Project report: Acidification mitigation plan for high priority salmon watersheds: effectiveness of liming to reduce toxic aluminum levels, year 2

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Contents

Executive summary

Increased streamwater concentrations of toxic cationic aluminum (Al_i) caused by terrestrial and freshwater acidification have demonstrated toxic effects on Atlantic salmon (*Salmo salar*). The only viable management option to reduce the impacts of acidification other than emissions reductions is the addition of calcium-bearing minerals to waters or soils, via “liming”. Studies of liming elsewhere have shown resulting decreases in streamwater Al_i concentrations and positive impacts on fish communities, but stream chemistry response to liming in Nova Scotia is poorly understood. Here we aim to increase this understanding by measuring concentrations of Al_i and other water chemistry parameters known to influence Al_i (pH, calcium, organic carbon, etc.) in four experimental catchments in Nova Scotia. Our results show that liming generally decreased Al_i concentrations in stream water 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, there are still some parameters that do not meet thresholds for aquatic health, indicating that further liming treatments are required. This study was limited by the period of data collection, and future liming trials using a before-after-control-impact (BACI) experimental design will be required to gain a full understanding of Al_i dynamics in Nova Scotia and their response to liming.

Introduction

Cationic aluminum (Al_i) is toxic to salmonids and increased concentrations of these aluminum (Al) species are one of the most lethal effects of terrestrial and freshwater acidification. Following reductions in sulfur emissions in the 1990s, many studies observed reduced concentrations of Al_i in rivers in the USA (Baldigo and Lawrence, 2000; Buchanan et al., 2017; Burns et al., 2006) and Europe (Beneš et al., 2017; Davies et al., 2005; Monteith et al., 2014). However, recent work has shown a delay in acidification recovery in some areas (Houle et al., 2006; Warby et al., 2009; Watmough et al., 2016), including Nova Scotia (NS), Canada (Clair et al., 2011; Sterling et al., 2020). A recent paper published with the support of ASCF, Sterling et al., 2020 shows that 9 out of 10 rivers monitored in NS have Al_i concentrations that exceed the suggested toxic threshold for aquatic health of 15 ug L^{-1} (Howells et al., 1990). High concentrations of Al_i in rivers have led to increased freshwater and marine mortality and the extirpation of native Atlantic salmon (*Salmo salar*) populations in many rivers, such as in Scandinavia (Henriksen et al., 1984; Hesthagen and Hansen, 1991), the eastern USA (Monette and McCormick, 2008; Parrish et al., 1998) and Nova Scotia (Watt, 1987).

Cationic species of Al, such as Al^{3+}, $Al(OH)_2^{1+}$, and $Al(OH)^{2+}$, are considered to be the most toxic to salmonids, as these positively charged species bind to negatively charged fish gills, causing morbidity and mortality through suffocation (Exley et al., 1991), reducing nutrient intake at gill sites, and altering blood plasma levels (Nilsen et al., 2010). Sub-lethal exposure to Al in the freshwater environment also causes osmoregulatory impairment (Monette and McCormick, 2008; Regish et al., 2018), which reduces survival in the marine environment (McCormick et al., 2009; Staurnes et al., 1996).

Al speciation is pH dependent (Helliweli et al., 1983; Lydersen, 1990), with Al being most toxic to salmonids between pH 4.8 and 5.8 (Driscoll and Schecher, 1990). Within this range, the cationic species $Al(OH)^{2+}$ and $Al(OH)_1^{2+}$ make up the highest proportions of total Al (Gensemer and Playle, 1999). At pH values below 4.8, conditions are still toxic to Atlantic salmon, but toxicity is dominated by the acidity itself (Lacoul et al., 2011; Sterling et al., 2014).

Current acid deposition rates remain above critical loads for large areas of Nova Scotia (NEG-ECP, 2007), and this ongoing deposition combined with slow rates of calcium (Ca) release from local bedrock could mean that rivers will not naturally begin to recover from chronic acidification for close to a century (Clair et al., 2004; Sterling et al., 2014). The only viable management option to begin to reduce the impacts of acidification is the application of Ca-bearing minerals (most commonly limestone) to soils and freshwaters to neutralize acidity, via “liming” (Lawrence et al., 2016). Liming to catchment soils has been shown to decrease the concentrations of Al_i in rivers in Scandinavia (Hindar et al., 2003; Hindar, 2005; Hultberg et al., 1995; Traaen et al., 1997; Westling and Zetterberg, 2007) and the eastern USA (Josephson et al., 2019; Shao et al., 2016), and studies investigating the impact of adding limestone directly to surface waters in Europe and the USA found that fish survival, reproduction, and density increased following liming (Clair and Hindar, 2005; Eriksson et al., 1983; Lawrence et al., 2016; McCahon et al., 1989; Rask et al., 2007). However, studies of the impact of liming in NS remain limited. The liming experiments studied here are part of a very small number in the province. Thus, we are just beginning to understand how liming affects stream chemistry and Atlantic salmon populations in NS.

The aim of this project is to increase the understanding of how the addition of Ca-bearing minerals to soils and freshwaters, via liming, might affect water quality and Al_i concentrations in chronically acidified watersheds in NS. We measure Al_i concentrations and a suite of other water chemistry parameters at four experimental catchment sites where liming has been conducted to determine current the current stream chemistry status and the impact of liming on these conditions.

Methods

Study area

We surveyed Al_i concentrations at four experimental catchment sites in NS, Maria Brook (MB) in the Gold River watershed, and Colwell Creek (CC), the Killag River (KR), and the West River (WR) in the West River watershed (Figure 1). For each catchment, a control and treatment site were sampled for a total of eight study sites. Our study sites are predominantly forested, and drain slow-weathering, base-cation poor bedrock. The catchments also have relatively high dissolved organic carbon (DOC) concentrations (Ginn et al., 2007), associated with the large number of wetlands in the region (Clair et al., 2008).

Liming treatments

In the MB and CC watersheds, partial catchment liming was conducted using crushed dolomitic limestone ($CaMg(CO_3)_2$). MB was treated via hand application of crushed limestone in three separate treatments (2012-2014), with dosages varying from 1-50 t/ha. Application in this watershed focused on hydrologic source areas (lowland wet areas). The area downstream of where the limestone was applied was designated as the treatment area, while the area upstream of where the limestone was applied was designated as the control area. CC was treated via helicopter application to hydrologically active areas (where the water table was within 2m of the surface), at a dosage of 10 t/ha. The paired catchment of Brandon Lake Brook remained untreated as the control catchment (referred to as CC-T henceforth).

In the KR and WR watersheds, crushed dolomitic limestone was added to directly to the stream water via lime dosers at a rate of 7.5g per m^3 of water. This treatment has been ongoing at WR since 2005 and at KR since 2016. For both rivers, the control samples were collected ~200m upstream of the lime doser, and treatment samples were collected ~4km downstream of the lime doser.

Data collection and analysis

We measured Al_i concentrations and other water chemistry parameters at the sample locations (Figure 1), including pH, water temperature (T_w), specific conductance (SPC), and concentrations of constituents such as dissolved Ca and total organic carbon (TOC). Measurements were taken from June to November in 2019, from September to December in 2020, and from June to December in 2021, on a biweekly to weekly frequency.

Al_i sampling events were comprised of grab samples for lab analysis and in situ measurements of pH, T_w, and SPC. We calculate Al_i as the difference between dissolved Al (Al_d) and organically complexed Al (Al_o), following Dennis and Clair, 2012, Poléo, 1995, and Sterling et al., 2020 (Eq. 1). Speciating metals samples in the field reduces errors caused by changes in temperature and pH during transport from field to lab.

$$Al_i = Al_d - Al_o \tag{1}$$

Al_d is measured as the Al concentration of a sample passed through a 0.45 um polyethersulfone (PES) filter. Al_o is measured as the eluate from passing water through a 3 cm negatively charged cation exchange column (Bond Elut Jr. Strong Cation Exchange Column). Water was passed through the cation exchange column at a rate of 30-60 drops per minute, to avoid underestimating Al_i (Dennis and Clair, 2012). From this method, Al_o is operationally defined as the non-labile, organically complexed species of Al, while Al_i is defined as the cationic species of Al (e.g., Al^{3+}, $Al(OH)_2^{1+}$, $Al(OH)^{2+}$).

Samples to be analyzed for metals content as described above were collected using sterilized polyethylene syringes into sterilized polyethylene tubes (15 mL). All metals samples were filtered in the field and preserved with nitric acid (HNO_3) within a week of arriving at the laboratory. Samples analyzed for TOC, anion content, and physical parameters were not filtered and were collected in sterilized amber glass bottles (1L). All samples were kept cooled to a temperature of 4 °C during transport to the lab and were delivered to the lab within 24 hours of being collected.

As the samples analyzed for organic carbon content were not filtered, results are therefore reported as TOC. However, the suspended loads in the study rivers are very low and it has been established that particulate matter typically contributes <5% of TOC, and that TOC can therefore be used as a proxy for DOC (Clair et al., 2008).

In situ measurements of pH, T_w, and SPC were taken using a portable water chemistry sonde. The sonde was calibrated at a minimum of once per week, typically the day before samples were collected.

Pre-treatment data was collected for MB in 2012 following the methods in Sterling et al., 2014. Pre-treatment data was collected for CC in 2016 following the methods in Sterling et al., 2020. No pre-treatment data was collected for KR or WR.

We examined Al_i concentrations and other water chemistry parameters at treatment and control sites, as well as between pre-treatment and post-treatment data for significant differences using an unpaired two-samples Wilcoxon test. Statistical analysis was carried out using R 4.1.2.

Results

Water chemistry conditions at unlimed sites are currently toxic to Atlantic salmon. Median Al_i concentrations at all sites are well above the 15 ug/L toxic threshold, ranging from 49.9 to 64.8 ug/L (Table 1, Figure 2). Median Ca concentrations at unlimed sites range from 1.01 to 1.68 mg/L (Table 1, Figure 3), falling below the threshold for aquatic health (2.0 mg/L) (Jeziorski et al., 2008; Sterling et al., 2014). Median pH levels at unlimed sites range from 4.35 to 4.79 (Table 1, Figure 4), falling into the range of pH values where the level of acidity is toxic to Atlantic salmon (Lacoul et al., 2011; Sterling et al., 2014).

Liming improved water chemistry conditions in the study catchments. Significant differences between limed and unlimed areas were found. Median Al_i concentrations were lower at all treated sites than at the corresponding control sites, however this difference was only statistically significant ($p<0.05$) at KR (Table 1, Figure 2). At CC, between the pre-liming monitoring period (2016) and the post-liming monitoring period (2019-2021), there was a significant increase in median Al_i concentrations of 102.5% at the control site (32 ug/L vs. 64.8 ug/L), while median Al_i concentrations in the treated site decreased, though insignificantly (Table 2, Figure 5).

Median Al_d concentrations were lower at treated sites than at the corresponding control sites, except at CC where the Al_d concentration was higher at the treated site (Table 1, Figure 6). However, this difference was only statistically significant at KR and WR. At CC, between the pre-liming monitoring period (2016) and the post-liming monitoring period (2019-2021), there was a significant increase in Al_d concentration of 27.6% at the control site (373 ug/L vs. 476 ug/L). Al_d concentrations also increased at the treated site, but the increase was smaller and not significantly significant (Table 2, Figure 7).

Median Ca concentrations were higher at all treated sites than at the corresponding control sites, and this difference was significant in all catchments except MB (Table 2, Figure 3). There was a significant increase in median Ca concentration at both CC sites between the pre-liming period (2016) and the post-liming monitoring period (2019-2021), however the control site saw an increase of only 44.5% while the treated site saw an increase of 398% (Table 2, Figure 8). The median Ca concentration at the control site remains below the threshold for aquatic health, while the Ca concentration at the treated site has surpassed this threshold. There was no significant change in median Ca concentration following liming in either the control or treated site at MB (Table 2).

pH levels were higher at all treated sites than at the corresponding control sites, and this difference was significant in all catchments except MB (Table 2, Figure 4). At CC, there was a significant decrease in median pH at the control site between the pre-liming monitoring period (2016) and the post-liming monitoring period (2019-2021) of 5.69%, while at the treated site median pH significantly increased by 15% (Table 2, Figure 9). There was no significant change in median pH following liming in either the control or treated site at MB (Table 2).

There was a range of differences in median TOC values between control and treatment sites depending on the catchment, with a significant increase between control and treatment at CC, a significant decrease between control and treatment at WR, and no significant difference between control and treatment at MB and KR (Table 1, Figure 10). At MB, there was a significant increase in median TOC concentration at the treatment site between the pre-liming monitoring period and the post-liming period of 40.7%, while the TOC also increased at the control site, though insignificantly (Table 2, Figure 11). There was no significant change in median TOC concentration following liming in either the control or treated site at CC (Table 2).

Discussion

Current water chemistry conditions at untreated sites do not conform to requirements for aquatic health, including for populations of Atlantic salmon. Median Al_i concentrations are well above the toxic threshold of 15 ug/L, median concentrations of dissolved Ca are below the 2.0 mg/L threshold for aquatic health, and median pH levels are below 4.8, meaning that the levels of acidity are toxic to Atlantic salmon (Table 1, Figures 2-4). Though this project only assessed conditions in two primary watersheds (Gold River and West River), the large geographic separation between the two watersheds (one located in southwest NS and one located in the Eastern Shore area) (Figure 1) suggests that these conditions may be widespread.

Liming reduced Al_i concentrations or prevented further increases in Al_i concentrations in all experimental catchments, although the difference was only significant in one catchment (KR, Tables 1 and 2, Figure 2). Despite these decreases, Al_i concentrations at all sites remain in the toxic range (>15 ug/L). Further liming treatments, over untreated areas of the catchments, may be required to decrease Al_i concentrations to a level that is not toxic to Atlantic salmon.

Liming increased pH or prevented further decreases in pH at all catchments (Tables 1 and 2, Figure 3), and these differences were statistically significant in all catchments except for MB. At CC and MB, median pH values in limed areas were increased to above 4.8, bringing them above the level where acidity is toxic to Atlantic salmon, but still within the pH range where Al conditions are most toxic (<5.8). Further liming treatments, over unlimed areas of the catchment, may be required in these catchments to raise the pH to a level that is not toxic to Atlantic salmon. At KR and WR, median pH values in limed areas were increased to above 5.8, bringing them outside the toxic range for Atlantic salmon.

Liming also increased median dissolved Ca concentrations in all catchments, and these differences were statistically significant in all catchments except for MB. In all catchments except for MB, the median dissolved Ca concentrations in limed areas were increased to above the 2.0 mg/L threshold for aquatic health. The liming methods used at these sites were sufficient to increase Ca concentrations to those suitable for Atlantic salmon.

These results imply that treatment via in-stream lime dosing is the most effective way to reduce impacts of acidification that negatively impact Atlantic salmon populations. The catchments treated with in-stream lime dosing (KR, WR) demonstrated statistically significant changes in all major indicator parameters, with the water chemistry conditions becoming more conducive to supporting Atlantic salmon populations. However, it is important to note that in-stream lime dosing is a very cost- and labour-intensive method of liming. The treatment must be consistently added to the stream water, and the positive effects will disappear almost immediately when the treatment is stopped. On the other hand, a single application of terrestrial-based liming treatment may have effects lasting multiple decades (Clair and Hindar, 2005). At CC, where limestone was applied to the catchment surface via helicopter, there were significant increases in both median pH and median dissolved Ca concentration in stream water. Although there was no significant decrease in Al_i concentrations following treatment, there was a 102.5% increase in median Al_i at the control site that was not reflected at the treatment site. The liming treatment likely prevented this significant increase from also occurring at the treatment site.

The liming treatment at MB was the least effective at reducing impacts of acidification. This catchment did not demonstrate any significant changes in the major indicator parameters. This treatment was applied via hand liming, with a highly variable dose across the catchment and a more clumped application pattern. The more successful treatment at CC was more evenly dispersed across the catchment with a steady dosage rate. For future liming projects, we therefore recommend that liming methods similar to those used at CC (even dispersal with a high, steady dosage rate) be used. A combination of in-stream lime dosing and terrestrial liming may be the most effective and efficient way to create both short- and long-term improvements in water chemistry to better support Atlantic salmon populations.

This project was limited by the period of data collection. Pre-treatment data was not collected at all sites, and where pre-treatment data was collected, it was limited to 2-4 samples depending on the site, which is insufficient to fully quantify pre-liming conditions. At MB, post-treatment data collection began 5 years after the liming treatment was applied, and at CC post-treatment data collection began 3 years after the liming treatment was applied. Future liming trials with a before-after-control-impact (BACI) experimental design are needed to better understand the impacts of liming on Al_i concentrations and other water chemistry parameters. We recommend that future liming projects include at least one year of pre-treatment monitoring, and consistent periodic monitoring in the post-treatment period.

Conclusion

Our results show that liming improved water chemistry, but some parameters still did not meet aquatic health thresholds for Atlantic salmon. Water quality at the untreated sites is unsuitable and toxic to Atlantic salmon. The results of this project demonstrate that addition of limestone to surface waters and catchment soils is an effective tool to decrease Al_i concentrations and increase the dissolved Ca concentrations and pH levels in streams. Liming may improve stream water chemistry to that suitable for Atlantic salmon, provided appropriate methodology is used (sufficiently high dose, even dispersal, and large treatment area). For best results, limestone should be applied to a larger fraction of the catchment, and in-stream liming may be used in addition to terrestrial liming to see a more immediate effect. Without this intervention, streams are unlikely to naturally recover to pre-acidification conditions on a timescale to support Atlantic salmon populations (Clair et al., 2004).

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Figures

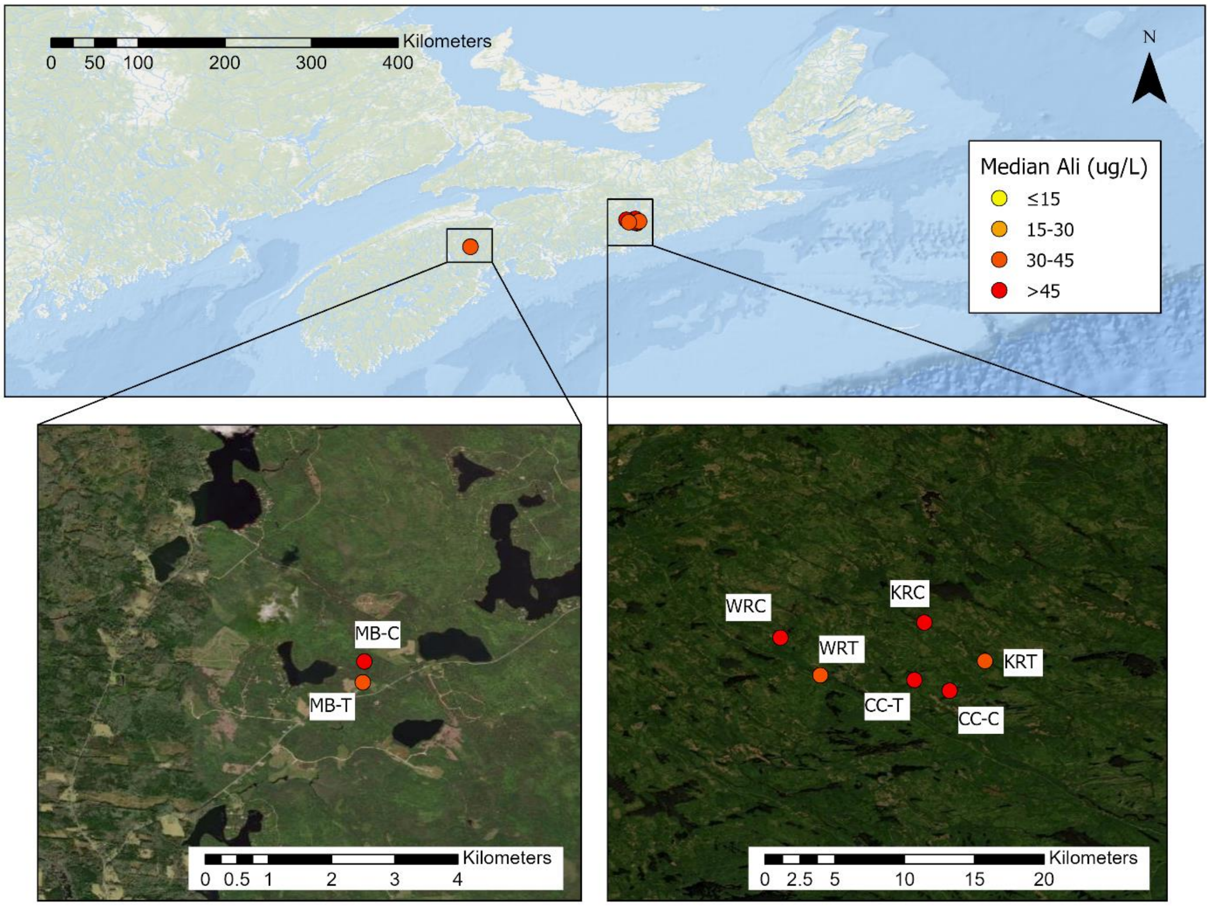

Figure 1. Median Al_i concentrations at eight stream sites surveyed in NS.

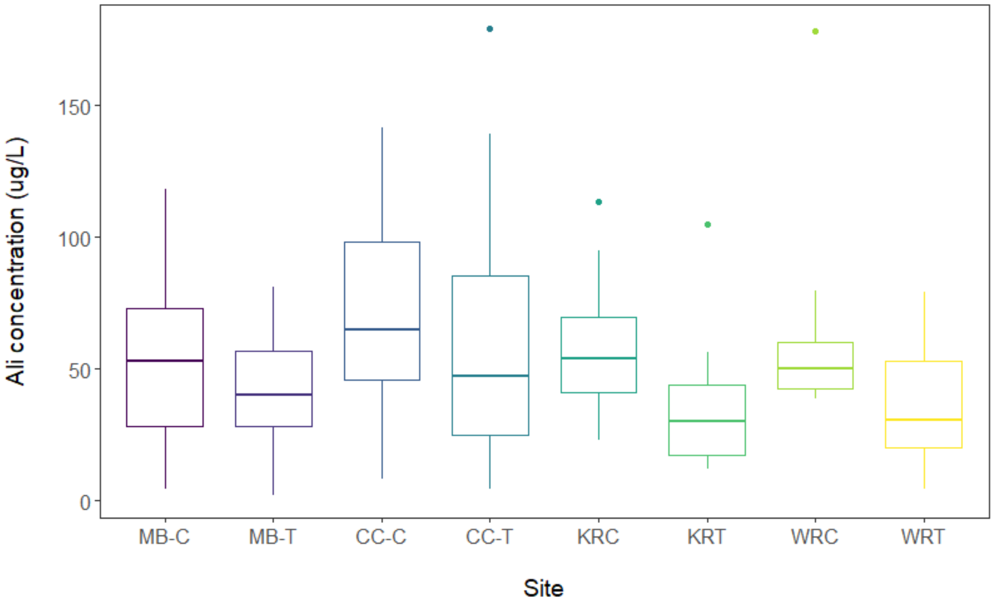

Figure 2. Al$_i$ values at study sites for post-liming monitoring period (2019-2021) (n=10-27 per site).

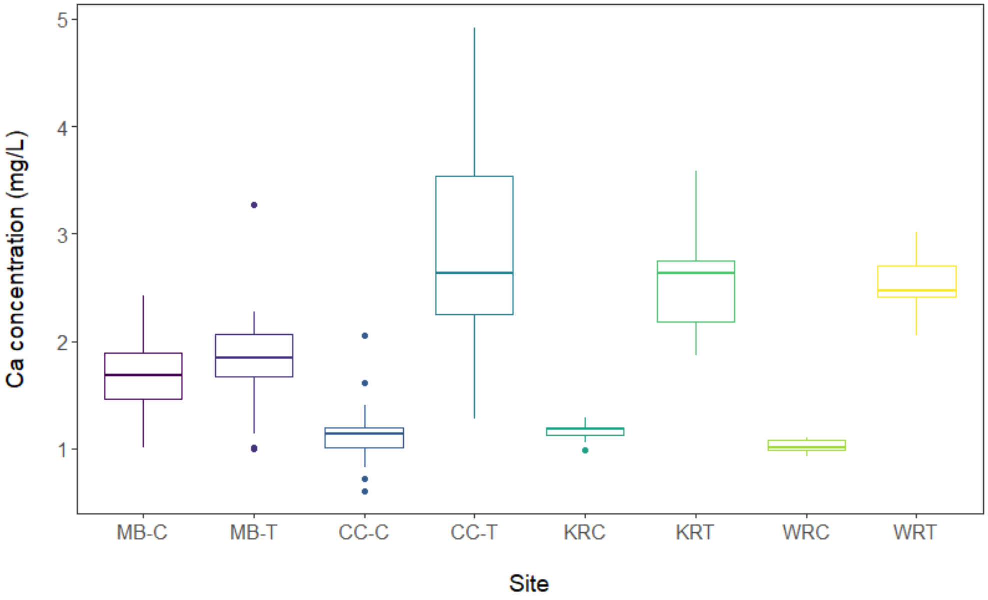

Figure 3. Dissolved Ca values at study sites for post-liming monitoring period (2019-2021) (n=11-31 per site).

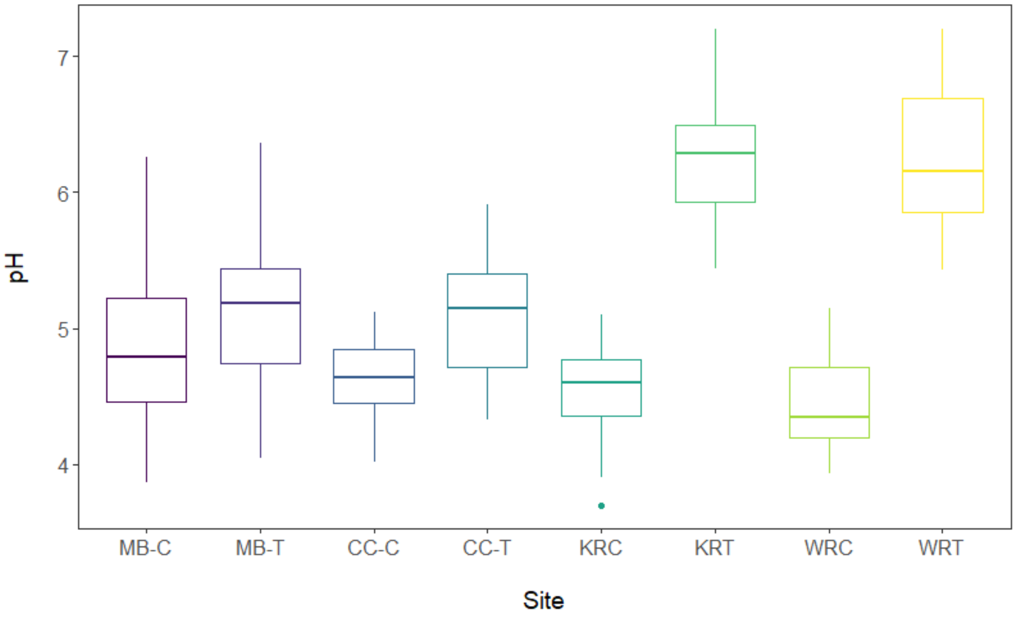

Figure 4. pH values at study sites for post-liming monitoring period (2019-2021) (n=15-35 per site).

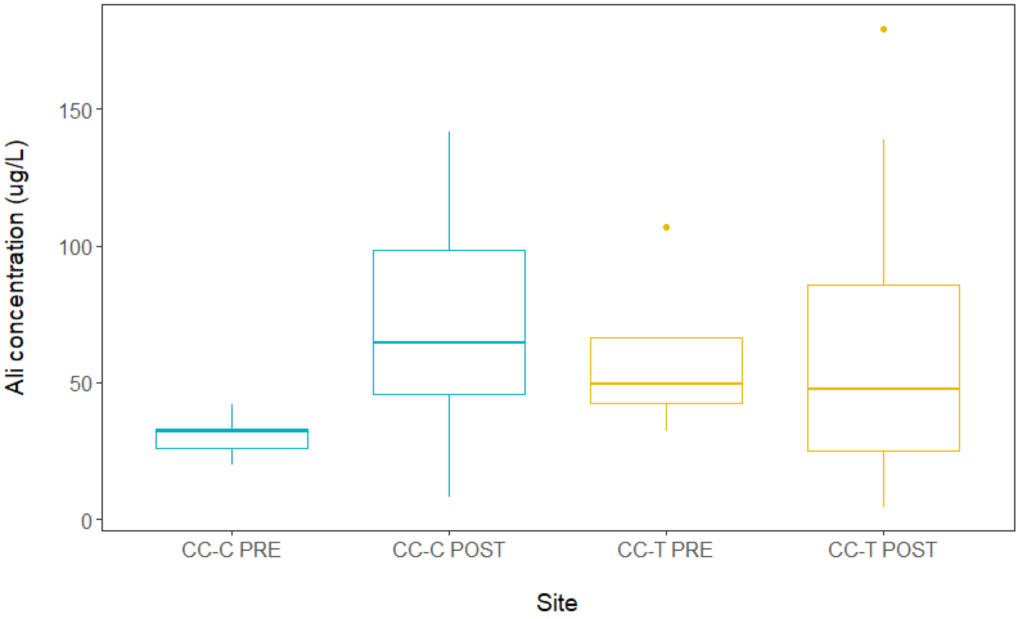

Figure 5. Change in Al_i concentrations for Colwell Creek sites between pre-treatment (2016, n=4-5) and post-treatment monitoring periods (2019-2021, n=22-23).

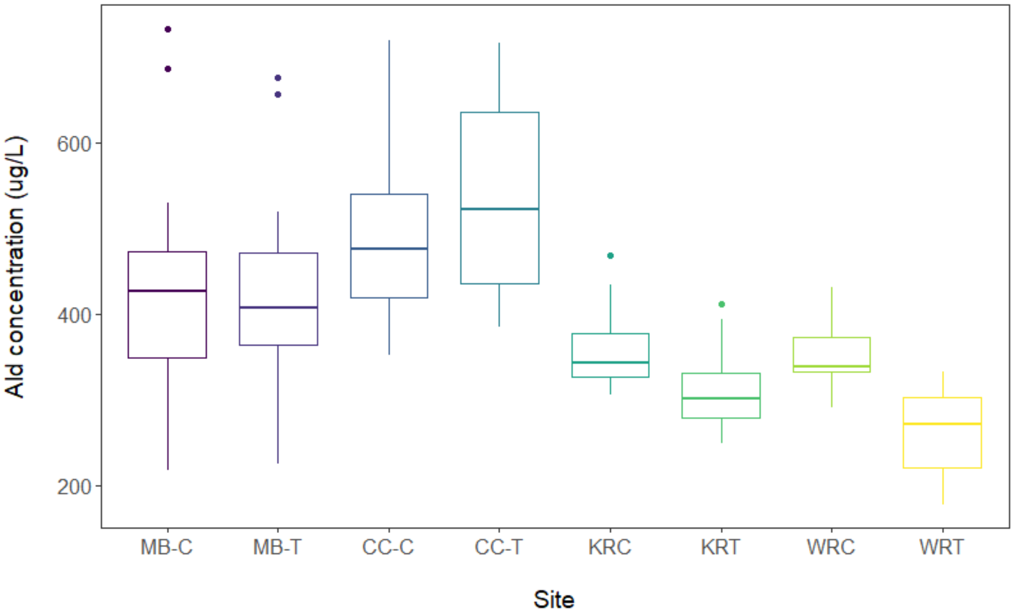

Figure 6. Al_d values at study sites for post-liming monitoring period (2019-2021) (n=11-27 per site).

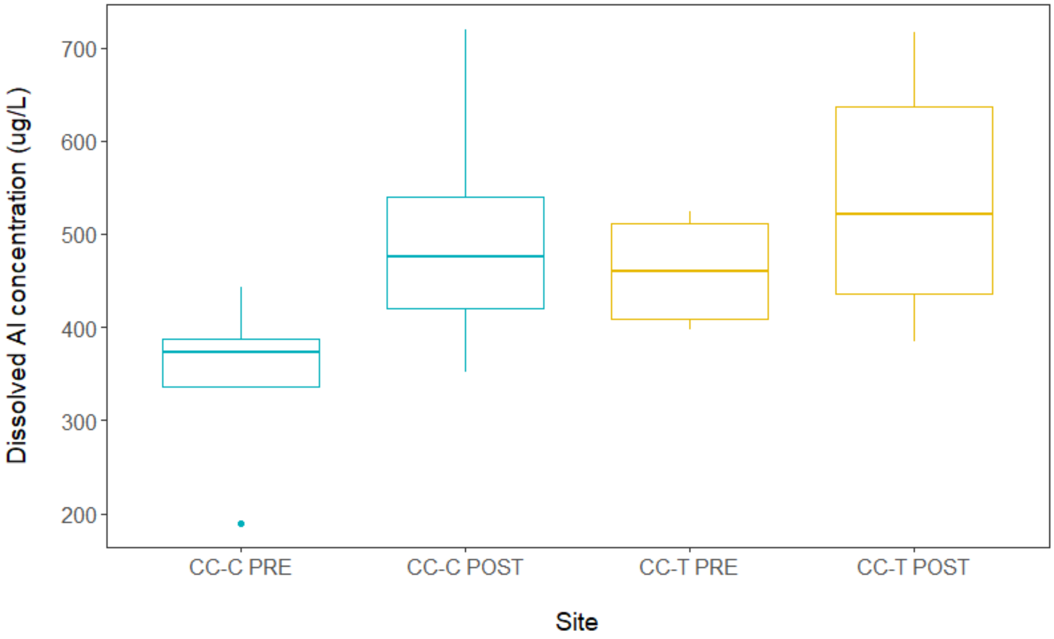

Figure 7. Change in Al_d concentrations for Colwell Creek sites between pre-treatment (2016, n=4-5) and post-treatment monitoring periods (2019-2021, n=23).

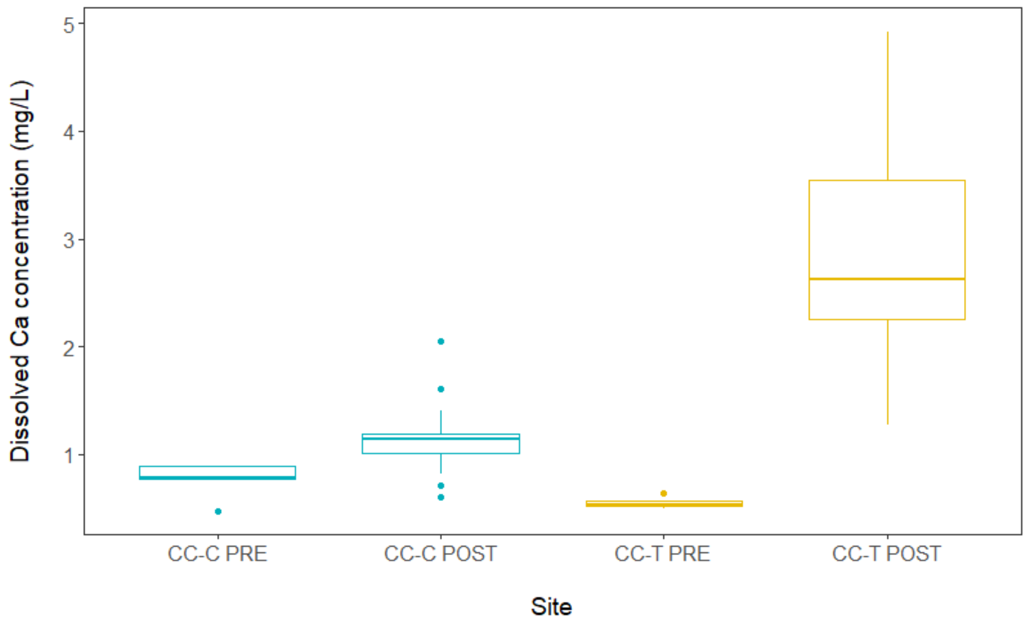

Figure 8. Change in dissolved Ca concentrations for Colwell Creek sites between pre-treatment (2016, n=4-5) and post-treatment monitoring periods (2019-2021, n=31).

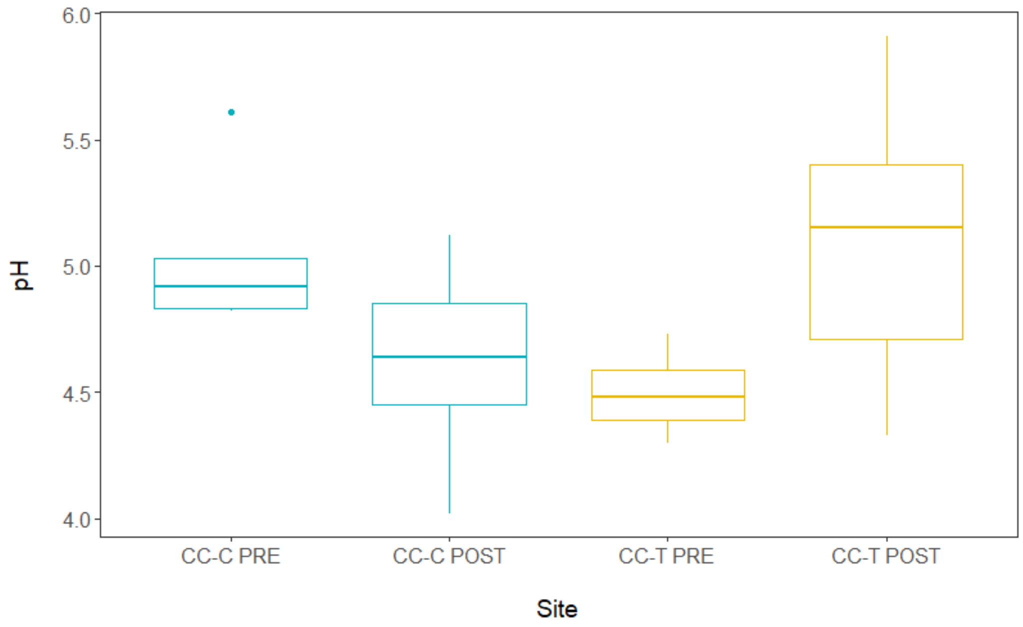

Figure 9. Change in pH for Colwell Creek sites between pre-treatment (2016, n=4-5) and post-treatment monitoring periods (2019-2021, n=31).

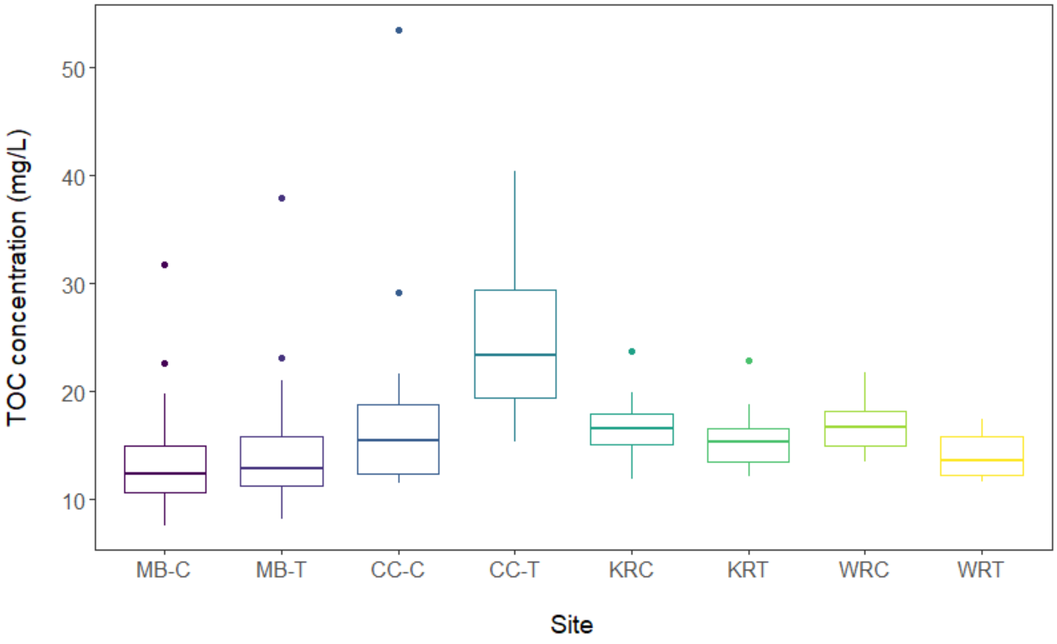

Figure 10. TOC values at study sites for post-liming monitoring period (2019-2021) (n=12-30 per site).

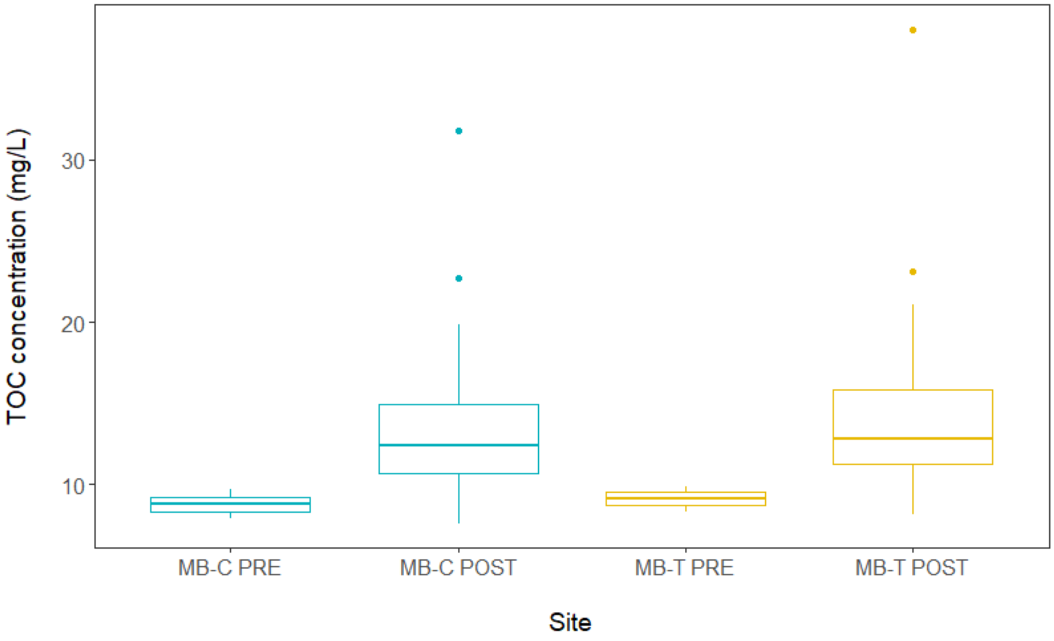

Figure 11. Change in TOC concentrations for Maria Brook sites between pre-treatment (2014, n=2) and post-treatment monitoring periods (2019-2021, n=30).

Tables

Table 1. Median values for water chemistry parameters at control and treated sites. Statistically significant differences ($p<0.05$) between control and treatment are indicated by bold text.

MARIA BROOK			
	Control	Treatment	P-Value
pH	4.79	5.18	0.0606
Al_i (ug/L)	53	40.2	0.3495
Al_d (ug/L)	426	407	0.7868
Ca_d (mg/L)	1.68	1.84	0.1234
TOC (mg/L)	12.4	12.8	0.3851
COLWELL CREEK			
	Control	Treatment	P-Value
pH	**4.64**	**5.15**	**<0.0001**
Al_i (ug/L)	64.8	47.4	0.2515
Al_d (ug/L)	476	522	0.0866
Ca_d (mg/L)	**1.14**	**2.63**	**<0.0001**
TOC (mg/L)	**15.4**	**23.4**	**<0.0001**
KILLAG RIVER			
	Control	Treatment	P-Value
pH	**4.6**	**6.28**	**<0.0001**
Al_i (ug/L)	**54.1**	**30.2**	**<0.0001**
Al_d (ug/L)	**342**	**300**	**0.0003**
Ca_d (mg/L)	**1.18**	**2.63**	**<0.0001**
TOC (mg/L)	16.5	15.4	0.1649
WEST RIVER			
	Control	Treatment	P-Value
pH	**4.35**	**6.15**	**<0.0001**
Al_i (ug/L)	49.9	30.6	0.13
Al_d (ug/L)	**338**	**271**	**0.0008**
Ca_d (mg/L)	**1.01**	**2.48**	**<0.0001**
TOC (mg/L)	**16.7**	**13.6**	**0.0141**

Table 2. Median values for water chemistry parameters during pre-liming and post-liming periods. Statistically significant differences ($p<0.05$) between pre-treatment and post-treatment are indicated by bold text.

MARIA BROOK CONTROL			
	Pre-liming	Post-liming	P-value
pH	5.08	4.79	0.3093
Ca_d (mg/L)	1.14	1.68	0.0582
TOC (mg/L)	8.8	12.4	0.0614
MARIA BROOK TREATMENT			
	Pre-liming	Post-liming	P-value
pH	5.27	5.18	0.699
Ca_d (mg/L)	1.24	1.84	0.0738
TOC (mg/L)	**9.1**	**12.8**	**0.0416**
COLWELL CREEK CONTROL			
	Pre-liming	Post-liming	P-value
Al_i (ug/L)	**32**	**64.8**	**0.0137**
Al_d (ug/L)	**373**	**476**	**0.0099**
pH	**4.92**	**4.64**	**0.0144**
Ca_d (mg/L)	**0.789**	**1.14**	**0.0025**
TOC (mg/L)	13.2	15.4	0.1375
COLWELL CREEK TREATMENT			
	Pre-liming	Post-liming	P-value
Al_i (ug/L)	49.5	47.4	0.8112
Al_d (ug/L)	460	522	0.2601
pH	**4.48**	**5.15**	**0.0159**
Ca_d (mg/L)	**0.528**	**2.63**	**0.0014**
TOC (mg/L)	19.4	23.4	0.1277