Final report on mapping toxic ionic aluminium levels in priority Nova Scotia rivers for Atlantic salmon

Prepared for: Nova Scotia Freshwater Fisheries Research Cooperative (FFRC)

Prepared by: Dalhousie Hydrology Research Group (DHRG)
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Motivation

Ionic aluminium (Al\textsubscript{i}) is toxic to Atlantic Salmon (Salmo salar) and is known to be a key cause of population declines. Increases in ionic aluminium concentrations in rivers are caused by chronic acid rain pollution (Committee on the Status of Endangered Wildlife in Canada, 2010; Dennis, Clair, & Kidd, 2012; Nilsen, et al., 2013)

It was only recently that aluminum was identified as a threat to Salmo salar populations in South Western Nova Scotia, Canada (SWNS) (Dennis, Clair, & Kidd, 2012). Previously, it was thought SWNS rivers contained enough dissolved organic carbon (DOC) to render the aluminum in rivers inactive. However, recently it has been demonstrated that although Nova Scotian freshwaters have high DOC levels, these levels are not correlated with decreased Al\textsubscript{i} levels (Tipping, Rey-Castro, Bryan, & Hamilton-Taylor, 2002). Data collected from years 1 and 2 of the Al\textsubscript{i} monitoring programme funded by the FFRC (Sterling, et al., in progress) indicate that the ionic aluminum concentrations frequently exceed the threshold recommended for aquatic health (15 µg·L\textsuperscript{-1}) as determined by the European Inland Fisheries Advisory Commission (Howells, Dalziel, Reader, & Solbe, 1990). However, little is known about the Al\textsubscript{i} concentrations in the 13 high priority watersheds for Atlantic Salmon in Nova Scotia.

Information on aluminium concentrations in Nova Scotian rivers is urgently needed because the local salmon population numbers are declining to near-extirpation levels (Department of Fisheries and Oceans, 2013). Planning measures require information on Al\textsubscript{i} levels to identify the most suitable restoration measures, without information on Al\textsubscript{i} levels, there is an increased risk that costly mitigation actions may be unsuccessful. A major problem is that without information on the aluminium levels, the mitigation activities for acid rain, such as instream and catchment liming, may not address the threat of aluminium or indeed worsen it.

Relevance of Project to FFRC Objectives

The Al\textsubscript{i} monitoring project closely supports the FFRC objectives to aid in evaluation of the strategies used to enhance and sustain the freshwater sport fishery. Our project will support these objectives by determining the health and status of the freshwater sport fishery through the assessment of the threat of ionic aluminium to key freshwater sport fishery species, including Salmo salar and trout species.

The goal of this project is to develop an aluminium component to the Southern Upland Watershed Acid Rain Mitigation Plan (submitted with this report), and thus to identify the best way to reduce the effects of acid rain on Atlantic salmon. The only way to actively mitigate the effects of acid rain is through the application of a neutralizing substance (limestone) to the waters or soils of a watershed. To be successful, the Acid Rain Mitigation Plan must identify where the limestone should be applied, how much, and by what method. For the Southern Upland Acid Rain Mitigation Plan to be effective in increasing Salmo salar productivity, it is essential that the plan addresses the patterns of toxic aluminium within the watersheds of the 13 high priority sites.
Importance of the Southern Upland Watershed Acid Rain Mitigation Plan in Sport Fisheries Management

This project forms an important component of the Southern Upland Watershed Acid Rain Mitigation Plan, which is overseen by the Southern Upland Priority Group (SUPG).

The SUPG was founded by the Department of Fisheries and Oceans (DFO following the Southern Upland Atlantic Salmon Recovery Potential Assessment (Department of Fisheries and Oceans, 2013) to identify action items to reverse declines in *Salmo salar* productivity in the region. Members of the SUPG include government, university, First Nations, and community groups. During the first meeting in July 2013 the SUPG stuck a committee, the Southern Upland Acid Rain Mitigation Committee (SUARMC), chaired by Dr. Shannon Sterling from 2012 to 2016, and Dr. Edmund Halfyard in 2017 to present, to identify actions to combat one of the largest threats to *Salmo salar* in the region: freshwater acidification from acid rain.

In October, 2013, the SUPG identified 13 watersheds as a priority watershed for *Salmo salar* recovery (Figure 1), and SUARMC identified the development of a mitigation plan for these 13 watersheds as a priority project.

![Figure 1](image.png)

Figure 1 The 13 priority watersheds in Nova Scotia, as determined by the Southern Upland Priority Group.

The Southern Upland Watershed Acid Rain Mitigation plan includes the Gold River Pilot Catchment Liming Study, the Ted Creek Catchment Liming Study, both led by Dr. Shannon Sterling, Dalhousie University, and Bluenose Coastal Action Foundation, and supported by Environment Canada and the Donner Foundation.

Beginning in fall 2016, the funding provided by FFRC to the Al monitoring project was additionally used for the collection of water quality data to assess the effectiveness of catchment liming conducted by the Nova Scotia Salmon Association (NSSA) at mitigating the threat of toxic aluminum to Atlantic salmon. The results of this study will be added to the Southern Upland Acid Rain Mitigation Plan upon completion to further inform freshwater habitat restoration initiatives, benefitting the sport fisheries management.
Al₃ Monitoring Project Objectives

The objectives of the three-year, nova Scotia-wide, Al₃ monitoring project are outlined below, along with an indication of if the objective was achieved (Table 1).

Table 1  Performance measures for Al₃ monitoring project, as agreed upon by the DHRG and FFRC.

<table>
<thead>
<tr>
<th>Project Objective</th>
<th>Outcome</th>
<th>Performance Measures</th>
<th>Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measure toxic aluminium levels in the Nova Scotia Southern Uplands River Watersheds.</td>
<td>An understanding of where in the 13 SU priority watersheds the waters have toxic aluminium levels, their severity, and seasonal variability. And an understanding of aluminium levels during the smoltification window.</td>
<td>1) Measures of levels of toxic (ionic) aluminium and water chemistry in the sub-basins and mainstem of the 13 high priority watersheds, four measurements per site per year over a three-year period.</td>
<td>Yes</td>
</tr>
<tr>
<td>Map ionic aluminium levels in the 13 priority watersheds.</td>
<td>Map of areas of toxic aluminium, showing target areas for liming and instream habitat</td>
<td>2) Map of areas of toxic aluminium as needed for watershed mitigation planning.</td>
<td>Yes</td>
</tr>
<tr>
<td>Amend acid rain mitigation plan for the SU priority Watershed to Include aluminium</td>
<td>List of sites priority for liming and for avoiding.</td>
<td>3) A map and a list of sites that are high priority for liming, and a list of sites that should be avoided for liming within the 13 Southern Upland priority Watershed.</td>
<td>Yes</td>
</tr>
<tr>
<td>Adapt guidebook for acid rain mitigation that addresses aluminium</td>
<td>Improved acid rain mitigation guidebook for Southwest Nova Scotia</td>
<td>4) A guidebook for catchment liming produced in conjunction with Bluenose Coastal Action Foundation that is improved to address aluminium.</td>
<td>Yes</td>
</tr>
</tbody>
</table>
**Methods**

Multiple research initiatives investigating Al levels in the Nova Scotia Southern Uplands were supported by FFRC funding, these projects included the 1) synoptic Al survey, the results of which will be reported in the work of MacLeod et al. (2018, in prep); 2) the Nova Scotia Freshwater Database (NSFwD), the results of which will be reported in the work of Rotteveel et al. (2018b, in prep); 3) an honours thesis reporting on the effectiveness of the NSSA liming project, the results of which will be reported in Rotteveel et al. (2018a, in prep); and 4) the Terrestrial Liming Guidebook for Southwestern Nova Scotia. Varying methods were used for these four sub-projects, as indicated below.

**Synoptic Al Survey**

**Sample Collection**

Water quality samples (including Al) were collected between April 2015 and September 2017 on a weekly to monthly basis during the snow-free season (approximately April to November). Water quality measurements and samples included in-situ stream pH, conductivity, and temperature, measured with a YSI Pro Plus multiparameter Sonde, and samples of dissolved organic carbon, sulphate, cations (total, dissolved, and organic) and metals (total, dissolved, and organic).

**Products Used:**

- Bond Elut Jr. SCX (strong cation exchange) columns
- 0.4 M ammonium acetate solution at pH 5
  - Made with solid ammonium acetate, creating the 0.4 M solution, and adding acetic acid to adjust pH to 5.0.
- Bottles, syringes, and filters
  - 250 mL polyethylene bottles for pH and SO$_4$
  - 200 mL amber glass bottles with nitrate preservative for DOC and TOC
  - 150 mL polyethylene bottles for metals and cations with nitrate preservative
  - 50 mL plastic syringes for DOC, metal, and cation sample collection
  - 0.45µm filters

**Sample Laboratory Analysis**

Water quality samples were analysed at three different laboratories due to budget constraints.

**Maxxam Laboratory**

Metal, cation, anion, DOC, and pH samples were analyzed at Maxxam Analytics Laboratory in Bedford, Nova Scotia. Maxxam Laboratory protocols adhere to the United States of America Environmental Protection Agency (US EPA) approved methods for identifying trace elements in water (United States Environmental Protection Agency, 1994) and analyzing samples using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (United States Environmental Protection Agency, 1998).

Metal, cation, and anion samples were analyzed using ICP-MS, DOC samples were analyzed using a Continuous Flow Analyzer, and laboratory pH was measured using a standard hydrogen electrode and reference electrode. All samples were prepared and analyzed in accordance with US EPA (1994; 1998) guidelines.
HERC Laboratory

$\text{SO}_4$ samples were analyzed at Dalhousie University Health and Environmental Research Center (HERC) in Halifax, Nova Scotia. This laboratory was selected by the DHRG as it provides a lower detection limit for $\text{SO}_4$ analysis. Samples were filtered using a 0.45 µm glass fiber filter and analyzed using an Ion-Chromatography System (ICS) 5000 Dionex detector.

AGAT Laboratory

Metal, cation, anion, total organic carbon (TOC), pH, and $\text{SO}_4$ samples were analyzed at AGAT Laboratories in Dartmouth, Nova Scotia. AGAT Laboratories are accredited by the International Organization for Standardization, and hold both the 9001:2015, and 17025:2005 accreditations (AGAT Laboratory, 2017).

Metal and cation samples were analyzed using ICP-MS, TOC samples were analyzed using Infrared Combustion (IR Combustion), laboratory pH was measured using a standard hydrogen electrode and reference electrode, and $\text{SO}_4$ and anions was measured using ICS (Canadian Association for Laboratory Accredidation Inc., 2017).

Quality Assurance and Control

To ensure results for samples analyzed at Maxxam Analytics and and HERC laboratories were comparable to results for samples analyzed at AGAT laboratory, three duplicate samples were taken at BLB and Upper Killag River (UKR) sample sites on April 19th, 2017, May 14th, 2017, and May 30th, 2017 and analyzed by both laboratories. Results were analyzed using the Wilcoxon Rank Sum statistical test in Python 3.6 using the SciPy 0.19 package. This analysis showed a significant difference in laboratory pH results ($T = 1$, $p = 0.04$). Therefore, analysis of pH was conducted using the corrected Sonde pH data. Comparison of the total, dissolved and organic aluminum results indicated a non-significant difference between laboratory results ($T = 8.5$, $p = 0.674$; $T = 5.0$, $p = 0.249$; and $T = 8.0$, $p = 0.600$, respectively), indicating Al results are comparable between laboratories. No significance difference was found between samples analyzed for total Ca ($T = 4.0$, $p = 0.173$), indicating that Ca results are also comparable between laboratories.

$\text{Al}_i$ Calculation Procedure

$\text{Al}_i$ is calculated as the difference between total aluminium (filtered stream water) and organic aluminium (filtered stream water passed through a SCX column) (Equation 1), following the protocol developed by the DHRG in collaboration with Environment Canada in 2014 (MacLeod, et al., 2018, in prep).

\[
\text{Al}_i = \text{Al}_d - \text{Al}_o
\] (1)

where $\text{Al}_d$ is quantity of dissolved aluminum (filtered sample) and $\text{Al}_o$ is the quantity of non-labile organically-completed colloidal aluminum (eluate of the cation exchange column).

$\text{Al}_i$ is defined as all positive ionic species of Al in this approach; consistent with Dennis & Clair (2012) and Poléo (1995).
Nova Scotia Freshwater Database

Site Selection

Study sites were selected from the publically-available Environment Canada National Long-Term Water Quality Monitoring Dataset (LT WQMD). The LT WQMD contains nationwide water quality data Environment Canada (EC) has collected since the mid-1890s, including data collected at 333 lakes and 302 rivers in Atlantic Canada, whereof 66 study sites have data dating back to the 1980s (Clair, Dennis, & Vet, 2011). For details on water quality sample analysis methods, please refer to the information provided on the online LT WQMD access point (http://open.canada.ca/data/en/dataset/67b44816-9764-4609-ace1-68dc1764e9ea). Since the Atlantic Canada subset of the LT WQMD contained 54,478 records, spread over 631 sites, the site selection process was automated via a script executed in Python 2.7, using the Pandas, NumPy, TQDM, Sys, and OS modules. Sites were selected based on four criteria: 1) minimum of five samples per decade (Table 2), 2) samples present in the 1990s decade or before, 3) samples present in the 2010s decade, and 4) minimum of five samples per season, per decade (Table 3).

Table 2 Decade definition based on date range. October 27th, 2015 was chosen as the final data point in the 2010s decade because it was the most recent data point available at the time of data collection (July 21th, 2016).

<table>
<thead>
<tr>
<th>Decade</th>
<th>Date Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980s</td>
<td>January 1st, 1980 to December 31st, 1989</td>
</tr>
<tr>
<td>1990s</td>
<td>January 1st, 1990 to December 31st, 1999</td>
</tr>
<tr>
<td>2000s</td>
<td>January 1st, 2000 to December 31st, 2009</td>
</tr>
<tr>
<td>2010s</td>
<td>January 1st, 2010 to October 27th, 2015</td>
</tr>
</tbody>
</table>

Table 3 Season definition based on date range.

<table>
<thead>
<tr>
<th>Season</th>
<th>Date Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter/Snowmelt</td>
<td>December 1st to April 30th</td>
</tr>
<tr>
<td>Spring/Summer</td>
<td>May 1st to August 30th</td>
</tr>
<tr>
<td>Fall</td>
<td>September 1st to November 30th</td>
</tr>
</tbody>
</table>

63 sites were selected based on the above criteria, and were mapped in ArcGIS 10.3.1 using coordinates specified in the LT WQMD (Figure 2).
Al\textsubscript{i} Estimation

The Al\textsubscript{i} concentration for each site in the NSFwD database was estimated using equations developed by MacLeod et al. (2018, *in prep*). The chemistry values used for Al\textsubscript{i} estimation were the average pH, DOC, Ca, and Al\textsubscript{t} values for the 2010s decade at each site. Al\textsubscript{i} concentrations were estimated using all equations in Table 4 and averaged to obtain a final Al\textsubscript{i} estimate. The equations developed by MacLeod et al. (2018, *in prep*) use dissolved aluminum, however, Al\textsubscript{d} data was unavailable, so total aluminum (Al\textsubscript{t}) was used. This may have biased the results by indicating higher Al\textsubscript{i} levels.

Figure 2  Map of the 63 selected study sites in Nova Scotia, Canada.
Table 4  Equations to predict $\text{Ali}$ for Mersey River (MR) and Moose Pit Brook (MPB). #N indicates sampling points included in the creation of the equation, $R^2$ (%) indicates regression fit, $p$-value <0.05 are significant regressions at 95%, Norm=Normality $p$-value, with $p$ <0.05 indicating normal residuals, and Appl.=Possible applications for the equations. The equation needs some parameters to be converted before application to the EC Database. [Get Sarah to Update to new seasons].

<table>
<thead>
<tr>
<th>Name</th>
<th>Season</th>
<th>Equation</th>
<th>$R^2$ (%)</th>
<th>$p$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRS1Ald1</td>
<td>1</td>
<td>$\text{Al}_i = -1.30 \times 10^{-2} - 8.53 \text{pH} + 1.33 \times 10^1 \sqrt{\text{Al}_d} + 2.30 \times 10^{-3} \text{SO}_4^2$</td>
<td>79</td>
<td>0.00</td>
</tr>
<tr>
<td>MRS1Ald2</td>
<td>1</td>
<td>$\text{Al}_i = -1.49 \times 10^2 + 1.68 \times 10^1 \sqrt{\text{Al}_d} - 3.08 \times 10^{-1} \text{DOC} + 2.19 \times 10^{-8} \text{SO}_4^2 - 9.98 \text{pH}$</td>
<td>82</td>
<td>0.00</td>
</tr>
<tr>
<td>MRS2Ald1</td>
<td>2</td>
<td>$\text{Al}_i = 5.07 \times 10^1 - 1.35 \times 10^1 \left( \frac{\text{Ca}_i}{\text{Al}_d} \right) + 1.30 \times 10^{-2} \text{SO}_4^2 - 2.64 \times 10^{-2} \text{DOC} + 1.42 \text{pH}$</td>
<td>45</td>
<td>0.39</td>
</tr>
<tr>
<td>MRS2Ald2</td>
<td>2</td>
<td>$\text{Al}_i = 5.07 \times 10^1 - 1.35 \times 10^1 \left( \frac{\text{Ca}_i}{\text{Al}_d} \right) + 1.30 \times 10^{-2} \text{SO}_4^2 - 2.64 \times 10^{-2} \text{DOC} + 1.42 \text{pH}$</td>
<td>85</td>
<td>0.04</td>
</tr>
<tr>
<td>MRS3Ald1</td>
<td>3</td>
<td>$\text{Al}_i = -1.48 \times 10^{-2} - 8.71 \times 10^{-4} \text{Al}_d^2 + 3.51 \times 10^{-1} \text{pH} + 7.51 \text{DOC}$</td>
<td>100</td>
<td>0.04</td>
</tr>
<tr>
<td>MPBS1Ald1</td>
<td>1</td>
<td>$\text{Al}_i = -6.90 - 0.067 \text{Al}_d + 8.21 \times 10^{-3} \text{SO}_4^2 + 1.60 \text{DOC}$</td>
<td>69</td>
<td>0.00</td>
</tr>
<tr>
<td>MPBS1Ald2</td>
<td>1</td>
<td>$\text{Al}_i = -1.65 \times 10^2 + 1.48 \times 10^1 \text{Al}_d^3 - 1.42 \times 10^1 \text{Dis}_2 + 7.90 \times 10^2 \text{pH}^{-1}$</td>
<td>86</td>
<td>0.00</td>
</tr>
<tr>
<td>MPBS2Ald1</td>
<td>2</td>
<td>$\text{Al}_i = -1.81 \times 10^1 - 9.01 \times 10^0 \left( \frac{\text{Ca}_i}{\text{Al}_d} \right) + 8.34 \times 10^{-4} \text{DOC}^3 + 2.00 \times 10^2 \text{pH}^{-1}$</td>
<td>72</td>
<td>0.04</td>
</tr>
<tr>
<td>MPBS2Ald2</td>
<td>2</td>
<td>$\text{Al}_i = 4.20 \times 10^1 + 3.98 \times 10^0 \left( \frac{\text{Al}_d}{\text{Ca}_i} \right) + 1.24 \times 10^{-3} \text{DOC}^3 - 8.80 \text{pH} - 1.17 \times 10^2 \text{Dis}_2^2$</td>
<td>94</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Helicopter Liming Project

Limestone Application

The pilot catchment liming project was a partnership between the NSSA and the province of Nova Scotia, with project oversight from Dr. Edmund Halfyard (NSSA) and funding from the Nova Scotia Freshwater Fisheries Research Cooperative, Nova Scotia Department of Natural Resources (NS DNR), Nova Scotia Department of Fisheries and Aquaculture, Nova Scotia Salmon Association, Atlantic Canada Opportunities Agency, Recreational Fisheries Conservation Partnerships Program (Fisheries and Oceans Canada), Northern Pulp and Paper, Dalhousie University, the Nova Scotia Sportfish Habitat Fund, and the Atlantic Salmon Conservation Foundation.

Powdered dolomitic limestone ($\text{CaMgCO}_3$) was applied at a concentration of 10 t·ha$^{-1}$ on land and 2 t·ha$^{-1}$ on lakes/ponds to 2.0 m Wet Area Model (WAM) buffer zone (treatment area). A 2.0 m WAM identifies watershed areas which have a proportionately larger influence on stream chemistry, as the water table lies within 2.0 meters of the surface (Sterling, et al., 2014). Limestone was applied using a MD 500E helicopter flown by NS DNR pilots. Limestone was applied in approximately 340 kg loads using a hopper suspended beneath the helicopter. Limestone was applied to two treatment catchments: Colwell Creek (CC) and MacGregor Brook (MacGB). Two catchments were used as control sites: Upper Killag River (UKR) and Brandon Lake Brook (BLB). During liming operations some limestone blew into the catchment of a fifth site: Cope Brook (CB). This site was also monitored, although it was not included in formal analysis of liming effectivity.
at mitigating freshwater acidification. The entire treatment area of CC was limed, 21.548% of the total catchment (Table 5). One small 0.23 ha pond in CC was limed as a landmass; at 10 t·ha⁻¹, although its direct connection with CC is ephemeral. One section of MacGB did not receive treatment because the hopper broke and could not be repaired within the allotted application period. The un-limed treatment section represented 11.004 % of the total watershed, while the limed treatment area represented 61.991 % of the MacGB watershed. It is unknown what portion of CB watershed received limestone or the mass of limestone deposited within the watershed resulting from blow out. Catchment liming was conducted between October 3rd, 2016 and November 19th, 2016.

Table 5  Catchment area treated with powdered dolomitic limestone, and quantity of limestone applied.

<table>
<thead>
<tr>
<th>Sub-catchment</th>
<th>Sub-catchment Area (km²)</th>
<th>Limed Treatment Area (km²)</th>
<th>Unlimed Treatment Area (km²)</th>
<th>Proportion Catchment Area Limed (%)</th>
<th>Lime Applied (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colwell Creek</td>
<td>0.930</td>
<td>0.200</td>
<td>0</td>
<td>21.548</td>
<td>200.42</td>
</tr>
<tr>
<td>MacGregor Brook</td>
<td>0.727</td>
<td>0.458</td>
<td>0.080</td>
<td>62.991</td>
<td>424.40</td>
</tr>
<tr>
<td>Cope Brook</td>
<td>0.633</td>
<td>unknown</td>
<td>unknown</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Total</td>
<td>2.290</td>
<td>0.658</td>
<td>0.080</td>
<td>n/a</td>
<td>624.82</td>
</tr>
</tbody>
</table>

**Sample Collection and Laboratory Analysis**

Sample collection and analysis, and Alᵢ calculations were conducted following the same protocol as was used in the Synoptic Alᵢ survey (above).

**Statistical Analysis**

Data was examined using descriptive statistics and Generalized Linear Mixed Model (GLMM) in the R 3.4.2 statistical analysis platform, using the car, MASS, bbmle, MuMIn, lme4, and lsmeans packages. GLMM was selected to account for inherent variation in site topographic, geologic, and hydrographic characteristics (Burnham & Anderson, 2002).
Results

Performance Measure 1: Ali measurements in 13 priority watersheds

The synoptic Ali monitoring programme indicated that Ali is a province-wide concern, and effects all of the sampled watersheds (Mersey-, Medway-, Gold-, and West River watersheds). Average toxic aluminum (Ali) level exceeded the 15 µg·L⁻¹ maximum juvenile Atlantic salmon threshold for 80% (n = 10) of the sites between April 2015 and September 2017 (Figure 4). Average site Ali levels ranged from 13 µg·L⁻¹ to 60 µg·L⁻¹.

Results from weekly and monthly sampling conducted by Macleod et al. (2018, in prep) of Mersey River and Moose Pit Brook indicated that Ali levels are lowest in the spring, corresponding with the smoltification window for Atlantic salmon, then increase and reach the highest annual level during the summer (Figure 4).
Figure 4  Timeseries for A) toxic aluminum (Ali), B) dissolved aluminum (Ald), and C) total aluminum (Alt) for Mersey River and Moose Pit Brook from April 2015 to July 2016. Background colors indicate a change of seasons, where season one (April 1st to August 5th) is indicated in blue, season two (August 12th to October 31st) in white, and season three (November 1st to March 31st) in pink. 14% error is associated with Al\textsubscript{i} concentrations, and 10% error is associated with Al\textsubscript{d} and Al\textsubscript{t} measurements due to laboratory equipment (MacLeod, et al., 2018, in prep).

Performance Measure 2: Map of areas with Al\textsubscript{i}

Analysis of 63 watersheds across Nova Scotia conducted by Rotteveel et al. (2018b, in prep) using Al\textsubscript{i} estimation equations developed by Macleod et al. (2018, in prep) found that Al\textsubscript{i} levels exceed the recommended 15 µg·L\textsuperscript{-1} limit for aquatic ecosystem health in all examined watersheds between 2010 and 2015 (Figure 2). Indicating that liming initiatives should be considered across the province.
14 of the 63 sites examined by Rotteveel et al. (2018b, in prep), coincided with the 13 SU Priority Watersheds (Table 6).

Since toxic aluminum levels were predicted to be above 15 µg·L⁻¹ for all sites in the Rotteveel et al. study, all the sites identified below are recommended for consideration in liming initiatives.
Table 6  Study sites examined by Rotteveel et al. (2018b, in prep) which are located within the 13 priority watersheds. The 'Avoid' column indicates whether to avoid liming the watershed due to acid drainage-producing bedrock as the dominant bedrock underlying the site.

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Site ID</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Medium</th>
<th>Avoid</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIRD LAKE ABOUT 200 M E OF NW SHORE</td>
<td>NS01EA0020</td>
<td>43.9731</td>
<td>-65.9442</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>LITTLE TUPPER LAKE</td>
<td>NS01EE0006</td>
<td>44.4167</td>
<td>-64.9667</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>MOOSE PIT BROOK AT OUTFLOW TO TUPPER LAKE</td>
<td>NS01EE0014</td>
<td>44.4619</td>
<td>-65.0483</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>HUEY LAKE</td>
<td>NS01EE0028</td>
<td>44.3906</td>
<td>-64.7333</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>HIRTLLE LAKE</td>
<td>NS01EE0030</td>
<td>44.4667</td>
<td>-64.7500</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>MATTHEW LAKE</td>
<td>NS01EE0031</td>
<td>44.3281</td>
<td>-64.6831</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>ANNIS LAKE</td>
<td>NS01EE0061</td>
<td>44.3331</td>
<td>-64.8383</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>LAHAVE RIVER @ WEST NORTHFIELD BRIDGE (WSC GAUGE)</td>
<td>NS01EF0002</td>
<td>44.4467</td>
<td>-64.5917</td>
<td>River</td>
<td>No</td>
</tr>
<tr>
<td>LITTLE WILES LAKE</td>
<td>NS01EF0016</td>
<td>44.4000</td>
<td>-64.6472</td>
<td>Lake</td>
<td>Yes</td>
</tr>
<tr>
<td>ROCKY LAKE</td>
<td>NS01EF0017</td>
<td>44.4831</td>
<td>-64.7331</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>ROUND LAKE</td>
<td>NS01EN0021</td>
<td>45.0667</td>
<td>-62.3331</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>KELLY LAKE</td>
<td>NS01EN0024</td>
<td>45.0497</td>
<td>-62.3331</td>
<td>Lake</td>
<td>No</td>
</tr>
<tr>
<td>ST. MARY'S RIVER AT HWY 7 BRIDGE IN STILLWATER</td>
<td>NS01EO0001</td>
<td>45.1739</td>
<td>-61.9800</td>
<td>River</td>
<td>No</td>
</tr>
<tr>
<td>TUSKET RIVER AT WILSONS BRIDGE</td>
<td>NS01EA0001</td>
<td>43.9242</td>
<td>-65.8667</td>
<td>River</td>
<td>No</td>
</tr>
</tbody>
</table>

Performance Measure 3: Map and list of priority sites for liming and sites to avoid

The chemistry values of the above sites (Table 6) were examined, and the priority watersheds were selected based on not meeting the minimum water quality standards for freshwater ecosystem health identified in the Terrestrial Liming Guidebook for Southwestern Nova Scotia: Al concentration above 15 µg·L⁻¹, dissolved calcium (Ca²⁺) concentration below 2 mg·L⁻¹, and pH below 6.0 units. Four high priority sites were selected based on the above criteria,
whereof one should be avoided during liming activities due to the acid drainage-producing underlying bedrock (Figure 5 and Table 7).

![Image of map]

**Figure 6** High priority sites for liming initiatives in the 13 Southern Upland Priority Watersheds. Orange points and polygons indicate high priority watersheds, red indicates watersheds within those designated as high priority which should be avoided due to acid drainage-producing bedrock.

**Table 7** High priority liming sites identified within the 13 SU Priority Watersheds. The 'Avoid' column indicates whether to avoid liming the watershed due to acid drainage-producing bedrock as the dominant bedrock underlying the site. Water chemistry sample collected between 2010 and 2015 were averaged.

<table>
<thead>
<tr>
<th>Site Name</th>
<th>Site ID</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Medium</th>
<th>Average Al (µg·L⁻¹)</th>
<th>Average Ca (µg·L⁻¹)</th>
<th>Average DOC (mg·L⁻¹)</th>
<th>Average pH (unit)</th>
<th>Average Estimated Al (µg·L⁻¹)</th>
<th>Avoid</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOOSE PIT BROOK AT OUTFLOW TO</td>
<td>NS01EE0014</td>
<td>44.4619</td>
<td>-65.0483</td>
<td>Lake</td>
<td>236</td>
<td>797</td>
<td>16.41</td>
<td>4.79</td>
<td>128</td>
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</tr>
<tr>
<td>TUPPER LAKE</td>
<td>NS01EF0016</td>
<td>44.4000</td>
<td>-64.6472</td>
<td>Lake</td>
<td>96</td>
<td>822</td>
<td>3.22</td>
<td>5.96</td>
<td>78</td>
<td>Yes</td>
</tr>
<tr>
<td>LITTLE WILES LAKE</td>
<td>NS01EN0021</td>
<td>45.0667</td>
<td>-62.3331</td>
<td>Lake</td>
<td>237</td>
<td>921</td>
<td>12.13</td>
<td>5.21</td>
<td>124</td>
<td>No</td>
</tr>
<tr>
<td>ROUND LAKE</td>
<td>NS01EA0001</td>
<td>43.9242</td>
<td>-65.8667</td>
<td>River</td>
<td>288</td>
<td>1097</td>
<td>12.09</td>
<td>4.82</td>
<td>141</td>
<td>No</td>
</tr>
<tr>
<td>TUSKET RIVER AT WILSONS BRIDGE</td>
<td>NS01EA0001</td>
<td>43.9242</td>
<td>-65.8667</td>
<td>River</td>
<td>288</td>
<td>1097</td>
<td>12.09</td>
<td>4.82</td>
<td>141</td>
<td>No</td>
</tr>
</tbody>
</table>
Performance Measure 4: Catchment liming guidebook

The Terrestrial Liming Guidebook for Southwestern Nova Scotia has been submitted with this report. This guidebook was developed in collaboration with and funding from the Freshwater Fisheries Research Cooperative, the Atlantic Salmon Conservation Foundation, the Bluenose Coastal Action Foundation, and the Natural Sciences and Engineering Research Council.

Additional Findings: Preliminary results of NSSA catchment liming initiative

The catchment liming initiative conducted by the Nova Scotia Salmon Association and partners improved water quality for all treatment sites: total Ca levels to above minimum recommended level (2 mg·L\(^{-1}\)), pH was raised, but has not yet met the recommended level (6.0 units), and Al\(_i\) decreased but has not yet met the recommended level (15 µg·L\(^{-1}\)). Since the limestone must first percolate through the soil before interaction with groundwater can occur, it is expected that pH and Al\(_i\) will improve further as more time passes since initial application.

While control sites showed no change in calcium concentration following liming (Tukey adjusted comparison, \( z = 0.00, p = 1.00 \)), treatment sites showed a significant increase calcium concentration following liming (Tukey adjusted comparison, \( z = 5.49, p < 0.001 \)) (Figure 7). Calcium levels were estimated to increase by \( 1.57 \pm 0.29 \) µg·L\(^{-1}\) following liming.

![Figure 7](image-url) Significant increases in calcium were observed post-liming in treatment catchments while no significant increases occurred in control catchments. Here, sites denoted with “Cont” indicate a control site, while sites denoted with “Treat” indicate treatment sites. "Blow - CB" indicates the Cope Brook catchment, which received a small quantity of lime as a result of liming operations, but was not intentionally limed.

Control sites showed significantly lower pH (worsening) following liming (Tukey adjusted comparison, \( df = 39.31, t = -3.21, p = 0.013 \)) and were estimated to be on average 0.25 ±
0.08 pH units lower (Figure 8). Conversely, limed sites showed significantly higher pH (improvement) following liming (Tukey adjusted comparison, df = 39.24, t = 8.06, p < 0.001) and were estimated to be on average 0.65 ± 0.08 units higher following liming.

![Figure 8](image)

Figure 8  pH significantly decreased for control sites, while significantly increasing for treatment sites following limestone application. Here, sites denoted with “Cont” indicate a control site, while sites denoted with “Treat” indicate treatment sites. "Blow - CB” indicates the Cope Brook catchment, which received a small quantity of lime as a result of liming operations, but was not intentionally limed.

Control sites showed a non-significant increase in Al₃ (worsened) following liming (Tukey adjusted comparison, df = 42.74, t = 1.76, p = 0.303) and Al₃ was estimated to increase by 19.80 ± 11.21 µg·L⁻¹ (Figure 9). Conversely, limed sites showed a non-significant decrease (improvement) in Al₃ following liming (Tukey adjusted comparison, df = 42.74, t = -1.04, p = 0.73) and Al₃ levels were estimated to decrease by 11.69 ± 11.21 µg·L⁻¹.
Figure 9  Al₃ concentration non-significantly increased in control watersheds (worsened), while non-significantly decreasing in treatment watersheds (improved) following limestone application. Here, sites denoted with “Cont” indicate a control site, while sites denoted with “Treat” indicate treatment sites. "Blow - CB” indicates the Cope Brook catchment, which received a small quantity of lime as a result of liming operations, but was not intentionally limed.
**Recommendations**

This research has found that ionic aluminum, which is toxic to freshwater ecosystems is a province-wide problem in Nova Scotia, with levels measured consistently above the maximum recommended level for freshwater ecosystem health (15 µg·L⁻¹), and maximum levels reaching as high as 60 µg·L⁻¹ during the summer, when Alᵢ levels were found to be at their worst. Furthermore, using Alᵢ estimation equations, toxic aluminum levels were predicted and found to exceed the maximum recommended level in all of the study sites located within many of the 13 high priority watersheds designated by the Southern Uplands Priority Group. Based on these findings, it is recommended that predicted Alᵢ levels are verified with in-stream sampling, and a feasibility study of a province-wide freshwater acidification mitigation initiative is conducted to improve the freshwater habitat of key fish species to improve population productivity.

Of the sites examined, three sites within the 13 high priority watersheds have been selected as high priority sites as they do not meet any of the minimum criteria for freshwater ecosystem health, and are located in areas with bedrock suitable for liming. It is recommended that liming initiatives are developed for these areas in particular to improve chemical habitat suitability for freshwater fish species, improving population productivity.

Initial results of the helicopter liming project in the West River watershed indicate that terrestrial liming via helicopter application is effective at improving freshwater habitat suitability for key fish species, including the Atlantic salmon which are threatened with extirpation from areas in Nova Scotia. Although the initial results of the NSSA helicopter liming project are positive, it is recommended that continued water quality samples are collected to monitor for changes in effectivity, including the expected further decrease in Alᵢ levels.
The DHRG would like to thank the many researchers and volunteers who have dedicated their time to this project:

- Dr. Shannon Sterling (Earth Sciences, Dalhousie University)
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- Dr. Rob Jamieson (Civil and Resource Engineering, Dalhousie University)
- Dr. Edmund Halfyard (Nova Scotia Salmon Association)
- Marley Geddes (Environmental Systems Research Institute)
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- Lobke Rotteveel (Environmental Sciences, Dalhousie University)
- Franz Heubach (Mechanical Engineering, Dalhousie University)
- Siobhan Takala (Environmental Sciences and Sustainability, Dalhousie University)
- Emily Bibeau (Environmental Sciences and Sustainability, Dalhousie University)
- Lorena Heubach (Biology, Dalhousie University)
- Bouke Rotteveel (Biology, Saint Mary’s University)

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- Nova Scotia Salmon Association
- Nova Scotia Freshwater Fisheries Research Cooperative
- Nova Scotia Department of Natural Resources
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