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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Abstract

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

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

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

2

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[1–3] in some areas, including Nova

27 Scotia (NS), Canada[4,5]. For example, in recent decades, pH has not increased significantly, and calcium

28 (Ca) concentrations remain extremely low[4] in rivers and lakes in southern mainland NS. This region was

29 one of the areas most strongly affected by acid precipitation[6] 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[4,7–10].

32   Increased concentrations of toxic cationic aluminum (Al_i) are one of the most lethal effects of

33 terrestrial and freshwater acidification, and include species such as Al^{3+}, $Al(OH)_2^{1+}$, and $Al(OH)^{2+}$. The

34 positively charged species bind to negatively charged fish gills, causing morbidity and mortality through

35 suffocation[11], reduced nutrient intake, and altered blood plasma levels[12]. Sub-lethal exposure to Al_i in the

36 freshwater environment also causes osmoregulatory impairment [13,14], which reduces survival in the

37 marine environment[15,16]. High concentrations of 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[17,18], the eastern USA[13,19] and NS[20].

40   Aluminum (Al) speciation is pH dependent[21,22], with Al being most toxic to salmonids between

41 approximately pH 4.8 and 5.8[23]. Within this range, the cationic species $Al(OH)^{2+}$ and $Al(OH)_1^{2+}$ make up

42 the highest proportions of total Al[24]. At pH values below 4.8, conditions are still toxic to Atlantic salmon,

43 but toxicity is dominated by the acidity itself[25,26].

44 Following reductions in sulfur emissions in the 1990s, many studies documented reduced concentrations

45 of Al_i in rivers in the USA[27–29] and Europe[30–32]. However, recent work shows that 90% of monitored rivers

46 in NS have Al_i concentrations that exceed the toxic threshold for aquatic health of 15 µg/L determined by

47 the European Inland Fisheries Commission (EIFAC)[5,33].

48   Current acid deposition rates remain above critical loads for large areas of Nova Scotia[34], and

49 studies project that that forests and rivers will not naturally begin to recover from chronic acidification

50 for decades[26,35]. 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"[36]. Application of minerals to catchment

53 soils (terrestrial liming) has decreased Al_i concentrations in rivers in Scandinavia[37–41] and the eastern

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54 USA[42,43]. 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_i concentrations in chronically

59 acidified watersheds in NS.

2.0 Materials and Methods

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21. Study area

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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[44] 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}).

2.2 Liming treatments

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75 Crushed dolomitic limestone ($CaMg(CO_3)_2$) 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)[45]. 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

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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).

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 μg/L for

88   Atlantic salmon in freshwaters with pH between 5.0 and 6.0, and 30 μg/L in pH < 5[33]. Here we use 15

89   μg/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[5,26]. The target value for Ca concentrations is 2.0 mg/L following

91   biological study of the impact of low Ca concentrations in lakes[46]. 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[46]. The 15 μg/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[33]. Our pH target is 5.8, as the toxic cationic species $Al(OH)^{2+}$ and $Al(OH)_1^{2+}$ make up the highest

96   proportions of total Al between pH values of 4.8 and 5.8[24]. At pH values below 4.8, conditions are still

97   toxic to Atlantic salmon, but toxicity is dominated by the acidity itself[25,26].

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[5,47,48] (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.

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

113 Al_d is the Al concentration of a sample passed through a 0.45 μm 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[47]. 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[5]: 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 μm) 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[49].

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.

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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 µg/L toxic threshold, ranging from 44-
154   54 µg/L at control sites during the post-liming period (Table 3, Figures 3 and 4). 18 samples had extreme
155   Al_i concentrations (> 100 µg/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 µg/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

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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.

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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[50]. 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[51].

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_i 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

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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[35].

238   6.0 Acknowledgements

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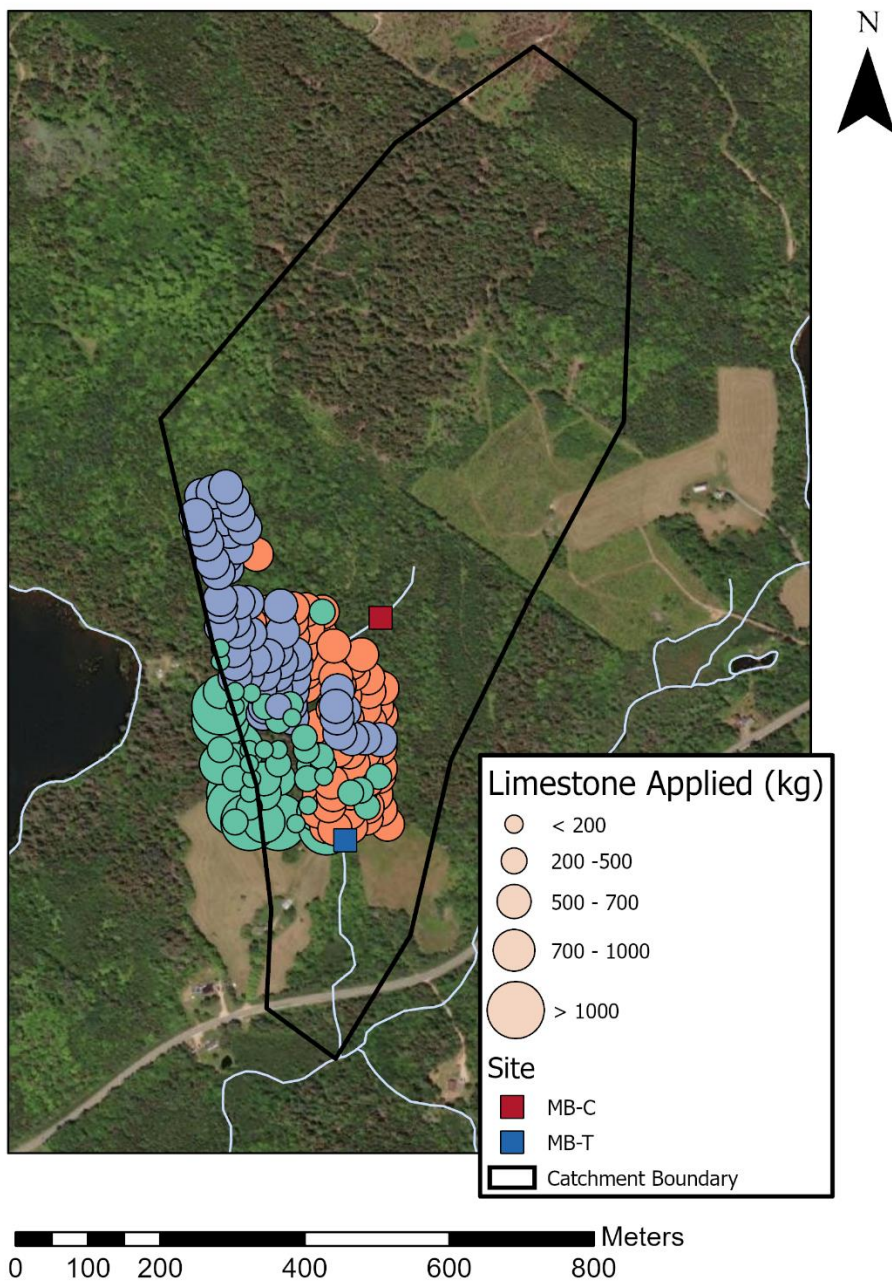391

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7.0 Figures

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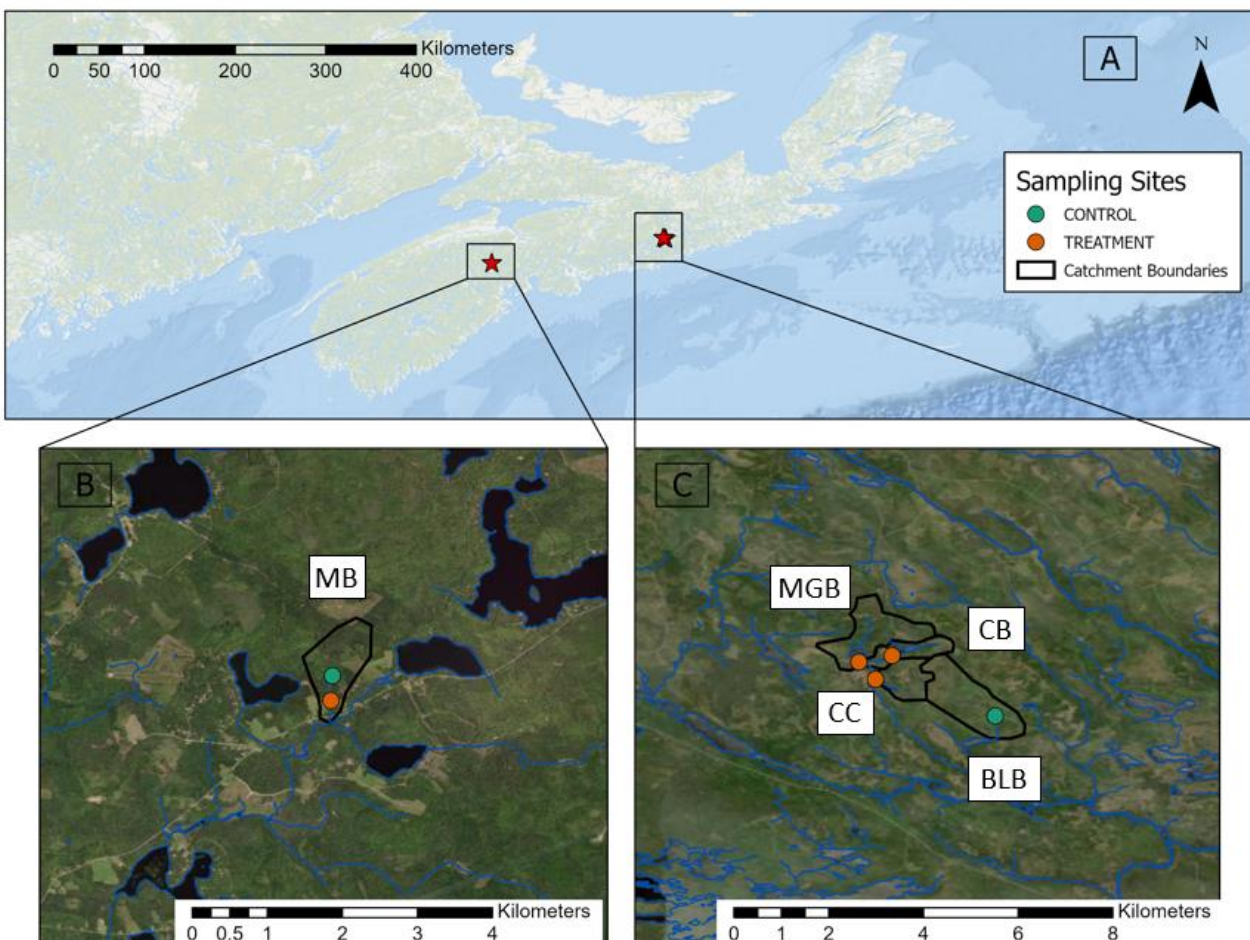
Figure 1. A) Location of Study catchments in Nova Scotia. B) Maria Brook catchment, with upstream
control site (MB-C) and downstream treatment site (MB-T). C) Keef Brook catchment (CC, MGB, CC) and
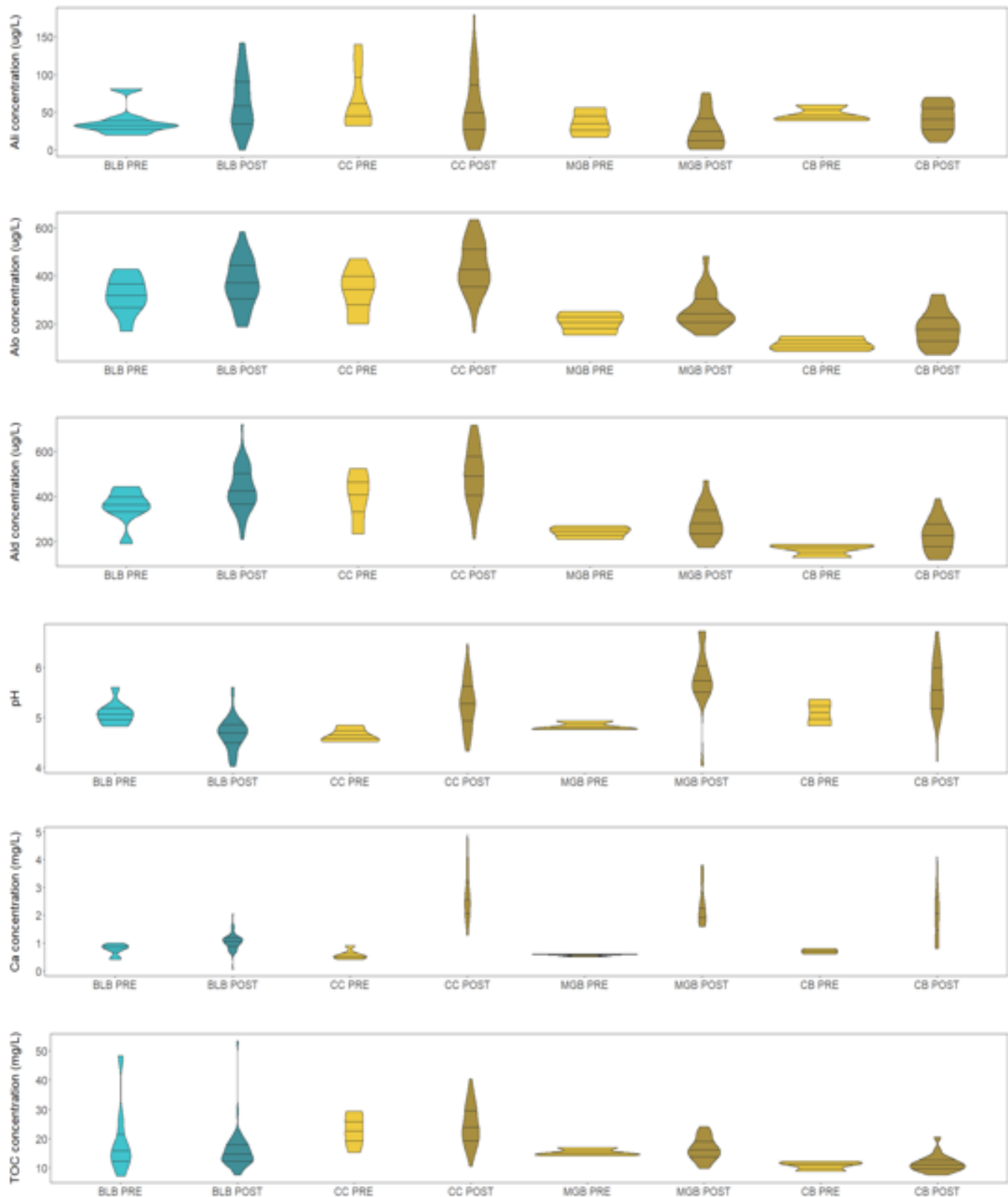Brandon Lake Brook catchment (BLB).

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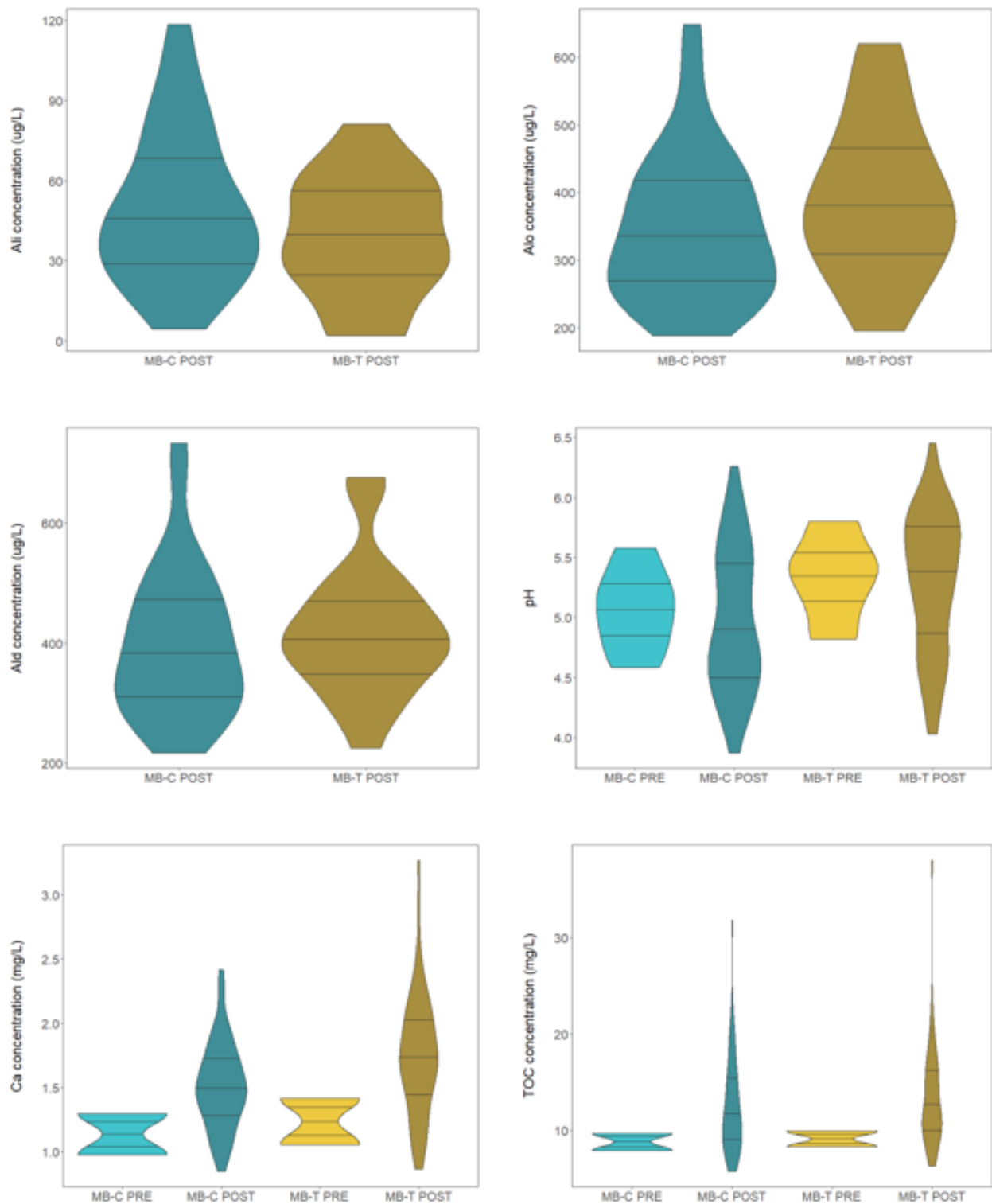
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Figure 3. Values of water chemistry parameters of interest for control and treatment sites in the Keef
Brook catchment during the pre- (2016) and post-liming (2017-2022) periods. Blue represents control
site values and yellow represents treatment site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

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

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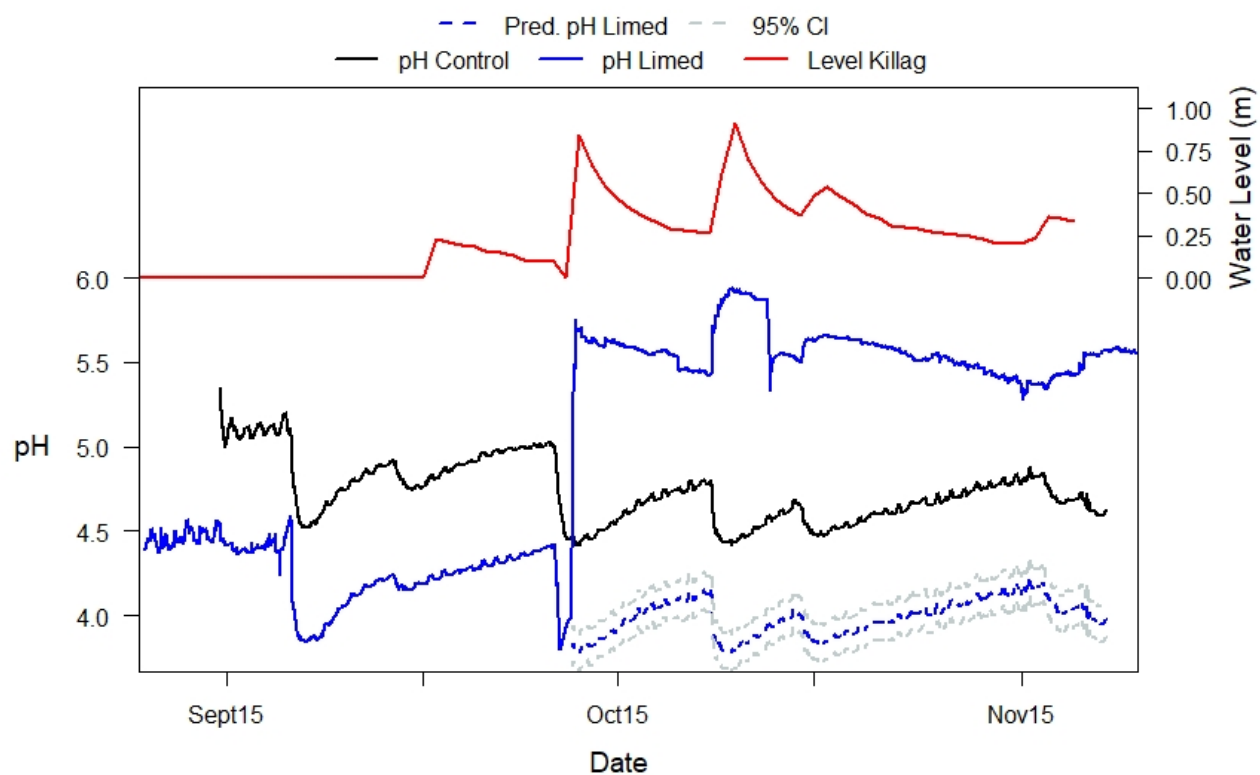
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413   Figure 5. Comparison of continuous pH measurements in 2016 at a control site (BLB) and treated site
414   (CC), including predicted pH data for treated site if treatment had not occurred. See Appendix C for
415   information on predictive modelling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

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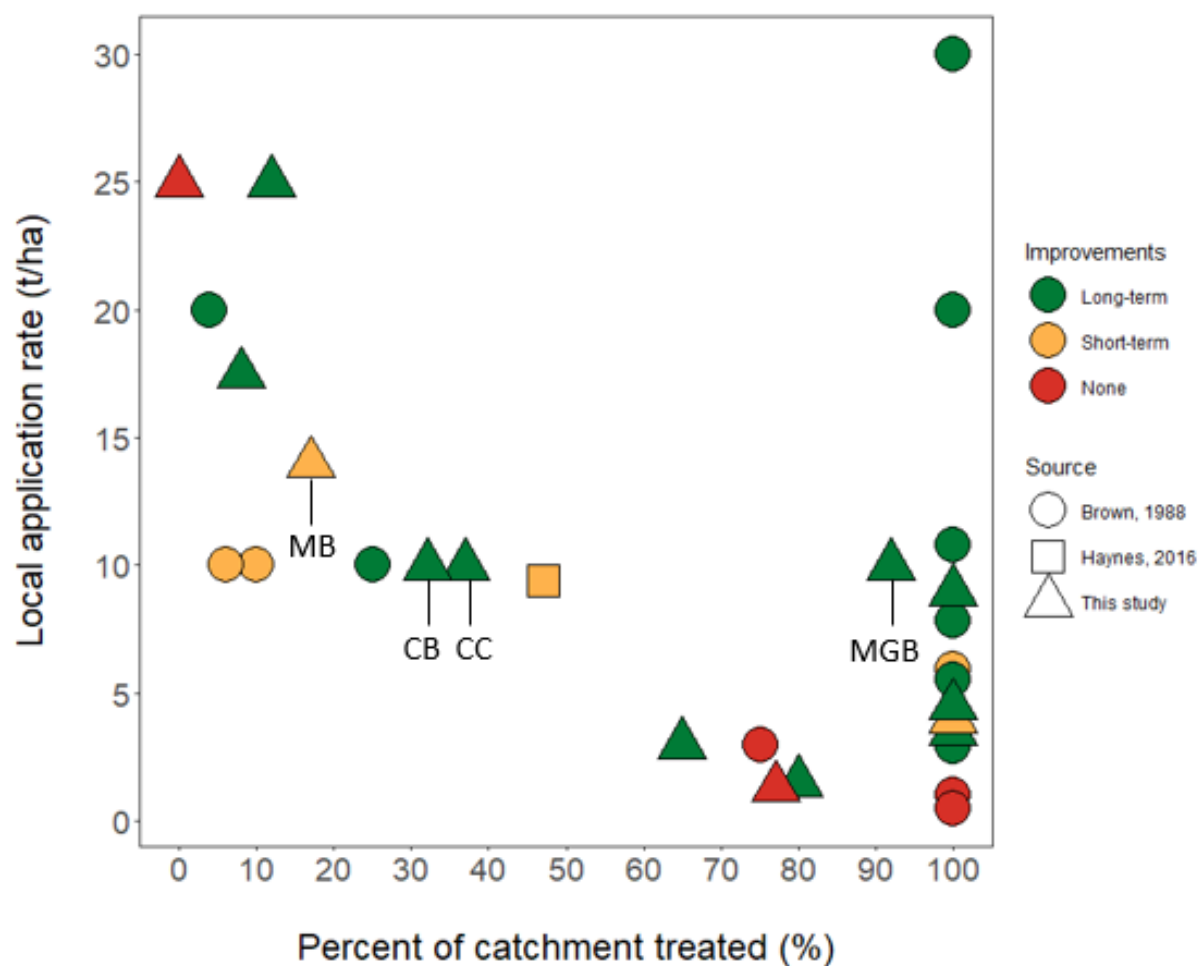
Figure 6. Comparison of effectiveness of liming studies in Europe and North America (Appendix A) with local application rate and percent of catchment treated. Long-term improvements indicate increased water quality indicators for greater than one year, short-term improvements indicated increased water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

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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[53]).

Site	Latitude	Longitude	Area (km^2)	% 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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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:

1. In MGB 2016, due to weather and mechanical failure some of the 45.8 ha treated were below 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 limed at only 5.2 t/ha.
2. Lakes and ponds were treated with a dose of only 2t/ha.
3. In CB 2016, it is possible that rain caused limestone runoff from the helicopter loading site 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_i (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_o (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_d (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_d (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_i (µg/L)	N/A	44 (n=32)	N/A	N/A	36 (n=20)	N/A
Al_o (µg/L)	N/A	330 (n=28)	N/A	N/A	378 (n=16)	N/A
Al_d (µg/L)	N/A	365 (n=32)	N/A	N/A	407 (n=20)	N/A
Ca_d (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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Table 4. Median values for water chemistry parameters across control and treated sites during the post-liming period. Statistically significant differences ($p < 0.05$) between control and treatment sites are 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_i (μg/L)	54 (n=39)	39 (n=79)	0.0264
Al_o (μg/L)	361 (n=36)	329 (n=75)	0.0446
Al_d (μg/L)	421 (n=41)	375 (n=82)	0.0286
Ca_d (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_i (μg/L)	44 (n=32)	36 (n=20)	0.2836
Al_o (μg/L)	330 (n=28)	378 (n=16)	0.1607
Al_d (μg/L)	365 (n=32)	407 (n=20)	0.3666
Ca_d (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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