-1}}$ (Roseway River). The lower levels of Al_i measured by Dennis and Clair (2012) in comparison with Maria Brook may be due to the former only being sampled during the Fall.

The strong correlation between TOC and Al_t corresponds with the observation that high concentrations of TOC percolating from the forest floor help to mobilize Al_t from soil minerals (Dijkstra and Fitzhugh, 2003). While Dennis and Clair (2012) observed a levelling of of Al_t at $450\,\mathrm{\mu g\,L^{-1}}$ and suggested there was a limit to how much aluminium can be weathered from soil solution or bedrock, we do not observe a clear levelling off of Al_t at Maria Brook (Fig. 5). The Al_t values at Maria Brook continue to increase with increasing TOC, reaching over twice as high as the Dennis and Clair (2012) threshold value of $450\,\mathrm{\mu g\,L^{-1}}$, suggesting aluminium may be more freely available in the system than previously thought.

Indeed, the maximum Al_t level measured ($1418\,\mathrm{\mu g\,L^{-1}}$) in Maria Brook is among the highest reported in the literature. Other high values found include $510\,\mathrm{\mu g\,L^{-1}}$ in the Vosges Mountains (Thiébaut and Muller 1999), and $350\,\mathrm{\mu g\,L^{-1}}$ in Nova Scotia (Lacroix and Townsend, 1987). In a survey of rivers in SWNS, (Watt et al., 2000) reported values as high as $320\,\mathrm{\mu g\,L^{-1}}$. While data on silicic acid levels were not available for this study, we recommend that silica levels be monitored for future studies because of the relation of silicic acid concentration and toxicity of aluminium to fish (Birchall et al., 1989). We also recommend that a regional aluminium study be done to look at spatial and temporal trends over larger scales in SWNS.

4.1 Considerations for terrestrial liming

4.1.1 Dose and identification of target parmeters and CSAs

Results from Phase 2 indicate that the current dose of 28 tonnes of powdered limestone in 4.3 % of a 47 ha catchment is not sufficient for water chemistry to reach target levels for aquatic health in SWNS, in contrast to results from the Røynelandsvatn (Hindar et al., 1996) where there was a rapid increase in stream pH and Ca^{2+} and a decrease in Al_i. However, on the range of terrestrial liming doses that have been successful in the past (Brown, 1988), the dosage applied at Maria Brook is on the lower end of this range. Further application of limestone, set for Phase 3, monitoring and modelling is required to project precise doses needed to reach target water chemistry levels.

Because the chronic water chemistry levels measured in Maria Brook for Al_i, pH, and Ca^{2+} are in the range considered detrimental to aquatic health, it is advisable that all three of these parameters be included in the target parameters for terrestrial liming programs in the region.

A key CSA for pH is the dynamic contributing area (i.e. the lowlying areas around the riparian-zone saturated soils) during storms because the minimum values of this target parameter are associated with storm flow. In contrast, because our data suggest that the highest concentrations of Al_i may be associated with base flow rather than storms, for Maria Brook there appears to be a different CSA for Al_i from the storm-related CSA of pH. Thus, to address the high Al_i concentrations it may be necessary to lime the entire catchment instead of only the dynamic contributing area. Further research on temporal and spatial patterns of Al_i in SWNS is recommended.

The most sensitive times of the life cycle of *Salmo salar* to low pH and high Al_i are during smoltification (Kroglund et al., 2008; McCormick et al., 2009) which typically occurs in April and May in SWNS, and during the alevin-emergence phase occurring in the summer (Daye and Garside, 1977). Smolitification is a crucial phase in the lifecycle as health during this phase determines probability of smolt survival upon reaching the ocean (Hansen and Quinn, 1998). Both smolts and parr may be especially vulnerable to impacts of short-term (days-week) acid and Al_i exposure (Monette and McCormick, 2008).

This analysis of critical time windows pertinent to terrestrial liming reveals two areas that need further study. If the CSA for Al_i includes areas outside the recharge zone, terrestrial liming aimed at the recharge zone may not reduce the supply of Al_i to streams.

Therefore, to protect aquatic life, it is important that the liming raise the pH above the target value of 5.8 for pH during times of high total aluminium levels. We recommend that stream water be monitored carefully for pH and aluminium levels following terrestrial liming.

Second, there is the possibility that the activity of buffering agents may be reduced during periods with frozen soils, as possibly suggested by the data from Maria Brook. We therefore suggest monitoring soil status, whether frozen or not, in the weeks before the smoltification period; this issue is particularly important because pH tends to be low during the smoltification window due to snow melt processes (Clair et al., 2001) and because following acid/Al exposure it takes at least two weeks for smolts to recover (Nilsen et al., 2013).

Because the pH concentration tend to drop with storm occurrence, the effectiveness of terrestrial liming in part will depend upon future climate, including when the soil is frozen in the spring, and the number and timing of storms, both of which have substantial interannual variation in SWNS.

4.1.2 Monitoring the effectiveness of terrestrial liming

Based on results from Phase 1 and 2 of sampling at Maria Brook, we suggest six considerations for monitoring the effectiveness of terrestrial liming in SWNS:

1. Use of transect method with a single pH sensor to detect changes in stream chemistry in experiments between pre- and post-liming. Our results suggest that this method can detect small changes in pH downstream of the liming relative to an upstream control. This method avoids uncertainties inherent when comparing pH and conductivity measured with two different sensors in the field.

2. Inclusion of acid episodes as a monitoring variable for the effectiveness of terrestrial liming, and measuring pH with a minimum 3 to 6 h frequency. Our results show that acid episodes are common and severe in Maria Brook. While annual average pH levels are customarily used as an index of river acidification status for

SWNS (e.g., DFO, 2013), acid episodes should be monitored because they have been shown to prevent biological recovery even if the annual average statistics of recovery have improved (Bradley and Ormerod, 2002; Mant et al., 2013). Further, acid episodes may not be adequately captured by weekly or bi-weekly grab samples, especially if there is a sampling bias in avoiding taking samples on the rising limb during storms due to safety concerns.

3. Inclusion of a wide array of parameters in grab samples, including pH, TOC, and extractible aluminium, and other metals that may be mobilized by changes in chemistry, such as uranium (Drage and Kennedy, 2013). Monitoring of groundwater wells downstream of terrestrial liming areas is also recommended.

4. Use of conductivity as a proxy for Ca^{2+} concentrations is an alternative method that is less expensive than grab sample analysis. This technique also opens the possibility of estimating continuous Ca^{2+} export from the stream, and therefore to estimate of the amount of Ca^{2+} that remains in the catchment in the years following liming. However, the Ca^{2+} conductivity relation is expected to be weaker on the rising limb of ocean-origin storms, when ocean seasalt (chloride) inputs are expected to increase the conductivity, and therefore the conductivity value would be less representative of the Ca^{2+} concentration.

5. Monitoring of stream chemistry response to terrestrial liming in all four seasons, as there is a risk of water going into the acidity toxic zone or Al_i toxic zone throughout the year in SWNS. Further, duration of monitoring should be longer than five years, and ideally 10 to 20 years, to verify the length of activity of the limestone application.

6. Monitoring of any adverse terrestrial and aquatic ecosystem effects, for example on *Sphagnum papillosum* (Bragg and Clymo, 1995), or shrews (Shore and Mackenzie, 1993).

These suggestions for monitoring build upon fundamental knowledge of terrestrial liming from Olem (1991) and Henriskon and Brodin (1995), taking into account local conditions and new technology such as high frequency sampling and portable sondes.

4.2 Limitations and future directions

This study reveals five areas needing further examination to guide terrestrial liming efforts in SWNS to reverse the declines of *Salmo salar*: (1) creation of Ca^{2+} budgets for the SWNS watersheds and their response to liming, in particular to determine how much of the limestone applied remains in the soil, and how much is taken up by vegetation, (2) completion of dosage calculations for terrestrial liming based on ANC and critical load exceedances, following (Hindar et al., 1998), (3) examination of aluminium dynamics in SWNS watersheds to pinpoint the CSAs for this parameter and development of a more robust model for estimating Al_i from readily measured parameters, (4) examination of spatial and temporal patterns of acidic episodes in SWNS, and (5) evaluation of other composition and forms of limestone to be used in terrestrial liming, such as with other grain sizes, and limestone pellets composed of powdered chalk, starch, and bentonite instead of crushed limestone.

5 Conclusions

Our results show that highly and chronically acidified conditions exist in a SWNS catchment despite over two decades of emissions cutbacks, in strong contrast to trends detected elsewhere in the world. Further, measured levels of pH, aluminium, and Ca^{2+} in Maria Brook are comparable to the most heavily acidified catchments in Norway during the height of acidification (Henrikson and Brodin, 1995; Seip et al., 1991). For most of the year the surface water conditions for pH, aluminium, and Ca^{2+} in Maria Brook are not within the recommended values for *Salmo salar* survival, with projected Al_i at toxic concentrations throughout the year. A mitigation program for acidification in

SWNS that targets these three parameters therefore is urgently needed to reduce the risk of extirpation of *Salmo salar* populations. Several lines of evidence demonstrate that Southern Upland Atlantic salmon are biologically unique and that their extinction would constitute an irreplaceable loss of Atlantic salmon biodiversity (Gibson et al., 2011). Terrestrial liming remains one of the most promising options for mitigation of this chronic acidification because of the need for a long-term solution; toxic conditions of streamwater for aquatic life are predicted to remain for many decades in SWNS (Clair et al., 2004). Yet, results indicate that the 28 tonnes applied to 4.3 % of the catchments in the hydrologic source area is not sufficient for water chemistry to reach target levels for pH, Ca^{2+}, and Al_i. Another phase of liming is needed to bring the water quality to acceptable levels for *Salmo salar* presumably needed to avoid the extirpation of this species.

Due to the the chronic acidification status of Maria Brook, we identify that liming plans in SWNS must be careful not to raise the chronic pH from the pH toxic zone into aluminium toxic zone while not directly reducing aluminium delivery to the stream, as this scenario could make aluminium toxicity worse for species such as *Salmo salar*. The study also identifies that transect and continuous monitoring sensors can be useful approaches for monitoring the effectiveness of terrestrial liming, given a controlled experimental layout, and that monitoring of pH, Ca^{2+}, and Al_i levels (both during base flow and storm events) is needed to evaluate the effectiveness of terrestrial liming. Since acid episodes were found to be severe in Maria Brook they need to be included in monitoring acidification of other SWNS rivers.

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Table 1. Data collection at Maria Brook experimental catchment. Site 5 is the downstream treatment site and Site 6 is the location of the control upstream of liming.

Type	Sites	Parameters measured	Sampling frequency	Sampling period
Grab sample	1 to 6	pH, conductivity, Ca^{2+}, magnesium, aluminium, sodium, nitrogen, sulfate, TOC, other metals and cations	Semi-monthly	December 2010 to present for Sites 1 to 3. May 2012 to present for Sites 4 to 6.
Transect	Eight station transect every 50 m from Site 6 to 5	pH, conductivity, stream temperature	Semi-monthly	February 2012 to Present
Continuous stream chemistry	5	pH, conductivity, stream temperature	15 min	12 Jun 2012 to 27 Nov 2012, 14 Mar 2013 to Present
	6	pH, conductivity, stream temperature	15 min	25 Apr 2012 to Present
Meteorology and water level	5, 6	Rainfall, wind, temperature, relative humidity, water level	15 min	Oct 2011 to Present

Table 2. Characterization of Maria Brook (Sites 1, 5, and 6) and Birkenes I SWAP field site (Seip et al., 1991 citing SFT, 1989). Physical characteristics and means ± standard error or approximate ranges of concentrations for streamwater; volume-weighted averages for Birkenes, non-volume-weighted averages for Maria Brook. Data range for Maria Brook pH encompass all collection methods.

	Maria Brook	Birkenes I
	Physical Characteristics	
Area of catchment studied/km^2	0.50	0.41
Altitude/m	190–225	205–300
Bedrock	Granite (Leucomonzogranite)	Granite
Precipitation/mm a^{-1}	1150–1500	1500
Soils		Podzol/peat
Land cover	Spruce forest	Spruce forest
	Chemical Characteristics	
Years representing	2010 to 2013	1981 to 1983 and 1985 to 1988
pH	4.0 to 6.5[a]	4.6
Ca^{2+} / mg L^{-1}	1.5 ± 0.1, 0.8 to 4.0	1.0
Mg^{2+} / mg L^{-1}	0.53 ± 0.02	0.38
K^{+} / mg L^{-1}	< 0.4 to 0.6	0.2
Na^{+} / mg L^{-1}	4.0 ± 0.2, 2.1 to 10.2	2.5
Al_t/µg L^{-1}	335 ± 20, 170 to 1420	
Al_i/µg L^{-1}	73 ± 4, 16 to 160[b]	110 to 650[c]
TOC/mg L^{-1}	12 ± 1, 6 to 25	3 to 11[c]
Characterization	acidified	acidified

[a] From in situ measurements only; higher pH values were measured ex situ (see Sect. 3.1.1) with a mean of 6.0 ± 0.1 and an extreme high value of 7.3.

[b] Of the calculated values of Al_i (for Sites 1, 5, and 6) three out of 61, ranging from 84 to 612 µg L^{-1}, were rejected due to the input values of Al_t being more than 10 % outside the range of those used to develop the regression model.

[c] For 1985 to 1988 only.

Table 3. Summary of acid episodes. Mean values of acid episode parameters for Site 5 and 6. Acid episodes that occurred during the winter (when soils were probably frozen) are reported separately from those during the rest of the year. We define acid episodes as a drop in pH of at least 0.2 units within 24 h of a rainfall event, provided the pH minimum is below 5.5. The duration of pH drop is considered to be the time from the maximum pH before rainfall to the minimum pH reached.

Site	Dates	# Acid Episodes	Mean Min. pH	Mean Max. pH before drop	Mean Magnitude of pH drop (µEq L^{-1})	Mean duration of pH drop (h)	Mean precipitation amount (mm/72 h before)
6	Jul 2012 to Nov 2012	14	4.36	4.94	31.9	17.5	32.2
5	Jul 2012 to Nov 2012	14	4.83	5.34	10.1	25.0	32.2
6 (Winter)	Dec 2012 to Mar 2013	5*	4.55	5.07	19.5	35.5	19.0

* During the winter period Site 6 had intermittent data collection during some acidic episodes due to a weak battery and up to four potential acid episodes may have been missed based on the partial pH data set and local weather data.

Table 4. Comparison of pH pre-liming (Phase 1) with post-liming (Phase 2) upstream and downstream of liming area, Sites 5 (treatment) and 6 (control). Phase 1 pH measurements include samples measured with the YSI Ecosense pH10 pen probe within four hours of collecting grab samples at each site (December 2011 to May 2012). Phase 1 data range from December 2010 to May 2012. Phase 2 data range from June 2012 to November 2012. A two sample *t* test for the relative difference of µEq L^{-1} H^+ was used to compare Phase 1 and Phase 2 pH measurements.

Stage	Method of pH Measurement	N	Site 6 (control) Mean pH ± Std. Error	Site 5 (treatment) Mean pH ± Std. Error	Mean Difference (µEq L^{-1} H^+) (Relative Difference: [Site 6 − Site 5]/ Mean Site 6)	Statistical Analysis for Relative Difference ($\alpha = 0.05$)	*p* value
Pre-liming	Discrete YSI 600 and Ecosense in situ + Ecosense *lab*	36	5.59 ± 0.05	5.63 ± 0.06	0.116 µEq L^{-1} (3.3 %)	1 sample *t* test failed to reject H_0: Difference of means (Site 5 from Site 6) = 0.	0.486
Post-liming	Discrete YSI 600 and Ecosense in situ	24	5.32 ± 0.13	5.43 ± 0.13	2.38 µEq L^{-1} (17.2 %)	1 sample *t* test failed to reject H_0: Difference of means (Site 5 from Site 6) ≥ 0	0.167
						2 sample *t* test failed to reject H_0: Mean (post-liming) − mean (pre-liming) ≥ 0	0.244

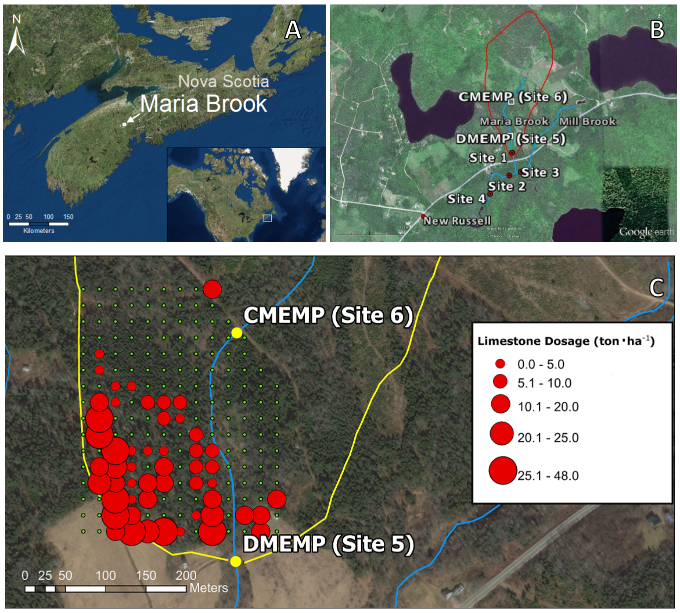

Figure 1. Maria Brook field site. **(A)** Location in Southwestern Nova Scotia (SWNS). **(B)** Maria Brook catchment boundary (red) and location of sampling sites. Streams flow downstream from Site 6 to Site 4. **(C)** Location and amount of Phase 2 limestone application. Red or green dots represent 20 m × 20 m quadrat. Quadrats demark approximate area of recharge zone. Green dots represent all quadrats that were not limed in May 2012.

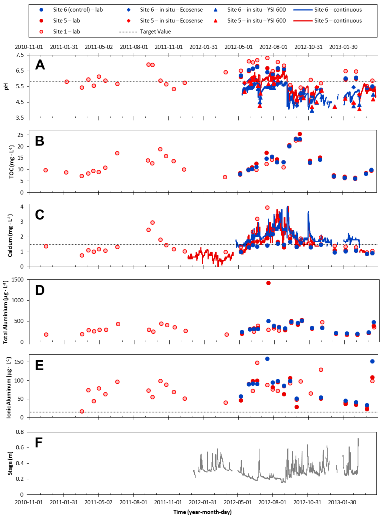

Figure 2. Stream chemistry at Maria Brook from Fall 2010 to Spring 2013. Blue dots are for control sites, red dots are treatment sites. Where appropriate, dotted line indicates target value (see Sect. 2.4). Lab values are from grab samples analyzed at ALET (Atlantic Laboratory of Environmental Testing) and in situ values are measured in the field using YSI 600 multiparameter sondes or YSI Ecosense pH10 pen probes. Site 5 and 6 continuous 15 min measurements are taken with a YSI 6600 multiparameter sonde. **(A)** pH. **(B)** Total Organic Carbon (TOC). **(C)** Calcium ion concentration; continuous Ca^{2+} values are estimated from conductivity data using a regression model (Supplement). **(D)** Al_t, **(E)** Estimated Al_i concentration (Eq. 1). Estimates were not made where input values were more than 10 % outside the range of data used to develop the regression model (resulting in the loss of five out of 146 data points), and negative estimates of Al_i (four, the most extreme being $-15\,\mu g\,L^{-1}$ and the rest no more extreme than $-7\,\mu g\,L^{-1}$) were set to zero. **(F)** Stage.

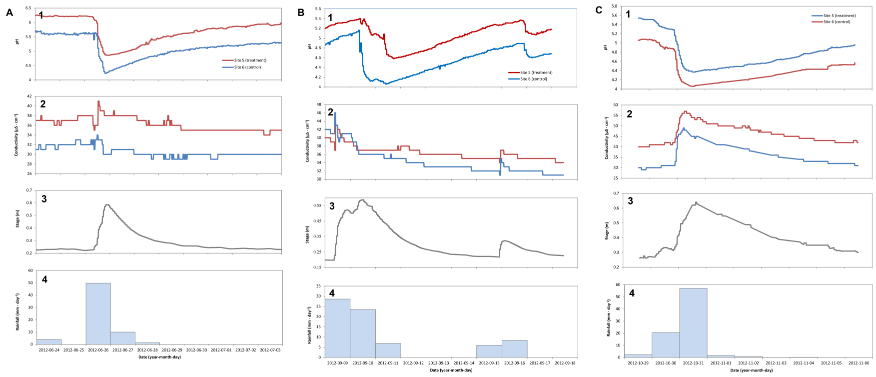

Figure 3. Acid episodes observed in Fall 2012. pH, conductivity, stage, and rainfall are displayed for all episodes. **(A)** Episode 1, 26 June 2012, **(B)** episode 2, 9 September 2012 to 10 September 2012 (Hurricane Leslie), and **(C)** episode 3, 30 October 2012 and 31 October 2012 (Hurricane Sandy). Rainfall data are from Site 5. Stage data are from Site 6.

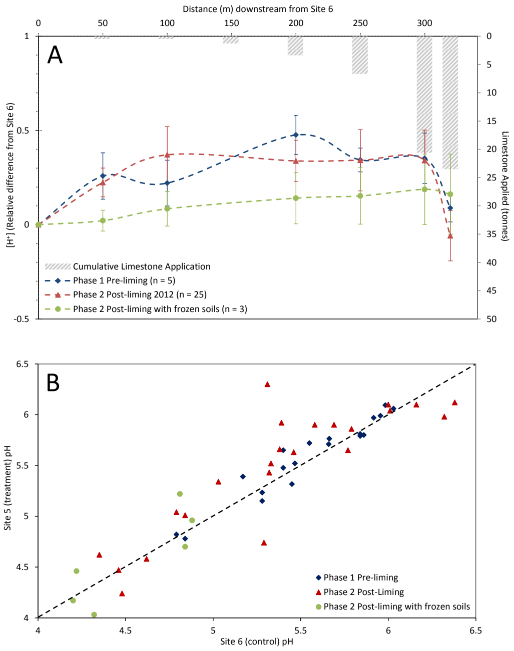

Figure 4. Transect data. Stream pH through the liming zone transect for data collected by a single YSI 600 or YSI Ecosense pH10 probe within a 2 h period. **(A)** H^+ concentration moving downstream from Site 6 (control) (0 m) to Site 5 (treatment) (320 m), as a proportion of value at the Site 6. Pre-liming (Phase 1), post-liming (Phase 2) and post-liming with presumed frozen soils (Phase 2), and Phase 2 cumulative limestone dose along transect (columns). **(B)** pH for Site 5 (treatment) and Site 6 (control), as measured by YSI 600 and Ecosense pH 10 pen probe. Note that Phase 1 data include duplicate grab samples measured one to four hours post sample collection with the Ecosense sensor ($n = 8$). Dashed line indicates the 1 : 1 relation.

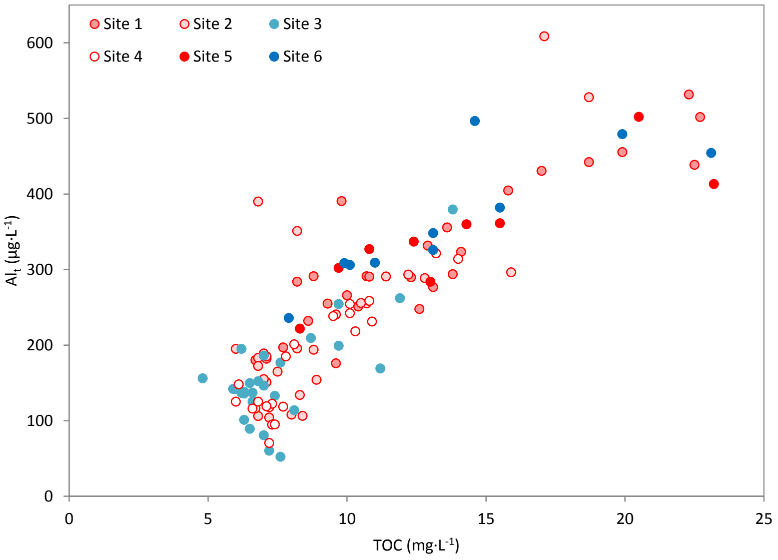

Figure 5. Total extractible aluminum (µg L^{-1}) and total organic carbon (TOC) at the six monitoring sites. The R^2 for a simple linear regression at Site 1 is 0.81, Site 2 is 0.61, Site 3 is 0.52, Site 4 is 0.84, Site 5 is 0.74, and Site 6 is 0.70.