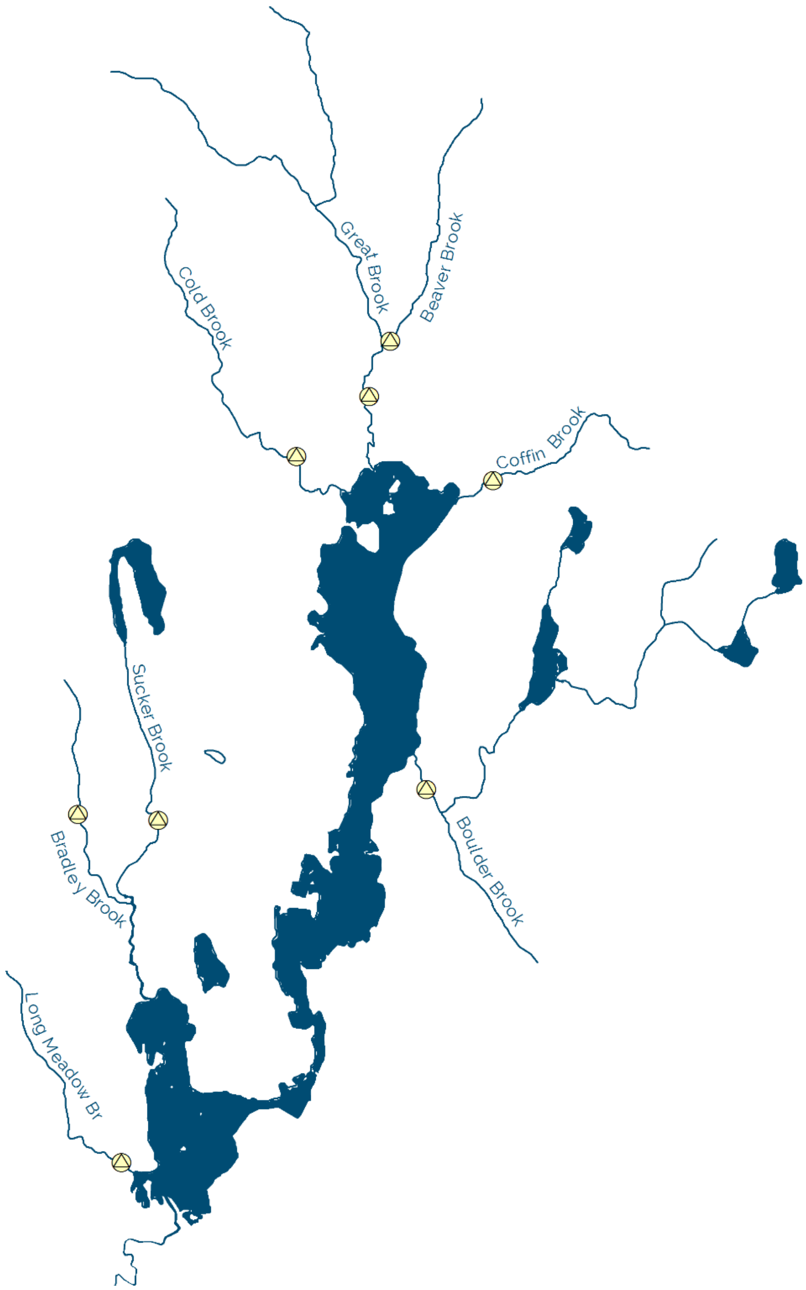
KEZAR LAKE WATERSHED

BASELINE ACIDITY STUDY

A Report on the Current State of Tributary Acidity to Kezar Lake



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INTRODUCTION

Due to its natural granitic geology, Kezar Lake and its ponds suffer from extremely low **alkalinity** (typically < 5 ppm), which has significantly degraded by 1 ppm or more in the last few decades at Kezar Lake, Cushman Pond, and Horseshoe Pond (Figure 1). Without adequate alkalinity to remove excess hydrogen ions in rain (~ pH 5.0) or acidic groundwater, pH in surface waters can fall below levels deemed safe for aquatic life (pH 6.0-8.5).

pH in Kezar Lake and its ponds over the same period shows a statistically significant decline at both Heald and Horseshoe Ponds (Figure 1). While most waterbodies with a longer record showed recovery from acidification following the Clean Air Act Amendments of 1990, pH in waterbodies of the Kezar Lake watershed, including tributaries, has shown a marked decline since 2014, without an obvious cause.

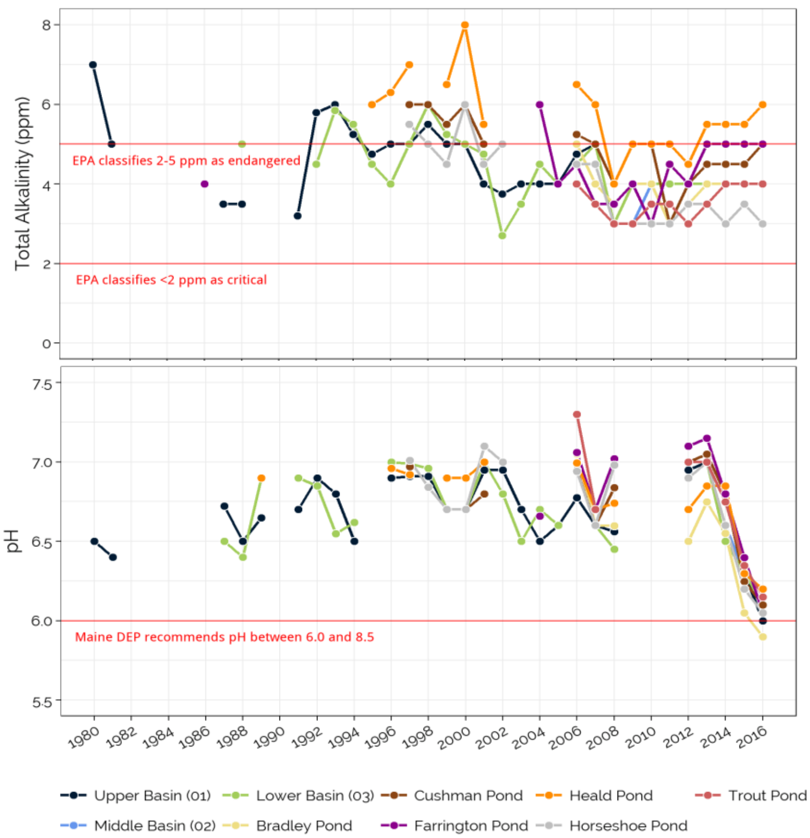


Figure 1. Mean annual total alkalinity (top) and pH (bottom) from 1980-2016 in Kezar Lake and six ponds.

In addition to the recent chronic acidification of surface waters in the Kezar Lake watershed, a sonde deployed in Great Brook in 2012 during a 1.5" storm event recorded a steep decline in pH from 6.1 to 5.5, suggesting that streams to Kezar Lake may regularly experience **episodic acidification** during major precipitation events and snowmelt (Figure 2).

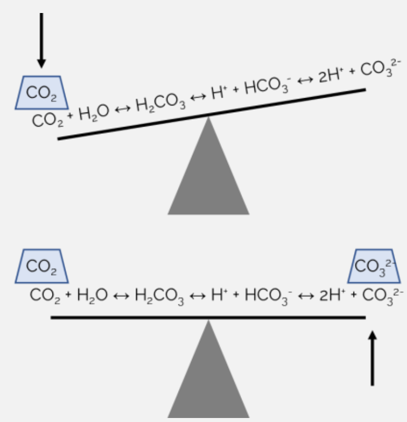
Alkalinity

Alkalinity or acid neutralizing capacity (ANC) is a measure of the buffering capacity of water, or the capacity of water to neutralize acids. It is measured as the concentration of naturally-available bicarbonates, carbonate, other "weak" acids, and hydroxide ions $(OH)^-$). Alkalinity is derived from weathering of soils and rocks, as well as biological processes in the watershed.

pH is a measure of hydrogen ion (H^+) concentration on a negative logarithmic scale of 1-14. A change in pH of 1 reflects a ten-fold change in acidity. If H^+ and OH^- concentrations are balanced, the pH is neutral, or 7.

Episodic Acidification is the depression of pH and alkalinity during rain or snowmelt events. It results from:

1) pre-existing low alkalinity water (<10 ppm as $CaCO_3$) unable to neutralize H^+ loading from acidic rainwater (~ pH 5.0),
2) dilution of pre-existing higher alkalinity runoff,
3) acidic groundwater pulse through shallow soil horizons rich in organic acids and acid deposition (nitrates and sulfates) and dilute in base cations, and
4) carbon dioxide (CO_2)-rich pulse of groundwater from high precipitation events.



Adding CO_2 to a system forces the above sequence of reactions to balance by releasing H^+ (causing acidification) with each reaction from carbonic acid (H_2CO_3) to bicarbonate (HCO_3^-) to carbonate (CO_3^{2-}). This is why increasing CO_2 in the atmosphere is causing global acidification of soil and water. In reverse, the above reaction can take up excess H^+ if enough carbonates are available.

Whether chronic (long-term) or episodic (short-term), acidification of soil pore water, groundwater, and surface water can dissolve, exchange, and leach naturally-occurring ions that can both benefit and harm aquatic life. Acidification is the lowering of pH and alkalinity of aquatic and terrestrial systems, which leaches critical nutrients and increases the availability of toxic metals like aluminum (Al), causing reduced reproductive capacity of sensitive organisms, lower body weight of fish, decreased species diversity, and forest mortality. Base cations (positively charged), such as calcium (Ca^{+2}) and magnesium (Mg^{+2}), are critical to metabolic function and are readily exported (lost) with anions deposited in acidic rain. In response to concerns of the impacts of chronic and episodic acidification, the Kezar Lake Watershed Association (KLWA) obtained funding for a study that determined a baseline for acidity metrics, including alkalinity, pH, Al, and Ca^{2+}, for major tributary streams to Kezar Lake.

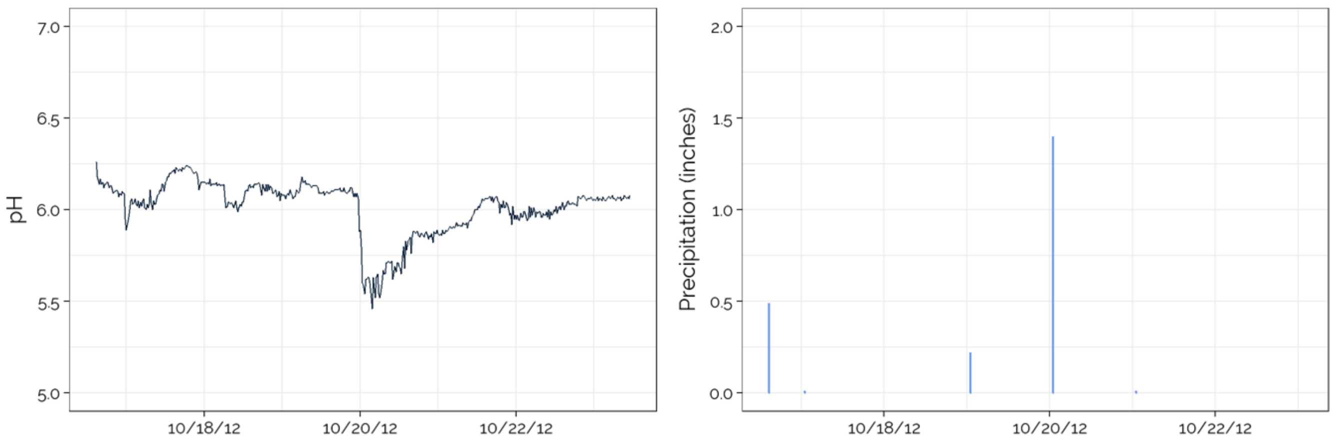
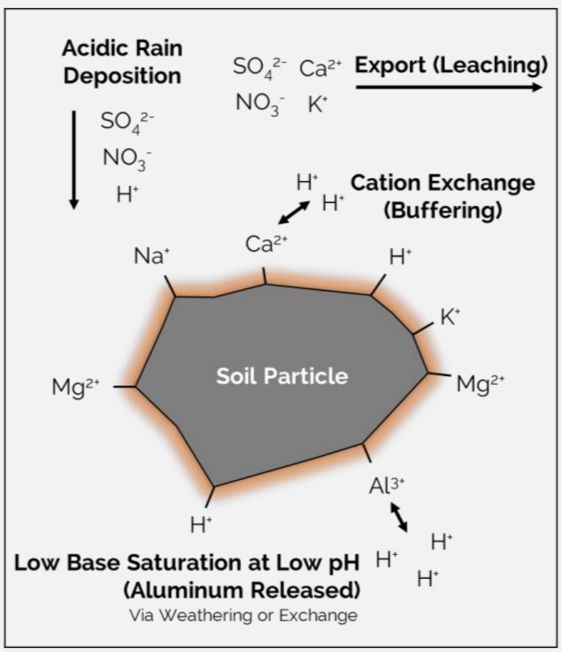


Figure 2. pH in Great Brook (at Adams Rd) dropped from 6.1 to 5.5 during a 1.5" rain event on 10/20/2012. Continuous data were collected by FBE using a YSI data sonde. Precipitation data taken from Creeper Hill NW Cove Kezar Lake weather station (Weather Underground).

ACIDIFICATION PROCESSES EXPLAINED

Fossil fuel combustion emits sulfur dioxide and nitrogen oxides to the atmosphere. These gases react with water vapor, oxygen, and other gases in the atmosphere to form sulfuric (H_2SO_4) and nitric (HNO_3) acids. The acids occur as hydrogen (H^+), sulfate (SO_4^{2-}), and nitrate (NO_3^-) in rain and snow, which falls on water and land surfaces. H^+ ions exchange with base cations such as Ca^{2+}, Mg^{2+}, sodium (Na^{2+}), and potassium (K^+) that are adsorbed by electrostatic force to negatively-charged sites on clay minerals and organic matter. These desorbed base cations are then leached (exported) from the system along with the anions, SO_4^{2-} and NO_3^-. A well-buffered system will export base cations (thus increasing alkalinity downstream); whereas, a poorly-buffered system with low cation exchange capacity will export more H^+ ions downstream (thus increasing acidity downstream). Note that explanation of these processes is simplified and that several other factors influence the behavior of cations and anions in these systems.



Loss of base cations from the soil causes a decrease in alkalinity or buffering capacity in streams, which over time can lead to reduced base saturation of soils (i.e., more H^+ and Al^{3+} comprising total cations in solution) and enhanced acidification of soils and surface waters. When base saturation is reduced and exchange sites are dominated by H^+ and Al^{3+}, H^+ loading at low pH will dissolve amorphous (non-crystalline) secondary $Al(OH)_3$ derived from weathering reactions, consuming the excess H^+ and releasing Al^{3+} and H_2O to solution.

$Al(OH)_3 \leftrightarrow Al(OH)_2^+ \leftrightarrow Al(OH)^{2+} \leftrightarrow Al^{3+}$

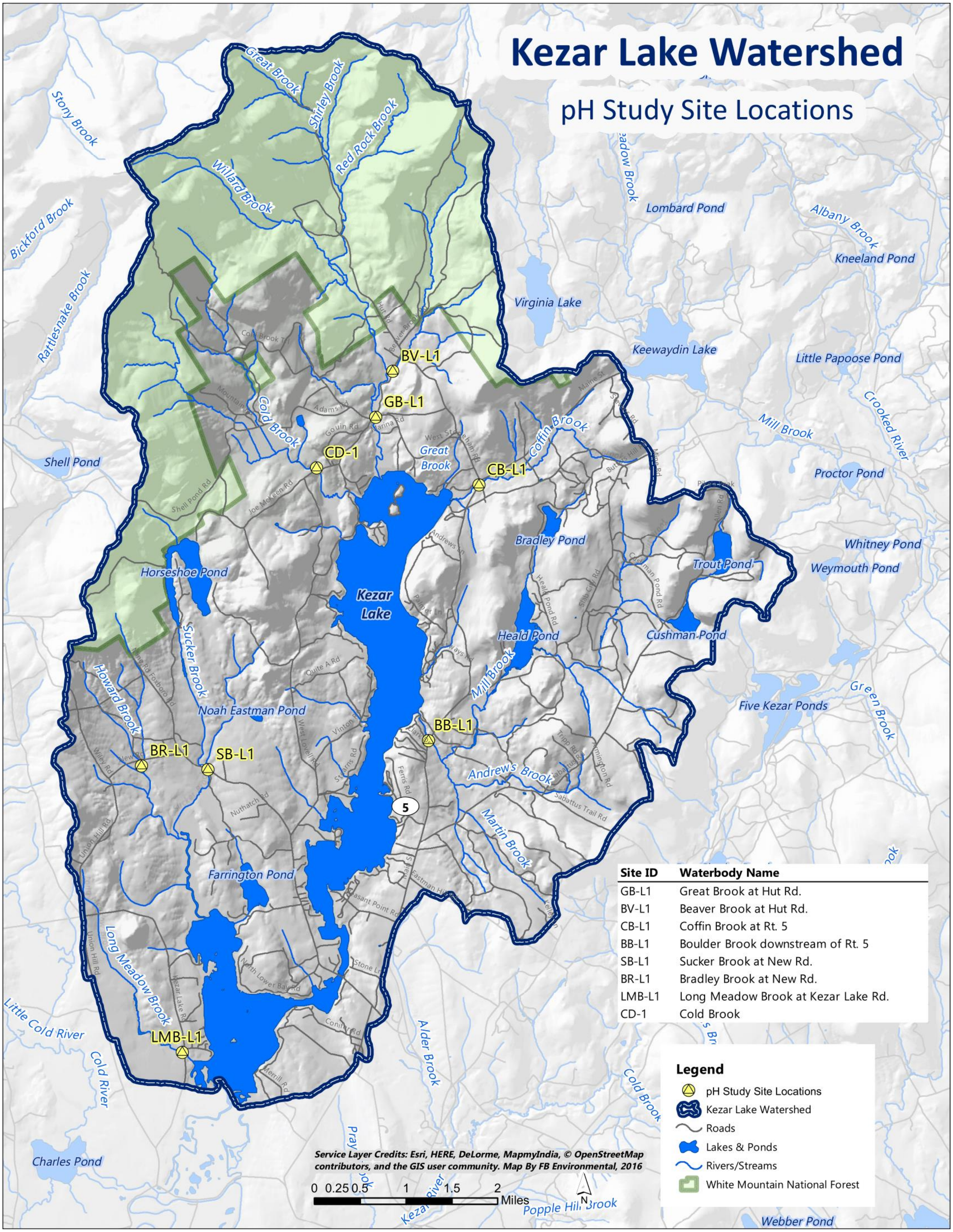


Figure 3. Sampling locations for the 2016-17 acidity study of Kezar Lake tributaries.

METHODS

With guidance from FB Environmental Associates (FBE), KLWA volunteers collected surface water grab samples from eight major tributaries to Kezar Lake: Great Brook, Beaver Brook, Cold Brook, Sucker Brook, Bradley Brook, Long Meadow Brook, Boulder Brook, and Coffin Brook (Figure 3). All sites were sampled six times. A subset was also sampled on 6/6/2016. Sampling targeted stormflow and baseflow weather conditions in summer, fall, and spring (during the snowmelt period) to capture seasonal variation in acidity (Table 1). Samples were analyzed for pH, total alkalinity, Al (total, dissolved, organic, and inorganic), and Ca^{2+} at the University of Maine Sawyer Water Research Laboratory. Research at the Hubbard Brook Experimental Forest in the White Mountain National Forest has shown distinct seasonal patterns in inorganic Al, including maxima during spring snowmelt, minima during summer baseflow, and steady increases throughout the fall until mid-winter; this research helped guide the seasonal timing of sample collection (Figure 4) and determine the threshold for stormflow at 0.75 inches of rainfall or more. Results were also compared to a subset of water quality data collected by the U.S. Forest Service in the Great Brook watershed from 2011-2014.

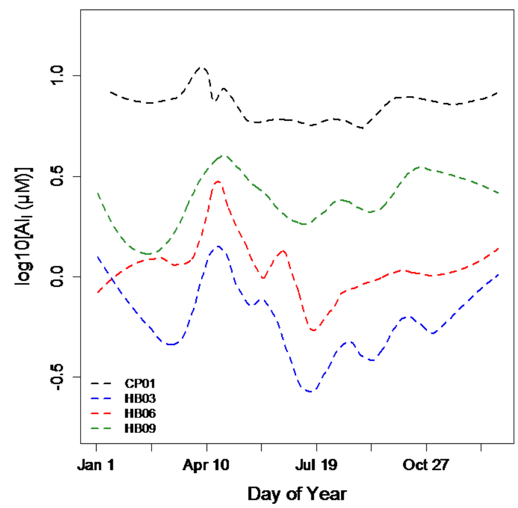


Figure 4. Seasonal patterns in inorganic Al at four small streams in the White Mountain National Forest. Locally Weighted Scatterplot Smoothing (LOWESS) determined from hundreds of data points. Courtesy of C. Ellis (Plymouth State University).

Table 1. Sampling dates and conditions.

Date Sampled	Season	Weather	Prior 24 hr Precip (in)	Prior 48 hr Precip (in)
6/6/16	Summer	Stormflow	2.46	2.46
7/28/16	Summer	Baseflow	0.00	0.00
8/13/16	Summer	Stormflow	1.18	1.18
10/29/16	Fall	Stormflow	0.24	1.11
12/10/16	Fall	Baseflow	0.00	0.00
4/7/17	Spring	Snowmelt	1.02	1.27
5/3/17	Spring	Snowmelt	0.00	0.29

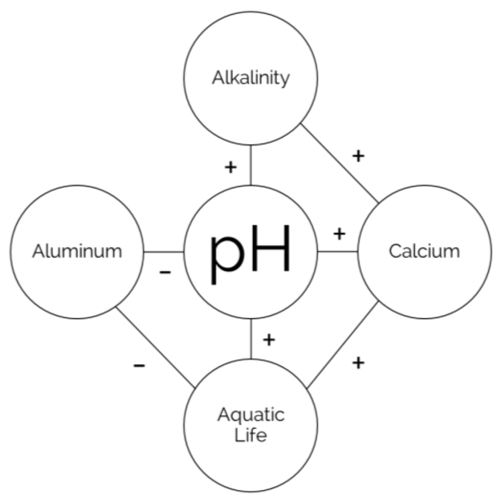
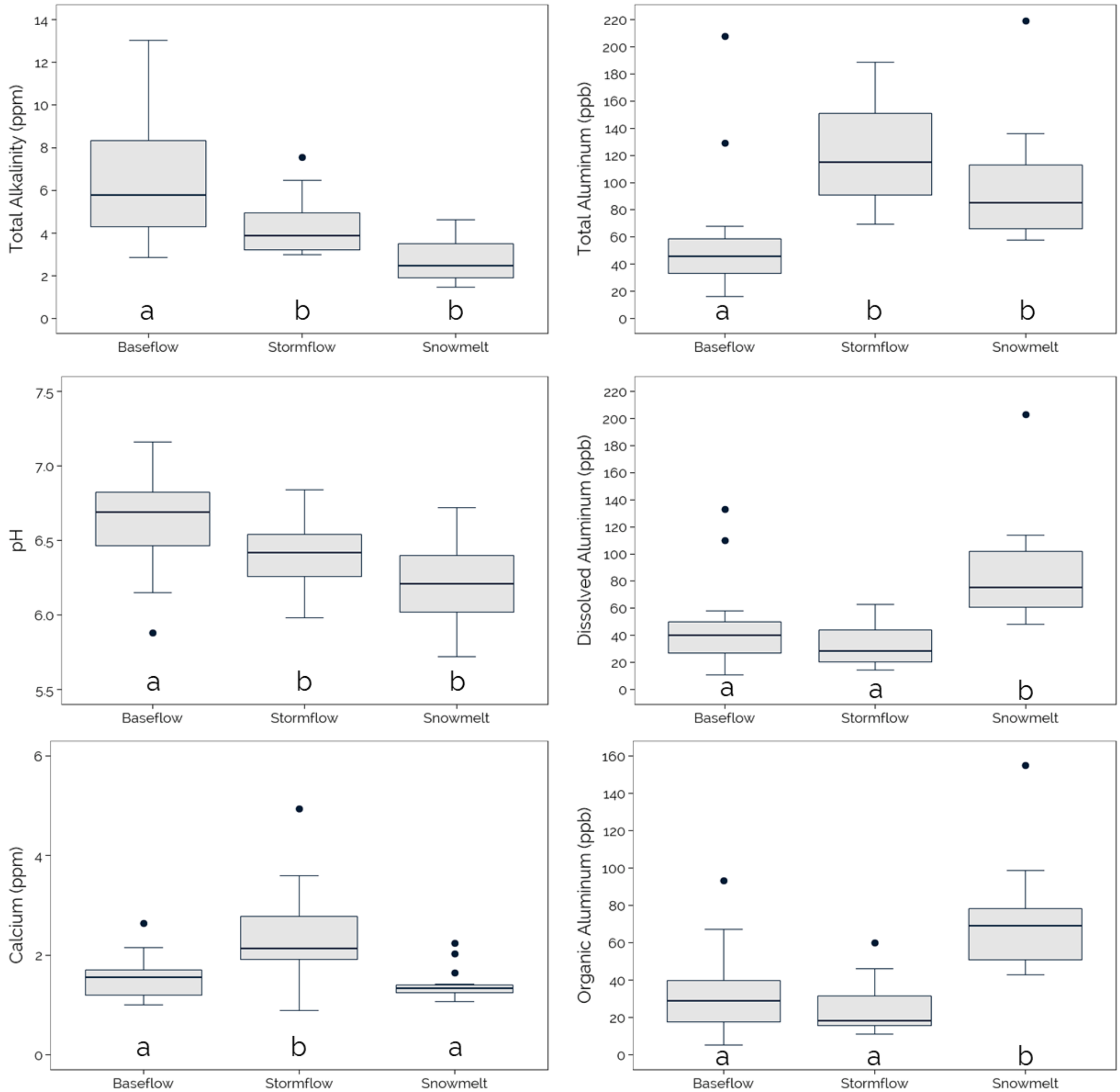


Figure 5. Simplified diagram showing the relationship between each acidity metric. A "+" represents a positive relationship (e.g., if Ca^{2+} increases, alkalinity increases; if Ca^{2+} decreases, alkalinity decreases). A "-" represents a negative relationship (e.g., if pH increases, Al decreases; if pH decreases, Al increases).

RESULTS & DISCUSSION

The interaction among the acidity metrics (alkalinity, pH, Al, and Ca^{2+}) are complex, but predictable (Figure 5), especially across longer times scales like seasons. Alkalinity and Ca^{2+} are typically lowest during spring snowmelt and fall rains and highest during summer and winter (not sampled) baseflow when most incoming water is from deeper flowpaths through mineral soil horizons. pH is typically most acidic during early snowmelt when acid deposition concentrates by ion separation within the snowpack, which forms an acid water layer that is released to surface waters during melting. Later snowmelt may acidify streams, largely through dilution of alkalinity. The seasonal increase in acidity triggers release of Al from soil and stream bed precipitates in spring. Acidity would also release base cations from soil during other times of the year or during rain events, but spring flowpaths extend mostly through shallow organic soil horizons where base cations are not as prevalent as acid anions. These processes were evident in our study's limited data set, which highlights the predictable patterns and interactions among these acidity metrics (Figures 6, 7).



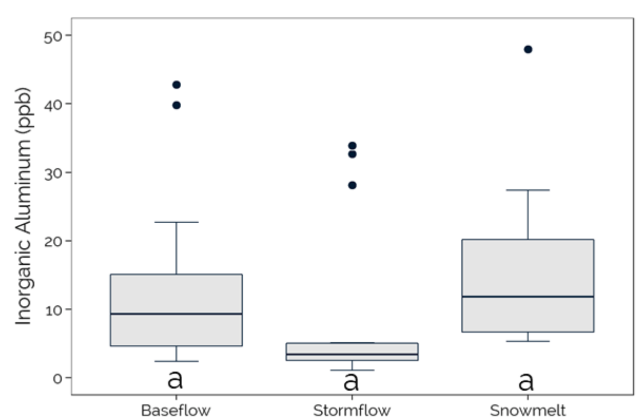


Figure 6. Boxplots summarizing results by weather condition (baseflow, stormflow, snowmelt) for eight tributary sites to Kezar Lake. Letters denote statistical significance by ANOVA and Tukey's HSD (α = 0.05). Different letters mean the conditions are statistically significantly different from each other. Individual points represent outliers. Horizontal lines within the boxes represent medians.

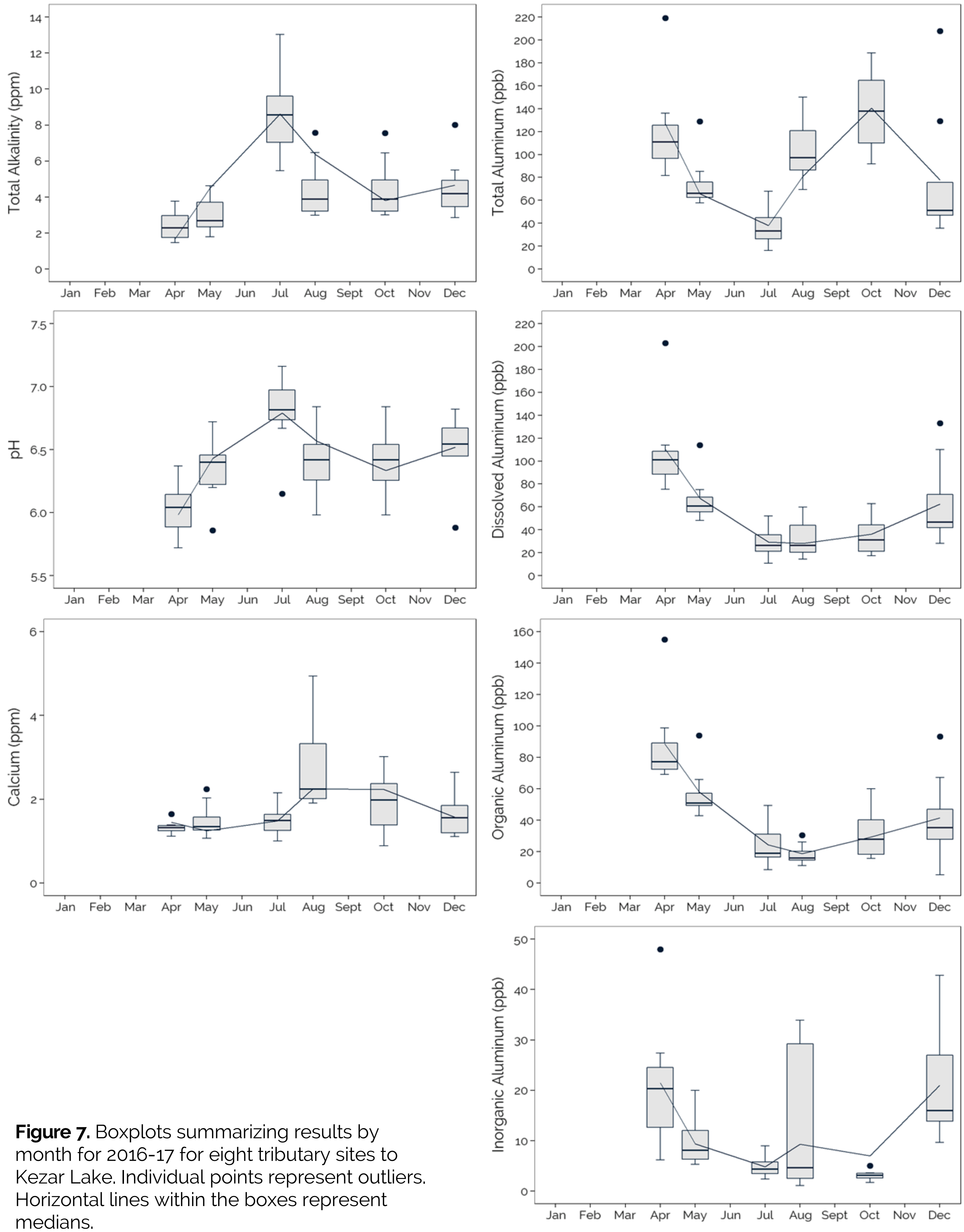


Figure 7. Boxplots summarizing results by month for 2016-17 for eight tributary sites to Kezar Lake. Individual points represent outliers. Horizontal lines within the boxes represent medians.

The recent chronic acidification observed from 2014-2016 in the surface waters of the Kezar Lake watershed may be the result of multiple back-to-back mild winters with little snow cover. Over the available long-term record for North Conway, NH (1959-2017), the number of days with snowpack depth greater than 1 inch significantly declined by about 10 days (Figure 8). This reduction in snowpack depth comes as temperatures and precipitation (as rain, not snow) increase with climate change. Long-term pH data are insufficient to adequately correlate annual pH with number of days with snowpack depth greater than 1 inch, but the recent rapid decline in annual pH in Kezar Lake and the ponds occurred after mild winters in 2014-2016. 2017 was also a mild winter and preliminary June testing results for the lake and ponds show low pH of 5.9-6.1.

Reduction in snowpack duration results in loss of soil CO_2 (degassing from soil horizons to the atmosphere) and thus lower alkalinity in spring runoff, leaving these systems more vulnerable to acidification. Drought (as we have experienced in the last few summers) can also lower water tables and result in evaporative concentration of acid deposition and slowed rates of mineral weathering of buffering elements, causing enhanced acidification.

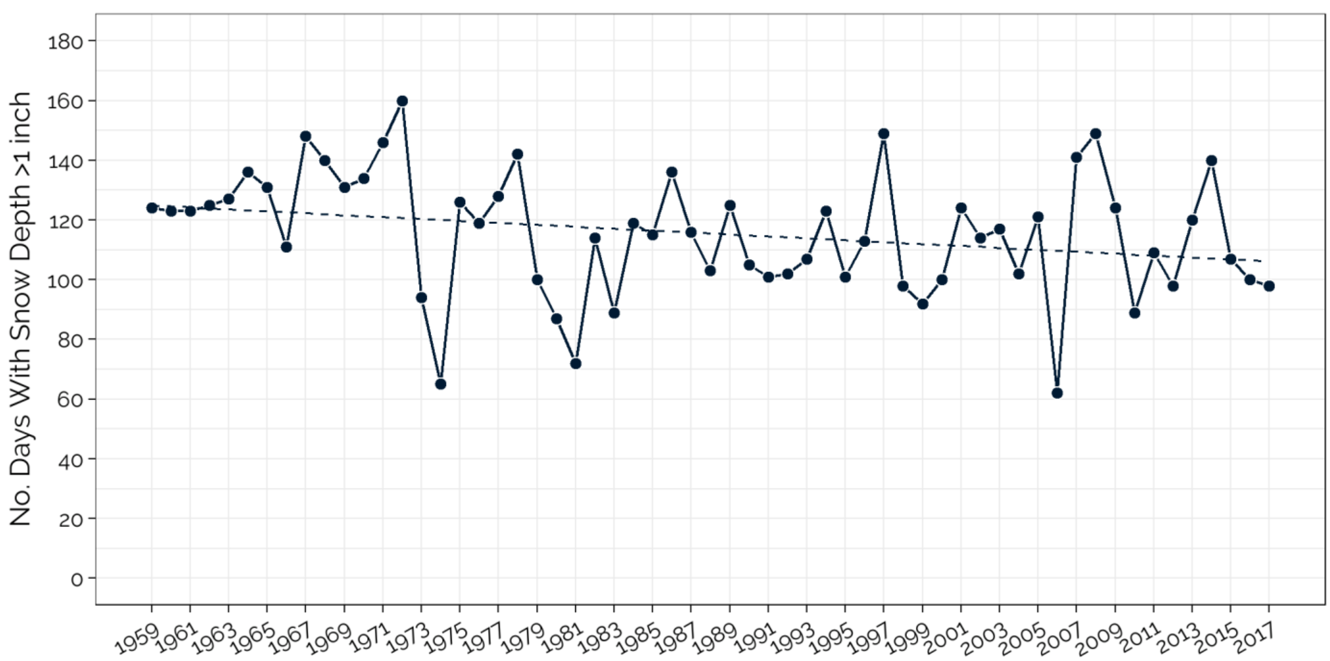


Figure 8. Number of days with snowpack depth of more than one inch. Data taken from the NOAA National Climatic Data Center for station CONWAY 1 N, NH US (ID# GHCND:USC00271732) for 1959-73 and station NORTH CONWAY, NH US (ID#GHCND:USC00275995) for 1974-present. Mann-Kendall trend test was performed. Statically-significant trend is shown as dotted trend line.

OTHER LINES OF EVIDENCE: ANECDOTES & RELATED STUDIES

Anecdotal evidence from expert local fishermen show that smallmouth bass populations in Kezar Lake have declined in the last 10-15 years, along with their food source, crayfish. A brief study of crayfish was conducted in Kezar Lake from August-September 2008 by Dr. Karen Wilson of the University of Southern Maine. The study found three native species and caught a total of 29 crayfish, which were mostly found around rocky islands. The spatial and temporal sample size were too small to gain any significant conclusions on population size, species composition, or size trends. However, given recent evidence of acidification occurring in surface waters of the Kezar Lake watershed, crayfish may be unable to obtain adequate amounts of Ca^{2+} (a base cation leached under acidic conditions) for shell production.

Other lines of evidence also show a marked change in the stability of Kezar Lake within the last decade. A sediment core study of the upper bay deep spot and the Great Brook outlet by Dr. Lisa Doner of Plymouth State University showed an accelerated increase in sediment accumulation rate and organic content after 2000, which Dr. Doner proposed was the result of intensified watershed runoff and erosion. Greater runoff and erosion may have also caused the notable increase in particle-size and decrease in Al concentrations in lake bottom sediments since 2000. Correlation of particle-size and Al concentrations in the lake sediments within recent years may reflect changes in Al-sediment export (from coarser to finer material) from streams. An alternative hypothesis for the increase in organic content in Kezar Lake may be enhanced soil organic matter solubility following recovery from acid rain deposition. Studies of acid-sensitive lakes in the northeast show increasing in-lake dissolved organic carbon (DOC) concentrations with decreasing sulfate deposition. DOC serves as an energy source for microbes, which may also help explain the observed change in sediment-core algal community composition since 2008. This theory is complicated by DOC's other abilities to bind with trace metals, such as Al, and photodegrade in surface waters (releasing Al to settle on lake bottom). It is recommended that DOC be added to the annual baseline water quality monitoring program.

The dense network of tributary streams draining to Kezar Lake in western Maine support some of the last remaining native, wild, and intact populations of brook trout (*Salvelinus fontinalis*) in the northeast. Brook trout are considered a keystone indicator coldwater fish species that is sensitive to watershed disturbances and changes in stream chemistry. The Maine Department of Inland Fish and Game also designated Kezar Lake as a trophy lake for Landlocked Salmon (*Salmo salar*).

The limit of safe exposure for aquatic life to acidic, high- Al, low- Ca^{2+} environments depends largely on the time of year (e.g., spawning in early spring), stage of life (e.g., egg, smolt, or adult phases), and type of species (e.g., brook trout vs slimy sculpin). In one study, exposure to episodic acidification (pH < 5-5.2 and inorganic Al > 100 ppb) during high flows (i.e., after rain events or during spring snowmelt) increased mortality rates in salmon smolts and brook trout fry. Other studies found the lower limit of adult trout survival to be at 5.2, trout egg hatchability at 6.5, and fry mortality at 4.5; these limits increase if Al is elevated. Most fish species, including brook trout, require baseflow conditions of pH 6.0-7.2 and inorganic Al < 60 ppb. Landlocked salmon require at least pH 6.0. Crayfish, mayflies, and frogs begin to die off at pH 5.5. Acidic water alters the blood chemistry of fish and increases the solubility of Al, which can bind to fish gills and disrupt egg and fry development. At least 2.5 ppm of Ca^{2+} is needed to avoid fry mortality, though > 4 ppm is preferred.

Results show that aquatic organisms in the tributaries to Kezar Lake could be impacted by lower alkalinity, pH, and Ca, and elevated Al. All tributaries contribute low alkalinity waters to the lake – a natural condition given the granitic bedrock geology of the region; however, acidic rain deposition (despite improvements since the Clean Air Act Amendments of 1990) continues to cause sustained depletion of base cations in already-low-base-cation forest soils in New England. All tributaries except Coffin Brook had average Ca^{2+} concentrations below the sub lethal level of 2.5 ppm for brook trout survival and reproduction. These low Ca^{2+} levels may be one cause of the anecdotally-observed reduction in crayfish (and subsequently smallmouth bass) in Kezar Lake. Total Al was also elevated at Beaver Brook, Bradley Brook, Long Meadow Brook, and Sucker Brook; however, the most mobile and toxic form of Al (inorganic) was generally low (though Bradley Brook was near the recommended threshold for slimy sculpin survival at 22 ppb). Multiple individual samples at these and other tributary sites did exceed these Al thresholds, indicating that aquatic life in these streams are more likely impacted by episodic acidification.

Interestingly, 2016 brook trout population indices were above average, indicating that brook trout were thriving despite episodic acidification and chronic acidification in the Kezar Lake watershed. There are several possible explanations:

- A significant trout habitat restoration project from 2005-6 in the Great Brook watershed resulted in measurable increases in brook trout biomass in post-treatment sampling from 2007-10 and may be continuing to foster growth in trout populations.
- Studies showed that episodic acidification caused net downstream movement of brook trout and other acid-sensitive species (such as slimy sculpin and blacknose dace) seeking refuge in higher alkalinity spring water along stream beds. Fish may be able to seek out these groundwater refuges during episodic acidification events.
- One study showed adaptation of juvenile brook trout to chronic acidification (pH of 5.2 and inorganic Al of 75 ppb), which caused severe gill damage and mortality in the first 4 days. After 10 days of exposure, juvenile brook trout showed signs of gill repair and less mortality, suggesting that sensitive fish species could be surviving acidification by acclimation.

Table 2. Summary of water quality data by stream sampling site. Values represent mean ± 1 standard deviation. Red values indicate that water quality parameter does not meet recommended threshold for aquatic life.

Stream	Total Alkalinity (ppm)	pH	Ca^{2+} (ppm)	Total Al (ppb)	Dissolved Al (ppb)	Organic Al (ppb)	Inorganic Al (ppb)
Threshold	**20.0**	**6.0**	**2.5**	**87.0**	**NA**	**NA**	**22.0**
Beaver Br	4.2 ± 1.9	6.5 ± 0.3	1.7 ± 0.5	98.4 ± 63.0	45.3 ± 30.4	34.4 ± 27.4	10.9 ± 8.8
Boulder Br	6.1 ± 2.4	6.5 ± 0.2	2.1 ± 0.6	69.0 ± 25.2	42.0 ± 25.2	34.8 ± 21.5	7.2 ± 5.8
Bradley Br	3.8 ± 2.7	6.3 ± 0.3	2.3 ± 1.4	124.7 ± 59.2	82.6 ± 73.6	61.7 ± 55.8	20.9 ± 20.0
Coffin Br	7.4 ± 3.3	6.8 ± 0.3	2.5 ± 0.8	64.6 ± 33.0	42.5 ± 24.7	31.9 ± 21.8	10.6 ± 12.2
Cold Br	4.4 ± 2.2	6.6 ± 0.2	1.4 ± 0.4	75.9 ± 25.7	43.7 ± 17.2	31.1 ± 19.5	12.7 ± 12.4
Great Br	3.1 ± 1.4	6.4 ± 0.3	1.3 ± 0.3	82.5 ± 45.7	52.2 ± 28.2	37.9 ± 22.5	14.3 ± 11.0
Long Meadow Br	4.7 ± 2.4	5.9 ± 0.1	1.6 ± 0.4	118.2 ± 54.3	70.6 ± 40.5	56.4 ± 28.0	14.2 ± 13.8
Sucker Br	3.3 ± 1.4	6.3 ± 0.3	1.5 ± 0.4	100.6 ± 58.0	58.0 ± 30.4	50.8 ± 26.6	7.1 ± 5.8

CONCLUSIONS

Overall, the study design allowed for adequate coverage of year-round variation in acidity metrics, alkalinity, pH, Al, and Ca^{2+}, and the resulting dataset serves as a good baseline of comparison to future studies. The acidity metrics followed expected seasonal patterns and storm event responses based on literature values and a subset of U.S. Forest Service data from 2011-2014 for tributary sites in the Great Brook watershed. Aquatic life in the tributaries to Kezar Lake may be impacted by low alkalinity, pH, and Ca^{2+}, and elevated Al, especially during episodic acidification events. All tributaries except Coffin Brook had average Ca^{2+} concentrations below the sub lethal level of 2.5 ppm for brook trout survival and reproduction. These low Ca^{2+} levels may be one cause of the anecdotally-observed reduction in crayfish (and subsequently smallmouth bass) in Kezar Lake. Since 2014, surface waters within the Kezar Lake watershed have become increasingly acidic; this chronic acidification may be the result of multiple back-to-back mild winters with little snow cover that allows soil CO_2 to be lost, which decreases alkalinity in spring runoff. Brook trout in Great Brook appear to be thriving despite impacts from acidification, which may be the result of habitat improvements, fish movement to groundwater refuges, or fish acclimation.

FUTURE STUDIES

Future studies in the Kezar Lake watershed should build on the existing baseline data set for acidity metrics. Recommendations include the following:

- **Include total phosphorus and phosphate in sample parameter suite.** Studies have found that phosphorus export in streams may be linked to particulate Al hydroxide.
- **Include dissolved organic carbon (DOC) to help interpret Al dynamics**, as well as the acidity status of stream and lake water. DOC should also be added to the annual baseline water quality monitoring program.
- **Collect acidity parameters plus phosphorus before, during, and after a major storm event.** Acidity parameters are at their minima or maxima at peak discharge. Concentrated sampling over the course of a storm could show how long aquatic life are exposed to episodic acidification.
- **Locate possible groundwater refuges.** A stream walk measuring specific conductivity, dissolved oxygen, and temperature continuously upstream could help identify the number and location of groundwater refuges for aquatic life during episodic acidification events.
- **Compile and analyze all U.S. Forest Service data for acidity metrics.** The U.S. Forest Service regularly collects water quality samples at multiple sites within the Great Brook watershed.

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