Reducing Acidification in Endangered Atlantic Salmon Habitat

Fourth Year of Clam Shells

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Americorps Emily Wilson spreading shells

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Introduction

Despite restored access to historic Atlantic salmon (*Salmo salar*) habitat in eastern Maine, population sizes have remained low (USASAC 2022). Most Downeast rivers and streams have been identified as acidic (pH <6.5), with headwaters chronically acidic and main stems episodically acidic, due to natural (wetlands, coniferous forests) and anthropogenic (acidified rain) sources (Haines et al. 1990; Whiting and Otto 2008). Loss of fish populations due to acidification of surface waters has been well documented in the North Atlantic region (as reviewed by Clair and Hindar 2005; Dennis and Clair 2012). In addition, numerous studies have demonstrated that episodic exposure to low pH can have detrimental, sub-lethal, or lethal impacts especially when coinciding with key salmon life stages during snow melt and spring runoff (e.g., Kroglund et al. 2008; Lacroix and Knox 2005; as reviewed by McCormick et al. 1998). Adding lime to acidic waters, through application of agricultural lime or lime slurry, has increased salmon populations in Scandinavia and Nova Scotia (as reviewed by Clair and Hindar 2005; Halfyard 2007; Hesthagen et al. 2011), and has been a recommended restoration action for Maine's acidic rivers and streams (NRC 2004). A 2009 Project SHARE pilot study investigating the efficacy of using clam shells to lime small streams suggested a trend towards improved habitat quality (Whiting 2014; for a more detailed project background, see Zimmermann 2018).

To further investigate using shells as a mitigation method, the Downeast Salmon Federation (DSF) started a five-year liming project in the East Machias River watershed in 2019. Clam shells were spread along the stream bottom, as well as along the banks to capture high flow events (i.e., rainfall and snowmelt, when episodic acidity is expected). The project goal is to increase juvenile salmon abundance by application of clam shells to achieve a target pH, and to evaluate changes in the macroinvertebrate community, which provides food sources for salmon. From 2017 through summer 2019, baseline data were collected (see Zimmermann 2019). Each summer starting in 2019, shells were spread along a treatment reach in Richardson Brook over multiple days, with the 2022 shell additions occurring Sept. 8-9. Most of the shells spread in 2022 were quahog (*Mercenaria mercenaria*). This report investigates any impacts to water quality from the addition of shells.

Methods

<u>Study Location</u>

Four tributary streams to the East Machias River were monitored (Fig. 1; for physical and geological characteristics see Appendix I Tables 1 and 2 in Zimmermann 2020). These are within the homeland of the Passamaquoddy Tribe of Wabanaki. The East Machias River watershed is typical of coastal eastern Maine, with extensive wetlands resulting in colored waters high in organic materials and low in pH, and with high summer temperatures (Project SHARE-USFWS 2009). The existing salmon population in the East Machias River system is low (median large parr density 13.1 per habitat unit, $100m^2$ in 2019), with an estimated 881 ± 167 smolts exiting the system in 2021 (Maine Department of Marine Resources, MDMR; DSF; USASAC 2022). In 2022, 14 redds were observed in the watershed (MDMR). Richardson Brook and Creamer Brook are stocked by DSF and MDMR, and the average large parr density observed during fall electrofishing is 11 parr/$100m^2$ and 16 parr/$100m^2$ respectively (Fig. 2, MDMR data). As in the prior year, five species of fish were present in Richardson Brook in 2022 (MDMR data). Beaverdam Stream is stocked by DSF, has an average of 13 parr/$100m^2$, and had 3 species present in 2021, lower than the average of the prior years (Fig. 2; MDMR data).

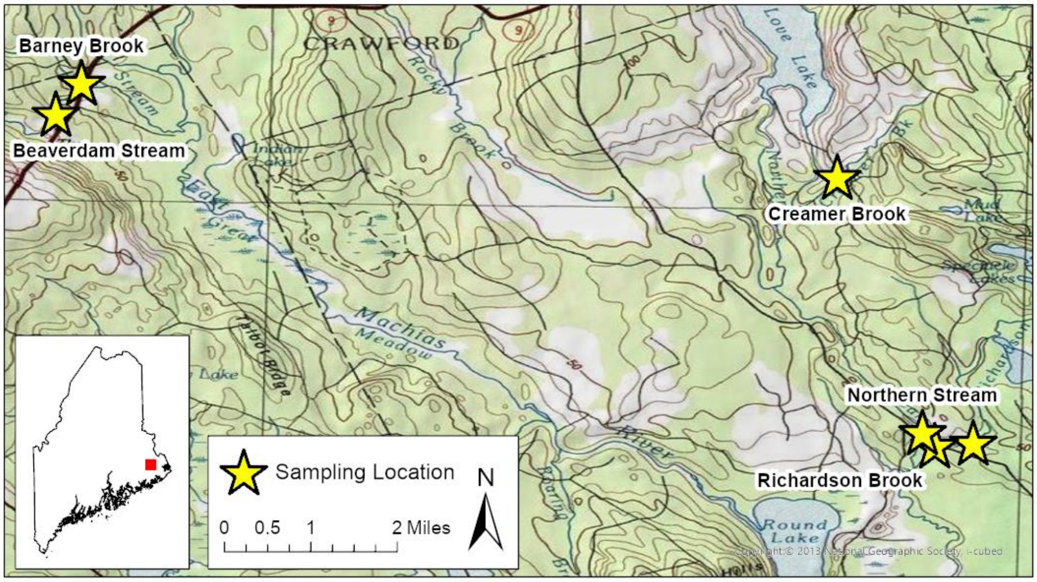


Figure 1. Map of the study sites on tributaries to the East Machias River. On Richardson Brook, samples were collected at two sites: within the shell treatment reach (Rich-B) and above the shell treatment reach (Rich09). Northern Stream was only sampled for macroinvertebrates.

Water Quality

All water quality monitoring activities followed the EPA-approved Salmon Habitat Monitoring Program Quality Assurance Project Plan (MDEP 2021). Continuous monitoring devices provided water quality data every half hour from April through November 2022 (see Zimmermann 2018 for detailed methods). Continuous data were corrected as needed based on quality control procedures as described in MDEP (2016) and using a sonde as a field meter (Eureka Manta2 Sub2 or Eureka Manta+ 20). Grab samples for acid neutralization capacity (ANC), calcium, aluminum species, dissolved organic carbon (DOC), closed-cell pH, and base cations were collected in April, August, September, and November (Appendix I Table 1; see Zimmermann 2018 for detailed methods). With the exception of Barney Brook, macroinvertebrate samples were collected at all sites during baseflow using rock bags following the Maine Department of Environmental Protection (MDEP) Biological Monitoring Program sampling methods (MDEP 2014). DSF staff collected additional macroinvertebrate data in October at three locations using rock bags, following the Izaac Walton League of America’s stream-side identification methods (IWLA 2021).

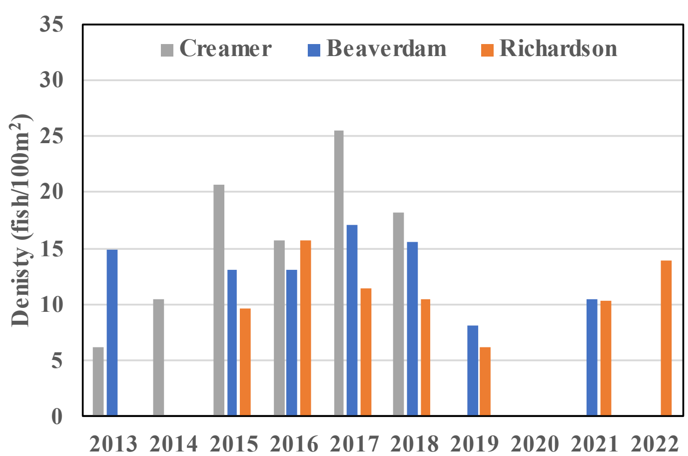


Figure 2. Salmon density in three of the study streams from 2013-2022. High flows prevented data collection in Creamer Brook in 2019 and 2021. Extremely low flows prevented data collection in 2020. Only Richardson Brook was surveyed in 2022 due to resource limitations. Data from MDMR electrofishing surveys.

Data Visualization and Analysis

Water quality data were analyzed using the Water Resources Database 7.0.0.31 (Wilson Engineering 2023) and R 4.2.2 (R Core Team 2022). Figures 5-7 were created using the *ggplot2* package (Wickham 2009). All data are presented as mean ± standard deviation (SD). Due to the small sample sizes, non-parametric Kruskal-Wallis tests were used to compare water grab sample results between sites, seasons, and years, with pairwise Wilcoxon rank sum post-hoc tests with Holm adjustment. Duration of stressful events, based on thresholds for the protection of salmon and other aquatic life, were calculated based on how many consecutive data points exceeded the water quality threshold before recovery. Continuous data across all sites had 4% of pH data and <1% of specific conductance and DO data rejected due to quality control issues. Equipment malfunction, primarily battery failure, resulted in loss of 4% of continuous data for all parameters. Flagged data (based on data corrections as per MDEP 2021 or best professional judgement) represented 13% of specific conductance data and 2% of DO data.

Results and Discussion

Weather

Maine had a warm, dry winter in 2022 followed by a warm spring and an abnormally hot, dry summer punctuated by late summer and fall storms, resulting in the second wettest shell treatment period of the study, behind 2019 (Fig. 3; NOAA 2022; U.S. Drought Monitor 2022). Most rain events were small (<10 mm), however larger rain events occurred September through November (Figs. 4 and 5; Weather Underground 2022).

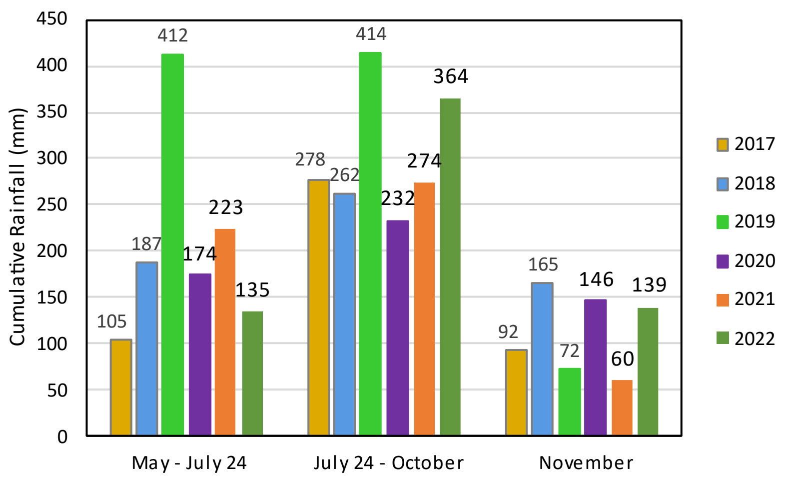


Figure 3. Cumulative annual rainfall. The three time periods represent spring pre-treatment, summer-fall shell treatment, and November post-treatment, based on shell applications in 2019-2022. Data from Weather Underground stations KMEALEXA2, KMEBAILE9, KMEBARIN2, and KMECOOPE3.

pH

Salmon prefer pH values that are circumneutral (6.5-7.5), rather than acidic (<6.5). The impacts of acidity depend on 1.) duration, magnitude, and frequency of the episode, 2.) the ability of the fish to avoid adverse water quality conditions, 3.) the concentration of exchangeable aluminum (Alx), 4.) the buffering capacity of the water (i.e., ANC and calcium) and 5.) life stage (see Zimmermann 2018 for overview). pH thresholds used in this analysis are estimates of anticipated impacts to salmon populations and do not include a detailed analysis of the impact of other factors.

Winter pH was lower in 2022 compared with 2021, but the treated Richardson Brook site remained consistently 0.4 units higher than the upstream control (5.5 ± 0.2 downstream vs. 5.1 ± 0.1 upstream; Fig. 4). pH remained above the critical stress threshold of 5.5, below which adverse impacts to salmon populations are expected (Haines et al. 1990; Stanley and Trial 1995), for 45% of the time at the treated downstream site, similar to winter 2019-2020. In comparison,

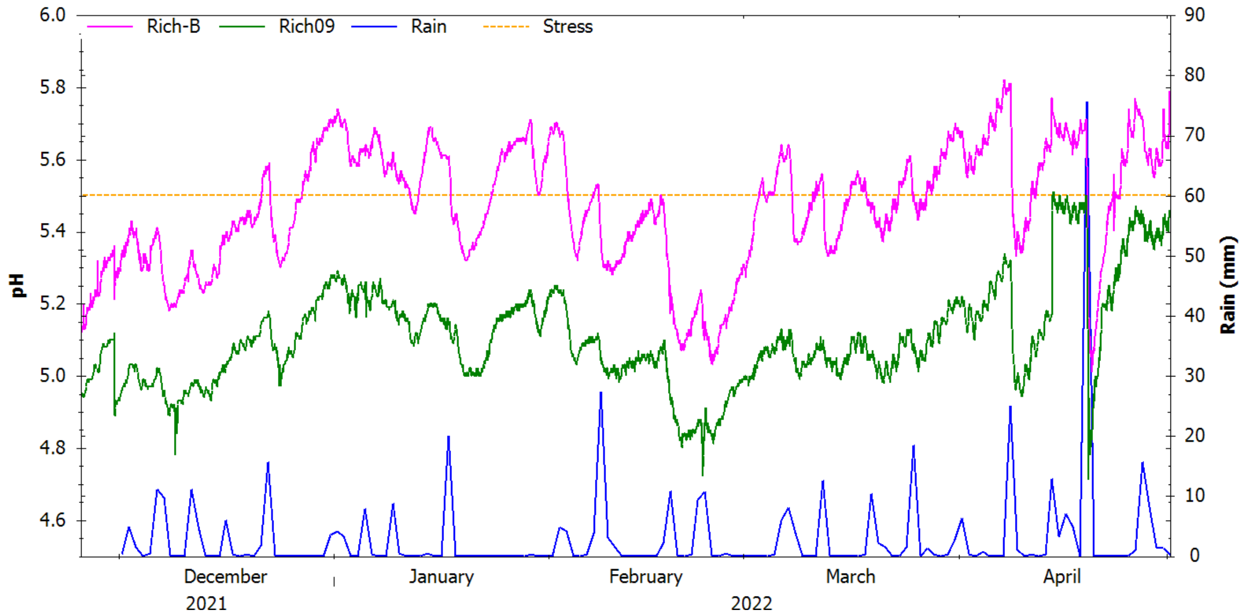


Figure 4. Winter 2021-2022 pH at the two Richardson Brook sites, the upstream control (Rich09) and the downstream treatment site (Rich-B). Stress threshold from Stanley and Trial 1995 and Haines et al. 1990.

the upstream control site remained consistently below the stress threshold of 5.5. Rainfall-driven episodic acidity events continued to occur, however shell additions have increased winter pH at the treatment site.

From spring through fall, at all sites combined, pH values remained mostly above the stress threshold of 5.5, as in prior years (Fig. 5; Appendix I Tables 2 and 6; Haines et al. 1990; Stanley and Trial 1995). Like prior years, both Barney Brook and Beaverdam Stream had pH above the threshold of 6.5, an optimal minimum pH for the protection of the most sensitive salmon life stages (alevins and smolts; Kroglund and Staurnes 1999; Kroglund et al. 2008). In addition, pH at the treated Richardson Brook site stayed above 6.5 for the longest yet observed at that site, for about the same amount of time as Beaverdam Stream (26.3%). Summer rain events were mostly too small to cause episodic pH depressions, except for one event in July which was not captured by the backyard weather station (Fig. 5; Weather Underground 2022). The largest rain event in late September (57 mm) caused Creamer Brook to fall below the survival threshold of 4.5 for 2.7 days (1.5% of the study period; Potter 1982). The pH at the treated Richardson Brook site (Rich-B) was 0.6 units higher in 2022 than in baseline years (2017-2019; Fig. 6). No other study site showed a change of more than 0.2 units from baseline conditions except Beaverdam Stream, which had higher minimum pH (by 0.42 units) and an overall increase of 0.31 units. In addition, the treated Richardson Brook site remained on average 0.57 units higher than the control site for the entire study period (Fig. 5; Appendix I Table 4). Shell additions have increased pH at the treated site to levels similar to streams with high buffering capacity (Beaverdam Stream and Barney Brook).

Stressful conditions still occurred at the treated Richardson Brook site, particularly in the fall (64% of November 2022 was <5.5; Baker et al. 1996; Henriksen et al. 1984; Lacroix and Knox 2005; Magee et al. 2003). Despite yearly variation in stressful acidic events (<5.5), the duration of these events was reduced at the treated site (average of 2.2 days with a maximum of

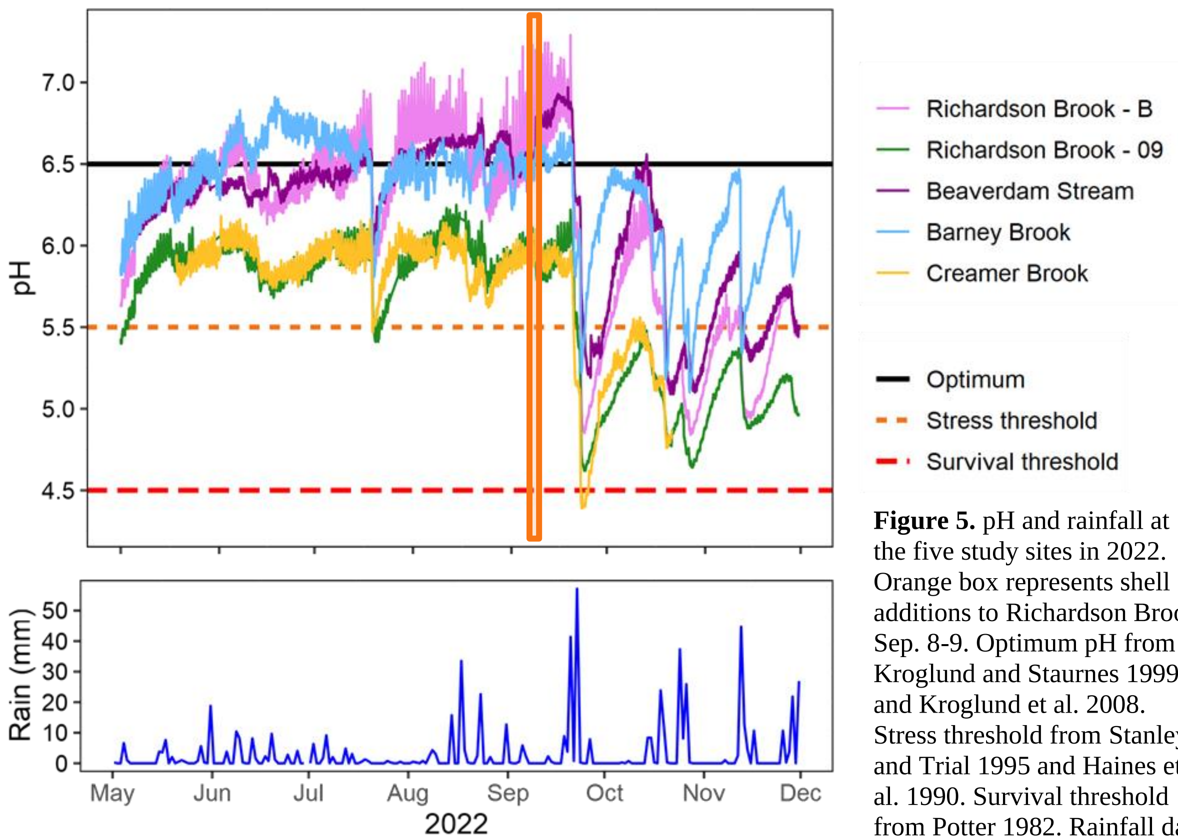


Figure 5. pH and rainfall at the five study sites in 2022. Orange box represents shell additions to Richardson Brook Sep. 8-9. Optimum pH from Kroglund and Staurnes 1999 and Kroglund et al. 2008. Stress threshold from Stanley and Trial 1995 and Haines et al. 1990. Survival threshold from Potter 1982. Rainfall data from Weather Underground.

16.6 days in 2022) compared to baseline years (average of 5.4 days with a maximum of 1 month) and to the upstream control site (average of 12 days with a maximum of 3.5 months in 2022). Although both the treatment and control sites experienced a decrease in the average duration of stressful events compared with baseline years, a greater reduction occurred at the treatment site (72%) than at the upstream control (36%). Although pH at the treated site has increased following shell additions, acidic episodes are still occurring, and recovery from these events has only slightly improved.

Stream Temperature

Salmon prefer cold waters. Stream temperatures in 2022 were similar to the prior years of the study in all study streams, remaining below the threshold for optimal growth of 20°C for most of the sampling period (84% at all streams combined; Appendix I Tables 2 and 6; Jonsson et al. 2001; USEPA 1986). the stress threshold of 22°C was exceeded 4.5% of the time (Cunjak et al. 2005; Elliott and Elliott 2010; Lund et al. 2002), USEPA's short-term maximum for survival of 23°C was exceeded 3.3% of the time (USEPA 1986), the lethal temperature for adult salmon survival (26-27°C) was exceeded only 0.08% of the time (Shepard 1995 as cited in Frechette et al. 2018), and the lethal temperature for parr (28-29°C) was never exceeded (Elliott 1991 as cited in Stanley and Trial 1995; Garside 1973 as cited in Lund et al. 2002; Grande and Andersen 1991 as cited in Elliott and Elliott 2010). During the hot, dry summer, Barney and Creamer Brooks remained the coldest, possibly due to the relative influence of groundwater

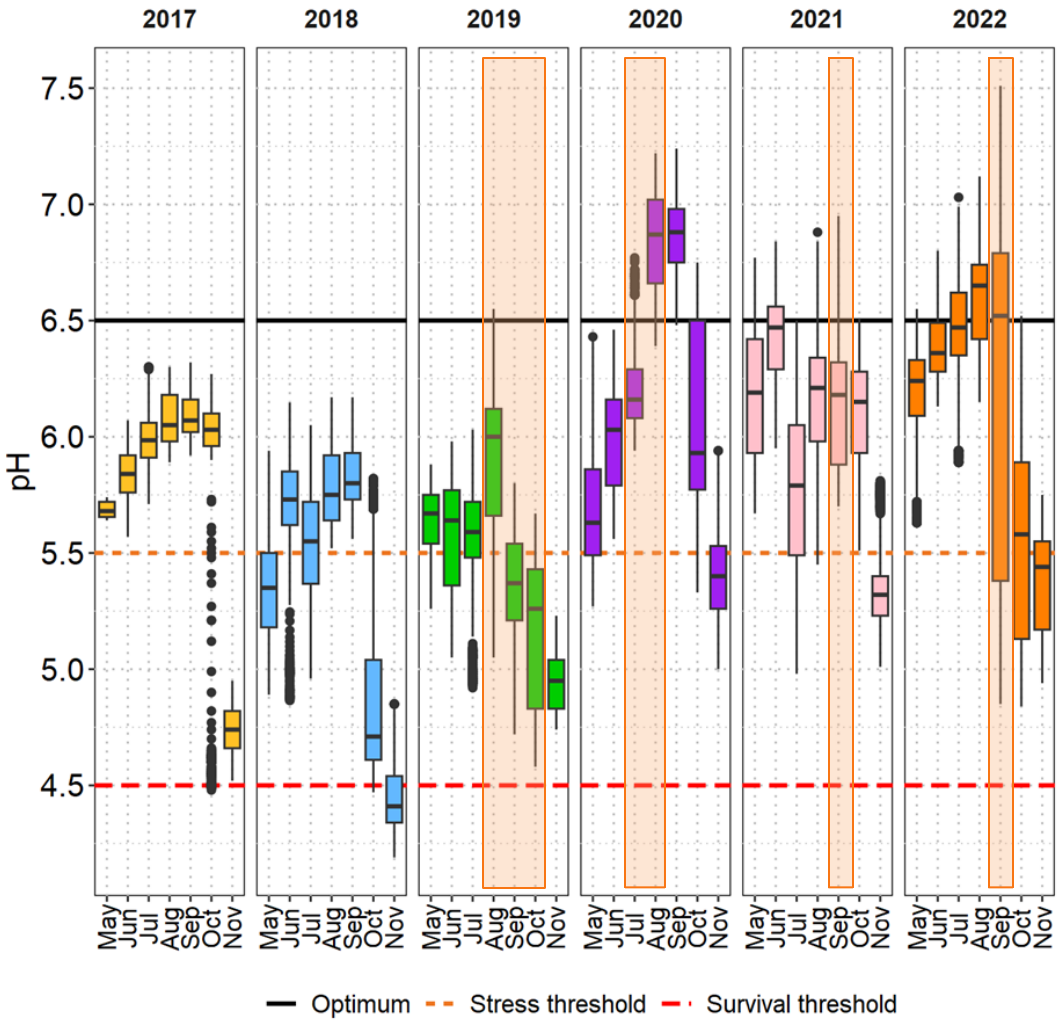


Figure 6. Monthly pH at the downstream Richardson Brook site (Rich-B). Each box represents the interquartile range, with the horizontal line representing the median, and whiskers extending to the minimum and maximum values observed, except where values are considered statistical outliers (dots). Optimum pH from Kroglund and Staurnes 1999 and Kroglund et al. 2008. Stress threshold from Stanley and Trial 1995 and Haines et al. 1990. Survival threshold from Potter 1982. Orange boxes represent shell additions 2019-2022.

during low flows (Appendix I Table 2). Exceedances of the stress threshold of 22°C lasted on average 9 hours at a time. The longest period above 22°C occurred at Beaverdam Stream in July, lasting 4.7 days. As in prior years, sub-lethal stress may be occurring during the hottest parts of the summer at all sites.

Specific Conductance

Specific conductance is a measure of the concentration of ions in the water, or the ability of water to conduct electricity. The streams in the study area have very low specific conductance (38 ± 18 µS/cm at all sites combined; Appendix I Table 2), which can increase the difficulty of accurate pH measurements and electrofishing (Hovind 2010 as cited in Garmo et al. 2014; Zimmermann 2018). Lab-analyzed closed-cell pH grab samples closely matched sonde pH (within 0.16 ± 0.20), with the closest match at the Richardson Brook sites (within 0.02 ± 0.11), providing confidence in the pH data discussed above. As observed in 2020, specific conductance at the treatment site in Richardson Brook increased during baseflow conditions, including immediately following shell additions, with rain events diluting concentrations to levels similar to the upstream control. The increase in specific conductance during baseflow was likely due to the dissolution of shells into dissolved solids such as sodium, calcium, and chloride. No negative impacts to aquatic life are expected from the increase in specific conductance, however increased ion concentrations (such as calcium) may increase buffering capacity.

Dissolved Oxygen (DO)

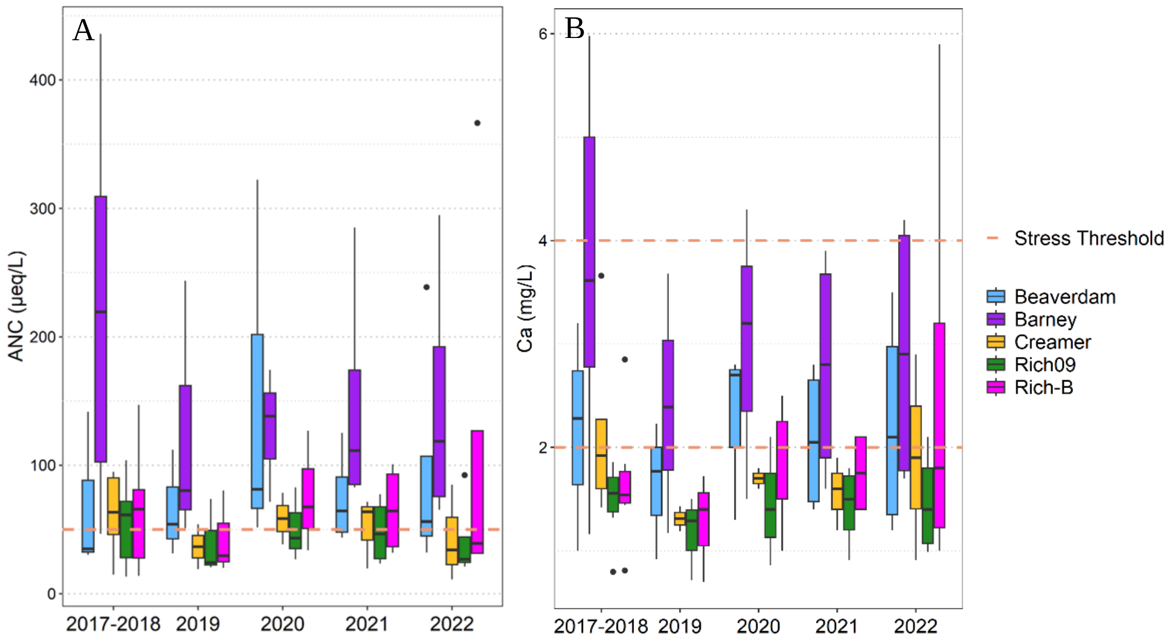
Salmon prefer well oxygenated waters. As in prior years, DO levels were within a healthy range for fish and aquatic life, in addition to the preferred range for salmon of >6-7 mg/L, for most of the study period (96%; Appendix I Tables 2 and 6; Stanley and Trial 1995; USEPA 1986). DO concentrations fell below the Maine Water Quality Standard of 7 mg/L at all sites, lasting on average 8 hours, with a maximum duration of 19.5 hours at the upstream Richardson Brook site (38 M.R.S. §§ 465.2.B). DO never dropped below USEPA's threshold for acute impairment of 5 mg/L (USEPA 1986). The hot dry summer resulted in DO minima that coincided with the warmest temperatures, increasing stress, as well as coinciding with the lowest flows, possibly preventing movement of salmon to oxygen and temperature refugia, if any existed nearby.

Acid Neutralization Capacity (ANC)

Streams with higher ANC have a higher capacity to buffer against changes in acidity. As in prior years, summer baseflow stayed consistently above the threshold of acid sensitivity for the protection of the most sensitive aquatic species and life stages of 50 μeq/L (Driscoll et al. 2001). ANC minima were below the Norwegian 20-30 μeq/L critical limit for salmon at three sites: Creamer and the treated site at Richardson Brook in the fall, and the upstream control at Richardson Brook in spring and late summer (Fig. 7 A; Appendix I Table 3; Baker et al. 1990; Lien et al. 1996; Kroglund et al. 2002). As in prior years, ANC was likely high enough (>100 μeq/L) for maintenance of the necessary calcium concentration (2 mg/L) during summer baseflows only at Barney Brook and Beaverdam Stream, but in 2022 also at the treated Richardson Brook site (Fig. 7 A; Brocksen et al. 1992). Despite higher ANC during 2022 baseflow, there were no statistically significant differences at the treated Richardson Brook site between years, compared to the other sites, or pre- and post- shell additions (Appendix I Table 4). In low DOC waters, ANC is an approximate surrogate for alkalinity (Garmo et al. 2014). As in prior years, no samples were above USEPA's recommended AWQC of 20 mg/L alkalinity (calculated from ANC), however this threshold does not apply where values are naturally lower (USEPA 1986). Relatively low ANC values indicate a deficit of buffering materials in the watershed due to thin soils (Potter 1982), allowing volatile swings in pH after rain inputs and increasing the potential for salmon mortality (Fig. 5; MacAvoy and Bulger 1995). Buffering capacity at the treated Richardson Brook site has increased during summer baseflow.

Calcium

Higher calcium values enable faster growth and higher survival in fish. As in the prior years of the study, calcium was below the survival threshold of 2 mg/L at all sites for most of the sampling events (58%; Fig. 7 B; Appendix I Tables 3 and 6; Baker et al. 1990; Baldigo and



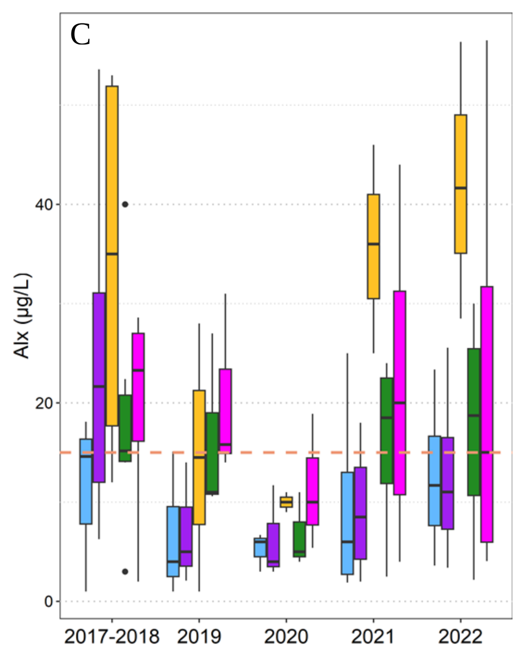


Figure 7. (A) Acid neutralization capacity (ANC), (B) calcium (Ca) and (C) exchangeable aluminum (Alx). 2017-2018 represents baseline conditions. Shells were added to Rich-B 2019-2022. Each box represents the interquartile range, with the horizontal line representing the median, and whiskers extending to the minimum and maximum values observed, except where values are considered statistical outliers (dots). Most sample sizes n = 3. ANC stress threshold of <50 µeq/L from Driscoll et al. 2001. Calcium stress thresholds of <4 mg/L from Marcus et al. 1986, as cited in Brocksen et al. 1992, and <2 mg/L from Baker et al. 1990 and Baldigo and Murdoch 2007. Alx stress threshold of >15 µg/L from EIFAC as cited in Dennis and Clair 2012.

Murdoch 2007). During summer baseflow, both Barney Brook and the treated Richardson Brook site were above the suggested threshold of 4 mg/L to prevent deformities and other stress (Marcus et al. 1986, as cited in Brocksen et al. 1992). Despite higher calcium during 2022, there were no statistically significant differences at the treated Richardson Brook site (Appendix I Table 4). As in prior years, calcium minima coincided with low pH, high aluminum, and low ANC, however the buffering capacity at the treated Richardson Brook site has improved, allowing for potential buffering of Alx during summer baseflow.

Aluminum

No significant changes in aluminum were observed between 2022 and prior years. Average total aluminum per stream ranged from 154 to 254 µg/L, well below the Maine AWQC maximum of 750 µg/L (based on a pH of 6.5-9 and dissolved organic carbon (DOC) <5 mg/L, which are significantly different from values observed in the study streams; Appendix I Tables 2, 3 and 5; MDEP CMR Chapter 584). USEPA's site-specific maximum criterion (CMC; ranging from 13-1,500 µg/L depending on DOC, total hardness, and pH at each sample site; USEPA 2018) was exceeded in 53% of samples, similar to baseline years. As in prior years, organic aluminum was the dominant species.

Exchangeable aluminum (Alx) can cause respiratory distress when it binds to the gills of fish. Alx values were similar to baseline years, representing 9.7 ± 8.8% of aluminum species. Approximately half of the 2022 samples exceeded the threshold for the protection of aquatic life of 15 µg/L (Fig. 7 C; Appendix I Tables 5 and 6; Howells et al. 1990 as cited in Dennis and Clair 2012; Kroglund and Staurnes 1999; McCormick et al. 2009). There were no statistically significant differences at the treated Richardson Brook site between years, compared to the other sites, or pre- and post- shell additions (Appendix I Table 4). As in prior years, sub-lethal stress due to toxic Alx may decrease smolt tolerance to saltwater when they migrate out of their freshwater habitat (Kroglund and Staurnes 1999; McCormick et al. 2009; Monette et al. 2008; Staurnes et al. 1995).

Dissolved Organic Carbon (DOC)

DOC can help buffer against the toxic impacts of Alx by binding aluminum into inert organic complexes (Baldigo and Murdoch 2007; Kroglund et al. 2008; Tipping et al. 1991). Downeast streams, including those studied here, are naturally highly colored, with relatively high organic content (and therefore high DOC) due to wetlands and coniferous forests (Haines et al. 1990). In 2022, DOC at all sites combined ranged from 6.7 to 23 mg/L, with an average of 14.0 ± 6.1 mg/L (Appendix I Table 3). Based on the high DOC values, it is expected that some buffering of Alx is occurring in the study streams despite low pH values.

Base Cation Surplus

Base cation surplus (BCS) reduces the influence of natural acidity from DOC, to help distinguish the impacts of natural acidity versus anthropogenic acidification (Lawrence et al. 2007; Baldigo et al. 2009). BCS is the difference between the sum of cations (calcium, potassium, magnesium, and sodium) and anions (chloride, nitrate, sulfate, and strong organic anions as defined as 0.071*DOC-2.1; Lawrence et al. 2007). The threshold for aluminum mobilization occurs at a BCS around 0, regardless of DOC values. In 2022, BCS ranged from a minimum of -32 at the upstream control to 305 at the treated site on Richardson Brook (Appendix I Table 7). Lowest values were observed in the fall, corresponding with the lowest pH values, when all sites had a negative BCS except for Barney Brook. As expected, based on calcium, ANC, and pH (Figs. 5 and 7), Beaverdam Stream and Barney Brook had the highest average BCS, and thus the highest capacity to buffer against the mobilization of toxic aluminum. During summer baseflow, the treated site at Richardson Brook also had a high BCS, allowing for potential buffering against toxic aluminum.

Macroinvertebrates

Results from the DEP rock bags were not available in time for this report, as analysis was delayed due to lack of resources at DEP and contract complications. Samples from DSF rock bags showed high variability between replicates at each site. A water quality index can be calculated based on occurrence of different taxa groups, with the presence of sensitive taxa increasing the index score (IWLA 2021). Ephemeroptera (mayflies), Plecoptera (stoneflies) and Trichoptera (caddisflies), collectively referred to as EPT, have low tolerance to water pollution, and are therefore indicators of good water quality. Although there were no statistically significant differences, EPT richness was higher at Richardson Brook than in previous years (Appendix I Table 8). As in most prior years of the study, the highest total abundance and water quality index score occurred at Northern Stream. Based on the DSF rock bag data, no significant differences have been observed in the macroinvertebrate community following the addition of shells, however full analysis of the more detailed taxonomic data from the DEP rock bags is still needed.

Conclusion

Following a fourth year of clam shell additions, pH in the treated section of Richardson Brook was higher than in baseline years, as well as higher than the upstream control site for the entire calendar year. Although not statistically significant, increases in acid neutralization capacity (ANC), calcium, and base cation surplus (BCS) were observed at the treated Richardson Brook site during summer baseflow, suggesting increased buffering capacity. Sub-lethal stress due to low pH and aluminum toxicity is likely still occurring during episodic, precipitation-driven acidity events, however these events are lasting for shorter durations at the treatment site due to increased buffering from the dissolution of the clam shells. The most sensitive salmon life stages (alevins and smolts) are present in the streams from March through June, when buffering capacity is low, however low pH events occurring during the autumn rainy season when buffering capacity is also low may impact hardier life stages (parr and adults). In addition, sublethal stress from warm temperatures and low dissolved oxygen may be occurring during summer baseflow conditions at all sites. To determine if the increases in pH, ANC and calcium provide enough buffering capacity of stressful acidic events to be biologically significant for salmon, the final year of water quality monitoring for this study will occur in 2023.

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Appendix I – Summary Data Tables

Table 1. Analytical laboratories, methods, and certification.

Analysis Lab	Analyte	Method	DEP Certified?
UMO Sawyer Water Research Lab	ANC	E600/4-87/26 5.53	No. This is a research method with no state certification, is approved by the DEP biologist, and is used for continuity of data to compare with prior liming projects.
	Aluminum (speciation)	SW6010B	No. This is a research method with no state certification, is approved by the DEP biologist, and is used for continuity of data to compare with prior liming projects.
	pH (closed-cell)	E600/4-87/26 19.0	No. This is a research method with no state certification, is approved by the DEP biologist, and is used for continuity of data to compare with prior liming projects.
Maine Environmental	Calcium and other cations	E200.7	Yes
	DOC	SM5310B	Yes
	Anions (chloride and sulfate)	E300.0	Yes
Eastern Analytic, Inc.	Nitrate	E300.0 and E353.2	Yes

Table 2. Continuous Data Summary. Summary statistics (mean, standard deviation (SD), minimum and maximum) of measurements from Manta+ 20 and YSI 600 XLM sondes, May to Nov. 2022 (n ~ 9,000). Dissolved oxygen data for Barney Brook are discrete measurements from a Eureka Manta+ 20 (n = 11).

Stream Name	pH				Temperature (°C)				Specific Conductance (µS/cm)				Dissolved Oxygen (mg/L)			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Barney Brook	6.33	0.33	5.10	6.91	12.96	4.76	-0.12	22.04	36	10	18	87	10.38	1.83	7.83	14.33
Beaverdam Stream	6.19	0.47	5.09	6.97	15.72	6.04	0.23	27.39	39	12	13	86	9.28	1.68	6.66	14.45
Creamer Brook	5.75	0.36	4.39	6.18	13.86	5.05	0.41	23.87	27	4	18	35	9.75	1.60	6.19	14.58
Richardson Brook – 09 (upstream control)	5.61	0.41	4.62	6.25	14.90	5.98	0.42	27.55	24	4	8	35	9.00	1.73	5.18	13.93
Richardson Brook – B (treatment)	6.11	0.58	4.84	7.51	14.96	5.81	0.27	27.91	27	6	17	50	9.49	1.75	5.59	14.76

Table 3. Discrete Data Summary. Summary statistics (mean, SD, minimum and maximum) from grab samples collected 2017-2022. n = 20*.

Stream Name	Calcium (mg/L)				Dissolved Organic Carbon (mg/L)				ANC (μeq/L)				pH (closed-cell)			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Barney Brook	3.07	1.39	1.16	5.98	11.7	6.1	3.4	27	163.5	109.9	46.6	435.9	6.42	0.36	5.82	6.96
Beaverdam Stream	2.15	0.80	0.92	3.50	12.7	6.0	6.1	26	94.4	81.3	31.4	322.3	6.13	0.47	5.28	6.88
Creamer Brook	1.82	0.70	0.91	3.66	12.7	4.8	7.6	23	52.3	28.6	11.2	94.9	5.79	0.45	4.96	6.37
Richardson Brook - 09+ (upstream control)	1.42	0.42	0.72	2.10	13.0	4.9	5.6	23	47.9	26.1	23.5	92.3	5.66	0.44	4.80	6.25
Richardson Brook – B (treatment)	1.84	1.11	0.70	5.90	12.7	4.5	6.8	22	74.0	78.4	13.9	366.5	5.95	0.52	4.94	6.86

* Creamer Brook was never sampled in April (n = 15). Beaverdam Stream was not sampled in 2017 (n = 16).
\+ Rich09 includes samples collected from Rich-A (a site 360m downstream) in 2017, 2018, and April 2019.

Table 4. Treatment Summary. Mean values (± SD) before any change in pH was observed at the treated Richardson Brook site ('pre': May 30, 2017 – July 26, 2020) and after pH increased ('post': July 26, 2020 – Nov. 30, 2022).

Stream Name	pH		Calcium (mg/L)		Exchangeable Aluminum (μg/L)		Acid Neutralization Capacity (μEq/L)	
	Pre *n ~ 30,000*	**Post** *n ~ 30,000*	**Pre** *n = 11**	**Post** *n = 9**	**Pre** *n = 11**	**Post** *n = 9**	**Pre** *n = 11**	**Post** *n = 9**
Barney Brook	6.3 ± 0.3	6.3 ± 0.3	3.2 ± 1.6	2.9 ± 1.1	16.5 ± 15.6	10.2 ± 7.8	177 ± 128	147 ± 87
Beaverdam Stream	6.1 ± 0.5	6.2 ± 0.5	1.9 ± 0.8	2.2 ± 0.8	8.9 ± 6.9	10.6 ± 8.6	107 ± 104	85 ± 64
Creamer Brook	5.7 ± 0.4	5.6 ± 0.4	1.9 ± 0.8	1.7 ± 0.6	29.5 ± 18.0	34.9 ± 15.0	58 ± 30	46 ± 28
Richardson Brook – 09+ (upstream control)	5.6 ± 0.4	5.4 ± 0.4	1.3 ± 0.4	1.5 ± 0.5	15.8 ± 10.6	15.2 ± 10.5	51 ± 31	46 ± 26
Richardson Brook – B (treatment)	5.5 ± 0.5	5.9 ± 0.6	1.5 ± 0.6	2.2 ± 1.5	18.6 ± 9.4	21.0 ± 18.7	62 ± 45	88 ± 108

* Creamer Brook was not sampled in April 2018-2022 (n = 8 pre, 7 post). Beaverdam Stream was not sampled in 2017 (n = 8 pre).
\+ Rich09 includes samples collected from Rich-A (a site 360m downstream) in 2017, 2018, and April 2019 (pre).

Table 5. Aluminum Species Data Summary. Summary statistics (mean, SD, minimum and maximum) from grab samples collected 2017-2022. n = 20*.

Stream Name	Total Aluminum (µg/L)				Dissolved Aluminum (µg/L)				Exchangeable Aluminum (µg/L)			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Barney Brook	195	117	40	537	169	103	32	465	14	13	2	54
Beaverdam Stream	154	79	54	386	130	71	32	332	10	13	<1	25
Creamer Brook	254	122	94	557	232	114	92	505	32	16	9	56
Richardson Brook – 09[+] (upstream control)	202	85	101	448	183	73	75	388	16	10	2	40
Richardson Brook – B (treatment)	194	87	88	474	180	81	79	432	20	14	2	57

* Creamer Brook was not sampled in April 2018-2022 (n = 15). Beaverdam Stream was not sampled in 2017 (n = 16).
+ Rich09 includes samples collected from Rich-A (a site 360m downstream) in 2017, 2018, and April 2019.

Table 6. Exceedance Summary. Percentage of data observations that exceeded stress threshold values for sonde data (pH, temperature and DO) April-Nov. 2022. Grab sample data (calcium and exchangeable aluminum) combine all six years of the study 2017-2022.

Stream Name	Continuous Data					Grab Sample Data		
	pH (n ~ 10,000)		Temperature (n ~ 10,000)	Dissolved Oxygen (n ~ 10,000)^		Calcium (n = 20)*		Exchangeable Aluminum (n = 16)*
Thresholds	*<5.5*	*<6.5*	*>20.0 °C*	*<5 mg/L*	*<7 mg/L*	*<2.0 mg/L*	*<4.0 mg/L*	*>15 µg/L*
Barney Brook	3.7	64.4	1.7	0	0	30.0	70.0	25.0
Beaverdam Stream[a]	15.0	73.7	28.0	0	1.2	43.8	100	25.0
Creamer Brook	27.7	100	6.6	0	1.2	80.0	100	73.3
Richardson Brook – 09[+] (upstream control)	42.7	100	19.9	0	9.4	90.0	100	40.0
Richardson Brook – B (treatment)	20.3	73.7	19.0	0	3.6	65.0	95.0	55.0

^ DO data for Barney Brook are discrete measurements from a Eureka Manta2 Sub2 sonde (n = 12).
* No grab samples were collected at Creamer Brook in April in 2018-2021 (n = 15)
a No grab samples were collected at Beaverdam Stream in 2017 (n = 16).
+ Rich09 includes samples collected from Rich-A (a site 360m downstream) in 2017, 2018, and April 2019.

Table 7. Base Cation Surplus (BCS). Summary statistics (mean and SD) from grab samples collected April-Nov. 2022. Cations include calcium, potassium, magnesium, and sodium. Anions include chloride, nitrate, sulfate, and strong organic anions (0.071*DOC-2.1, from Lawrence et al. 2007). Data converted from mg/L. n = 15*.

Stream Name	Cations (µEq/L)		Anions (µEq/L)		BCS (µEq/L)			
	Mean	SD	Mean	SD	Mean	SD	Min	Max
Barney Brook	290.1	99.6	156.3	48.8	133.8	91.4	23.8	301.3
Beaverdam Stream	285.8	91.4	220.4	74.7	65.4	46.4	-3.8	148.7
Creamer Brook	210.1	72.3	186.2	47.3	23.9	61.0	-42.5	193.7
Richardson Brook – 09 (upstream control)	184.5	48.0	161.0	41.8	23.4	33.7	-32.1	85.7
Richardson Brook – B (treatment)	211.7	81.6	160.6	42.8	51.1	76.4	-14.5	305.5

* Creamer Brook was not sampled in April 2019-2021 (n = 12).

Table 8. Macroinvertebrate Summary. Mean values (± SD) before any change in pH was observed at the treated Richardson Brook site (‘pre’: 2017 – 2019, n =7 at Beaverdam Stream, n = 6 at Northern Stream, and n = 9 at Richardson Brook) and after pH increased (‘post’: 2020 – 2022, n = 9). Macroinvertebrates were identified to the family in the field by DSF. Water quality index values are based on the occurrence of different taxa groups (IWLA 2021).

Stream Name	Mean Abundance		Mean Family Richness		EPT Family Richness		Water Quality Index	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Beaverdam Stream	69 ± 35	42 ± 19	11 ± 5	11 ± 3	9 ± 3	9 ± 2	13 ± 3	13 ± 2
Northern Stream	115 ± 25	53 ± 25	15 ± 2	14 ± 3	11 ± 1	10 ± 2	17 ± 3	15 ± 3
Richardson Brook (treatment)	62 ± 24	41 ± 15	10 ± 4	12 ± 2	9 ± 2	10 ± 2	14 ± 2	12 ± 3