

# Application of dolomite to forested catchments in Nova Scotia improves water quality - but more is needed to meet water quality targets

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## 1 Abstract

2 Populations of Atlantic salmon (*Salmo salar*) in Nova Scotia have plummeted in recent decades.  
3 One of the major threats for these populations is freshwater acidification, which has caused toxic water  
4 conditions including elevated stream water concentrations of toxic cationic aluminum ( $Al_i$ ). The only  
5 viable management option to reduce the threats of acidification to Atlantic salmon within the timeline  
6 needed to save the remaining populations is the addition of alkaline materials to waters or soils, via  
7 "liming." While studies in Europe, the UK, and the northeastern USA show that stream water  $Al_i$   
8 concentrations decrease in response to terrestrial liming with positive impacts on fish communities,  
9 stream chemistry response to terrestrial liming in Nova Scotia has not yet been examined. Here we  
10 examine the response of stream water chemistry to terrestrial liming in two types of experimental  
11 treatments in Nova Scotia. Our results show that liming decreased streamwater  $Al_i$  concentrations and  
12 increased dissolved calcium concentrations and pH levels. Untreated sites have water chemistry  
13 conditions that are toxic to Atlantic salmon, and although water chemistry was improved at treated sites,  
14 some parameters still do not meet thresholds for aquatic health, indicating that higher doses or  
15 repeated liming treatments are required. Results suggest that expansion of liming activities with higher  
16 liming doses may help avoid loss of the remaining wild salmon populations.

17

18 **Keywords:** Terrestrial liming, catchment liming, forests, Nova Scotia, aluminum, *Salmo salar*,  
19 freshwater acidification, soil amendments

20

21 **Synopsis:** Dolomitic soil amendments in Nova Scotia, Canada reduce toxic aluminum  
22 concentrations and improve water quality, but the dose/coverage needs to be increased to meet  
23 targets required to sustain Atlantic salmon populations.

## 24 1.0 Introduction

25 Despite reductions in anthropogenic sulfur and nitrogen emissions in North America and Europe in the  
26 past decades, recent work has shown a delay in acidification recovery<sup>1-3</sup> in some areas, including Nova  
27 Scotia (NS), Canada<sup>4,5</sup>. For example, in recent decades, pH has not increased significantly, and calcium  
28 (Ca) concentrations remain extremely low<sup>4</sup> in rivers and lakes in southern mainland NS. This region was  
29 one of the areas most strongly affected by acid precipitation<sup>6</sup> due to its base-cation poor and slow-  
30 weathering bedrock, thin soils with low acid neutralizing capacity, extensive wetlands, and episodic sea  
31 salt inputs<sup>4,7-10</sup>.

32 Increased concentrations of toxic cationic aluminum ( $\text{Al}_i$ ) are one of the most lethal effects of  
33 terrestrial and freshwater acidification, and include species such as  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_2^{1+}$ , and  $\text{Al}(\text{OH})_2^{2+}$ . The  
34 positively charged species bind to negatively charged fish gills, causing morbidity and mortality through  
35 suffocation<sup>11</sup>, reduced nutrient intake, and altered blood plasma levels<sup>12</sup>. Sub-lethal exposure to  $\text{Al}_i$  in the  
36 freshwater environment also causes osmoregulatory impairment<sup>13,14</sup>, which reduces survival in the  
37 marine environment<sup>15,16</sup>. High concentrations of  $\text{Al}_i$  in rivers have led to increased freshwater and marine  
38 mortality and the extirpation of native Atlantic salmon (*Salmo salar*) populations in many rivers, such as  
39 in Scandinavia<sup>17,18</sup>, the eastern USA<sup>13,19</sup> and NS<sup>20</sup>.

40 Aluminum (Al) speciation is pH dependent<sup>21,22</sup>, with Al being most toxic to salmonids between  
41 approximately pH 4.8 and 5.8<sup>23</sup>. Within this range, the cationic species  $\text{Al}(\text{OH})_2^{2+}$  and  $\text{Al}(\text{OH})_1^{2+}$  make up  
42 the highest proportions of total Al<sup>24</sup>. At pH values below 4.8, conditions are still toxic to Atlantic salmon,  
43 but toxicity is dominated by the acidity itself<sup>25,26</sup>.

44 Following reductions in sulfur emissions in the 1990s, many studies documented reduced concentrations  
45 of  $\text{Al}_i$  in rivers in the USA<sup>27-29</sup> and Europe<sup>30-32</sup>. However, recent work shows that 90% of monitored rivers  
46 in NS have  $\text{Al}_i$  concentrations that exceed the toxic threshold for aquatic health of 15  $\mu\text{g}/\text{L}$  determined by  
47 the European Inland Fisheries Commission (EIFAC)<sup>5,33</sup>.

48 Current acid deposition rates remain above critical loads for large areas of Nova Scotia<sup>34</sup>, and  
49 studies project that that forests and rivers will not naturally begin to recover from chronic acidification  
50 for decades<sup>26,35</sup>. The only viable management option to reduce the impacts of acidification is the  
51 application of Ca-bearing minerals (most commonly dolomite or calcite) to soils and freshwaters to  
52 neutralize acidity and replenish lost base-cations, via "liming"<sup>36</sup>. Application of minerals to catchment  
53 soils (terrestrial liming) has decreased  $\text{Al}_i$  concentrations in rivers in Scandinavia<sup>37-41</sup> and the eastern

54 USA<sup>42,43</sup>. Addition of mineral amendments to soils is increasing in NS, as it is becoming clear that the  
55 ecosystems are not recovering from acidification, but peer-reviewed studies of the impact of liming in  
56 the province are not yet available. Here, we report on the results of two experimental terrestrial liming  
57 projects in NS to increase our understanding of how the addition of Ca-and Mg-bearing carbonate  
58 minerals to forest soils, via liming, might affect water quality and Al<sub>i</sub> concentrations in chronically  
59 acidified watersheds in NS.

## 60 2.0 Materials and Methods

### 61 21. Study area

62 We examined the impact of terrestrial liming at two experimental catchments in NS, Maria Brook  
63 (MB) in the Gold River watershed and Keef Brook (KB) in the West River (Sheet Harbour) watershed  
64 (Figure 1, Table 1). The study catchments are predominantly forested, drain slow-weathering, base-  
65 cation poor bedrock, and have high dissolved organic carbon (DOC) concentrations<sup>44</sup> associated with  
66 extensive areas of wetlands and poorly drained soils with peat accumulation. Both catchments have  
67 been partially disturbed by previous forest harvesting.

68 We use a before-after-control-impact (BACI) study design for both experiments. The MB catchment  
69 experiment uses an upstream control site (MB-C) above the liming treatment and a downstream  
70 treatment site (MB-T) (Figure 2). The KB experiment uses a paired catchment control, where three sub-  
71 catchments within the KB catchment were treated: Colwell Creek (CC), Macgregor Brook (MGB), and  
72 Cope Brook (CB), and the neighbouring Brandon Lake Brook (BLB) catchment is used as the experimental  
73 control. All six sites were monitored before (denoted as  $X_{pre}$ ) and after treatment (denoted as  $X_{post}$ ).

### 74 2.2 Liming treatments

75 Crushed dolomitic limestone ( $\text{CaMg}(\text{CO}_3)_2$ ) from Mosher Limestone, NS was used as the soil amendment  
76 in both experiments. Crushed dolomite was applied to MB by hand over three summers (2012-2014),  
77 following a grid that targeted lowland wet areas, with a final local application rate of 14 t/ha over 17.4%  
78 of the total catchment area (Figure 2)<sup>45</sup>. The location of the control sampling site was moved in 2014, as  
79 the original site was located such that it may have been affected by the 2013 application. For the  
80 purposes of this study, eight samples collected at the original MB-C site prior to 2013 were used in the  
81 analysis. Crushed dolomite was applied to CC, CB, and MGB via helicopter targeting hydrologic source

82 areas (mapped to be where the water table was within 2 m of the surface), at a local application rate of  
83 10 t/ha, covering 32-92% of each sub-catchment (Table 2).

### 84 **2.3 Target water chemistry values**

85 We select target values for water chemistry parameters following standards set in previous  
86 studies. Toxic thresholds of  $Al_i$  vary based on the pH and calcium concentrations. Based on toxicological  
87 and geochemical studies on Al and Atlantic salmon, the EIFAC suggested a toxic threshold of 15  $\mu\text{g/L}$  for  
88 Atlantic salmon in freshwaters with pH between 5.0 and 6.0, and 30  $\mu\text{g/L}$  in  $\text{pH} < 5^{33}$ . Here we use 15  
89  $\mu\text{g/L}$  as a toxic threshold as most pH values at the treated sites are greater than or equal to 5.0,  
90 consistent with previous work in NS<sup>5,26</sup>. The target value for Ca concentrations is 2.0 mg/L following  
91 biological study of the impact of low Ca concentrations in lakes<sup>46</sup>. The abundance of *Daphnia* spp., a  
92 genus of common aquatic invertebrates and important organisms in the aquatic food chain were found  
93 to decrease in lakes where the Ca concentration was below 2.0 mg/L<sup>46</sup>. The 15  $\mu\text{g/L}$  threshold used for  
94  $Al_i$  is also representative of waters with “low” Ca concentrations, which were defined as concentrations <  
95 2.0 mg/L<sup>33</sup>. Our pH target is 5.8, as the toxic cationic species  $\text{Al}(\text{OH})^{2+}$  and  $\text{Al}(\text{OH})_1^{2+}$  make up the highest  
96 proportions of total Al between pH values of 4.8 and 5.8<sup>24</sup>. At pH values below 4.8, conditions are still  
97 toxic to Atlantic salmon, but toxicity is dominated by the acidity itself<sup>25,26</sup>.

### 98 **2.4 Data collection and analysis**

99 We measured water chemistry parameters at the six sample sites, including *in-situ*  
100 measurements of pH, water temperature ( $T_w$ ), specific conductance (SPC), and grab samples for lab  
101 analysis of concentrations of cations, anions, and metals and DOC. At MB, pre-treatment data were  
102 collected from 2011-2012, and post-treatment data were collected from 2012-2021. At KB sites, pre-  
103 treatment data were collected in 2016, and post-treatment data were collected from 2017-2022. At both  
104 sites, samples were collected on a weekly to monthly frequency through the spring-fall season, with  
105 irregular samples collected during the winter season (Figure B1).

106 We calculate  $Al_i$  as the difference between dissolved Al ( $Al_d$ ) and organically complexed Al ( $Al_o$ ),  
107 following previous studies<sup>5,47,48</sup> (Eq. 1). We speciated metals samples in the field to reduce errors caused  
108 by changes in temperature and pH during transport from field to lab. In 8 out of 190 (4%)  $Al_i$  samples  
109 collected during this project, the  $Al_d$  and  $Al_o$  values were very similar, and the result of equation 1 was  
110 negative. In these cases, we considered the  $Al_i$  concentration to be below the detection limit of our  
111 method.

112 
$$Al_i = Al_d - Al_o \quad (1)$$

113  $Al_d$  is the Al concentration of a sample passed through a 0.45  $\mu\text{m}$  polyethersulfone (PES) filter.  $Al_o$   
114 is the Al concentration in the eluate from passing filtered water through a 3 cm negatively charged cation  
115 exchange column (Bond Elut Jr. Strong Cation Exchange Column). Water was passed through the cation  
116 exchange column at a rate of 30-60 drops per minute, to avoid underestimating  $Al_i$ <sup>47</sup>. From this method,  
117  $Al_o$  is operationally defined as the non-labile, organically complexed species of Al, while  $Al_i$  is defined as  
118 the cationic species of Al (e.g.,  $Al^{3+}$ ,  $Al(OH)_2^{1+}$ ,  $Al(OH)^{2+}$ ).

119 Grab samples for metal analysis were collected using sterilized polyethylene syringes into  
120 sterilized polyethylene tubes (15 mL). Metal samples were filtered in the field and preserved with nitric  
121 acid ( $HNO_3$ ) within a week of arriving at the laboratory. Samples analyzed for DOC, anion content, and  
122 physical parameters were not filtered and were collected in sterilized amber glass or polyethylene  
123 bottles (1 L). All samples were kept cooled to a temperature of 4 °C during transport to the lab and were  
124 delivered to the lab within 24 hours of being collected.

125 Due to the long-term nature of the study, sample collection methods for pre-treatment data  
126 differed in the following ways<sup>5</sup>: 50 mL stream chemistry samples were collected instead of 1L samples,  
127 metal samples were preserved with nitric acid ( $HNO_3$ ) in the field instead of after arrival the lab, samples  
128 for DOC analysis were filtered (0.45  $\mu\text{m}$ ) in the field and transported in amber glass bottles containing  
129 sulfuric acid preservative ( $H_2SO_4$ ) to prevent denaturation instead of being filtered and preserved after  
130 arrival at the analysis lab. For some earlier samples (collected in 2016-2018), only the total Ca  
131 concentration (unfiltered) was measured. For the 15 samples where both total and dissolved Ca  
132 concentrations were measured, a two-sample Wilcoxon test showed no significant difference between  
133 total and dissolved Ca ( $p=1$ ). Therefore, in cases where only total Ca was measured, this value was used  
134 in place of dissolved Ca.

135 Some samples analyzed for organic carbon content were not filtered but results are reported as  
136 DOC, following Canadian Government water chemistry monitoring protocol, who established that  
137 particulate matter typically contributes < 5 % of TOC in rivers in this area, and that TOC can be used as a  
138 proxy for DOC<sup>49</sup>.

139 *In situ* measurements of pH,  $T_w$ , and SPC were taken using a portable water chemistry sonde (YSI  
140 ProQuatro). The sonde was calibrated at a minimum of once per week, typically the day before samples  
141 were collected but, in some cases, up to 6 days before the day of sample collection.

142 Continuous measurements of pH were collected at CC, MGB, and BLB using in-situ water  
143 chemistry sondes in hourly to 15-minute increments before and after treatment during 2016, allowing  
144 for visualization of immediate pH changes following the liming treatment.

145 We examined  $Al_i$  concentrations and other water chemistry parameters at treatment and control  
146 sites, as well as between pre-treatment and post-treatment data for significant differences using an  
147 unpaired two-samples Wilcoxon test. 4% of  $Al_i$  concentration values and 0.3% of Ca concentration values  
148 in the dataset were below detection limit values. In these cases, we substituted the value with half of the  
149 detection limit. When comparing control and treatment sites, only post-treatment data was used.  
150 Statistical analysis was carried out using R 4.2.2.

### 151 3.0 Results and Discussion

152 Our results confirm that current untreated water quality conditions are do not meet target  
153 values. Median  $Al_i$  concentrations at all sites are well above the 15  $\mu\text{g/L}$  toxic threshold, ranging from 44-  
154 54  $\mu\text{g/L}$  at control sites during the post-liming period (Table 3, Figures 3 and 4). 18 samples had extreme  
155  $Al_i$  concentrations ( $> 100 \mu\text{g/L}$ ) (9.5% of  $Al_i$  samples). Median Ca concentrations at control sites range  
156 from 1.1 to 1.5 mg/L during the post-liming period (Table 3, Figures 3 and 4), falling below targets.  
157 Median pH levels at control sites are well-below target values, ranging from 4.7 to 4.8 during the post-  
158 liming period (Table 3, Figures 3 and 4).

159 Median  $Al_i$  concentrations decreased or remained the same at all treated sites in the KB catchment after  
160 liming treatment occurred, while the median  $Al_i$  concentration at the control site increased by 64%  
161 during the same time period (Table 3, Figure 3). None of these changes are statistically significant;  
162 however, when comparing the control site to samples across all treatment sites for the post-liming  
163 period, the median  $Al_i$  concentration is significantly lower ( $p < 0.05$ ) at the treated sites (Table 4). No pre-  
164 treatment Al data was collected for the MB catchment sites, however when comparing the control and  
165 treatment site during the post-liming period, the median  $Al_i$  concentration is lower at the treated site  
166 though the difference is not statistically significant (Table 4). Despite reductions in  $Al_i$  concentrations, the  
167 median concentrations for all sites remain above the 15  $\mu\text{g/L}$  threshold.

168 Median  $Al_d$  concentration significantly increased by 16% at the KB catchment control site (BLB) between  
169 the pre- and post-liming periods (Table 3, Figure 3). Median  $Al_d$  concentration increased at each of the  
170 treated sites as well, though none of these changes were statistically significant. Median  $Al_d$

171 concentrations were not significantly different between the control and treatment sites at MB, though  
172  $Al_d$  concentration was higher at the treatment site (Table 4). The decreasing  $Al_i$  concentrations discussed  
173 above imply that the increase in  $Al_d$  at the treated sites must be predominantly driven by increasing  $Al_o$   
174 concentrations. This hypothesis is confirmed by the data, which show  $Al_o$  increased by 12-56% at  
175 treatment sites in the KB catchment after liming, with one site having a statistically significant increase  
176 (BLB; Table 3, Figure 3). The  $Al_o$  concentration is also higher at the treatment site than the control site at  
177 MB, though this difference is not statistically significant (Table 4).

178 Median Ca concentrations significantly increased at all sites in the KB watershed between the pre- and  
179 post-liming periods. While the Ca concentration at the control site (BLB) increased by 34%, the Ca  
180 concentration at the treated sites increased by 200-380% (Figure 3, Table 3). While the Ca concentration  
181 at BLB remains below the threshold for aquatic health, the Ca concentrations at all treated sites now  
182 exceed this threshold. Though the Ca concentration at the MB treatment site did increase after the  
183 liming treatment, this change was not statistically significant (Table 3, Figure 4). However, when  
184 comparing the control and treated site during the post-liming period, the Ca concentration at the treated  
185 site was significantly higher (Table 4). The Ca concentration at both MB sites remains below the  
186 threshold for aquatic health.

187 Median pH levels increased by 10-19 % at all treated KB sites between the pre- and post-liming  
188 periods, though only two of these increases were statistically significant (CC and MGB; Table 3, Figure 3).  
189 pH levels increased at limed sites almost immediately following treatment, while predictive modelling  
190 showed they would have remained low had treatment not occurred (Figure 5, Appendix C). During the  
191 same time period at the control site, median pH significantly decreased by 6% (Table 3, Figure 3).  
192 Despite these increases, median pH values at all sites remain below the target threshold of 5.8. There  
193 was no significant change at either the control or treatment site at MB between the pre- and post-liming  
194 periods, however when comparing the control and treated site during the post-liming period, the  
195 median pH at the treated site was significantly higher (Tables 3 and 4, Figure 4).

196 Our results show that the helicopter limestone application treatment at KB was more effective at  
197 reducing impacts of acidification than the hand application at MB, with significant improvements in pH  
198 and Ca at treated sites. Although there was no significant decrease in  $Al_i$  concentrations following  
199 treatment results suggest that the treatment prevented an increase of  $Al_i$  found at the control site, and  
200 that increasing concentrations of  $Al_d$  at treatment sites were driven predominantly by  $Al_o$  rather than  $Al_i$ .



201 Results suggest that, to meet water quality targets, more intensive application of dolomite is needed,  
202 either a higher dose (greater than 10 t/ha) or a higher percentage of the catchment treated. Previous  
203 studies on liming treatments have shown that obtaining long-term improvements to water quality  
204 requires either a high local application rate or a large treatment area, ideally both (Figure 6).

205 A delay in treatment effect could also be the reason we have not observed larger improvements  
206 in water quality. At the time of the most recent sampling events, six to seven years had passed since the  
207 liming treatment at KB and seven years had passed since the most recent liming treatment at MB.  
208 Though the impact on stream pH was almost immediate after treatment (Figure 5), previous studies have  
209 shown that soil can be slow to respond to amendment application, and Ca may take a prolonged period  
210 of time (~7 years) to migrate through the soil horizons and into runoff<sup>50</sup>. We recommend continued  
211 monitoring at these sites to determine if water quality improvements will increase with time, or whether  
212 an increase in application rate or treatment area may be necessary.

213 This project was limited by the short period of time available to collect pre-treatment data.  
214 Future liming trials with a longer pre-treatment data collection period are needed to improve our  
215 understanding of the impacts of liming on water chemistry. Further, with the current toxic water  
216 chemistry conditions in NS, establishment of a permanent reference catchment in the province would  
217 increase our ability to determine the impact of future liming trials.

218 Our study is also limited by a seasonal bias in sampling, where the monthly distribution is  
219 strongly skewed towards the summer and fall months, with few samples collected in the winter and  
220 spring period (Figure B1). Previous studies have identified strong seasonal patterns in Al concentrations  
221 and speciation, therefore we may be missing a key part of the Al picture in these catchments due to  
222 uneven distribution of samples throughout the year<sup>51</sup>.

223 Our results show that liming improved water chemistry, but many parameters still did not meet  
224 aquatic health thresholds for Atlantic salmon. Water quality at the untreated sites is unsuitable and toxic  
225 to Atlantic salmon. The results of this project demonstrate that addition of limestone to catchment soils  
226 can be an effective tool to decrease Al<sub>i</sub> concentrations and increase the dissolved Ca concentrations and  
227 pH levels in streams. Liming may improve stream water chemistry to that suitable for Atlantic salmon,  
228 provided appropriate methodology is used (sufficiently high dose, even dispersal, and large treatment  
229 area). For best results, limestone should be applied to a larger fraction of the catchment at a high  
230 application rate. We recommend continued monitoring of these catchments to detect any temporal

231 delay in the impact of terrestrial liming, as well as the establishment of further liming trials with a longer  
232 pre-treatment monitoring period. The establishment of reference catchments where long-term  
233 continuous monitoring takes place will also be helpful for future trials similar to this study. Soil  
234 amendments also have the potential to be applied as a carbon drawdown technology, therefore  
235 increasing our understanding of the effects of these amendments may be of use in the fight against  
236 climate change. Without this intervention, streams are unlikely to naturally recover to pre-acidification  
237 conditions on a timescale to support Atlantic salmon populations<sup>35</sup>.

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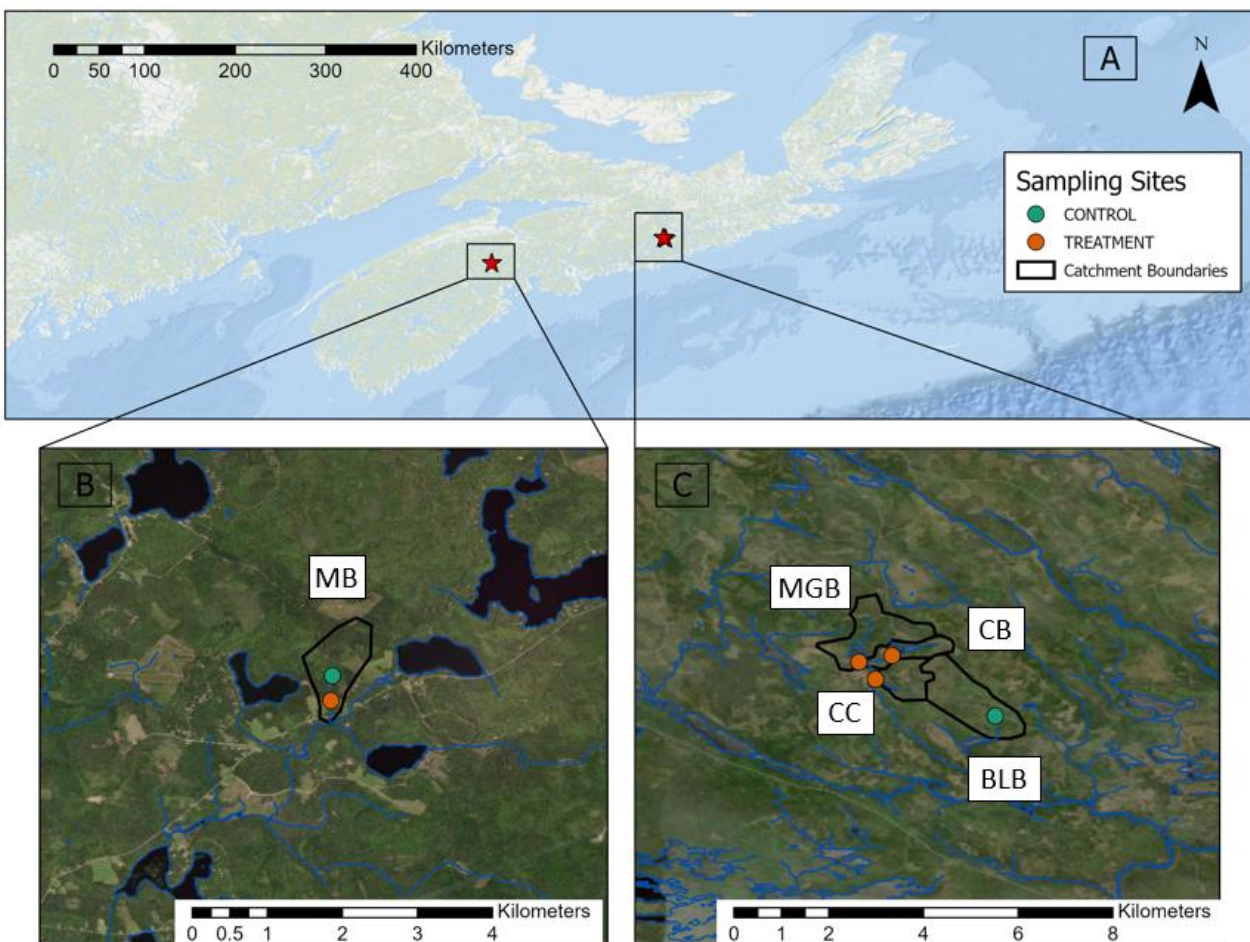
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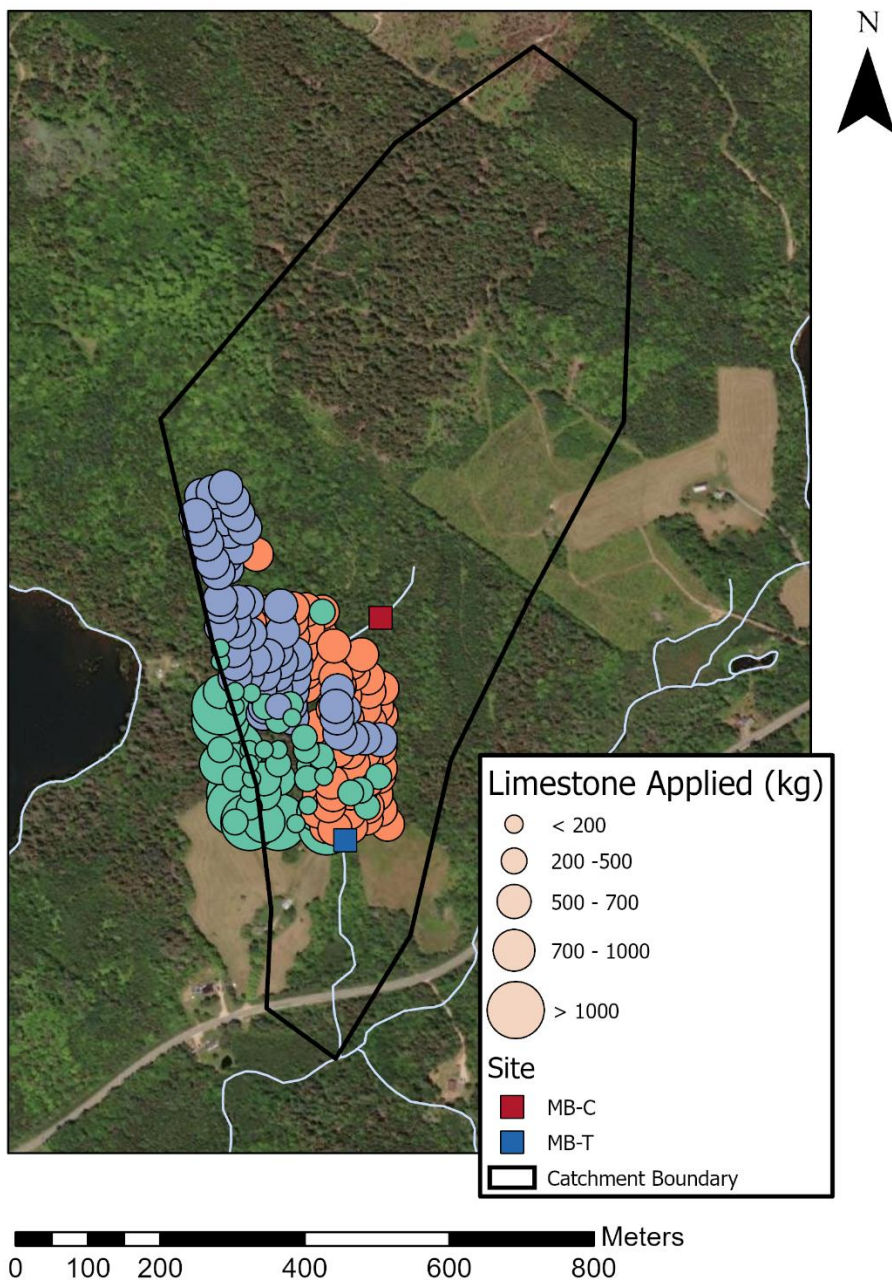
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392 7.0 Figures



393  
394 Figure 1. A) Location of Study catchments in Nova Scotia. B) Maria Brook catchment, with upstream  
395 control site (MB-C) and downstream treatment site (MB-T). C) Keef Brook catchment (CC, MGB, CC) and  
396 Brandon Lake Brook catchment (BLB).

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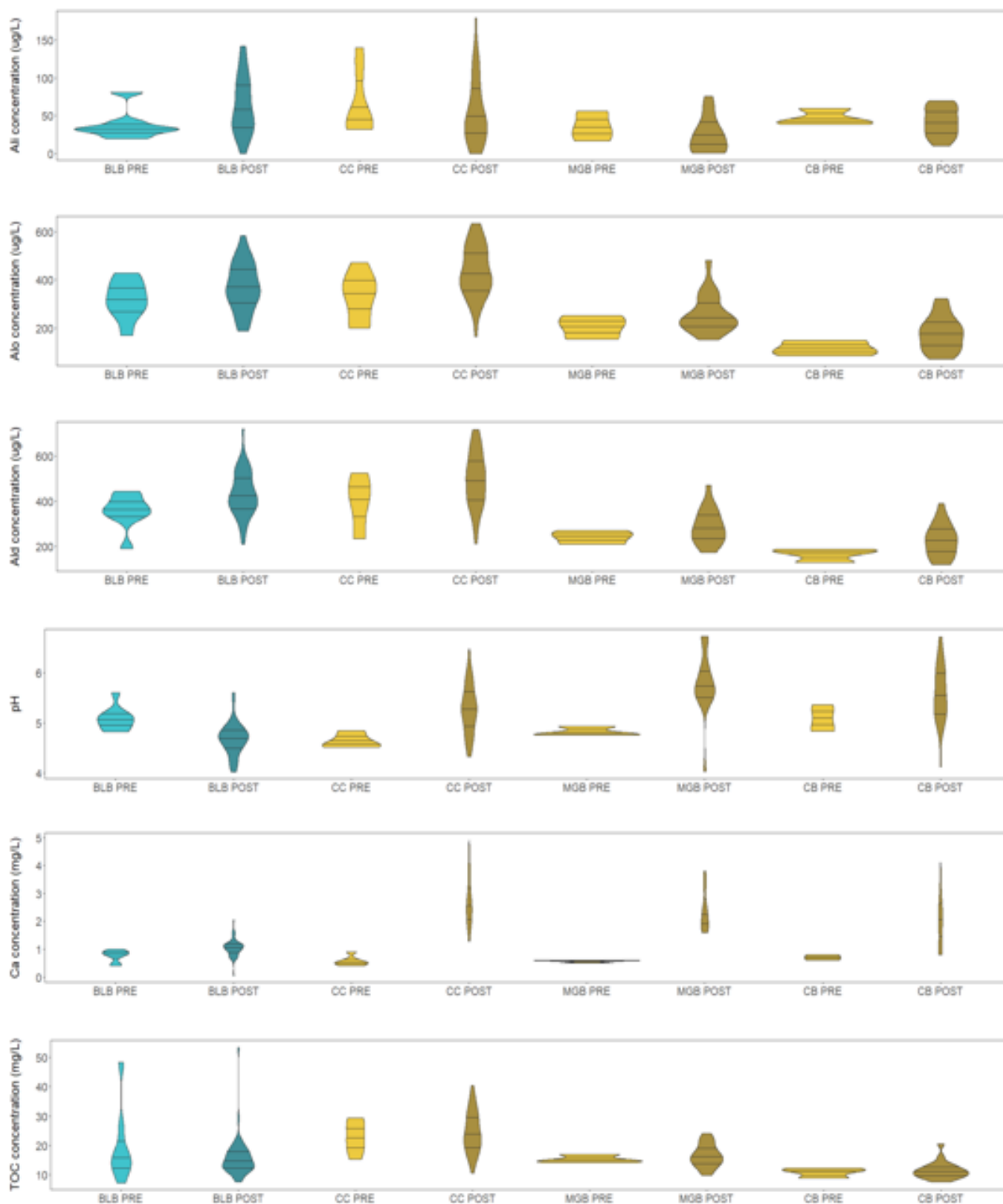


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399 Figure 2. Locations and amounts of limestone application during three treatment phases at MB. Teal  
 400 sites were treated in 2012, orange sites were treated in 2013, and purple sites were treated in 2014.

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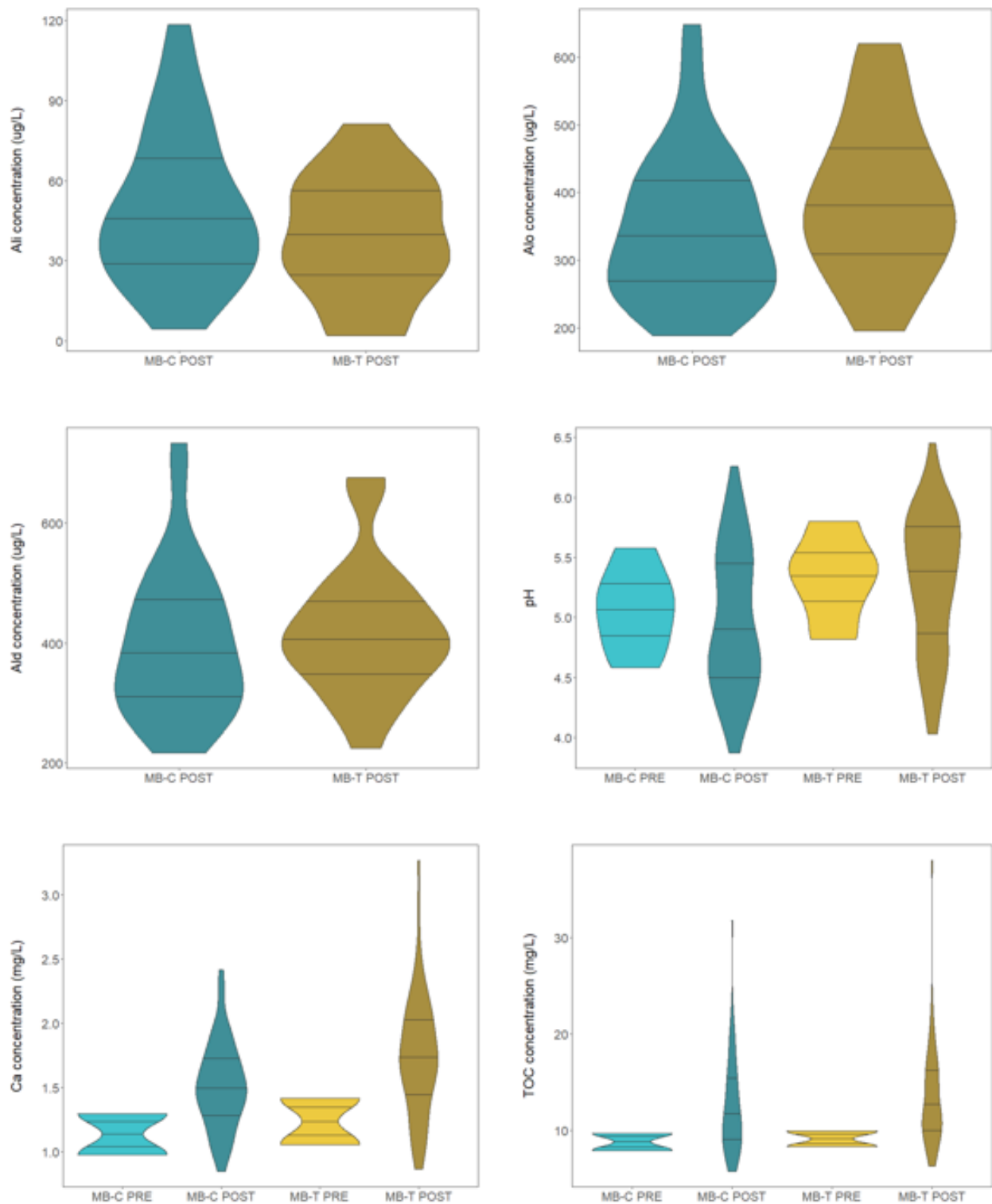




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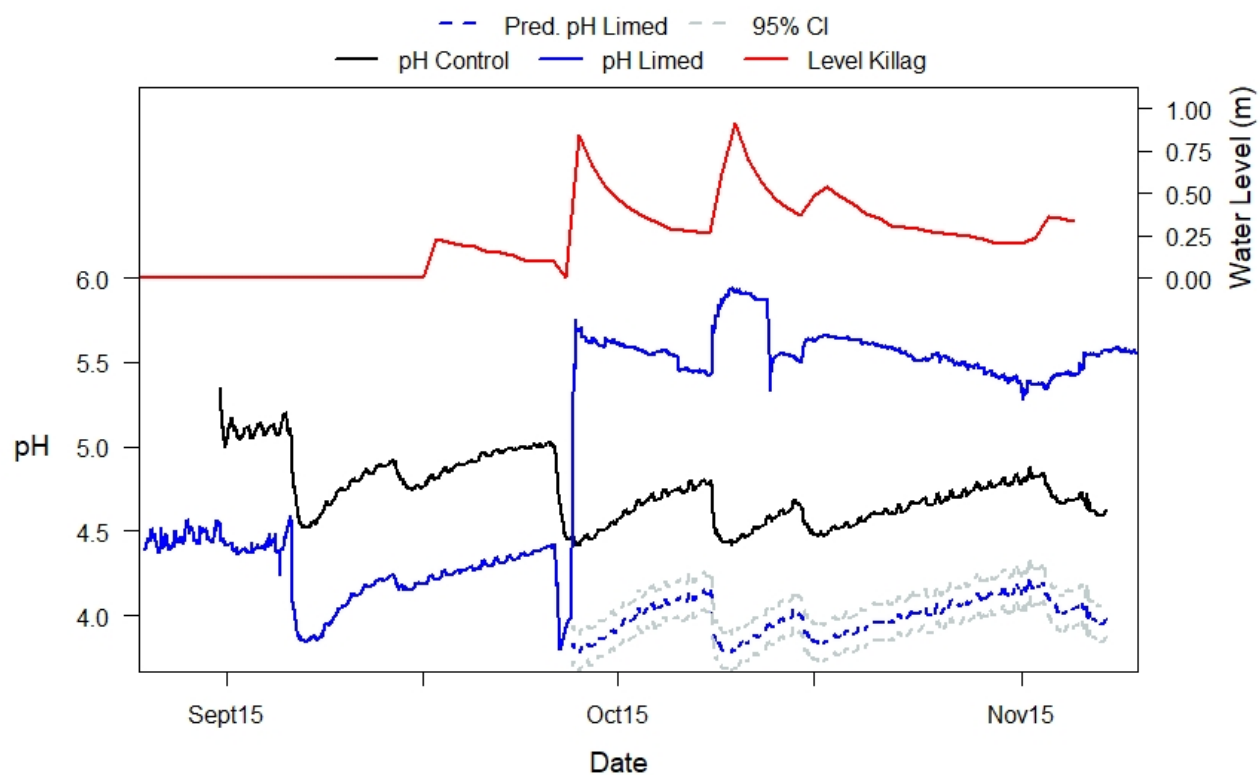
403 Figure 3. Values of water chemistry parameters of interest for control and treatment sites in the Keef  
 404 Brook catchment during the pre- (2016) and post-liming (2017-2022) periods. Blue represents control  
 405 site values and yellow represents treatment site values. Lighter shades represent pre-liming values and  
 406 darker shades represent post-liming values.

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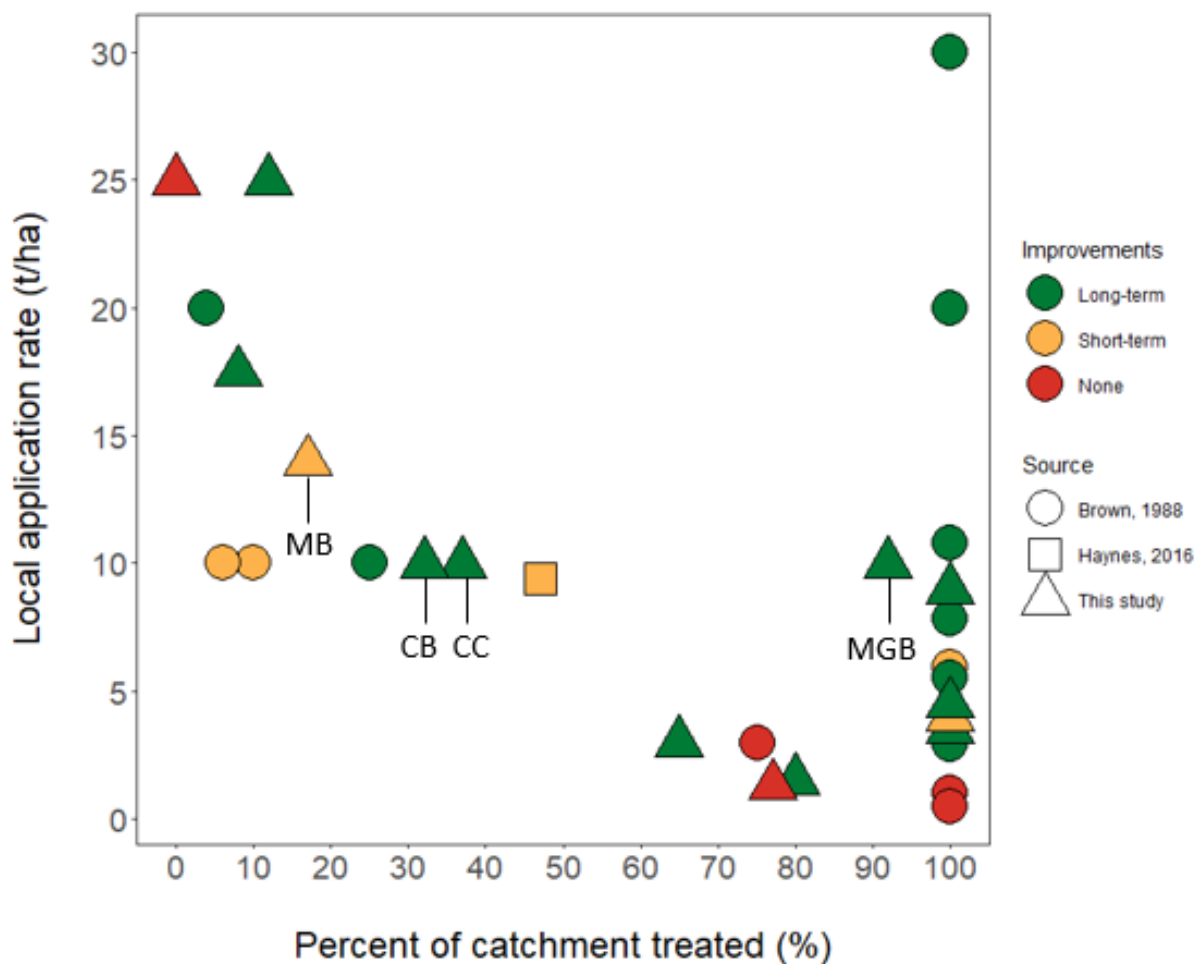
408 Figure 4. Comparison of water chemistry for control and treatment sites in the Maria Brook catchment  
 409 during the pre- (2011-2012) and post-liming (2012-2021) periods. Blue represents control site (MB-C)  
 410 and yellow represents treatment site (MB-T). Lighter shades represent pre-liming values and darker  
 411 shades represent post-liming values. No pre-treatments measurements of AI were taken.



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413 Figure 5. Comparison of continuous pH measurements in 2016 at a control site (BLB) and treated site  
 414 (CC), including predicted pH data for treated site if treatment had not occurred. See Appendix C for  
 415 information on predictive modelling used.

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 418 Figure 6. Comparison of effectiveness of liming studies in Europe and North America (Appendix A) with  
 419 local application rate and percent of catchment treated. Long-term improvements indicate increased  
 420 water quality indicators for greater than one year, short-term improvements indicated increased water  
 421 quality indicators for less than one year (adapted from Haynes, 2016 and Brown, 1988)<sup>45,52</sup>.

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426 **8.0 Tables**

427 Table 1. Study catchment characteristics. “n” refers to the number of sampling events. Hydrologically  
 428 active areas are defined as areas where the water table is within 2 m of the land surface (derived from  
 429 the Province of Nova Scotia’s wet areas mapping<sup>53</sup>).

| Site                     | Latitude  | Longitude  | Area (km <sup>2</sup> ) | % hydrologically active | n                         | Dominant bedrock type     | Forest type  |
|--------------------------|-----------|------------|-------------------------|-------------------------|---------------------------|---------------------------|--|
| Brandon Lake Brook (BLB) | 45.016543 | -62.689981 | 1.4                     | 45.8                    | 61                        | Sandstone/slate           | Mixed wood dominated by red spruce, red maple, and balsam fir                              |
| Colwell Creek (CC)       | 45.027892 | -62.712669 | 0.54                    | 52.7                    | 71                        | Sandstone/slate           | Mixed wood dominated by balsam fir, red spruce, and red maple                              |
| Cope Brook (CB)          | 45.0324   | -62.7096   | 0.47                    | 48.9                    | 39                        | Sandstone/slate           | Mixed wood dominated by black spruce, balsam fir, red maple, red spruce, and eastern larch |
| Macgregor Brook (MGB)    | 45.0312   | -62.7159   | 1.1                     | 48.2                    | 27                        | Sandstone/slate/granitoid | Mixed wood dominated by balsam fir, black spruce, red maple, and red spruce                |
| Maria Brook (MB)         | 44.778403 | -64.414356 | 0.47                    | 27.5                    | 64 control, 106 treatment | Granite                   | Mixed wood dominated by balsam fir, white spruce, and red maple                            |

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436 Table 2. Summary of area (ha) treated with dolomitic limestone at study sites from 2012-2014 for MB  
 437 and 2016-2018 for KB sites.

| Site | Total sub-catchment area (ha) | 2012 | 2013 | 2014 | 2016 | 2017 | 2018 | Total limed area (ha) | Percent area limed | Local application rate (t/ha) |
|------|-------------------------------|------|------|------|------|------|------|-----------------------|--------------------|-------------------------------|
| CC   | 54.6                          |      |      |      | 20.0 | N/A  | N/A  | 20.0                  | 36.6               | 10.0                          |
| CB   | 47.1                          |      |      |      | N/A  | 15.3 | N/A  | 15.3                  | 32.4               | 10.0                          |
| MGB  | 112.5                         |      |      |      | 45.8 | 6.0  | 51.5 | 103.0                 | 91.8               | 10.0                          |
| MB   | 47                            | 2.08 | 3.72 | 2.36 |      |      |      | 8.16                  | 17.4               | 14.3                          |

438 Notes:

- 439 1. In MGB 2016, due to weather and mechanical failure some of the 45.8 ha treated were below  
 440 the target dose of 10.0 t/ha. Specifically, 5.4 ha were limed at only 8.9 t/ha while 1.9 ha were  
 441 limed at only 5.2 t/ha.  
 442 2. Lakes and ponds were treated with a dose of only 2t/ha.  
 443 3. In CB 2016, it is possible that rain caused limestone runoff from the helicopter loading site  
 444 located within the CB sub-catchment to enter the brook.

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459 Table 3. Median values for water chemistry parameters at control and treated sites during pre- and post-liming periods. Statistically significant  
 460 differences ( $p < 0.05$ ) between pre- and post-liming periods are indicated by bold text. “n” refers to the number of sampling events. Control data  
 461 are indicated by manila-coloured cells. Note that no pre-liming Al data were collected at Maria Brook.

|                        | Brandon Lake Brook (Control) |                         |         | Colwell Creek (Treatment) |                         |         | MacGregor Brook (Treatment) |                         |         | Cope Brook (Treatment) |                         |         |
|------------------------|------------------------------|-------------------------|---------|---------------------------|-------------------------|---------|-----------------------------|-------------------------|---------|------------------------|-------------------------|---------|
|                        | Pre-liming (2016)            | Post-liming (2016-2022) | p-value | Pre-liming (2016)         | Post-liming (2016-2022) | p-value | Pre-liming (2016)           | Post-liming (2016-2022) | p-value | Pre-liming (2016)      | Post-liming (2016-2022) | p-value |
| pH                     | 5.0 (n=9)                    | 4.7 (n=47)              | 0.0003  | 4.6 (n=9)                 | 5.3 (n=54)              | 0.0003  | 4.8 (n=3)                   | 5.7 (n=18)              | 0.0182  | 5.0 (n=4)              | 5.5 (n=28)              | 0.0562  |
| Al <sub>i</sub> (µg/L) | 33 (n=7)                     | 54 (n=39)               | 0.054   | 46 (n=7)                  | 43 (n=42)               | 0.5677  | 34 (n=3)                    | 22 (n=18)               | 0.3914  | 43 (n=3)               | 43 (n=19)               | 0.8859  |
| Al <sub>o</sub> (µg/L) | 321 (n=8)                    | 361 (n=36)              | 0.1856  | 365 (n=7)                 | 417 (n=38)              | 0.0345  | 209 (n=3)                   | 235 (n=18)              | 0.3397  | 114 (n=3)              | 178 (n=19)              | 0.1513  |
| Al <sub>d</sub> (µg/L) | 364 (n=8)                    | 421 (n=41)              | 0.0499  | 413 (n=7)                 | 496 (n=43)              | 0.099   | 243 (n=3)                   | 265 (n=19)              | 0.3892  | 174 (n=3)              | 228 (n=20)              | 0.2732  |
| Ca <sub>d</sub> (mg/L) | 0.84 (n=8)                   | 1.1 (n=47)              | 0.0054  | 0.52 (n=7)                | 2.5 (n=50)              | <0.0001 | 0.6 (n=3)                   | 2.1 (n=18)              | 0.0077  | 0.70 (n=3)             | 2.1 (n=19)              | 0.011   |
| TOC (mg/L)             | 15 (n=8)                     | 15 (n=47)               | 0.6761  | 22 (n=7)                  | 24 (n=50)               | 0.5037  | 15 (n=3)                    | 16 (n=19)               | 0.774   | 11 (n=3)               | 11 (n=20)               | 0.9272  |

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|                        | Maria Brook (Control) |                         |         | Maria Brook (Treatment) |                         |         |
|------------------------|-----------------------|-------------------------|---------|-------------------------|-------------------------|---------|
|                        | Pre-liming (2012)     | Post-liming (2014-2012) | p-value | Pre-liming (2012)       | Post-liming (2014-2012) | p-value |
| pH                     | 5.1 (n=6)             | 4.8 (n=67)              | 0.567   | 5.4 (n=5)               | 5.4 (n=94)              | 0.9681  |
| Al <sub>i</sub> (µg/L) | N/A                   | 44 (n=32)               | N/A     | N/A                     | 36 (n=20)               | N/A     |
| Al <sub>o</sub> (µg/L) | N/A                   | 330 (n=28)              | N/A     | N/A                     | 378 (n=16)              | N/A     |
| Al <sub>d</sub> (µg/L) | N/A                   | 365 (n=32)              | N/A     | N/A                     | 407 (n=20)              | N/A     |
| Ca <sub>d</sub> (mg/L) | 1.1 (n=2)             | 1.5 (n=61)              | 0.0993  | 1.2 (n=2)               | 1.7 (n=71)              | 0.0942  |
| TOC (mg/L)             | 9 (n=2)               | 11 (n=63)               | 0.2314  | 9 (n=2)                 | 12 (n=54)               | 0.1276  |

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466 Table 4. Median values for water chemistry parameters across control and treated sites during the post-  
 467 liming period. Statistically significant differences ( $p < 0.05$ ) between control and treatment sites are  
 468 indicated by bold text. “n” refers to the number of sampling events.

| Keef Brook             |             |             |         |
|------------------------|-------------|-------------|---------|
|                        | Control     | Treatment   | p-value |
| pH                     | 4.7 (n=47)  | 5.4 (n=100) | <0.0001 |
| Al <sub>i</sub> (µg/L) | 54 (n=39)   | 39 (n=79)   | 0.0264  |
| Al <sub>o</sub> (µg/L) | 361 (n=36)  | 329 (n=75)  | 0.0446  |
| Al <sub>d</sub> (µg/L) | 421 (n=41)  | 375 (n=82)  | 0.0286  |
| Ca <sub>d</sub> (mg/L) | 1.1 (n=47)  | 2.4 (n=87)  | <0.0001 |
| TOC (mg/L)             | 15 (n=47)   | 19 (n=89)   | 0.0020  |
| Maria Brook            |             |             |         |
|                        | Control     | Treatment   | p-value |
| pH                     | 4.8 (n=67)  | 5.4 (n=94)  | 0.0004  |
| Al <sub>i</sub> (µg/L) | 44 (n=32)   | 36 (n=20)   | 0.2836  |
| Al <sub>o</sub> (µg/L) | 330 (n=28)  | 378 (n=16)  | 0.1607  |
| Al <sub>d</sub> (µg/L) | 365 (n=32)  | 407 (n=20)  | 0.3666  |
| Ca <sub>d</sub> (mg/L) | 1.5 (n=61)  | 1.7 (n=71)  | 0.0019  |
| TOC (mg/L)             | 11.2 (n=63) | 11.9 (n=54) | 0.2150  |

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