Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project

Volume 2: 2019 Comprehensive Review Report Technical Appendices V.3 Final

[Appendix 7: Aquatic Ecosystems (Lakes, Streams and Aquatic Biota)]

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7 APPENDIX TO SECTION 7 OF THE COMPREHENSIVE REVIEW REPORT: AQUATIC ECOSYSTEMS (LAKES, STREAMS AND AQUATIC BIOTA)

7.1 Aquatic Appendix A: Review Results for Aquatic Ecosystems (Lakes, Streams and Aquatic Biota)

NOTE: The structural and organization in Aquatic Appendix A are intended to align directly with the detailed Terms of Reference (TOR). Due to the nested nature of the appendices, the absolute numbering does not align but the higher level headings *within Section 7.1* correspond, in content, with the higher level headings *within Section 7 of the TOR*. That is, Section 7.1.x aligns with Section 7.x of the TOR and Section 7.1.x.y aligns with Section 7.x.y of the TOR. Certain sections of the TOR are covered exclusively in the main chapter and not further replicated here, although the associated headings have been retained in order to facilitate comparison among the TOR, the main report chapter, and this appendix. This is explicitly noted in these sections. However, the numbering of some of the sub-headings has changed due to either the addition of new sections that were not part of the original TOR or reordering of certain topics for a more logical flow.

The subsequent appendices (Appendix B through Appendix H) provide additional information on some topics in Appendix A. For these topics, Appendix A maintains the original headings of the TOR as an organizational placeholder and directs readers to the appropriate subsequent appendix.

Text in this format provides comments intended to help readers understand where certain topics or sections as defined in the Terms of the Reference have been shifted to another location, addressed exclusively in the main report chapter, or moved to a supplementary appendix.

7.1.1 What Did We Set Out to Learn?

NOTE: The content of this section exists solely in the Aquatic Ecosystems chapter of the main report.

7.1.2 What Methods Did We Use?

This section provides details on the methods used in the data preparation and analyses applied in the Comprehensive Review. These methods are referenced but not described in any detail in the main chapter. For the comprehensive statistical analyses of changes in water chemistry and for the updated modeling of critical loads, exceedances and future pH, the methods are described in their respective appendices and not repeated here.

7.1.2.1 Data we collected

Data collection and monitoring within the Aquatic Ecosystems component of the EEM Program are summarized in Table 7.2 and mapped in Figure 7.2 and Figure 7.3. Figure 7.2 shows the location of all of the lake and stream sites within the study area, as sampled during the STAR, KAA and/or EEM programs. Figure 7.3 focuses on the locations, frequency and types of sampling implemented as part of the EEM Program specifically.

The bulk of data collection efforts have focused on the annual monitoring of water chemistry for the 14 lakes selected for the EEM Program. Additionally, we have collected data on water chemistry of non-EEM sites, including a few streams of interest, data on fish presence in accessible lakes, intensive monitoring of pH in sensitive lakes, and other data (e.g., lake bathymetry, surface water levels) needed to answer the questions and uncertainties that provided the foundation for the EEM Program and/or emerged during its implementation. The water chemistry metrics that were measured as part of the EEM sampling program align with the sampling in the STAR (which included 41 lakes and 20 stream sites). Table 7.2 provides a chronological summary of data collected for the aquatic receptor in STAR/EEM programs in the period 2012-2018.

<u>The STAR Lakes</u>

The KMP sulphur deposition technical assessment (ESSA et al. 2013a) initially identified 57 candidate lakes (with a surface greater than 1 ha) in the area potentially affected by the prospective increase in deposition following the implementation KMP, including the following sampling groups based on their location relative to the modeled SO_4 deposition plume:

- 31 lakes situated within the three-year average 10 kg SO_4/ha/yr isopleth of total sulphur deposition;
- 9 lakes north of the isopleth that would be potentially exposed to total sulphur deposition of more than 7.5 kg SO_4/ha/yr based on meteorological conditions in 2008;
- 5 lakes south of the smelter that potentially receive SO_4 deposition during wind outflows; and
- 12 lakes within bedrock acid sensitivity class (ASC) 1 or 2 that could potentially receive acid deposition from the smelter.

The sampling strategy focused on lakes rather than streams because they are less influenced by episodic storm and snowmelt events, which makes their water chemistry more temporally stable and thus better suited for estimating critical loads for surface water (ESSA et al. 2013a). However, the STAR sampling program nonetheless still included streams to be precautionary.

After field reconnaissance to confirm accessibility conditions and ground-truthing the spatial information from the BC Watershed Atlas, 16 lakes were excluded from the sample set resulting in a final sampling population of 41 lakes. These 41 lakes represent 30.6 % of the lakes greater than 1 ha in size and 88.4 % of the area of lakes in the study area. The sampling design included 20 stream sites on 14 streams. Water sampling and measurements on these lakes and streams were completed during August 14-20, 2012.

<u>The EEM Lakes</u>

The current composition of lakes that comprise the lake chemistry sampling program within the EEM Program are outlined in Table 7.1.

Table 7.1. Summary of EEM Lakes.

Lake	Initial Sampling	Added to EEM Program	Rationale
EEM Sensitive Lakes			
LAK006	2012	2013	Sensitive lake chemistry
LAK012			
LAK022			
LAK023			
LAK028			
LAK042			
LAK044			
EEM Less Sensitive Lakes			
LAK007	2012	2013	Insensitive
LAK016		2013	Moderately sensitive
LAK024		2014	High public value
LAK034		2013	Moderately sensitive
EEM Control Lakes			
DCAS014A	2013 (KAA)	2015	Control site
NC184			
NC194			

The critical loads analysis (e.g., SSWC model) and risk acidification assessment was applied to these 41 lakes and 20 streams sites. Based on the results of the technical assessment (ESSA et al. 2013_a), we recommended careful monitoring of the chemistry of 7-10 lakes potentially vulnerable to acidification under KMP, baseline studies of their fish populations, and further biological studies if any of these lakes show biologically significant changes in pH (i.e., 0.30 pH units or more). The 7 sensitive lake chosen for the EEM program included all of lakes for which the STAR predicted pH changes greater than 0.1 pH units, including 5 lakes with predicted exceedances of their critical loads (Figure 7.1). These sensitive lakes were complemented by the inclusion of 3 additional lakes predicted to be moderately sensitive to extremely insensitive to increased acidic deposition – i.e., the "less sensitive EEM lakes" were not predicted to show any change in pH under increased levels of sulphur deposition. Lakelse Lake (LAK024) was not initially included in the EEM Program due to being highly insensitive; however, it was added as a fourth "less sensitive EEM lake" in 2014 because of its great importance to local communities and First Nations. Lakelse Lake is the largest lake in the study area (1,374 ha) and is accessible to fish populations.

These 11 lakes were grouped in two categories according to their sensitivity to acidification; there are seven lakes considered sensitive to acidification (i.e., predicted pH changes greater than 0.1 units) and three are considered less sensitive (i.e., predicted pH changes less than 0.1 units):

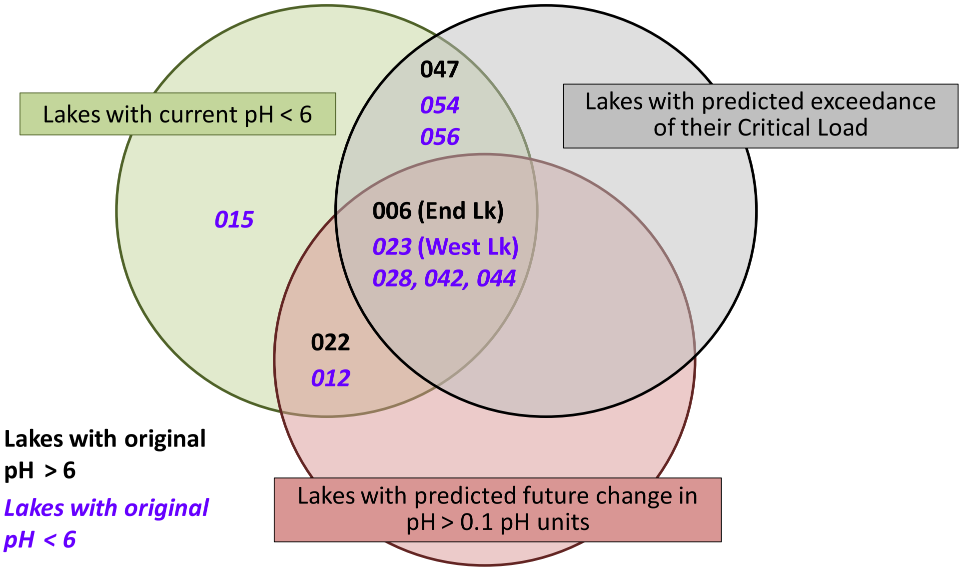

Figure 7.1. Conceptual diagram of criteria for lake vulnerability (ESSA et al. 2013a)

In 2015 three control lakes were added to the EEM Program. These lakes are similar to the sensitive EEM lakes in terms of their low ANC and relatively comparable annual runoff but they are located well outside the KMP deposition zone and therefore predicted to receive only background levels of acidic deposition. The inclusion of control sites addresses multiple objectives: improving the estimates of natural variability; improving the understanding of regional trends independent of KMP effects; and improving our ability to detect potential KMP effects in the sensitive lakes.

Table 7.2. Overview of data collection efforts for the aquatic receptor through the 2012-2018 period.

Year	Annual water chemistry monitoring	Intensive sampling and continuous pH monitoring	Fish sampling	Water chemistry at non-EEM sites	Other data collected[1]
Pre-KMP baseline period					
2012	41 lakes 20 streams as part of STAR (including 11 EEM lakes)				
Transition period					
2013	7 EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) 3 EEM less sensitive lakes (LAK007, LAK016, LAK034)		Conducted in four acid-sensitive lakes: LAK006, LAK012, LAK023, and LAK044	Cecil Creek (receives drainage from LAK023) sampled in three locations	
2014	7 EEM sensitive lakes 4 EEM less sensitive lakes[2]	Intensive sampling and continuous pH monitoring added to LAK006, LAK012, LAK023		Lake MOE6 and six sites within the Goose Creek watershed	Reconnaissance of habitat and water chemistry in Goose Creek
2015	7 EEM sensitive lakes 4 EEM less sensitive lakes 3 EEM control lakes	Continuation of existing program. Continuous pH monitoring in Anderson Creek	Completed in the three less sensitive lakes: LAK007, LAK016, and LAK034	Additional sampling in Goose Creek watershed to assess sensitivity	Bathymetric surveys of LAK006, LAK012, LAK023
Post-KMP period					
2016	14 EEM lakes (sensitive, less sensitive, and controls)	Continuation of existing program Continuous monitoring of Anderson Creek was unsuccessful			Lake levels monitoring in LAK006, LAK012, LAK023
2017	14 EEM lakes (sensitive, less sensitive, and controls)	Continuation of existing program	Fish sampling was done in LAK028		Lake levels monitoring continued Amphibian literature review
2018	14 EEM lakes (sensitive, less sensitive, and controls)	Continuation of existing program LAK028 was added		7 stream sites within the Goose Creek network	Lake levels monitoring continued Bathymetric survey of LAK028

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[1] Other data further discussed in Section 7.1.2.8
[2] LAK024 re-added in 2015

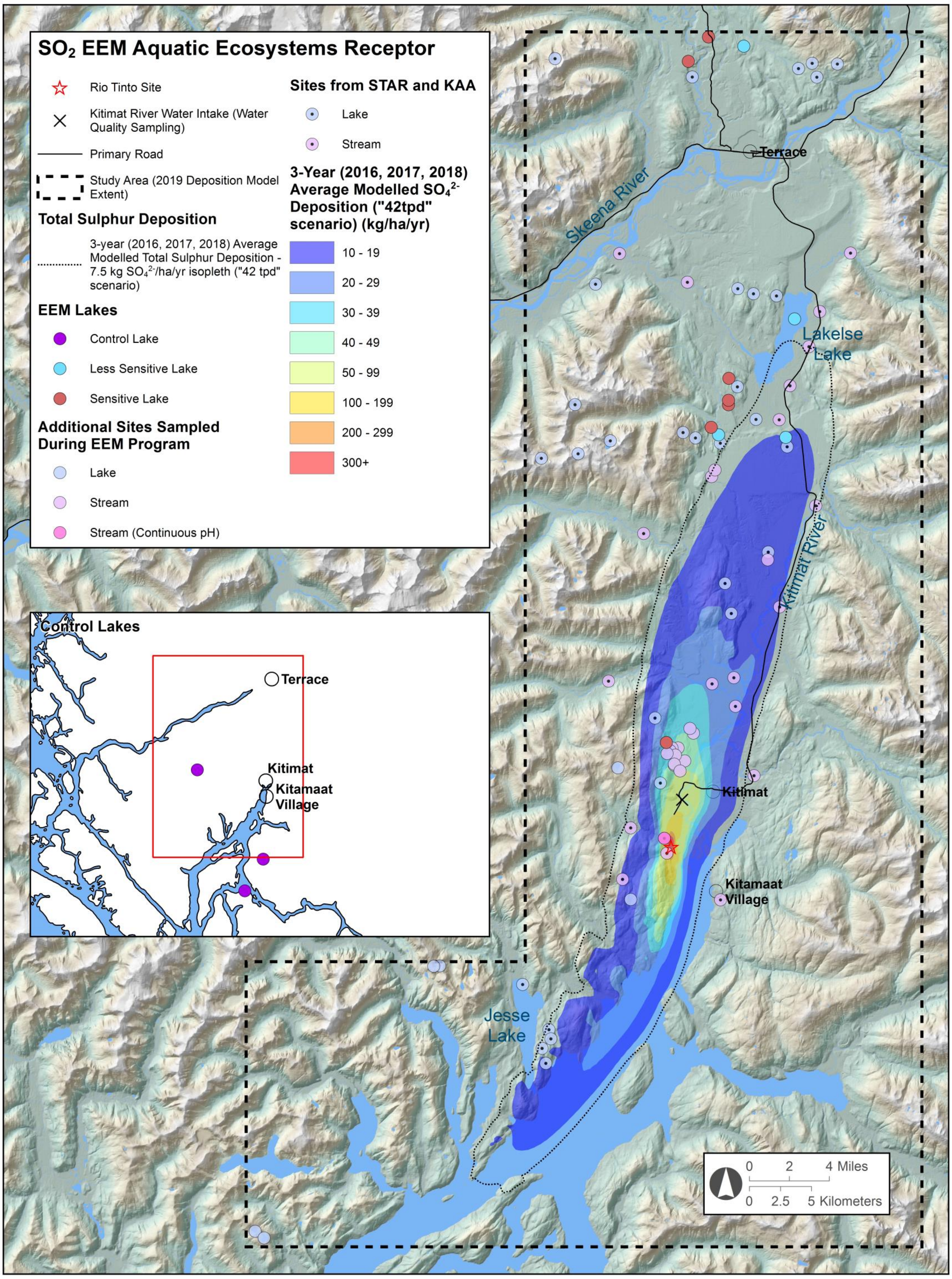

Figure 7.2. Locations of ongoing and existing monitoring and sampling for the aquatic receptor of the EEM Program.

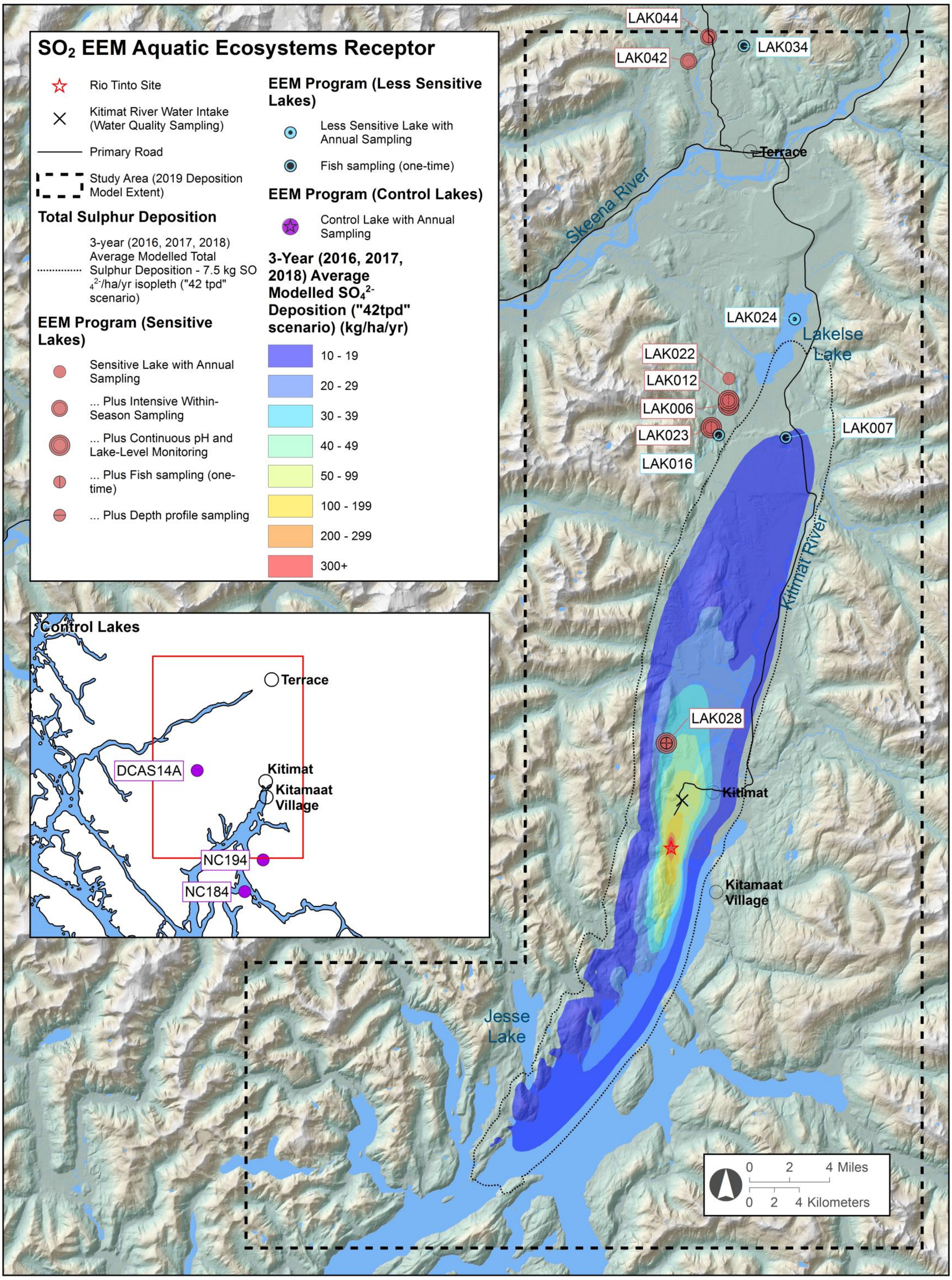

Figure 7.3. Locations of the study lakes of the EEM Program. Lakes are grouped by their classification as sensitive lakes, less sensitive lakes and control lakes. The map also shows the frequency and type of monitoring conducted at each of the lakes.

Water Chemistry Sampling

The annual water chemistry sampling program provides the data foundation for the assessment of inter-annual changes and long-term trends in water chemistry within the EEM lakes. Water chemistry samples are taken annually from all 14 EEM lakes and more intensively for 6 of the sensitive lakes (i.e., three additional samples within the fall index period). The frequency of sampling for each of the lakes over time is summarized in (Table 7.3).

The field and laboratory methods associated with the water sampling are documented in detail each year in Limnotek's technical report (e.g., Bennett and Perrin 2017, 2018; Limnotek 2016, 2019; Perrin et al. 2013; Perrin and Bennett 2015). Please refer to those documents for comprehensive technical details as these methods are only briefly summarized here.

Because most of the lakes in the EEM Program are only accessible by helicopter, annual water sampling was completed from a helicopter in hover position, approximately 4 m above the water surface. In more recent years, some of the lakes have been accessed by foot for the additional within-season sampling and "calibration visits" for the continuous pH monitors. Sampling included field measurements of temperature, dissolved oxygen and total dissolved solids. Laboratory analyses involved the measurement of major ions, dissolved organic carbon (DOC), total alkalinity and Gran ANC, obtained by titration.

The collection, handling, transport, and analyses of water quality samples were conducted with numerous quality checks, to ensure the highest quality data possible. Details on the methods for quality control and quality assurance for the water samples are described in the Limnotek technical reports from each of the years of annual sampling.

In addition to the data quality control and assurance procedures applied during the sampling and subsequent laboratory analyses, we applied two additional methods to confirm the quality of the data input prior to their use for the analyses and modeling described in this technical memo. First, we assessed the charge balance for each sample, and then examined the average charge balance across all samples within a particular data set (i.e., the EEM lakes were considered separately from non-EEM sites). Second, we compared the estimated conductivity based on ion concentrations for each sample to the measured conductivity for that site, then examined average relative differences across all samples. These two tests integrate the cumulative errors in any of the measured parameters, therefore giving an indication of the overall quality of the entire data set.

Table 7.3. Frequency of water chemistry sampling for EEM lakes, 2012-2018.

		Pre-KMP			Transition									Post-KMP								
		2012			2013			2014			2015			2016			2017			2018		
	Lake	Annual	Multiple	Continuous (pH only)	Annual	Multiple	Continuous (pH only)	Annual	Multiple (n=5)	Continuous (pH only)	Annual	Multiple (n=4)	Continuous (pH only)	Annual	Multiple (n=4)	Continuous (pH only)	Annual	Multiple (n=4)	Continuous (pH only)	Annual	Multiple (n=4)	Continuous (pH only)
EEM Sensitive Lakes	LAK006	✓			✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	LAK012	✓			✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	LAK022	✓			✓			✓			✓			✓			✓			✓		
	LAK023	✓			✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	LAK028	✓			✓			✓			✓			✓	✓		✓	✓		✓	✓	✓
	LAK042	✓			✓			✓			✓			✓	✓		✓	✓		✓	✓	
	LAK044	✓			✓			✓			✓			✓	✓		✓	✓		✓	✓	
EEM Less Sensitive Lakes	LAK007	✓			✓			✓			✓			✓			✓			✓		
	LAK016	✓			✓			✓			✓			✓			✓			✓		
	LAK024	✓						✓			✓			✓			✓			✓		
	LAK034	✓			✓			✓			✓			✓			✓			✓		
Control Lakes	NC184				✓						✓			✓			✓			✓		
	NC194				✓						✓			✓			✓			✓		
	DCAS14A				✓						✓			✓			✓			✓		

Continuous and bi-weekly pH monitoring

Starting in 2014, continuous pH monitors were installed each year in three of the acid-sensitive lakes – West Lake (LAK023), End Lake (LAK006) and Little End Lake (LAK012). A similar monitor was installed in LAK028 in 2018. The objective of intensive pH monitoring was to document natural variability in pH and related chemistry in acid-sensitive lakes over the fall season in order to assess the potential for episodic acidification.

The implementation of continuous pH monitoring facilitated an opportunity for an additional time series of pH data for these lakes. The pH monitors that were installed required calibration approximately every two weeks during their period of installation each year, which necessitated a field visit. On each visit, a field measurement of pH was taken[3] and recorded. This "calibration data" thus comprises a data set of bi-weekly field pH for each lake for 2014-2018 (during the ice-free period of the year). In 2017 and 2018, the calibration visit also included taking a water sample and sending it to Trent University to measure laboratory pH and Gran ANC.

A continuous pH monitor was also operated in Anderson Creek for multiple years but experienced significant issues with operating consistently.

7.1.2.2 Quality of Water Chemistry Data

Sampling and laboratory quality control and quality assurance

The collection, handling, transport, and analyses of water quality samples were conducted with numerous quality checks, to ensure the highest quality data possible. Details on the methods for quality control and quality assurance for the water samples are described in the annual technical reports from Limnotek, who are responsible for the implementation of the water chemistry sampling program.

Analyses of Charge Balance and Estimated vs. Measured Conductivity

In addition to the data quality control and assurance procedures applied during the sampling and subsequent laboratory analyses, we applied two additional methods to confirm the quality of the data input prior to their use for the analyses and modeling described in this technical memo. First, we assessed the charge balance for each site, and then examined the average charge balance across all sites. Second, we compared the estimated conductivity based on ion concentrations for each site to the measured conductivity for that site, then examined average relative differences across all sites. These two tests integrate the cumulative errors in any of the measured parameters, therefore giving an indication of the overall quality of the entire data set.

Further details on the methods and rationale are described in greater detail in the STAR (ESSA et al. 2013, Section 8.6.3.2) and the KAA (ESSA et al. 2014a, Section 6.1.1.1).

pH measurements

Water chemistry samples taken have multiple measures of pH, including a field measurement and two lab measurements (Trent University and ALS). As described in Section 7.1.2.1, several lakes also have additional measurements of pH from continuous meters. As described in the

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[3] Usually three separate field measurements were taken.

STAR, lab measurements of pH, rather than field measurements, have been used for the analyses of lake chemistry; lab pH measurements have lower variability, and therefore are more relevant to the detection of long term trends.

The 2012 data collected during the STAR included laboratory measurements of pH only from Trent University. Inter-annual comparisons of trends in pH have therefore been conducted using the pH measurements from Trent University. Limnotek has analyzed differences among the different methods of measuring pH for quality assurance purposes, repeating similar comparisons over multiple years.

7.1.2.3 Analyses we conducted with these data

7.1.2.3.1 Variable organic charge density

In the STAR, KAA, and EEM programs, we have calculated the charge concentration of organic anions using the method of Oliver et al. (1983). This method (as with others) requires specification of the average organic charge density (μeq/mg C) in the organic content of the water (as measured by DOC in mg/L). We assumed a charge density of 7.5 μeq/mg C for the STAR, KAA, and EEM. However, the actual organic charge density may vary significantly by lake, depending on the specific composition of organic compounds present and their relative concentrations. Therefore, the difference between the estimated charge concentration of anion and cations for a particular sample may partly be explained by having over or underestimated the contribution of organic acid anions to the charge balance.

As part of the present Comprehensive Review we have explored whether changing the assumed organic charge density would improve the overall charge balance across all lakes (i.e., all samples of all STAR lakes, EEM lakes, and additional lakes sampled during the EEM Program). First, we explored changes in a single, regional value for the organic charge density applied across all lakes (as done in the STAR, KAA, and EEM). Second, we allowed the assumed organic charge density to vary by lake (but keeping the value for each lake constant across years).

The effects on the average charge balance of changing the assumed value for a single, regional organic charge density are shown in Table 7.4. The best overall charge balance is achieved when applying an organic charge density of approximately 4.5-5.5 μeq/mg C, depending on the specific metric used to characterize the average charge balance.

Next we estimated the lake-specific value of organic charge density that produced the best charge balance for each lake – that is, we allowed each lake to be represented by a different value but assumed that value to be a constant property of the lake over time. To facilitate this exploration, we evaluated the average charge balance for each lake across all samples and all years using organic charge density values of 0.5 to 10.0 μeq/mg C (in increments of 0.5 μeq/mg C). The organic charge density value that produced the best charge balance (i.e., closest to zero) was identified as the "best" value for that lake. For this evaluation we focused on two metrics, the *average of the relative difference (%)* and the *average of the absolute differences (μeq/L)*[4] – if

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[4] Note that both these metrics are indicators of the effect *on measures of charge balance* of changing the assumed values for *organic charge density* and therefore the correct units are i.e., *μeq/L.*

these two metrics led to different answers we prioritized the latter. Table 7.5 shows the overall charge balance when applying the lake-specific estimates of organic charge density developed through this approach. Table 7.7 shows the lake-specific estimates that we applied.

By applying the results of either of the approaches described above for modifying the organic charge density assumption – i.e., revising the regional organic charge density value or developing lake-specific estimates – produces a much better average charge balance across all the lakes across all four charge balance metrics in most years (Figure 7.4).

These adjustments significantly improve the charge balance reported in previous annual reports, but changing the organic charge density does not affect the water chemistry statistical analyses in Appendix F or the modelling of critical loads, exceedances and future pH because those analyses do not use the charge concentration of organic anions as an input.

Table 7.4. Average charge balance under alternative assumptions for the average regional organic charge density across all samples for all samples from all STAR/EEM lakes from all years.

		Overall Charge Balance across all Lakes and Years			
Organic Charge Density (μeq/mg C)	Number of Samples	Average Percent Difference (%)	Average of the Absolute Value of the Percent Differences (%)	Average Difference (μeq/L)	Average of the Absolute Value of the Differences (μeq/L)
0.5	199	12.6%	13.9%	17.7	25.9
2.5	199	7.0%	9.0%	9.3	20.0
4.0	199	3.3%	6.1%	3.0	16.0
4.5	199	2.1%	5.4%	0.9	14.8
5.0	199	1.0%	4.8%	-1.2	13.9
5.5	199	-0.1%	4.3%	-3.3	13.2
6.0	199	-1.1%	4.0%	-5.4	12.8
7.5	199	-4.1%	5.1%	-11.7	14.8
10.0	199	-8.5%	8.9%	-22.1	23.9

Table 7.5. Overall average charge balance (four different metrics) using the lake-specific estimates of organic charge density that produce the best charge balance for each lake.

		Overall Charge Balance across all Lakes and Years			
Organic Charge Density (μeq/mg C)	Number of Samples	Average Percent Difference (%)	Average of the Absolute Value of the Percent Differences (%)	Average Difference (μeq/L)	Average of the Absolute Value of the Differences (μeq/L)
Lake-specific	199	-0.3%	3.0%	-2.9	9.2

Table 7.6. Lake-specific estimates of organic charge density by lake. The sensitive, less sensitive, and control lakes of the EEM Program are bolded and with blue fill. Orange fill indicates lakes that were assigned either the maximum or minimum values of the range tested (see description in text).

Lake	Estimated Organic Charge Density
LAK001	0.50
LAK002	7.75
LAK003	2.00
LAK004	5.75
LAK005	6.75
LAK006	**6.00**
LAK007	0.50
LAK008	0.50
LAK011	5.25
LAK012	**6.50**
LAK013	3.75
LAK014	9.75
LAK015	7.25
LAK016	**6.00**
LAK017	4.25
LAK018	0.50
LAK022	**6.00**
LAK023	**5.75**
LAK024	**1.75**
LAK027	6.50
LAK028	**0.50**
LAK030	0.50
LAK032	0.50
LAK034	**6.75**
LAK035	4.25
LAK037	3.25
LAK038	8.50
LAK039	7.00
LAK041	10.00
LAK042	**6.00**
LAK044	**4.00**
LAK045	10.00
LAK047	10.00
LAK049	10.00
LAK050	10.00
LAK051	8.50
LAK053	1.00
LAK054	7.50
LAK055	5.75
LAK056	7.25
LAK057	6.00
DCAS14A	**4.75**
NC184	**6.75**
NC194	**10.00**
MOE3	0.50
MOE6	9.50

Figure 7.4. Charge balance by year across all lakes under three different assumptions for the organic charge density. "Base Case" applies a value of 7.5 μeq/mg C (as per the STAR, KAA and EEM). "Alt Case" applies a value of 5.0 μeq/mg C (as per the sensitivity analyses described in the text). "Variable CD" applies the lake-specific estimate of organic charge density that produces the best charge balance (as described in the text; values between 0.5-10.0 μeq/mg C). The four metrics of charge balance are: %DIFF = average of the relative difference (%); ABS(%) = average of the absolute value of the relative differences (%); Diff = average of the absolute differences (μeq/L); AbsDiff = average of the absolute value of the absolute differences (μeq/L).

7.1.2.3.2 Exploration of ANC Values and Metrics

Acid neutralizing capacity (ANC) is the buffering capacity of a solution to neutralize strong acids and therefore mitigate acidification[5]. Gran ANC has been the primary measure of ANC for all the analyses in the STAR and EEM. It is determined by titration to the inflection point of the pH-alkalinity titration curve. Gran ANC includes the buffering effect of organic anions. Based on recommendations from other QPs, ENV, and external experts prior to the Comprehensive Review, we have explored alternative measures of ANC, including charge balance ANC (CBANC), Base Cation Surplus (BCS), and organic anion adjusted ANC (ANC_{OAA}). Figure 7.5 shows an idealized comparison of Gran ANC, CBANC and BCS based on hypothetical data.

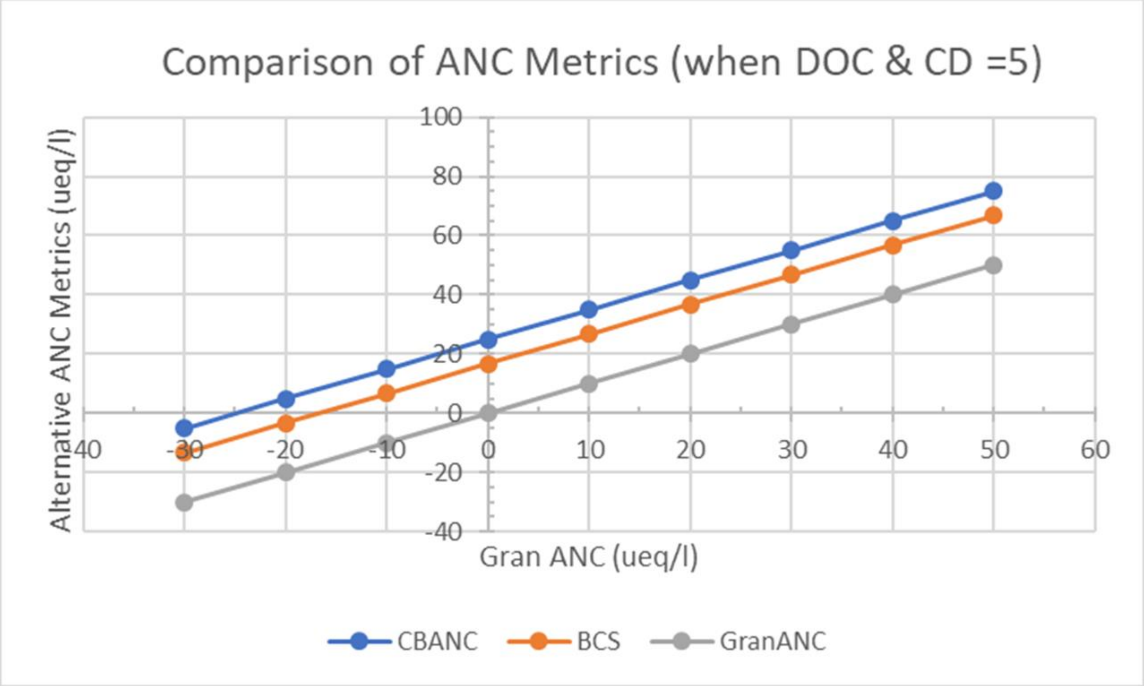

Figure 7.5. Comparison of three alternative measures of ANC – charge balance ANC (CBANC), base cation surplus (BCS), and Gran ANC. The contribution of organic acid anions is based on assumed values of a DOC of 5.0 mg/L and an organic charge density of 5.0 μeq/mg C.

<u>Exploring Relationship between Gran ANC and CBANC</u>

CBANC is generally calculated as the equivalent sum of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) minus the equivalent sum of strong acid anions (SO_4^{2-}, NO_3^{-}, Cl^{-}). CBANC has the benefits that it has been used in many studies of long term trends (e.g., Stoddard et al. 1998, 2003), and it can be analyzed in commercial labs without specialized equipment for Gran ANC titrations. However, the usual formulation of CBANC has the detriments that it does not take into account buffering by organic anions (which are very important in some of the EEM lakes) and that it is calculated

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[5] As defined in the STAR: acid neutralizing is the equivalent capacity of a solution to neutralize strong acids; ANC and alkalinity are often used interchangeably; ANC includes alkalinity plus additional buffering from dissociated organic acids and other compounds.

from the sum of seven different measurements and therefore can potentially accumulate measurement errors (Evans et al. 2001).

Estimating CBANC from Gran ANC

Although CBANC is a calculated measurement (based on the laboratory measurement of major ions) and Gran ANC is measured through an independent laboratory analysis, the two metrics are empirically related as described by the following equation:

CBANC = Gran ANC + CD * DOC,

where CD is an estimate of charge density, generally in the range of 4-6 μeq per mg DOC, but can be from 2-10 μeq per mg DOC (Hemond 1990, Marmorek et al. 1996). As discussed above in Section 7.1.2.3.1, the best overall estimate of CD for the EEM lakes is about 5.0 μeq/mg C, in the middle of the range observed in other studies.

Based on the recommendations from ENV's external expert during the development of the terms of reference for the Comprehensive Review, we calculated a lake-specific charge density (CD) to achieve the best possible charge balance (Section 7.1.2.3.1), and then applied that value to the above equation to compare CBANC vs Gran ANC, for the purposes of understanding the relationship between these two indicators. Figure 7.6 shows the results for all the samples taken during the STAR and EEM programs. The results show a very strong relationship between the estimated and calculated values for CBANC – i.e., CBANC and Gran ANC are very strongly correlated once CBANC is adjusted for the influence or organic anion, as expected. Of the 244 samples included, the only ones with notable deviations from the regression are the five deep-water samples from LAK028 taken in 2018 (which have substantially different water chemistry than the surface water samples) and one Goose Creek site. Figure 7.7 shows how the relationship between estimated and calculated CBANC changes with different assumptions about the organic charge density, which reaffirms the earlier conclusions from Section 7.1.2.3.1 regarding the merits of using lake-specific estimates of organic charge density.

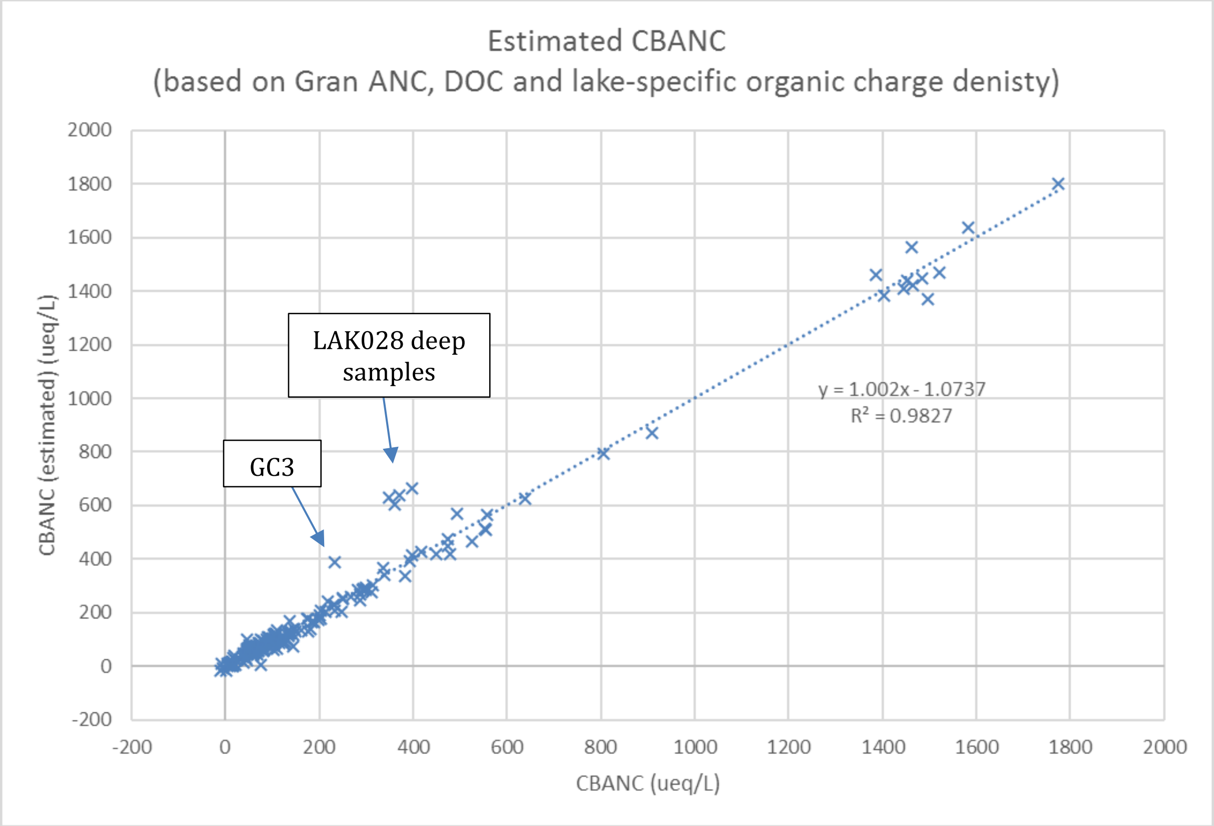

Figure 7.6. Estimated CBANC versus calculated CBANC for all lake and stream site samples from the STAR and EEM programs (n=244). Estimated CBANC is based on the empirical relationship with Gran ANC – i.e., CBANC = Gran ANC + CD * DOC (where CD = organic charge density, using lake-specific values in this implementation).

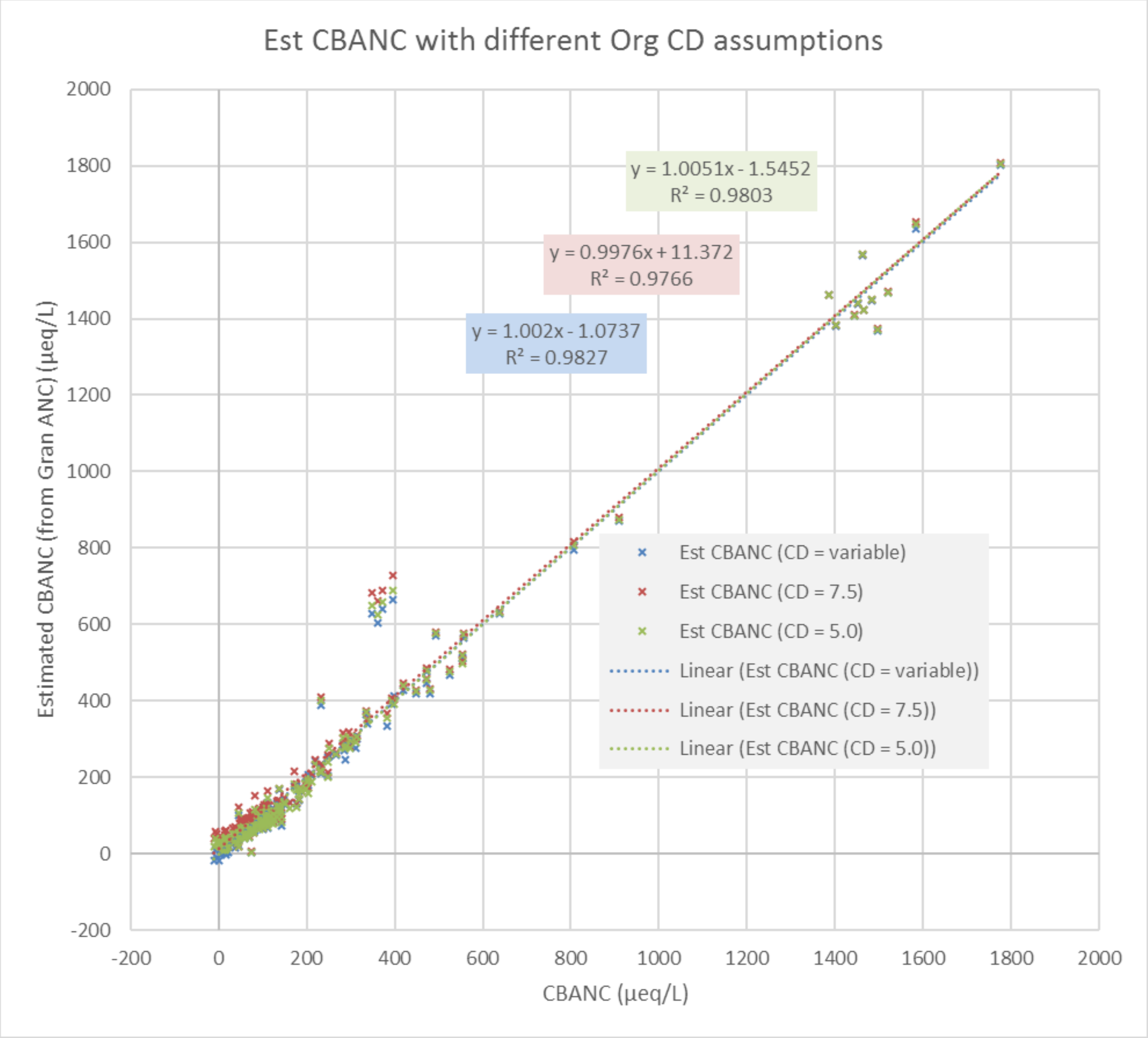

Figure 7.7. Comparison of estimated CBANC (based on varying values for organic charge density (CD)) versus calculated CBANC.

Gran ANC estimated from CBANC

In the Terms of Reference, the empirical relationship between CBANC and Gran ANC was framed as estimating CBANC from adjusted Gran ANC (as presented above). However, ultimately the more pragmatic need is to understand if we can use CBANC instead of Gran ANC, because Gran ANC is difficult to measure and only relatively few laboratories have the ability to do so. Thus we should also look at how closely we can estimate Gran ANC from CBANC. Figure 7.8 shows the relationship between estimated and measured Gran ANC, where *Gran ANC = CBANC – CD * DOC.* The structure of this equation is analogous to the calculation of BCS and ANC_{OAA} (as detailed later), which similarly start with CBANC and apply a reduction to account for the influence of strong organic acid anions. Figure 7.8 shows that when applied across the full set of all samples, both CBANC and estimated Gran ANC have very strong relationships with measured Gran ANC that do not appear markedly different. However, the figure also suggests that these relationships could be strongly influenced by the largest values, which are an order of magnitude larger than the bulk of the samples.

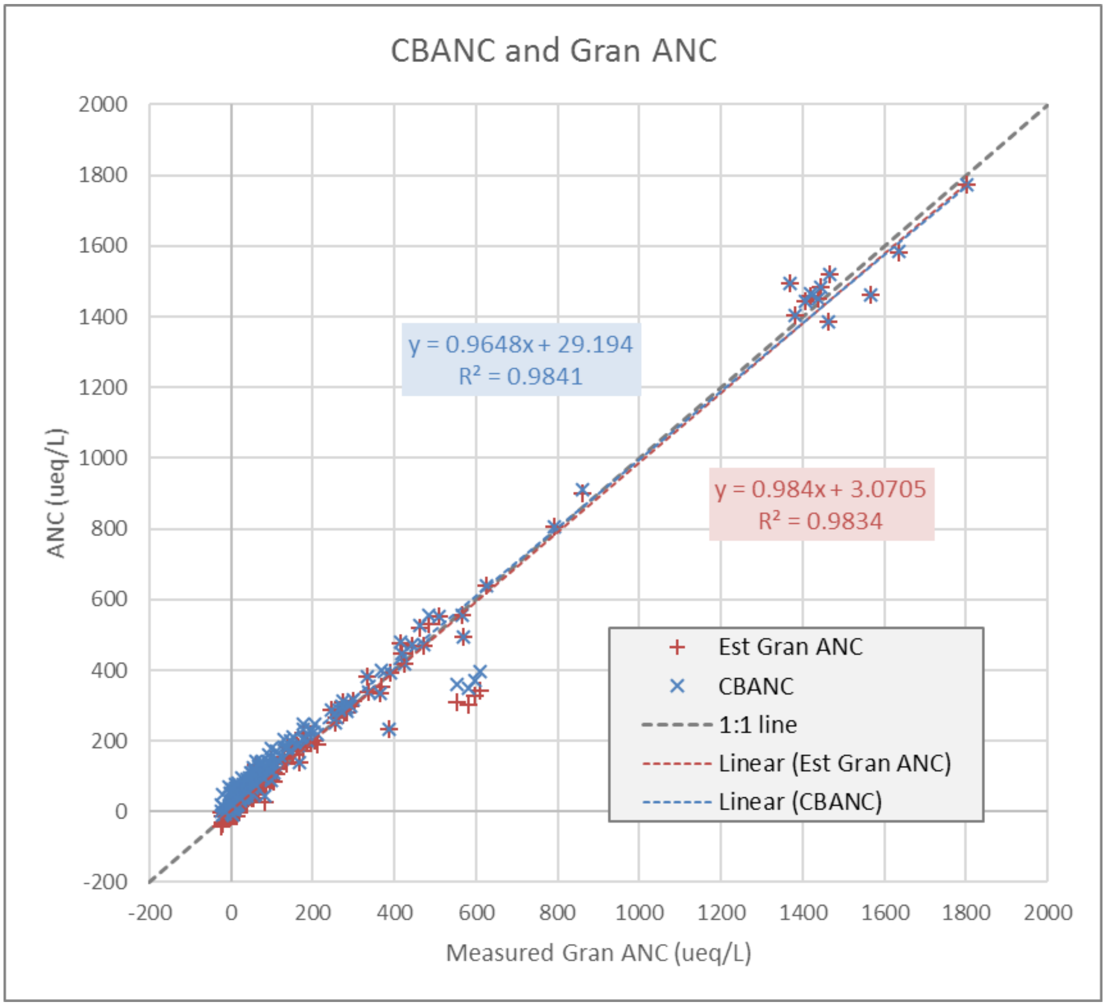

Figure 7.8. CBANC and estimated Gran ANC (based on CBANC) versus measured Gran ANC for all samples. Estimated Gran ANC = CBANC – CD * DOC, where CD is the lake-specific estimate of organic charge density.

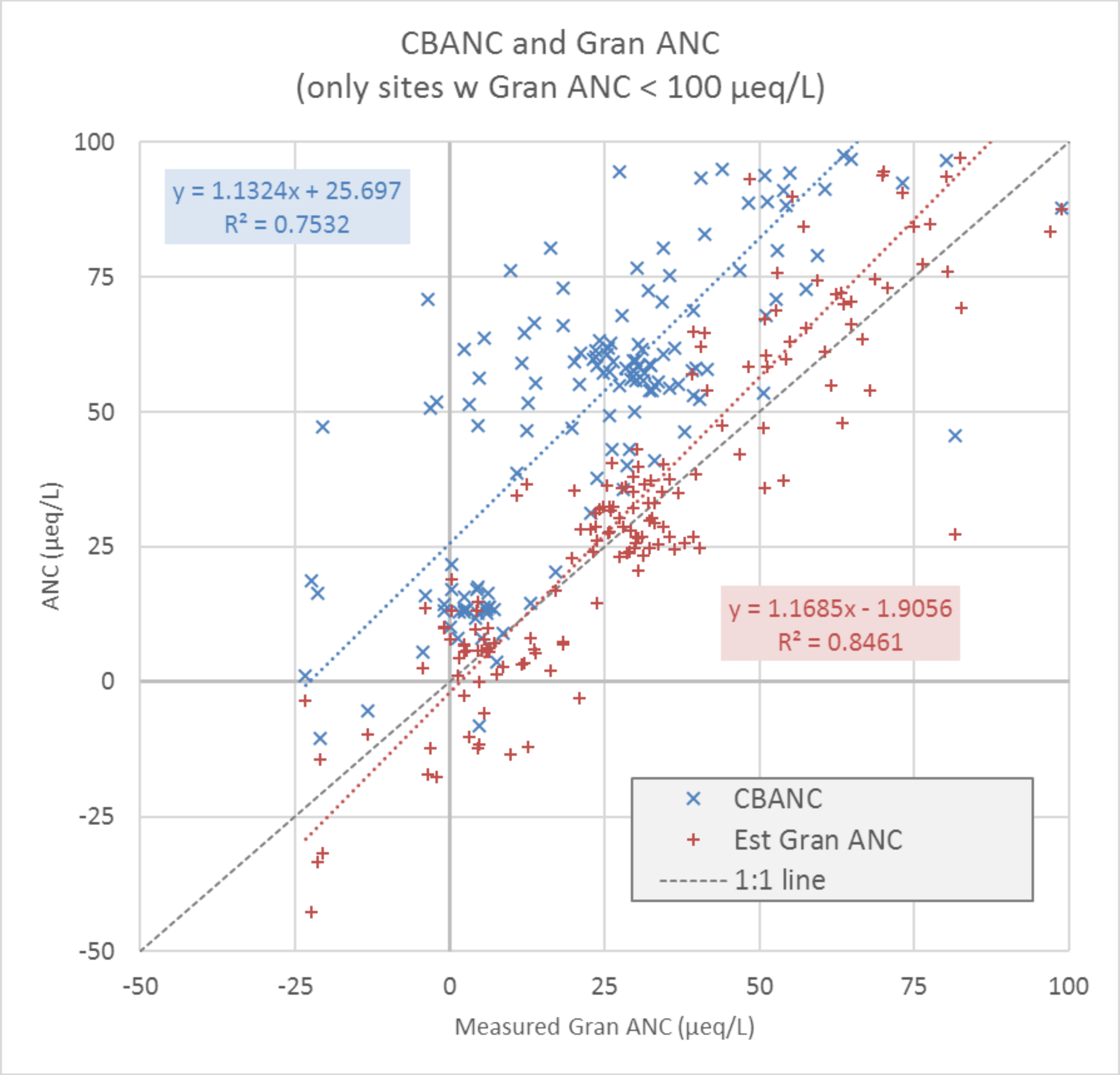

Figure 7.9. CBANC and estimated Gran ANC (based on CBANC) versus measured Gran ANC for all samples with Gran ANC < 100 µeq/L. Estimated Gran ANC = CBANC – CD * DOC, where CD is the lake-specific estimate of organic charge density.

Figure 7.9 shows the same data and relationships but constrained to only those samples with Gran ANC values less than 100 µeq/L) since it is the sites with low to moderate ANC that are of the greatest interest. The results show that when only considering samples with Gran ANC < 100 µeq/L, there are notable differences both from the relationship defined across the full data set and between the metrics. Comparing Figure 7.8 and Figure 7.9 shows that when focusing on sites of lower ANC, the strength of the relationship between estimated and measured Gran ANC is not as strong (but still strong), further from the 1:1 line, and that there is a clear improvement in adjusting CBANC based on organic anions (i.e., estimated Gran ANC) that is not readily apparent when looking at all samples across the full range of ANC values. For the next few years, it would be prudent to use Gran ANC, ANC_{OAA} and BCS (discussed below) as metrics of ANC, and compare their patterns, as implied by Recommendation 11 in the main report.

Alternative Estimates of ANC that Account for Organic Anions

BCS is equal to CBANC minus strongly acidic organic anions (called $RCOO_s^-$), which Lawrence et al. (2007, 2013) estimate from a linear regression of anion deficits vs. DOC for samples with a pH between pH 4 and 4.5 (33 stream samples in their 2007 paper, 200 lake samples in their 2013 paper). $RCOO^-_s$ is set equal to the anion deficit from this linear regression, for all water samples (i.e., both those with pH ≤ 4.5, and those with pH > 4.5), since the strong acid fraction of DOC is not likely to change with pH. The advantage of BCS as a measure of lake condition is that inorganic aluminum (which is associated with acidification and is toxic to fish and other organisms) consistently increases as BCS declines below zero (i.e., BCS < 0 is a concern).

In the EEM data set we do not have any samples with a pH < 4.5, so we proposed three alternative potential approaches in the Terms of Reference:

A. directly apply the regression lines from Lawrence et al. 2013 (derived from lakes in Adirondacks NY);
B. derive similar linear regressions using EEM and other regional data for lakes within a pH range from 4.5 to 5.1; or
C. assume a triprotic model for organic acids as per Lydersen et al. 2004, Hruska et al. 2001, or Driscoll et al. 1994 (i.e., ANC_{OAA}).

Method A has the advantage of relying on data in a pH range where it can be assumed that the anion deficit is entirely due to strong organic acids (weaker organic anions will be protonated), but has the weakness that those data and the resulting relationship defined by Lawrence et al. (2013) are for lakes in the Adirondacks and the acid-base properties of DOC and organic anions in the EEM lakes could be different. Thus in order to apply Method A, we must assume that the properties of the organic acid anion component of the water chemistry of the EEM lakes is on average comparable to the lakes in the Adirondacks and, similar to Lawrence et al. (2013), we must also assume that the acid-base properties of DOC are relatively similar across the lakes in the study area.

BCS is calculated as:

$BCS = (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) – (SO_4^{2-} + NO_3^{-} + Cl^{-} + RCOO_S^{-})$, or

$BCS = CBANC – RCOO_S^-$

Where $RCOO_S^-$ represents the strongly acidic organic anions, as defined above.

Method B theoretically has the advantage of using local data but ultimately we do not have sufficient data required to derive the relationships similar to Lawrence et al. (2007, 2013). First, we do not have any lake samples with pH values <4.5, although we could potentially use data from a higher pH than recommended (e.g., 4.5-5.1). Second, we have an extremely limited sample size – we have 14 samples with pH values in the range from 4.5 to 5.1 but 11 of them are from the same lake. By comparison Lawrence et al. (2007) used samples from 195 streams and Lawrence et al. (2013) had 200 samples from 13 lakes with pH values less than 4.5. Third, we cannot apply the method of Lawrence et al. (2013) to our lakes because we do not have data for either inorganic monomeric aluminum or organic monomeric aluminum, both of which are required to estimate the anion deficit.

Therefore, in order to estimate BCS for the EEM lakes, we have estimated $RCOO_S^-$ based directly on the results of Lawrence et al. (2013) – i.e., based on the relationship between anion deficits and DOC for 200 samples with pH < 4.5 from 13 Adirondack lakes.

For Method C, we have applied the Lydersen et al. (2004) method to estimate ANC_{OAA}, which uses a triprotic model of organic acids to characterize the organic anions. Lydersen et al. (2004) state that "using a model with a 3-protic acid, the first pKa-value is low, and hence 1/3 of the CD of organics will always be negatively charged in most natural waters". The formulation of their recommended method for estimating ANC_{OAA} is described as follows (Lydersen et al. 2004):

> *We have used these data from Hruska et al. (2001a) and Kohler et al. (1999), both data sets from Swedish humic lakes. We have used a charge density of 10.2 µeq/mg C in our calculation, according to Hruska et al. (2001a). This is also close to the value presented by Kohler et al. (1999) (i.e. 8.6 ± 1.6 µeq/mg C). The amount of permanent organic anions, to be incorporated in the* ANC_{OAA}*, is, therefore 1/3 of the charge density. Hence, we suggest the following expression:*
> $ANC_{OAA} = ANC - (10.2/3) * TOC$
> *[where ANC = CBANC, and TOC = total organic carbon]*

Lydersen et al. (2004) cite earlier research from a study of Norwegian lakes that found that particulate carbon is usually <10% of total carbon and therefore TOC ≈ DOC (Lydersen 1998 in Lydersen et al. 2004). Therefore, we have used the following equation:

$ANC_{OAA} = ANC - (CD/3) * DOC$,

However, we use the lake-specific values for organic charge density rather than an average value from the literature (i.e., 10.2 µeq/mg C as applied in Lydersen et al. (2004).

Comparison of BCS and ANC_{oaa} values for the full STAR / EEM data set

For all the samples across sites and years, we calculated BCS using the method Lawrence et al. (2013; "method A" above) and ANC_{OAA} using the method of Lydersen et al. (2004; "method C" above). Figure 7.10 shows the relationship between these two metrics across all samples. These two metrics demonstrate a very strong relationship and the only sites with notable deviation from the regression are the deep-water samples from LAK028 and a couple individual stream sites.

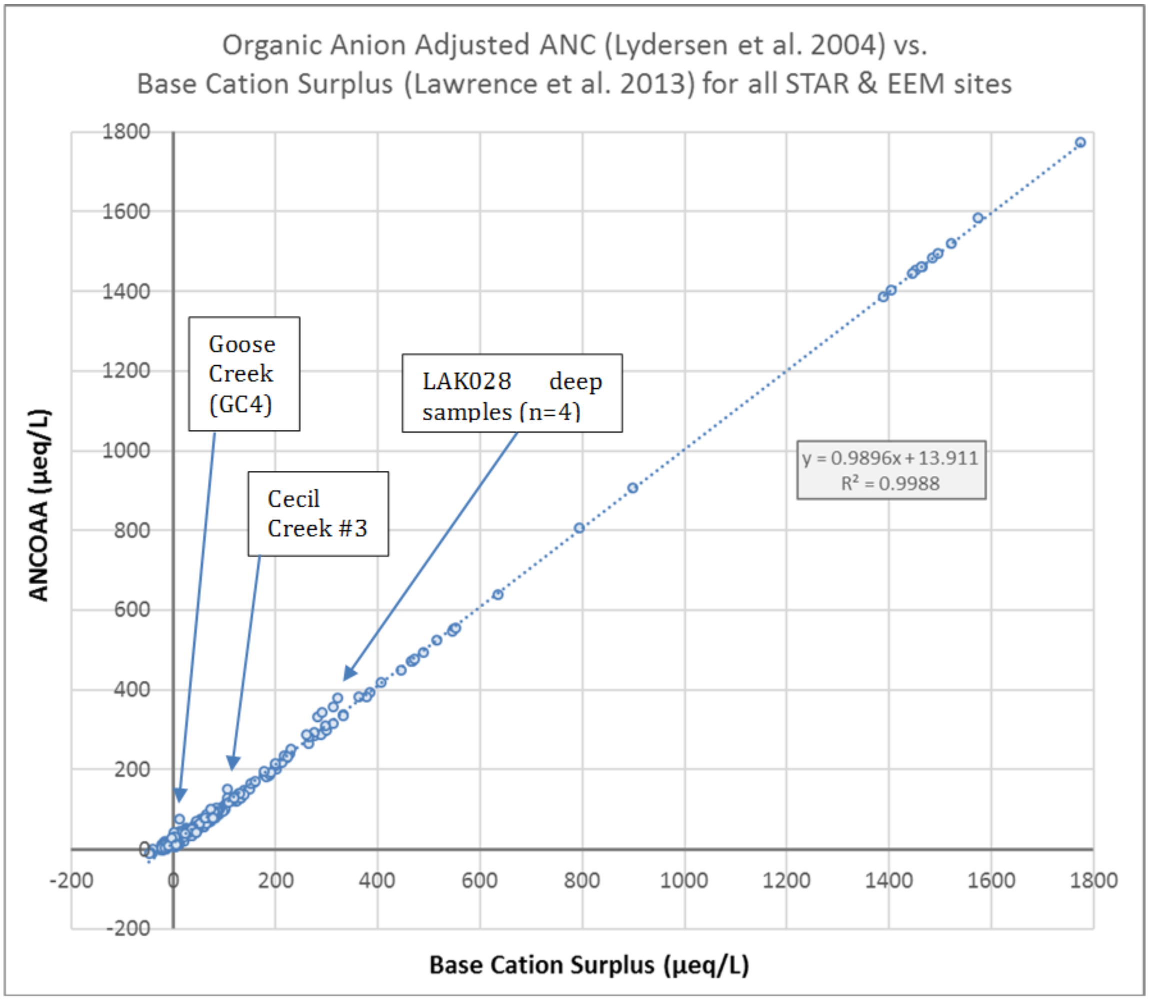

Figure 7.10. ANC$_{oaa}$ versus base cation surplus for the entire data set of all samples within the study area, 2012-2018. Sites with a visible deviation from the trendline at this scale are identified.

Figure 7.11 also shows ANC$_{OAA}$ and BCS values but only for samples with values <100 µeq/L (for either metric) and highlights any lakes with one or more samples below levels identified in the literature as potentially relevant thresholds for the protection of aquatic ecosystems (i.e., ANC$_{OAA}$ < 20 µeq/L or BCS < 0 µeq/L; see Aquatic Appendix B for a literature review of potential ANC thresholds). The lakes highlighted on Figure 7.11 include:

- **LAK042:** only two samples are below the BCS threshold but not below the ANC$_{OAA}$ threshold. However, these two samples are not temporally consistent as one is from 2012 and the other from 2018.
- **LAK044:** all samples are below the ANC$_{OAA}$ only.
- **LAK028:** Most of the samples are below both thresholds; however, the only two of the samples that are above the thresholds occurred in 2014 and 2015, which were the years in which smelter emissions were lowest. LAK028 has four samples that have the lowest BCS values observed and ANC$_{OAA}$ < 0 µeq/L, which is below the threshold for acute toxicity. However, these four samples represent only some but not all of the samples

from the post-KMP period of increased emissions (i.e., 2 of 4 samples from 2016, 1 of 4 samples from 2017, and 0 of 6 samples from 2018), plus one pre-KMP sample (2013).

- **LAK047, LAK054, LAK056:** These lakes were only sampled during the STAR. LAK047 is slightly below the ANC_{OAA} threshold but well above the BCS threshold and the other two are well below both. However, these three lakes were all identified in the STAR as being naturally acidic lakes that were not expected to change in pH (and thus not included in the EEM).

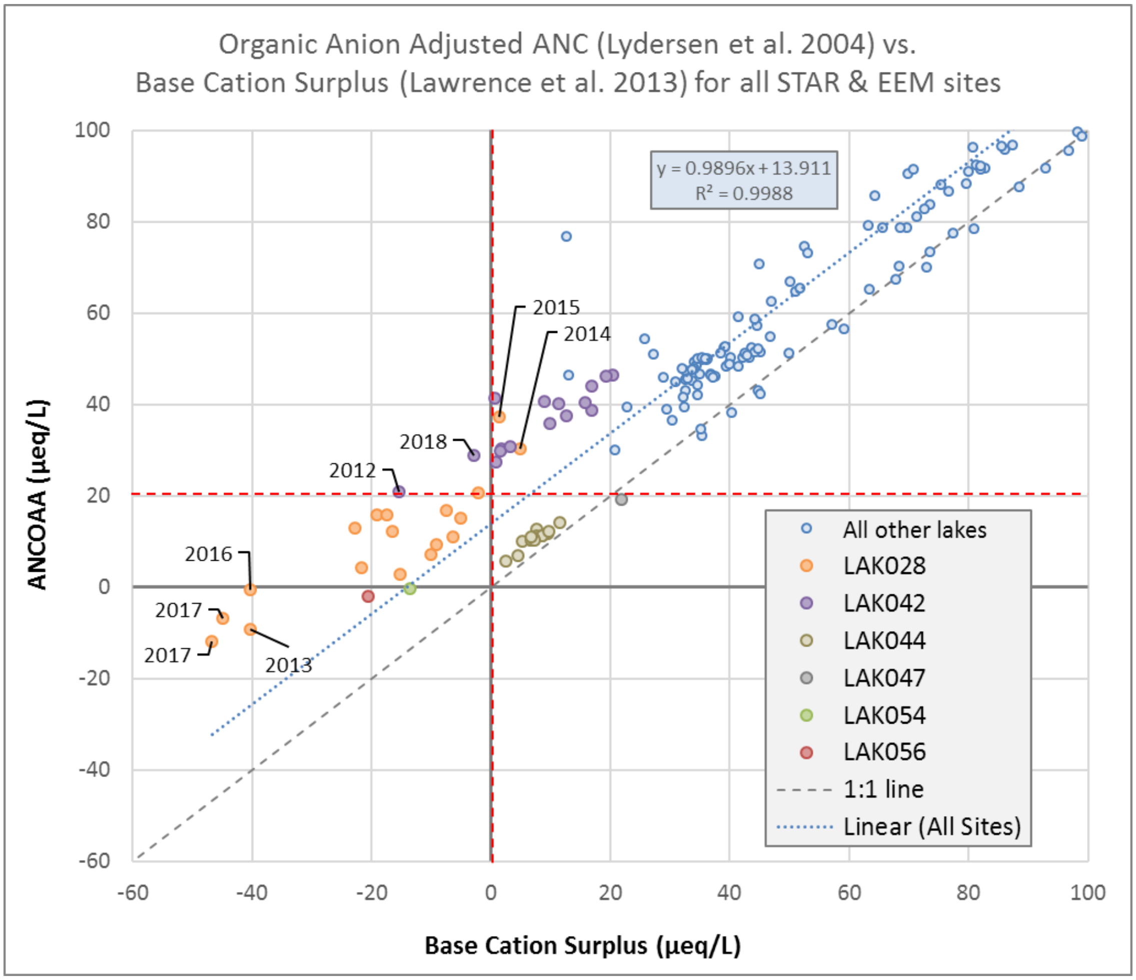

Figure 7.11. Organic anion adjusted ANC (ANC_{oaa}) and base cation surplus (BCS) values for all individual samples within the full data set with values <100 µeq/L. For any lakes with at least *some* samples with BCS<0 or ANC_{oaa}<20 µeq/L (dashed red lines), the full set of samples from the lake are identified. For LAK028 and LAK042, samples that appear to be anomalous within that lake are identified by year of sampling.

Figure 7.10 and Figure 7.11 are based on individual samples across all sites. For the EEM sensitive lakes and less sensitive lakes, we calculated the average BCS by year (Table 7.7). The results show that LAK028 is the only EEM lake with consistent values of BCS < 0 µeq/L. BCS values less than zero are indicative of water chemistry conditions potentially harmful to biota (Lawrence et al. 2007, 2013, Baldigo et al. 2019), especially via chronic toxic levels of aluminum (Baldigo et al. 2009; see Appendix B). For LAK028, BCS has been below this threshold for 5 of the 7 years of the EEM program, including periods both before and after the increase in emissions. The two years that BCS was greater than zero were the two years with lowest emissions. However, the only year with BCS < -35 μeq/L (identified in the literature review as a threshold for "acute Al toxicity"; see Appendix B) was 2013, which was also a year of low emissions. LAK042 had a negative value for BCS in 2012 (under pre-KMP emissions) but values remained positive from 2013 through 2018.

Table 7.7. Average base cation surplus (BCS) values by lake and year for the EEM lakes. Red cells indicate BCS<0μeq/L.

LAKE	2012	2013	2014	2015	2016	2017	2018
LAK006	34.6	30.3	37.2	38.7	38.9	42.1	43.6
LAK012	94.5	79.5	71.8	71.8	81.0	78.2	70.5
LAK022	44.5	33.9	51.0	47.0	50.1	44.2	51.8
LAK023	29.3	20.7	34.3	34.4	33.6	36.0	36.3
LAK028	-5.1	-40.2	4.8	1.5	-24.9	-32.5	-8.4
LAK042	-15.4	10.0	1.8	16.9	18.0	8.4	0.7
LAK044	2.5	4.5	6.8	11.6	7.0	9.1	7.0

LAK007	1452.5	1388.3	1484.5	1463.9	1495.2	1404.3	1445.7
LAK016	112.0	90.9	115.6	128.8	118.3	107.8	118.4
LAK024	311.7		468.1	465.0	514.8	472.3	548.8
LAK034	158.1	199.4	217.2	198.5	177.6	150.7	161.0

Inorganic Aluminum

Aluminum is of interest because of the concern for toxic effects on aquatic ecosystems.

As described in the STAR (see Section 9.4.1.2.4; based on the 2012 sampling data):

> *Levels of both dissolved aluminum and dissolved organic carbon (DOC) increased as pH decreased, consistent with other studies (Baker et al. 1991). This pattern is expected due to greater solubility of aluminum at low pH, and increased acidity (lower pH) with higher contributions of organic anions. It is likely that most of the aluminum in lower pH sites was complexed with organic anions, which renders it less toxic to fish (Baker et al. 1990). Lakes in the study area have higher levels of both aluminum and DOC than streams for a given pH.*

Inorganic monomeric aluminum (Al_{im}) is strongly linked with toxicity to fish and other aquatic organisms and is therefore frequently interpreted to represent the bioavailable fraction of aqueous aluminum. Differing levels of particulate matter and aluminum complexation in natural surface waters mean that total aluminum and dissolved aluminum do not always correlate well with aquatic toxicity. As part of the EEM Program, Al_{im} was measured in 2013 for 12 of the 14 water chemistry samples taken[6]. Al_{im} is more difficult to measure and therefore

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[6] Sites sampled in 2013 included 7 sensitive EEM lakes, 3 less sensitive EEM lakes (LAK024 was only added in 2014), lake MOE6, and 3 sites in Cecil Creek. The three control lakes, which were added to the EEM Program in 2015, have data from 2013 but these data were collected under other water chemistry monitoring programs. LAK044 does not have a measurement for Al_{im}; however, its total Al is among the very lowest (i.e., ~0.01 mg/L). MOE3 does not have a measurement for Al_{im} because its total Al was below the detection limit.

was only a one-time addition only to the water chemistry analyses. It was also added again in 2019. However, total aluminum and dissolved aluminum have been measured ever year. This subsection includes some basic exploration of the one year of data on Al_{im}. The following graphs show the relationship between Al_{im} and total Al (Figure 7.12), pH (Figure 7.13), and (Figure 7.14).

Figure 7.12 shows that there is a positive, potentially non-linear relationship between Al_{im} and total Al and that that only those sites with total Al values greater than 0.1 mg/L have appreciable levels of Al_{im}. LAK028 has the highest levels of Aluminum, then Cecil3, then LAK042. However, although Cecil3 has greater total Al than LAK042, its level of Al_{im} is approximately half.

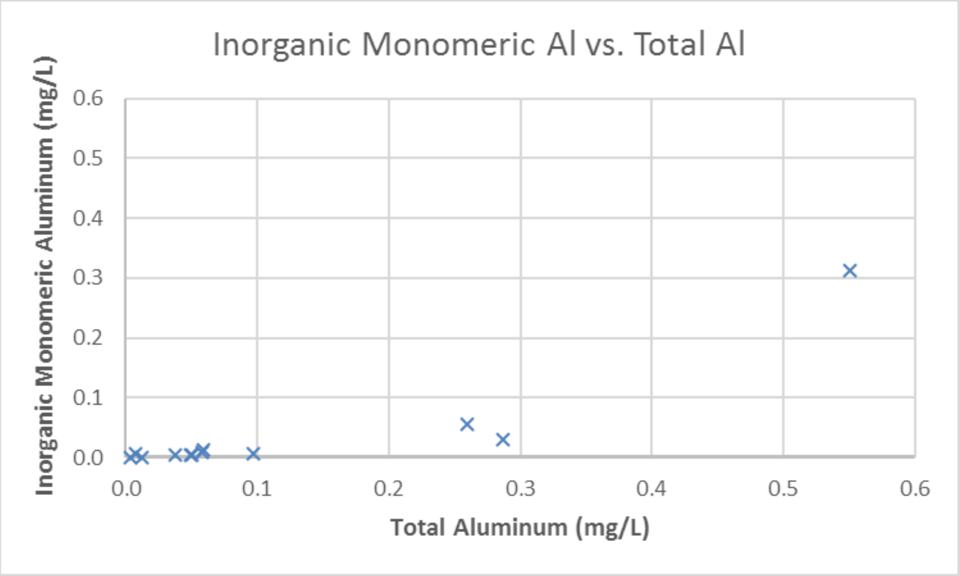

Figure 7.12. Inorganic monomeric aluminum versus total aluminum for the 12 water chemistry samples with Al_{im} values taken in 2013. These data include the non-EEM sites lake MOE3 and three stream sites in Cecil Creek.

As expected, Al_{im} increases with decreasing pH and is most apparent in lakes with pH<5.5 (Figure 7.13). The lakes with low pH and higher Al_{im} are also among the sites with the highest DOC levels. Also as expected, Al_{im} is highest for sites where BCS < 0 μeq/L and relatively negligible for sites where BCS is appreciably greater than zero (Figure 7.14). As discussed previously, one of the strengths of the BCS metric is that Al_{im} consistently increases as BCS declines below zero. LAK028 was the only lake with BCS < 0 μeq/L in 2013 and correspondingly has the highest Al_{im} value. LAK042, which has the second highest Al_{im} value is the only other lake with BCS < 20 μeq/L.

Based on these simple exploratory analyses of Al_{im} from 2013, LAK028 would be the only lake for which concerns regarding potential aluminum toxicity are strongly indicated but LAK042 might also be flagged for further observation based on these results. It appears from this preliminary analysis that BCS provides sufficient information on the potential for toxic conditions without the additional measurement of Al_{im} , but we can check on this preliminary conclusion with the data on Al_{im} collected in the fall of 2019.

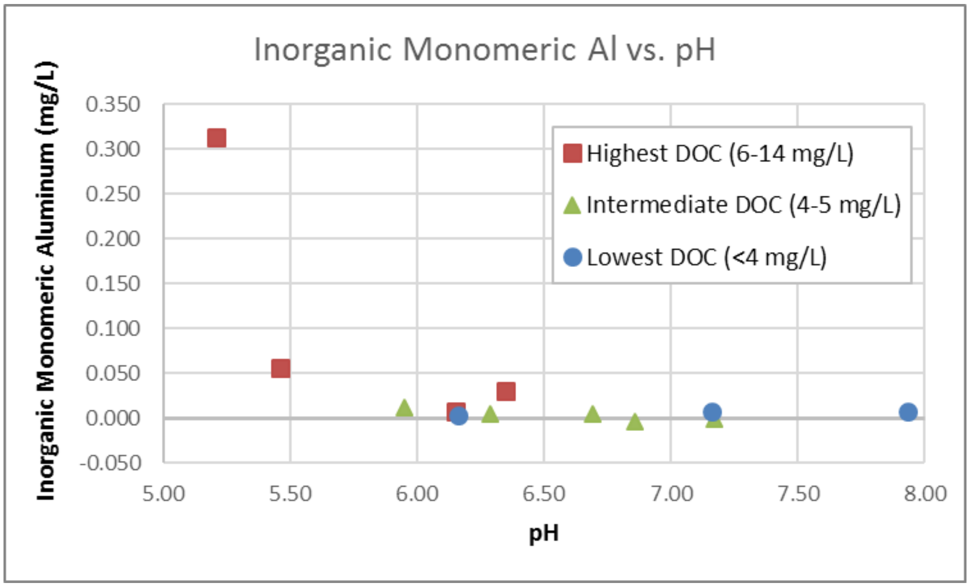

Figure 7.13. Inorganic monomeric aluminum versus pH for the 12 water chemistry samples with Al_{im} values taken in 2013. The sites are stratified into three classes of DOC based on natural breaks in the data. These data include the non-EEM sites lake MOE3 and three stream sites in Cecil Creek.

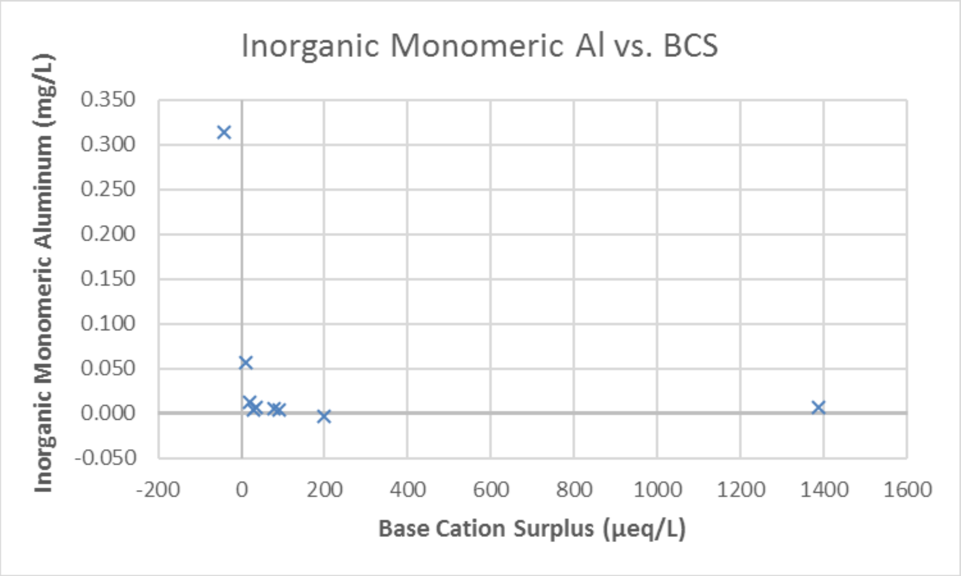

Figure 7.14. Inorganic monomeric aluminum versus Base Cation Surplus (BCS) for EEM lakes. These data include the 9 EEM lakes with Al_{im} values taken in 2013. BCS values were not calculated for the non-EEM sites.

7.1.2.3.3 Temporal patterns in water chemistry

Comparison of August vs. October water chemistry

We used the laboratory pH and Gran ANC measurements for samples taken during the calibration visits to LAK006, LAK012 and LAK023 in 2017 and 2018, and LAK028 in 2018 only, to test for differences between August and October water chemistry values. We tested for differences between the two months using a t-test.

Temporal Patterns in the Empirical Observations

We examined changes in the empirical data for major water chemistry metrics between the pre-KMP baseline (2012) and the post-KMP period (average of 2016-2018). These basic observational results are presented in the same format as used for EEM Annual Report each year. The time series graphs that are included in the Annual Reports have been updated to include the 2018 data (see Appendix C).

Statistical Analyses of Temporal Patterns

The detailed methods and results of the extensive statistical analyses of the water chemistry data are documented in Appendix F.

7.1.2.3.4 *Assessing observed changes in water chemistry relative to STAR predictions*

The STAR included predictive analyses of future changes in water chemistry under increased deposition at maximum emissions levels (i.e., the permit level of 42 tpd SO_2). In the STAR (as again in the Comprehensive Review, see Appendix G), we used the Steady-State Water Chemistry model (SSWC) to estimate critical loads and exceedances and the modified ESSA-DFO model to estimate future changes in ANC and pH and the eventual steady state water chemistry. As part of the current review, we compared the changes observed thus far to those predicted changes, after accounting for the fact that average post-KMP emissions have been much lower than the maximum permit level (i.e., 29.3 tpd SO_2). We therefore adjusted the STAR predictions based on current emissions to facilitate an equivalent comparison[7].

Post-KMP emissions have been much lower than the maximum allowable emissions under the permit as modelled in the STAR. Over 2016 to 2018, emissions have been an average of 29.3 tpd SO_2 compared to the permit level of 42 tpd. We explored two different methods for adjusting the STAR predictions based on this difference in emissions levels. In the STAR, the simulated changes in emissions were based on the increase from 20.6 tpd (average of 2006, 2008 and 2009, as per the CALPUFF "pre-KMP" scenario) to 42.0 tpd.

In Method A, we assumed that post-KMP deposition was 70% of what was modelled in the STAR and was proportional to emissions (i.e., (29.4[8] tpd for 2016-2018) / (42.0 tpd in STAR) = 0.70). We kept pre-KMP deposition at the values used in the STAR (average of 2006, 2008 and 2009 simulated deposition).

In Method B, we assumed that the observed change in sulphate deposition since 2012 was proportional to the change in emissions over the period from 2012 (16.1 tpd) to the average of

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[7] Note: The underlying analyses described here were conducted based on "actual" emissions of 29.4 tpd rather than the correct 29.3 tpd. The difference was due to minor differences in 2016 data resulting from use of preliminary data that was later revised. However, the analyses have been retained as is because this difference would have a negligible impact on the results and therefore not affect the conclusions of these comparisons.

[8] See previous footnote

2016-2018 (29.4[9] tpd), for a net change in emissions of 13.3 tpd over 2012-2018. Comparing this 13.3 tpd change in emissions with what we simulated in the STAR (i.e., 21.4 tpd = 42.0 tpd permitted emissions – 20.6 average emissions in 2006, 2008 and 2009), we obtain a ratio of 0.621, and applied that ratio to the change in deposition we had simulated in the STAR.

We then compared the results of both sets of adjusted predictions to the changes actually observed through the monitoring program.

7.1.2.4 Weight-of-Evidence approach for assessing causality

The evidentiary framework developed for the EEM Plan applies a weight-of-evidence approach for identifying patterns in the empirical lake chemistry data that are consistent with smelter-driven acidification. It is described in full in the EEM Plan[10] The definition of the KPI for aquatic ecosystems comprises two components: 1) an observed change in pH of greater than a specified threshold *and* 2) that the observed change to be causally linked to the smelter. Lake chemistry is naturally dynamic and there are additional mechanisms or natural variability that could lead to observed changes in pH that are not driven by increases in smelter emissions. The purpose of the evidentiary framework is to consider the patterns of change in the empirical observations of multiple lake chemistry metrics (i.e., different lines of evidence) in an integrated manner to determine whether the observed changes are or are not consistent with smelter-driven acidification.

We have applied the evidentiary framework as outlined in the EEM Plan, as well as a simplified version that maintains the most critical components of the full implementation. Because of its central importance as an integrated framework for assess evidence of the causal linkage between empirical observations of lake chemistry and KMP, the application of the evidentiary framework is presented in full in the main report (Section 7.3.4.5).

7.1.2.5 Episodic acidification studies

As discussed in EEM Annual Reports, there were two sources of information intended[11] to provide the inputs for exploring this topic. The first source is the continuous pH monitoring data from multiple lakes. Continuous pH monitoring has occurred since 2015 in three lakes: LAK006 (End Lake), LAK012 (Little End Lake) and LAK023 (West Lake). From 2015 to 2018, a Manta2 model 2.5 multiprobe was used to take pH measurements every half hour and was recalibrated every two weeks against known buffer solutions (Limnotek 2019).

The second source is the independent, parallel research project being conducted by Dr. Paul Weidman to determine (among other research objectives) the extent of episodic acidification within the Kitimat watershed – "*Impacts of Industrial Sulfur and Nitrogen Deposition and Climate Change on Salmon Stream Habitat in the Kitimat Watershed*"

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[9] See previous footnote

[10] In particular refer to Table 17, pg. 43 in EEM Plan

[11] As described in the "learnings" in Section 7.1.3.2.7, it has not been possible to use either of these sources for exploration of potential patterns of episodic acidification in the Comprehensive Review.

7.1.2.6 Critical loads, exceedances and predicted changes in pH

The modeling, analyses and sensitivity analyses associated with critical loads, exceedances and predicted change in pH are documented in Appendix G.

7.1.2.7 Kitimat River water quality

Rio Tinto conducts water quality monitoring at their intake on the Kitimat River.

7.1.2.8 Other data and/or analyses previously reported

In addition to the core water chemistry sampling program for the 14 EEM lakes (as described above), the we also conducted other data collections and analyses over the course of 2013-2018 in support of the Aquatic Ecosystems component of the Program. These other initiatives and analyses have been documented elsewhere (especially in the Annual Reports) during the program and are only briefly summarized here.

Fish sampling
In order to measure the presence/absence of fish in the acid-sensitive lakes, Limnotek conducted fish sampling in 2013 (LAK006, LAK012, LAK023, and LAK044), 2015 (LAK007, LAK016 and LAK034), and 2017 (LAK028). The EEM Plan established that fish populations in these lakes could potentially be resampled if it were determined that a lake's pH had declined by more than 0.3 pH units.

Fish sampling was done using standard gill netting techniques. Gill nets were left overnight, and each captured fish was identified with lake number, date, unique set code, mesh size where the capture occurred, unique fish code, species code, and scale number (Perrin et al. 2013).

DNA analysis of tissue was done in 2013 to confirm the presence of resident Coho salmon (i.e., non-anadromous, not going to sea) in West Lake (LAK023). More information on sampling methods and results can be found in the detailed sampling results report (Perrin et al. 2013).

Bathymetric surveys
In 2015, bathymetric surveys were done by Limnotek (2016) on the three lakes with continuous monitoring (LAK006, LAK012, LAK023) in order to be able to generate a precise estimate of lake volume and therefore a more accurate estimate of the water residence time for each lake. In 2017, a similar survey was done for LAK028.

Water residence time
Water residence time is relevant to understanding one of the possible factors contributing to variability (especially intra-annual variability) within individual lakes; i.e., lakes with shorter water residence times would be expected to demonstrate higher variability in water chemistry.

An estimate of water residence time of all the lakes in the EEM Program was estimated based on a coarse approximation of lake volume.

Water residence time (or retention time) is calculated as:

$$Residence\ time\ (years) = \frac{Lake\ volume\ (m^3)}{Annual\ outflow\ (\frac{m^3}{year})}$$

where annual outflow is estimated as: watershed area (m^2) * mean annual runoff (m/yr), with mean annual runoff for the period from 1960 to 1990, as described in the STAR.

Regional amphibians and potential risks of aquatic acidification

Acidification effects on amphibian species were not explicitly addressed in the 2013 sulphur dioxide technical assessment report - STAR (ESSA et al. 2013_a and 2013_b) - and were n0t including for monitoring in the aquatic ecosystems' component of the EEM Program.

However, in response to the interest expressed by the Kitimat Public Advisory Committee in learning about the risks KMP might pose to amphibians, ESSA conducted a literature review (ESSA 2017) and compiled regional data on amphibians in order to understand potential acidification risks.

The literature review focused on answering three questions addressing the current uncertainty about acidification risks for amphibians in the Kitimat area:

- Which effects/impact pathways are most relevant (e.g., life stage, habitat, mechanism)?
- What is the level of risk of acidification under KMP for local amphibian species? Are any local amphibian species at significant risk under KMP?
- What are the most critical knowledge gaps/uncertainties? What are the implications?

To answer these questions, we compiled relevant peer-reviewed research, government research and grey literature to understand the occurrence of amphibian species in the Kitimat Valley, their sensitivity to acidification, and the spatial distribution of potential habitats.

We defined a study area (Figure 7.15) encompassing the original STAR study area but with broader boundaries which account for the habitat patterns of amphibian species common to the region (i.e., (e.g., Western Toads, *Anaxyrus boreas*, are known to cover distances greater than 10 km) and also to include control areas which are not affected by KMP deposition.

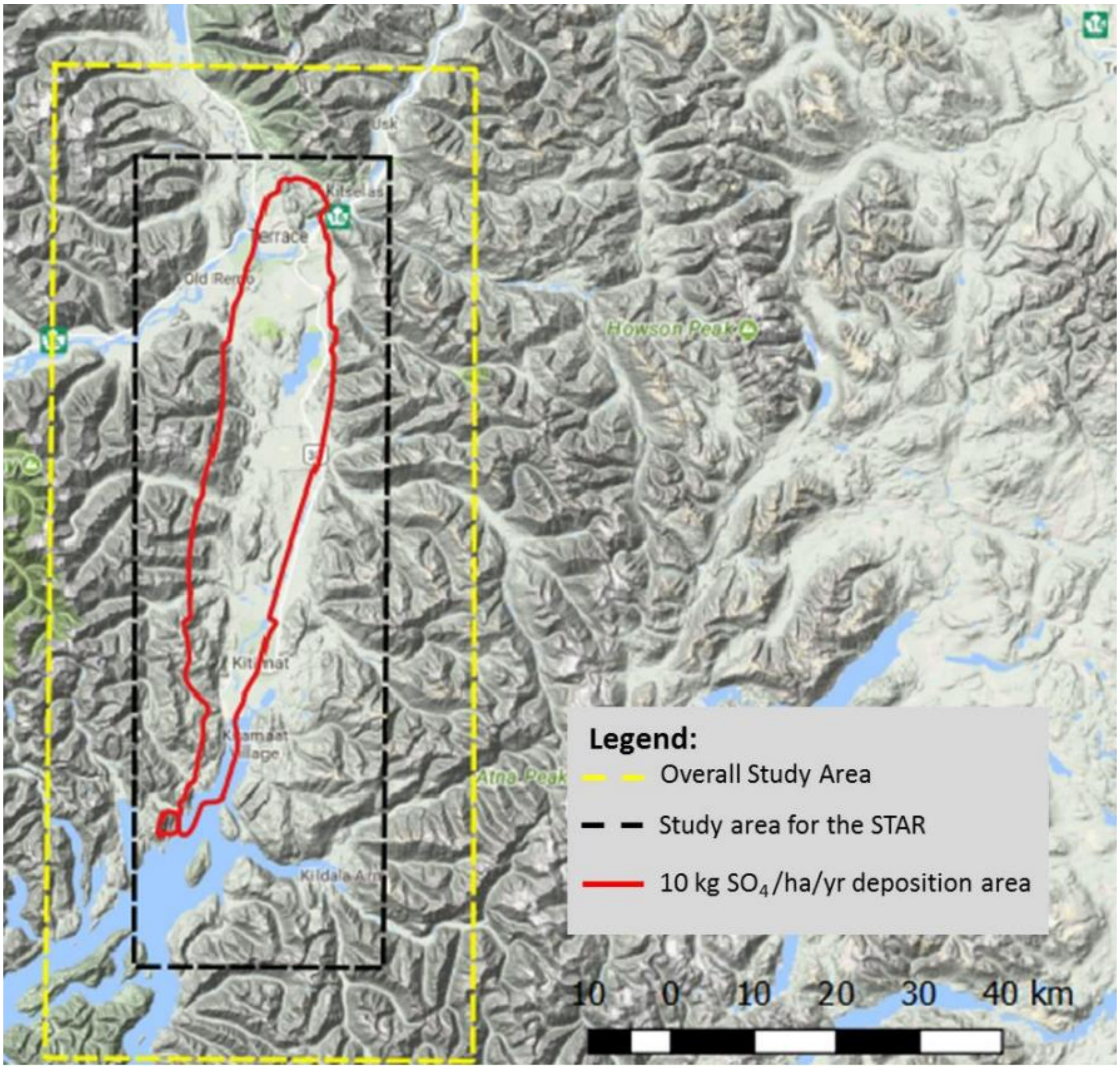

Figure 7.15. Overall study area for the amphibian literature review (hatched yellow line), and the two subareas: the study area for the STAR (hatched black line), and the 10 kg SO_4/ha/yr deposition isopleth as projected from KMP (solid red line). Source: ESSA 2017.

To study amphibian species occurrence and their distribution, we mapped amphibian observations assembled from government spatial databases, specifically the Species Inventory Database, the Conservation Data Centre (CDC), and Frogwatch BC. Additionally, and in order to identify potential amphibian habitat types within the overall study area, we mapped the occurrence of potential aquatic habitats within the overall study area, including lakes, wetlands, streams and rivers.

Lake level monitoring

Surface water level monitoring was done by installing a staff gauge near the lake's border. The staff gauge was attached to an 8-foot-long piece of angle iron and a one-inch wood post that were hammered into the lake bottom.

During the bi-monthly visits to each lake to calibrate the Mantas and collect water samples in June to November, the depth on the staff gauge was recorded on the field notes and the logger installations were checked for signs of tampering or vandalism.

In 2016, lake levels were monitored in End Lake, Little End Lake, and West Lake to provide an accurate, local measure of the timing of storm events, so as to better explain observed variation in pH (monitored continuously) and other water quality parameters of interest monitored during October (particularly sulphate, nitrate, DOC, ANC, and base cations).

Flow data

For some Annual Reports, we looked at regional stream flow data to supplement interpretation of observed patterns in lake chemistry (especially with respect to examining late-season decreases in pH and/or apparent dilution effects in the intensively monitored lakes). For this purpose we downloaded available stream flow data from Environment Canada's Water Survey of Canada (https://wateroffice.ec.gc.ca/) for the available stations within the study area. The three stations in the study area are: Kitimat River below Hirsch Creek (08FF001), Hirsch Creek near the mouth (08FF002), and Little Wedeene River below Bowbyes Creek (08FF003).

Depth profile, water column chemistry, and deep water sampling for LAK028

In 2017, a profile of the water chemistry was conducted at a deep location near the centre of lake LAK028 to gain a more comprehensive understanding of the lake's chemistry. Samples were taken every 1 m for temperature, pH, conductivity, total dissolved solids concentration, turbidity, dissolved oxygen concentration.

Water column sampling from LAK028 strongly suggests the presence of meromixis (i.e., surface and bottom waters do not mix), which was also implied by the small surface area relative to lake depth. The results of the water column sampling (see Bennett and Perrin 2018) show that thermal and chemical conditions change significantly at depths >9 m.

The surface mixed layer (<9 m) had water temperature typical of north coast lakes in the fall, high dissolved oxygen that could support fish, conductivity and inorganic nitrogen concentrations typical of nutrient deficient lakes, and a surface pH (~ 5) at the low end of tolerances for aquatic organisms. The bottom water layer was anoxic and would not support fish, with higher pH, higher conductivity, a warming thermocline, an odour of H2S, and other evidence of sulphur-reducing green and/or purple bacteria.

In 2018, deep water samples were taken from near the bottom of LAK028, in addition to the standard surface water sampling program, to examine chemical differences between surface and bottom mixed layers that were first described in 2017.

Non-EEM sites

In addition to the lakes sampled annually within the EEM Program, multiple other "non-EEM" (i.e., outside the core program) lake and stream sites were identified for exploratory water chemistry sampling in particular years over the course of the EEM Program. These sites were either requested by BC Ministry of Environment (MOE, now ENV) or selected by Rio Tinto to determine their sensitivity to acidic deposition. Table 7.2 provides a summary of the "non-EEM" sites sampled during the course of the EEM Program to date, including: Cecil Creek, lakes MOE3 and MOE6, and multiple sites within the Goose Creek drainage. Most of these sites were only sampled once but some of the Goose Creek sites have been sampled twice.

7.1.2.9 Assessment of acceptable or unacceptable impacts to aquatic receptor

The assessment of the impacts to the aquatic receptor as “acceptable” or “unacceptable”[12] is directly linked to the KPI. If the KPI threshold associated with facility-based mitigation in the EEM is exceeded, this is identified as an “unacceptable” impact for the aquatic receptor. Impacts to the aquatic receptor that do not exceed the KPI threshold associated with facility-mitigation in the EEM are identified as “acceptable”.

7.1.3 **What did we learn, and did we make any adjustments to the EEM Program?**

7.1.3.1 Empirical Data from Lake Chemistry Monitoring Program

7.1.3.1.1 Quality of Water Chemistry Data

Sampling and laboratory quality control and quality assurance

The results of the sampling and laboratory quality control and quality assurance methods are presented in the annual technical reports from Limnotek. The laboratory data show high precision and accuracy, with no apparent problems. Measurements of pH from ALS have common shown a statistically significantly different from pH measurements in the field, and from pH measurements in the laboratory at Trent University, but these differences were still within the specified limits of ± 0.3 pH units for the equipment used by ALS.

Charge Balance Check

The charge balance has been examined for each year of sampling, based on the data from each water chemistry sample. Table 7.8 shows four diagnostics metrics of the charge balance (i.e., the average value and the average of the absolute values, for both percent difference and difference in µeq/L). The charge balance in 2013, although acceptable, was worse than the other years in the series. In all cases, the average charge balance represents an excess of anions relative to cations. In order to be consistent with the results presented throughout the EEM, including those reported in the EEM 2018 Annual Report, the charge balances reported here are calculated using an assumed organic charge density of 7.5 µeq/mg C, rather than the revised and/or lake-specific estimates of organic charge density that we discussed in Section 7.1.2.3.1.

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[12] Section 4.2.6 of the P2-00001 permit, dated March 15, 2016, states “If any unacceptable impacts are determined through the use of the impact threshold criteria pertaining to emission reduction, then the maximum SO_2 daily discharge limit shall revert back to 27 Mg/d, unless the Director amends the discharge limit.”

Table 7.8. Measures of the charge balance check for all lake samples from 2012 to 2018. Negative (red) values for the two "Average Difference" values indicate less total charge from cations than from anions. See text for explanation of the assumed values for the organic charge density.

Year	Number of samples	Average Percent Difference (%)	Average of the Absolute Value of the Percent Differences (%)	Average Difference (µeq/L)	Average of the Absolute Value of the Differences (µeq/L)
2012	41	0.8	3.9	-6.3	14.4
2013	14	-10.3	10.3	-33.1	33.1
2014	24	-5.3	5.4	-12.2	12.9
2015	22	-3.2	3.3	-12.8	13.2
2016	32	-3.1	3.8	-4.8	12.0
2017	32	-0.3	3.5	-3.7	8.7
2018	34	-3.1	4.1	-7.7	9.6

Measured versus Estimated Conductivity

Measured and estimated conductivity were compared for each year of sampling, based on the data from each water chemistry sample. Table 7.9 shows two diagnostic metrics of the conductivity check for the water chemistry samples for all the lakes from 2012 to 2018. The average difference was highest in 2013. Overall the data demonstrate an acceptable relationship between measured and estimated conductivity. Although most years show an average negative results (i.e., estimated conductivity is lower than measured conductivity), the number of individual samples with negative values cross the entire data series reported shows only slightly more lake samples with negative values than positive values – 53% versus 47%, respectively.

Table 7.9. Measures of the conductivity check for all lake samples from 2012 to 2018. Positive values of "Average %Diff" indicate that the estimated conductivity was higher than the measured conductivity. Negative values (shown in red) indicate that the estimated conductivity was lower than the measured conductivity. The annual range of measured conductivity values is provided for context.

Year	Number of Samples	Average Difference (%)	Average of the Absolute Value of the Differences (%)	Measured Conductivity Values (µS/cm)*		
				Minimum sample value	Mean sample value	Maximum sample value
2012	41	6.6	7.4	2.5	35.4	184.3
2013	14	10.8	13.3	3.3	23.3	147.0
2014	24	-2.9	5.6	3.6	21.0	154.2
2015	22	-2.3	5.9	3.5	18.1	151.2
2016	32	-5.1	10.5	3.8	17.9	153.7
2017	32	-6.0	9.9	3.5	17.7	149.0
2018	34	-1.0	6.8	3.5	17.0	147.4
2018	34	-1.0	6.8	3.5	17.0	147.4

* The minimum, mean and maximum values are based on the total data set of all lake samples from a particular year, therefore the mean value is weighted toward lakes sampled more frequently and should be interpreted accordingly.

pH measurements

Lab measurements of pH were made at two different labs in 2013 to 2018. Limnotek has examined the differences in pH measurements among the two labs and the field measurement each year and concluded that the differences were within the expected ranges (i.e., factory/lab specified measurement error associated with each instrument). The values measured at ALS have generally been higher than those measured by Trent University or those measured in the field. Both labs apply substantial quality control, quality assurance and equipment calibration procedures. However, we know that in lake water with low ionic strength it is very important to allow lots of time for pH measurements to stabilize. This appears to have occurred at Trent University, but possibly not at ALS, where most of the samples they process are from waters with much higher ionic strength (Limnotek 2019). However, throughout the EEM Program, we have used the Trent University measurements for analyses of temporal patterns in pH to be consistent with the data from the STAR – the 2012 samples were only analyzed by Trent University and not ALS.

7.1.3.1.2 *Water Chemistry Sampling Results*

Appendix D reports the results of the annual water chemistry sampling for the EEM lakes and control lakes from the sampling conducted from 2012 to 2018, for major water chemistry metrics (pH, DOC, Gran ANC, base cations, and major anions).

Changes in pH, Gran ANC, SO_4^{2-}, DOC, sum of base cations, and chloride over the period of the EEM Program are shown in terms of absolute change in Table 7.10 and Table 7.11. The time period of comparison is from the baseline year (2012) to the post-KMP period (the average of 2016-2018). The sensitive EEM lakes and less sensitive EEM lakes are presented separately within each of the tables. The values presented use the mean annual values whenever multiple within-season samples were taken for a given lake in a given year.

Figure 7.16 and Figure 7.17 show the changes in the same water chemistry parameters graphically. These figures allow better visualization of the distribution and variability in the observed changes between the 2012 baseline and the post-KMP period.

Appendix C provides a detailed set of figures showing the inter-annual changes in major water chemistry metrics (Gran ANC, base cations, SO_4^{2-}, chloride, pH and DOC) for each of the EEM lakes across the seven years of monitoring data (2012-2018). Similar figures are also included for the three control lakes based on their five years of annual monitoring (2013, 2015-2018).

However, annual changes should be interpreted with substantial caution due to the combination of large natural variation (both within and between years) and limitations on measurement precision. The power analyses conducted and reported in the 2015 EEM Annual Report (see Section 7.1.3.2.2) illustrated that at least five years of post-KMP of observations are required to reliably detect changes in mean pH, Gran ANC and SO_4.

Given these caveats and the rigid schedule for the Comprehensive Review to occur in 2019 (with only three years of post-KMP observations), we have performed an extensive set of rigorous statistical analyses on the empirical data to ensure that any conclusions are as robust and scientifically defensible as possible given the limited number of post-KMP observations thus far (see Aquatic Appendix F).

These results are examined, analyzed and discussed in detail in Section 7.1.3.2.

Table 7.10. Changes in pH, Gran ANC and SO_4^{2-} from baseline conditions (2012) to the post-KMP period (2016-2018). Green cells indicate increases and red cells indicate decreases.

	pH			Gran ANC (μeq/L)			SO_4^{2-} (μeq/L)		
EEM sensitive lakes	2012	Post-KMP	ΔpH	2012	Post-KMP	ΔANC	2012	Post-KMP	ΔSO_4^{2-}
LAK006	5.8	6.0	0.24	25.7	27.7	2.0	11.4	14.0	2.5
LAK012	5.6	6.2	0.52	57.0	58.3	1.3	6.1	12.9	6.8
LAK022	5.9	6.1	0.15	27.8	33.0	5.1	30.2	38.8	8.6
LAK023	5.7	5.9	0.22	19.8	26.4	6.7	19.0	12.3	-6.7
LAK028	5.0	5.0	0.02	-4.0	-3.5	0.5	56.9	128.4	71.5
LAK042	4.7	5.2	0.54	-20.4	5.6	26.1	6.2	5.4	-0.8
LAK044	5.4	5.6	0.15	1.3	5.0	3.7	6.2	4.4	-1.9
Total lakes with increase			**7**			**7**			**4**
Total lakes with decrease			**0**			**0**			**3**

EEM less sensitive lakes	2012	Post-KMP	ΔpH	2012	Post-KMP	ΔANC	2012	Post-KMP	ΔSO_4^{2-}
LAK007	8.0	8.0	0.03	1437.6	1385.9	-51.6	51.4	47.0	-4.4
LAK016	6.3	6.7	0.34	68.7	89.8	21.1	39.0	44.5	5.4
LAK024	7.1	7.5	0.36	299.5	463.2	163.7	24.8	38.9	14.1
LAK034	6.7	6.4	-0.29	99.4	139.6	40.2	24.1	0.1	-24.0
Total lakes with increase			**3**			**3**			**2**
Total lakes with decrease			**1**			**1**			**2**

Control lakes	2013	Post-KMP	ΔpH	2013	Post-KMP	ΔANC	2013	Post-KMP	$\Delta\ SO_4^{2-}$
DCAS14A	6.5	6.6	0.2	50.6	55.9	5.4	33.4	36.4	3.0
NC184	5.7	5.8	0.1	16.2	27.0	10.8	5.7	6.2	0.5
NC194	6.6	6.4	-0.2	28.0	22.4	-5.6	3.6	2.5	-1.1
Total lakes with increase			**2**			**2**			**2**
Total lakes with decrease			**1**			**1**			**1**

Table 7.11. Changes in dissolved organic carbon (DOC), total base cations (∑BC), and chloride (Cl) from baseline conditions (2012) to the post-KMP period (2016-2018). Green cells indicate increases and red cells indicate decreases.

	DOC (mg/L)			∑ BC (μeq/L)			Cl (μeq/L)		
EEM sensitive lakes	2012	Post-KMP	ΔDOC	2012	Post-KMP	ΔBC*	2012	Post-KMP	ΔCl
LAK006	3.6	3.9	0.4	60.6	72.1	11.5	5.8	5.7	-0.1
LAK012	4.6	5.0	0.3	120.6	111.5	-9.1	4.2	6.3	2.1
LAK022	5.3	6.1	0.7	98.1	114.7	16.5	6.9	7.4	0.5
LAK023	4.2	5.6	1.5	65.9	72.8	6.9	4.5	4.7	0.2
LAK028	4.9	6.6	1.7	72.9	136.7	63.8	6.1	8.4	2.4
LAK042	13.2	10.7	-2.5	53.4	64.8	11.4	6.1	6.7	0.5
LAK044	1.7	1.8	0.1	14.2	18.1	3.9	5.6	6.2	0.6
Total Lakes with Increase			**6**			**6**			**6**
Total Lakes with Decrease			**1**			**1**			**1**

EEM less sensitive lakes	2012	Post-KMP	ΔDOC	2012	Post-KMP	ΔBC	2012	Post-KMP	ΔCl
LAK007	0.6	0.4	-0.2	1503.9	1494.3	-9.6	24.6	26.4	1.8
LAK016	3.7	4.6	0.9	166.3	179.5	13.2	6.3	7.7	1.4
LAK024	1.4	2.1	0.7	340.0	558.5	218.4	27.3	68.3	41.0
LAK034	4.5	6.2	1.7	201.7	191.2	-10.5	5.8	4.5	-1.3
Total Lakes with Increase			**3**			**2**			**3**
Total Lakes with Decrease			**1**			**2**			**1**

Control lakes	2013	Post-KMP	ΔDOC	2013	Post-KMP	ΔBC	2013	Post-KMP	ΔCl
DCAS14A	1.4	1.3	-0.0	90.6	109.7	19.1	9.2	7.1	-2.0
NC184	11.6	10.3	-1.3	86.2	94.8	8.6	24.0	17.5	-6.5
NC194	0.7	1.0	0.3	39.2	45.8	6.6	7.6	5.9	-1.7
Total Lakes with Increase			**1**			**3**			**0**
Total Lakes with Decrease			**2**			**0**			**3**

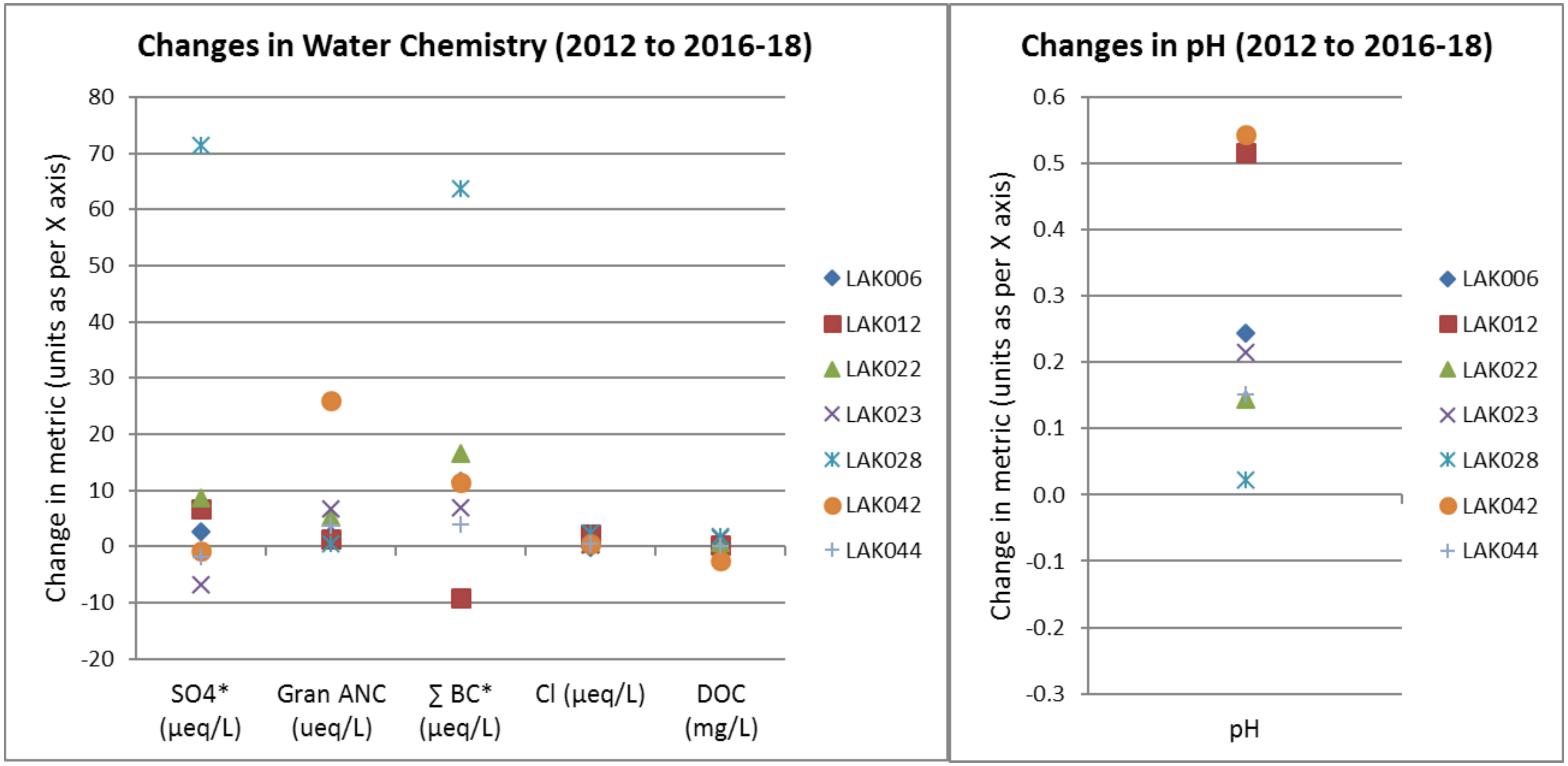

Figure 7.16. Changes in water chemistry metrics (left panel) and pH (right panel) across all of the sensitive EEM lakes, from the baseline (2012) to the average of post-KMP conditions (2016-2018). Values shown are the post-KMP value minus the baseline value.

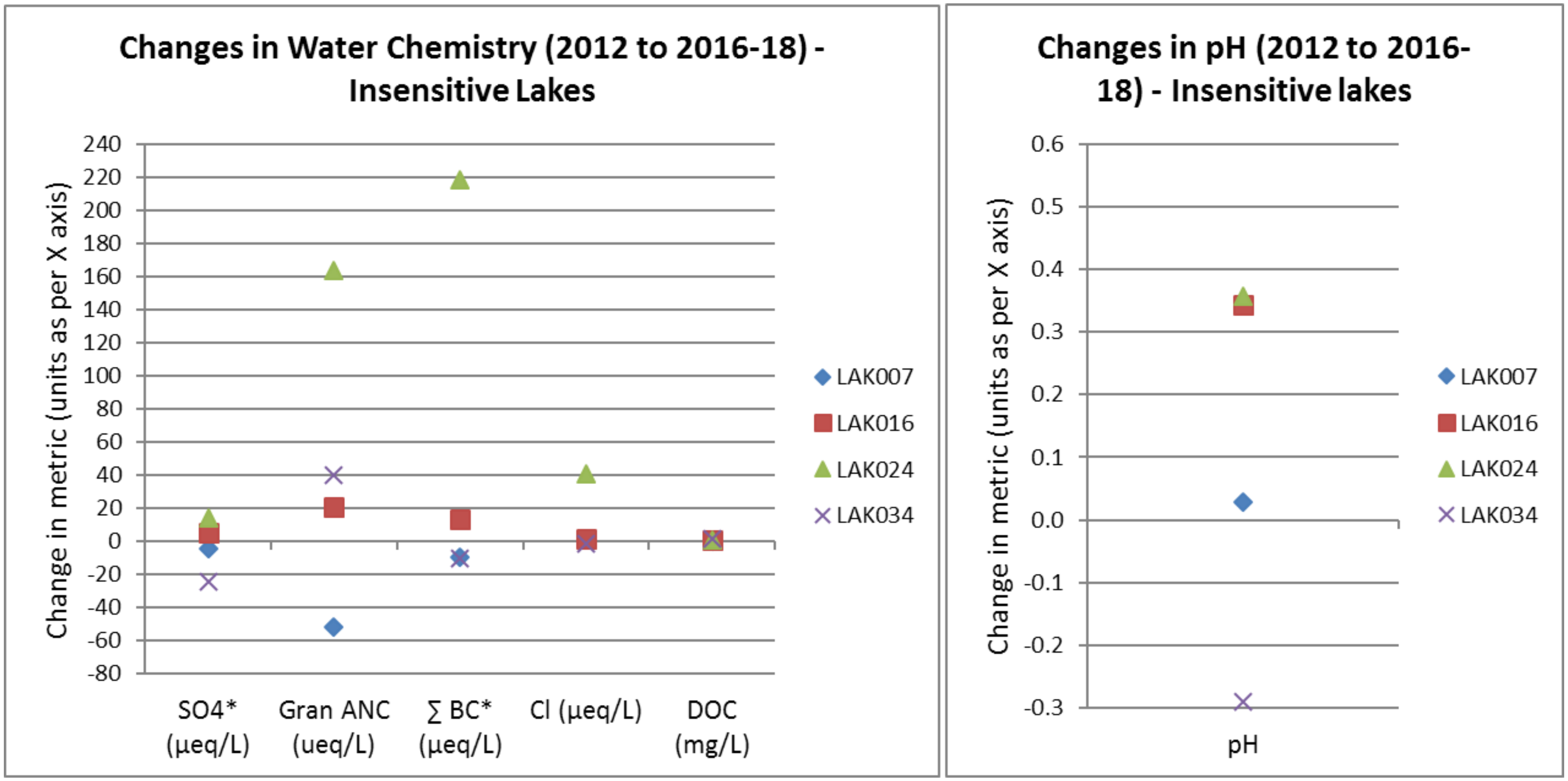

Figure 7.17. Changes in water chemistry metrics (left panel) and pH (right panel) across all of the less sensitive EEM lakes, from the baseline (2012) to the average of post-KMP conditions (2016-2018). Values shown are the post-KMP value minus the baseline value.

7.1.3.2 Knowledge gained

7.1.3.2.1 Measuring pH

Measuring pH accurately, especially in waters with low ionic strength (as is the case for the EEM lakes), is difficult. Skjelkvale et al. (2005) report that *"pH is among the most difficult variables to measure well in the laboratory and variability in measurements makes it more difficult to detect trends".* The details on what we have learned with respect to measuring pH during the course of the EEM program are predominantly reported in the annual technical reports from Limnotek on the water chemistry sampling program. However, some of the major insights are repeated here.

The pH data from the EEM lakes show a high degree of variability. The power analyses study in 2015 showed that the variability in the 2012-2014 pH data from the EEM lakes was much higher than similar pH data collected from a set of lakes studied by Environment Canada in southwestern BC. The data from the continuous pH monitors showed that pH can be highly variable on a seasonal or monthly basis and even over a period of only a few hours. This observed variability has been much greater than anticipated during the design of the EEM Program.

Starting in 2013, water samples were also sent to a commercial laboratory in addition to the laboratory at Trent University for analysis of certain parameters, including pH. The pH values measured by the commercial laboratory have consistently been higher than those measured by the Trent University laboratory, as well as showing greater deviation between values for field duplicates (i.e., two identical samples from the same lake). Work by Limnotek has shown that a critical factor for achieving consistent, reliable measures of pH in these waters of low ionic strength is allowing a long stabilization period (i.e., up to 10 minutes or longer) for each measurement. The lack of time for stabilization is one of the major factors behind Limnotek's recommendations with respect to use of the existing continuous pH monitors (see Section 7.1.3.2.7) and is suspected to be the underlying cause of the consistently higher pH values measured by the commercial laboratory.

Within the program, pH has been measured with multiple field and laboratory instruments. Every year Limnotek conducts analyses of potential instrument effects. Overall, their general conclusions have been that the laboratory analyses conducted at Trent University and the WTW field monitor generate the most reliable measures of pH in the Program, and therefore we have relied on those pH data for our analyses.

7.1.3.2.2 Ability to detect changes in water chemistry

The ability of the EEM Program to detect changes in water chemistry has been significantly informed by the power analyses conducted in 2014-15. The results and implications of this work are summarized in the 2015 EEM Annual Report and reiterated in Appendix F (Section 7.6.3). However, some of the most critical conclusions are repeated here:

1. The power to detect changes in pH, Gran ANC and SO_4^{2-} is highly variable among lakes and metrics
2. On average, the power to detect changes in pH in the EEM lakes is quite low
3. The power for Gran ANC or SO_4^{2-} is higher than for pH

4. Increased sampling frequency increases the power, especially for pH
5. For 4 lakes the power for Gran ANC or SO_4^{2-} is actually relatively high
6. Across most of the lakes, metrics and scenarios, power was low or very low in the first few years after KMP.
7. The EEM Program should not make any strong conclusions about the changes in lake chemistry that have occurred until there have been at least five years of post-KMP data collected.

7.1.3.2.3 Spatial and temporal patterns in water chemistry

NOTE: The following two topics for this subsection (as per the Terms of Reference) are addressed elsewhere (i.e., integrated into other sections as appropriate for improved logical flow and organization). Implementation of the original TOR exposed some areas of overlap and redundancy among sections and we have endeavoured to avoid repeating the same material unnecessarily.

- *"Application of multiple lines of evidence"*
    - *e.g., addressed in Sections 7.2.4, 7.3.2.3, and 7.3.4 in the main report*
- *"Results of Sensitivity Analyses"*
    - *e.g. addressed in Aquatic Appendices F, G and I*

August vs. October Sampling

The seasonal timing of the water chemistry sampling changed from August in 2012 to October from 2013 onwards. In the 2013 EEM Annual Report, the critical loads and exceedances were re-estimated using the October 2013 data to evaluate whether the shift in seasonal timing resulted in substantially different estimates. In more recent annual reports we conducted additional comparisons between August and October sampling values using the data from the continuous pH monitors. However, we have not found any consistent differences between August and October through these previous comparisons. In the present work, we have expanded upon these comparisons using two additional sets of data that allow comparison between August and October lake chemistry values. First, we have field pH data from each of the bi-weekly "calibration visits" to the lakes with continuous pH monitors for 2015-2018 and in 2017 and 2018 samples were also collected for laboratory analysis of pH and Gran ANC. These lakes include LAK006, LAK012, LAK023 and LAK028 (2018 only). Second, in 2018 for LAK028 only, two additional samples prior to the fall index period were collected and sent for full water chemistry analysis. These two samples were collected in early August and early September.

Using the data from the calibration visits, we tested for differences between August and October samples using a t-test. Table 7.12 shows the number of samples available in August and October for each of the metrics, lakes and years for which appropriate data were available. The results are shown below for field pH, lab pH and Gran ANC (Table 7.13, Table 7.14, and Table 7.15, respectively). The results show that we could not detect any differences between the sample values for August and October for these three metrics – i.e., there were no significant results.

Table 7.12. Number of samples available for comparisons of August vs. October sampling.

Metric	Lakes	Year	August samples	October samples
Field pH	LAK006, LAK012, LAK023	2015	2	4
		2016	3	4
		2017	2	5
		2018	3	3
	LAK028	2018	1	4
Lab pH, Gran ANC	LAK006, LAK012, LAK023	2017	2	4
		2018	3	3
	LAK028	2018	1	4

Table 7.13. T-test results for differences between August and October for field pH.

site	year	pval	lwr	upp
Lak006	**2015**	0.322	-0.57	0.935
Lak012	**2015**	0.012	-0.026	0.796
Lak023	**2015**	0.782	-1.066	1.186
Lak006	**2016**	0.036	-0.117	0.656
Lak012	**2016**	0.74	-0.746	0.671
Lak023	**2016**	0.638	-0.226	0.288
Lak006	**2017**	0.106	-1.041	1.641
Lak012	**2017**	0.811	-1.346	1.274
Lak023	**2017**	0.658	-1.26	1.424
Lak006	**2018**	0.348	-0.477	0.75
Lak012	**2018**	0.072	-1.195	0.502
Lak023	**2018**	0.241	-0.291	0.498

Table 7.14. T-test results for differences between August and October for lab pH.

year	lake	pval	lwr	upp
2017	**Lak006**	0.0395	-0.116	0.536
2018	**Lak006**	0.263	-0.209	0.337
2017	**Lak012**	0.572	-2.118	2.408
2018	**Lak012**	0.052	-0.985	0.342
2017	**Lak023**	0.179	-0.648	0.448
2018	**Lak023**	0.389	-0.51	0.338
2018	**Lak028**	0.0381	-0.496	0.121

Table 7.15. T-test results for differences between August and October for Gran ANC.

site	year	pval	lwr	upp
Lak006	**2017**	0.398	-20.076	28.056
Lak012	**2017**	0.245	-27.746	48.111
Lak023	**2017**	0.052	-22.509	6.474
Lak006	**2018**	0.146	-6.474	14.781
Lak012	**2018**	0.088	-56.734	124.854
Lak023	**2018**	0.066	-19.775	7.415

Figure 7.18 shows the ion composition for the six samples for LAK028 in 2018 that were collected and analyzed for full water chemistry. Figure 7.19 compares the ion composition between the August sample and the average of the four samples taken during the fall index period (i.e., Sept 30th through October). Based on qualitative, visual assessment, there does not appear to be any dominant change in ion composition between the August sample and later samples. However, we did not conduct any quantitative analyses on any of the constituent ions.

The results of both of these comparisons (i.e., the t-tests with the data from the calibration visits and the visual assessment of the ion composition for LAK028 in 2018) continue to indicate that we cannot identify a dominant difference between August and October water chemistry sampling results.

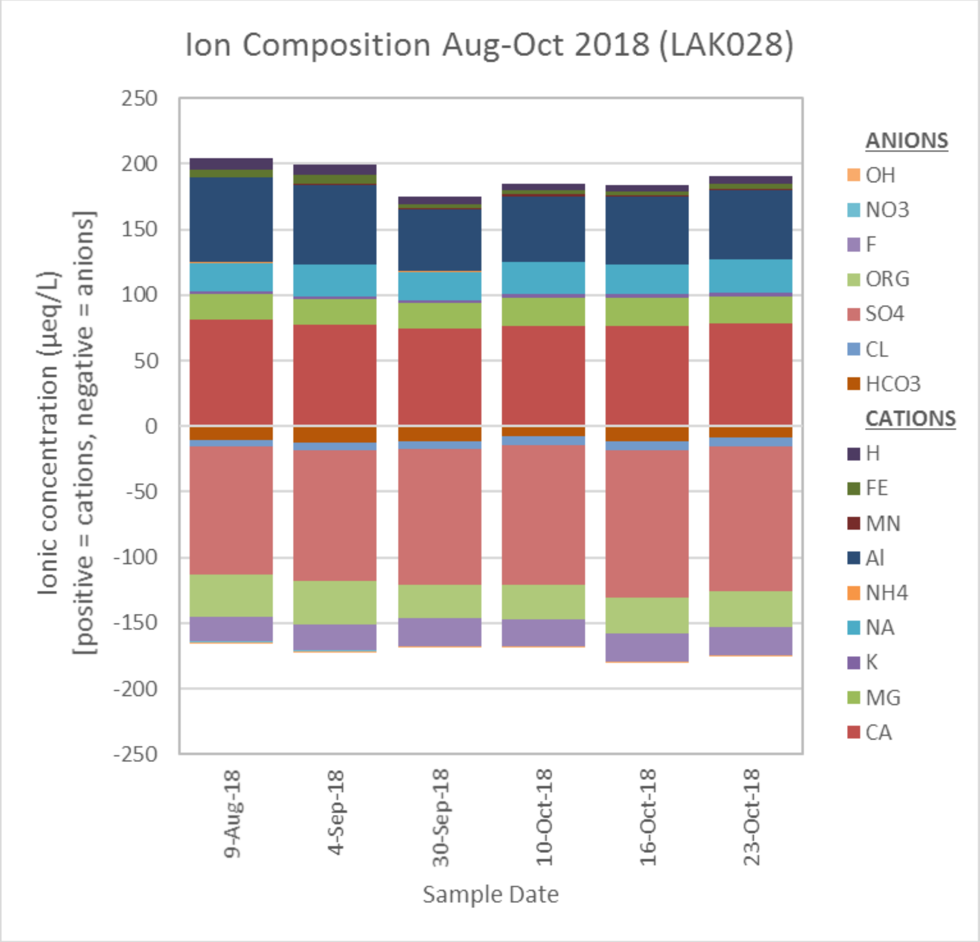

Figure 7.18. Ion composition over six water chemistry samples from LAK028 from August to October 2018. Cation concentrations are displayed as positive values and anion concentrations are displayed as negative values.

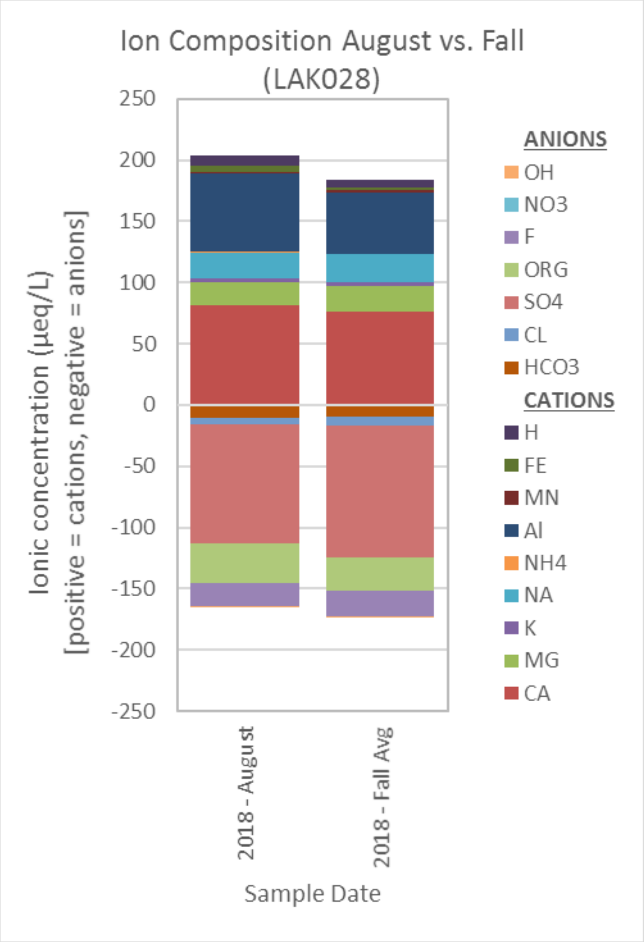

Figure 7.19. Ion composition for LAK028 for the sample taken in August 2018 (n=1) compared to the average of samples taken during the fall index period (i.e., September 30 plus 3 samples in October; n=4). Cation concentrations are displayed as positive values and anion concentrations are displayed as negative values.

Observed Changes in Water Chemistry

NOTE: The following two topics for this subsection (as per the Terms of Reference) are addressed in Section 7.1.3.1.2 and Appendix F:

- *"Observed Changes and Variability"*
- *"Observed Changes Relative to KPI Thresholds"*

The following subsections are addition sub-topics not explicitly included in the Terms of Reference that still fall under this topic.

Relative Changes in Base Cations versus SO_4^{2-}

We compared the changes in base cations versus changes in sulphate for all of the lakes to understand whether changes in base cations tracked changes in sulphate. For lakes with a non-zero F-factors, we would expect to see increases base cations that are correlated (but proportionally smaller, depending on the value of the F-factor) with increases in sulphate. The results are shown below only for LAK028 because it has shown the largest changes in base cations and sulphate, having increased substantially in both. shows that For LAK028, changes in base cations have tracked changes in sulphate as expected (Figure 7.20) and there is a strong relationship between the two metrics (Figure 7.21). The empirical relationship between base cations and sulphates could theoretically provide another estimate of the F-factor, by using the slope of the regression. For LAK028, the changes in base cations and sulphate appear to have been sufficiently large to produce a seemingly valid estimate of the F-factor (i.e., a positive slope, strong fit). However, this was not the case for any of the other lakes. Seven of the lakes did not even have positive slopes, potentially indicating that for lakes with small changes in sulphate, the magnitude of natural variability in lake chemistry greatly exceeds the magnitude of this pattern.

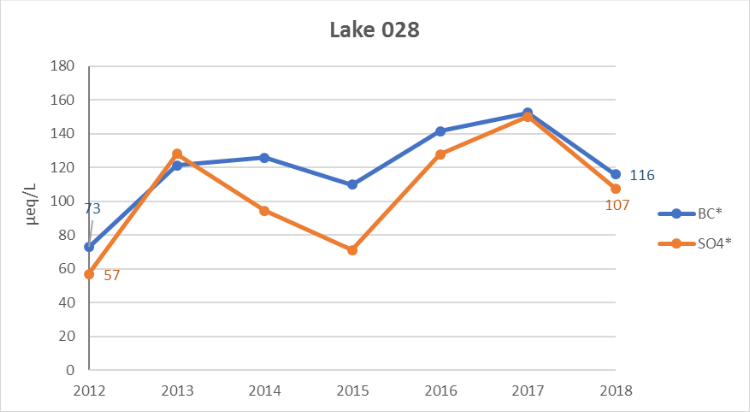

Figure 7.20. Average sulphate and total base cation concentrations over time, 2012-2018.

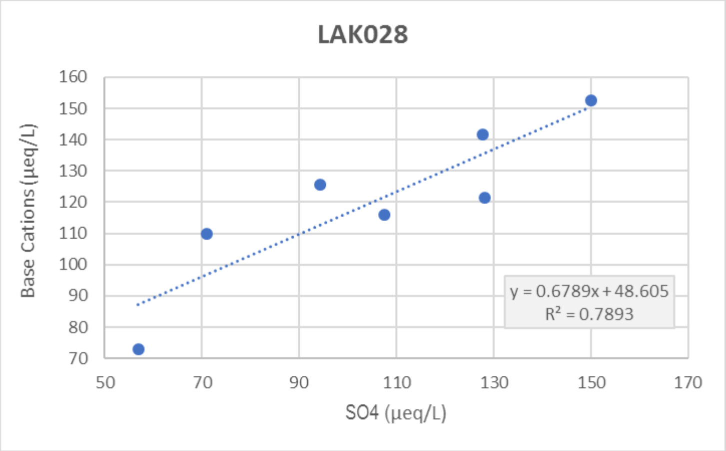

Figure 7.21. Total base cation concentration versus sulphate concentration (average values for each year). The slope of the trend line could be used as an estimate of the F-factor (i.e., how much of an increase in total base cations is, on average, associated with a given increase in sulphate.

Changes in Ion Composition Over Time

We have included figures presenting the change in anion composition on an annual basis in Appendix E and an example of the changes in the full suite of measured anions and cations composition for LAK028 below (Figure 7.22). These figures are included in these Appendices for exploratory purposes only but are not analyzed or interpreted in detail.

Based on visual inspection, Figure 7.22 indicates that there can be significant variation in the total ionic strength of an individual lake between years and that the variability in ionic composition and strength can sometimes be greater within a single year than across multiple years.

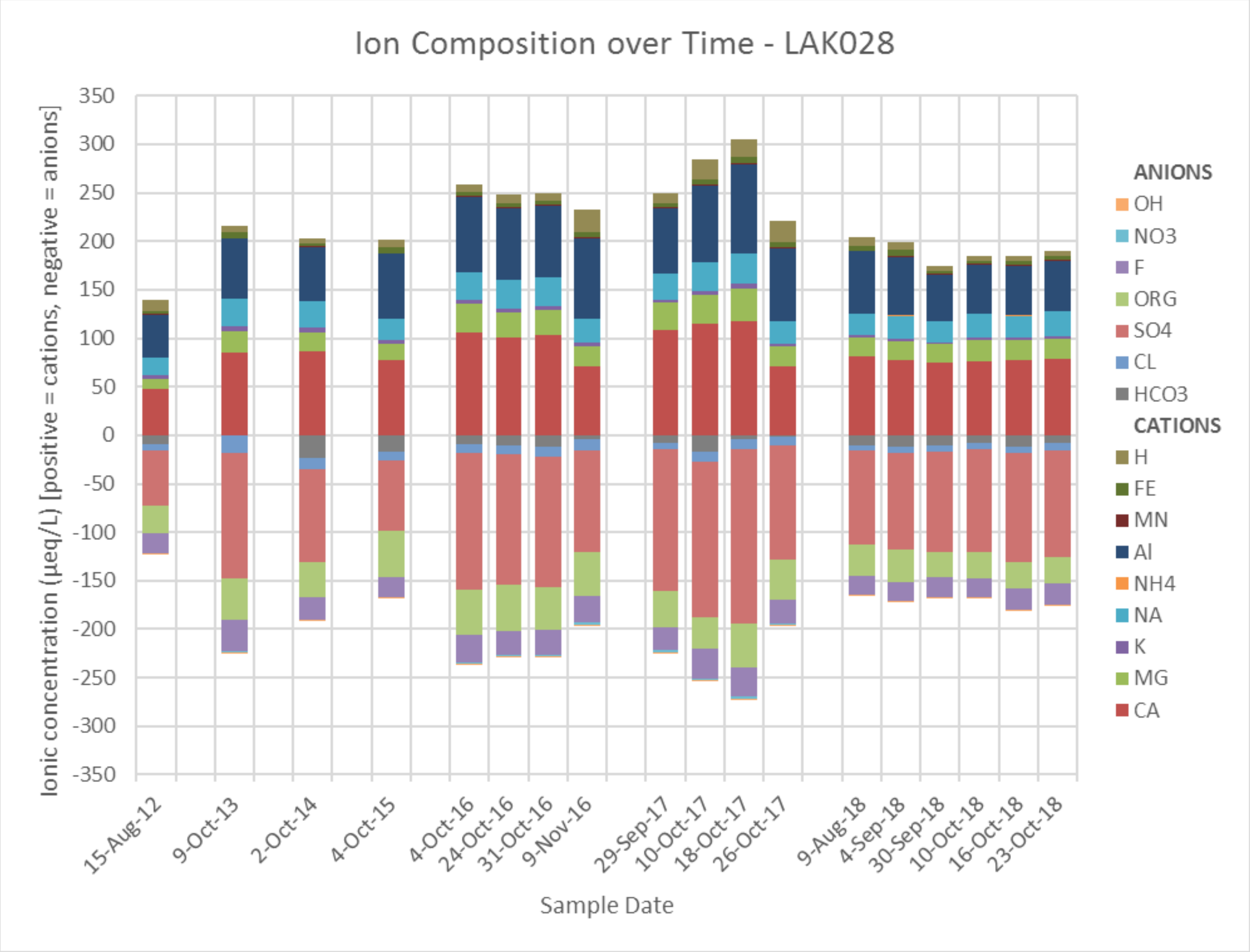

Figure 7.22. Changes in ion composition over time for LAK028. All of the sample events with full water chemistry analyses are shown. Samples from the same year are grouped together.

Magnitude of Changes in Nitrate

In the STAR, nitrate was excluded from analyses of potential acidification as it was assumed to represent a negligible contribution. To validate this assumption, we explored the magnitude of changes in NO_3 relative to changes in SO_4 (Figure 7.23, Figure 7.24), which confirmed that the changes in NO_3 have been negligible.

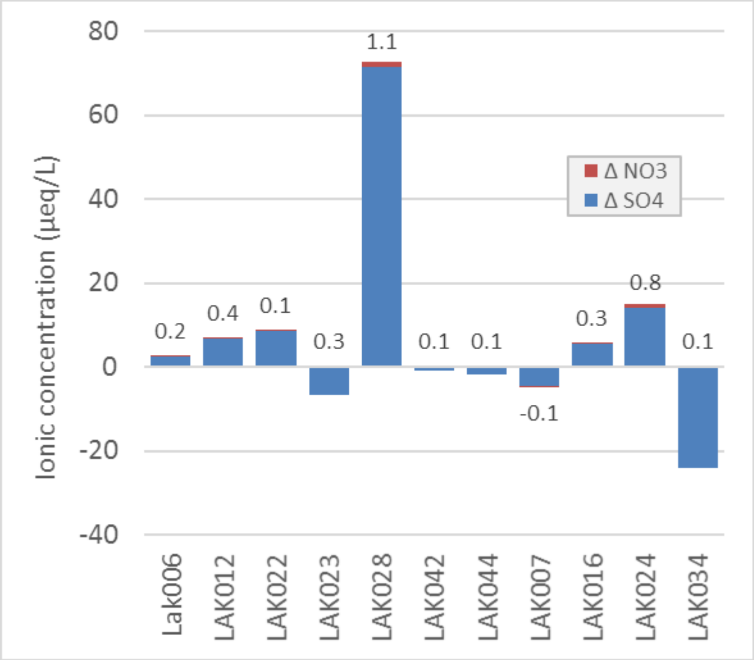

Figure 7.23. Changes in SO_4 and NO_3 from baseline (2012) to post-KMP (2016-2018). The blue bars show ΔSO_4 and the labels display ΔNO_3 because the red bars are barely visible.

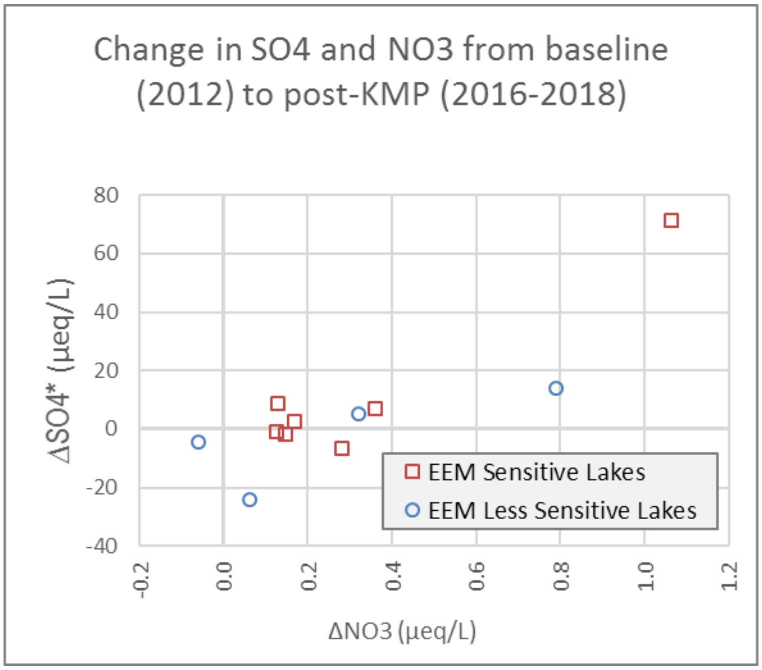

Figure 7.24. Changes in SO_4 relative to changes in NO_3 for the EEM lakes, from 2012 to the post-KMP period (2016-2018).

Statistical Analyses of Trends and Temporal Patterns

NOTE: The following two topics from the Terms of Reference for this section are addressed in depth in Appendix F (Statistical Analyses of Water Chemistry Data)

- *"Statistical Analyses of Trends and Temporal Patterns"*
- *"Statistical Evaluation of Observed Changes Relative to KPI Thresholds"*

7.1.3.2.4 Observed changes in water chemistry relative to STAR predictions

Observed Changes vs. Unadjusted STAR Predictions

The first six columns of Table 7.16 compare predictions from the modified ESSA-DFO model with observed changes. In general, all of the 7 sensitive lakes were predicted to show decreases in both ANC and pH, but none of them have. The main pattern that stands out is much less of a deposition effect (i.e., increased [SO_4^{2-}], decreased ANC and pH) than predicted in the sensitive lakes except that LAK028 had an observed increase in lake [SO_4^{2-}] which was 3.5 times that predicted (pink cell in Table 7.16) but with no decrease in ANC and pH. LAK023 (West Lake) is notable in that [SO_4^{2-}] has declined by 6.7 µeq/l over 2012-2018.

In the rightmost two columns of Table 7.16, we compare the SSWC prediction for critical load exceedances with observed changes in ANC over 2012-18. In the STAR we predicted that under 42 tpd of SO_2 emissions, five of the seven sensitive lakes would receive deposition in exceedance of their CL (LAK006, LAK023, LAK28, LAK042, LAK044, yellow shaded cells in Table 7.16). Of these 5 lakes, none of them showed a decline in ANC. Therefore, all five sensitive lakes showed less of a deposition effect than predicted (and hence are coloured green in Table 7.16). LAK007, an alkaline lake with an ANC > 1350 µeq/l (ESSA 2018b, Tech Memo W07) showed a 3.6% decrease in ANC, but no change in pH (remained constant at 8.0); this ANC change is of no concern.

Table 7.16. Predicted changes in lake chemistry in STAR vs. observed changes from 2012-2018. Green cells and red cells indicate observations less than or greater than, respectively, the predicted deposition effect. SO$_4^*$ is the marine-adjusted sulphate concentration.

Predicted Changes in STAR vs Observed Changes (2012 to 2016-18)

	Predictions from Modified ESSA-DFO model						SSWC model	
	Δ[SO4*]		ΔANC		ΔpH		Predicted Critical Load Exceedance meq/m^2/yr	Observed ΔANC 2012 to 16-18 µeq/l
	Predicted in STAR	Observed 2012 to 16-18 µeq/l	Predicted in STAR	Observed 2012 to 16-18 µeq/l	Predicted in STAR	Observed 2012 to 16-18		
Sensitive Lakes								
LAK006	24.8	2.5	-19.6	2.0	-0.5	0.2	14.3	2.0
LAK012	25.1	6.8	-15.2	1.3	-0.1	0.5	-37.5	1.3
LAK022	26.4	8.6	-18.1	5.1	-0.4	0.1	-12.3	5.1
LAK023	22.8	-6.7	-17.6	6.7	-0.5	0.2	9.1	6.7
LAK028	21.2	71.5	-11.8	0.5	-0.4	0.0	49.8	0.5
LAK042	15.0	-0.8	-13.2	26.1	-0.2	0.5	0.2	26.1
LAK044	14.9	-1.9	-14.3	3.7	-0.5	0.2	16.7	3.7
Less Sensitive Lakes								
LAK007	19.3	-4.4	0.0	-51.6	0.0	0.0	-1358.4	-51.6
LAK016	24.6	5.4	-10.8	21.1	-0.1	0.3	-71.0	21.1
LAK024	10.1	14.1	0.0	163.7	0.0	0.4	-347.6	163.7
LAK034	14.9	-24.0	-6.7	40.2	0.0	-0.3	-105.5	40.2

Observed Changes vs. STAR Predictions Adjusted using Method A

With Method A assumptions, LAK028 now shows a 23-fold greater increase in [SO$_4^{2-}$] than predicted (i.e., 71.5 µeq/l / 3.6 µeq/l; Table 7.17). LAK024 (Lakelse Lake) also shows a greater observed change in [SO$_4^{2-}$] than would be predicted. However, emissions in 2012 were less than in 2006, 2008 and 2009, so Method A underestimates the actual change in deposition since 2012. Method B (below) is a more accurate approach to testing the predictions of the ESSA-DFO model.

Predictions of exceedance in the SSWC model are driven just by the difference between long term deposition and the critical load, not by the change in deposition. So Method A is defensible for application of SSWC. As shown on the right side of Table 7.17, under Method A, only three lakes show an exceedance of their critical load (LAK006, LAK028, and LAK044). However, none of these lakes have shown a decrease in ANC over 2012-2018.

Table 7.17. Predicted changes in lake chemistry vs. observed changes from 2012 to 2018, assuming that sulphate deposition is 70% of what was modelled in the STAR, and using STAR estimate of pre-KMP deposition from 2006, 2008 and 2009 (Method A, as described in Section 7.1.3.2.4). SO_4^* is the marine-adjusted sulphate concentration.

Predicted Changes with 29.4 tpd emissions (avg of 2016-2018) vs Observed Changes (2012 to 2016-2018)

	Predictions from Modified ESSA-DFO model						SSWC model	
	Δ[SO4*]		ΔANC		ΔpH		Predicted CL Exceedance meq/m^2/yr	Observed ΔANC 2012-18 µeq/l
	Predicted w 29.4 tpd	Observed 2012-18 µeq/l	Predicted w 29.4 tpd	Observed 2012-18 µeq/l	Predicted w 29.4 tpd	Observed 2012-18		
Sensitive Lakes								
LAK006	10.3	2.5	-8.1	2.0	-0.2	0.2	1.5	2.0
LAK012	10.6	6.8	-6.4	1.3	-0.1	0.5	-50.0	1.3
LAK022	11.5	8.6	-7.8	5.1	-0.1	0.1	-24.7	5.1
LAK023	9.2	-6.7	-7.1	6.7	-0.2	0.2	-3.1	6.7
LAK028	3.1	71.5	-1.7	0.5	-0.1	0.0	20.8	0.5
LAK042	7.1	-0.8	-6.3	26.1	-0.1	0.5	-4.5	26.1
LAK044	7.1	-1.9	-6.9	3.7	-0.3	0.2	11.7	3.7
Less Sensitive Lakes								
LAK007	8.4	-4.4	0.0	-51.6	0.0	0.0	-1368.8	-51.6
LAK016	10.0	5.4	-4.4	21.1	0.0	0.3	-84.3	21.1
LAK024	4.6	14.1	0.0	163.7	0.0	0.4	-354.2	163.7
LAK034	7.2	-24.0	-3.2	40.2	0.0	-0.3	-111.1	40.2

Observed Changes vs. STAR Predictions Adjusted using Method B

Using Method B, which we think is the most accurate approach for making adjustments to the predictions of the modified ESSA-DFO model, the observed changes in $[SO_4^{2-}]$ in LAK028 are now 5.4 times what was predicted (Table 7.18). Predicted decreases in ANC and pH are now of a greater magnitude than those under Method A. LAK024 still has a greater observed change in $[SO_4^{2-}]$ than predicted.

It was not necessary to run the SSWC model for Method B. SSWC only depends on the ultimate long term deposition level, which was simulated under Method A.

Table 7.18. Predicted changes in lake chemistry assuming that the change in deposition is 62.1% of what was modelled in the STAR vs. observed changes from 2012 to 2018. (Method B, as described in Section 7.1.3.2.4). SO_4^* is the marine-adjusted sulphate concentration.

Predicted Changes with 0.621 of STAR deposition vs Observed Changes (2012 to 2016-2018)

	Predictions from Modified ESSA-DFO model					
	Δ[SO4*]		ΔANC		ΔpH	
	Predicted with 0.621 * STAR depn	Observed 2012 to 16-18 µeq/l	Predicted with 0.621 * STAR depn	Observed 2012 to 16-18 µeq/l	Predicted with 0.621 * STAR depn	Observed 2012 to 16-18
Sensitive Lakes						
LAK006	15.4	2.5	-12.2	2.0	-0.2	0.2
LAK012	15.6	6.8	-9.4	1.3	-0.1	0.5
LAK022	16.4	8.6	-11.2	5.1	-0.2	0.1
LAK023	14.2	-6.7	-10.9	6.7	-0.3	0.2
LAK028	13.2	71.5	-7.3	0.5	-0.3	0.0
LAK042	9.3	-0.8	-8.2	26.1	-0.1	0.5
LAK044	9.2	-1.9	-8.9	3.7	-0.4	0.2
Less Sensitive Lakes						
LAK007	12.0	-4.4	0.0	-51.6	0.0	0.0
LAK016	15.3	5.4	-6.7	21.1	0.0	0.3
LAK024	6.2	14.1	0.0	163.7	0.0	0.4
LAK034	9.2	-24.0	-4.2	40.2	0.0	-0.3

These results suggest that the STAR modelling predictions were generally conservative since the they have almost exclusively predicted changes of greater magnitude than have been observed. The one notable exception is the result for SO_4 at LAK028 that suggests that deposition levels close to the smelter (LAK028 is by the far the closest to the smelter and all of the other lakes are much further north) have been much higher than the model estimates of deposition from the STAR.

7.1.3.2.5 Critical loads, exceedances and predicted changes in pH

The modeling, analyses and sensitivity analyses associated with critical loads, exceedances and predicted change in pH are documented in Appendix G.

7.1.3.2.6 Application of the Evidentiary Framework

NOTE: The application of the evidentiary framework is described and discussed in the chapter of the main report.

7.1.3.2.7 Episodic acidification studies

Continuous pH monitoring

The data collected from the continuous pH monitors has been judged to be insufficient quality to use for the intended studies of acidifications, episodic events, and temporal trends in pH (Limnotek, 2019)).

Limnotek (2019) make the following recommendations with respect to instrument effects on pH measurement (quoted direction from Section 4.2 in Limnotek, 2019):

Recommendation 1: *Develop a curve showing time to stabilization of pH to determine the minimum time needed for a stable pH to be attained. Observations in 2018 and in earlier years showed that if a measurement was occurring after calibration in buffer solutions that have high conductivity, a stable reading was attained after a longer period than if a reading occurred following a measurement in a solution having a similar conductance to the sample being tested. This observation suggests the test of time effects on stabilization of a pH reading should be stratified according to conductivity of a previously measured solution (calibration buffer or sample) to which the sensor was exposed. Those strata are: (1) buffer solution during calibration (buffers have high conductance), (2) lower conductance water compared to the sample being tested, (3) higher conductance water compared to the sample being tested.*

Recommendation 2: *It is recommended that time course pH measured by the Mantas in a moored setting (autonomous recording of pH while moored in a lake or stream) not be used to interpret temporal variation in actual pH of the EEM lakes or streams for three reasons:*

1. *Insufficient time allowed in factory settings on the instruments for electrode stabilization between measurements that can lead to erroneous pH data,*
2. *Evidence of pH drift by up to 0.5 pH units between dates of calibration that can lead to erroneous data, and*
3. *Absence of features that prevent bio-fouling that may interfere with ion exchange at the glass bulb electrode and produce erroneous pH readings.*

Recommendation 3: *It is recommended that instantaneous measurements following sensor stabilization defined in Recommendation 1 be used for analyses of temporal and spatial variation in pH among the EEM Lakes and streams. Data from the Manta moorings should not be used for this purpose for reasons given in Recommendation 2. Of the instruments and labs used in the EEM program to date, data from WTW field pH meter and the lab at Trent University meet the requirement of adequate time for sensor stabilization in addition to standard sample handling and calibration protocols. This attention to how the pH is measured provides confidence in the resulting data.*

Recommendation 4: *Given that Manta instruments designed for a moored application have been purchased for the EEM program, it is recommended that options be explored with the manufacturer to change the factory set stabilization period from 5 seconds to at least 10 minutes. The Mantas should then be tested to examine pH drift and variability against other instruments (e.g. WTW and Trent Lab) to determine future suitability for providing pH data in a moored application.*

Recommendation 5: *If the Mantas are used in 2019, the glass bulb electrodes on all instruments that have been used in End Lake, Little End Lake, West Lake, and LAK028 require replacement in 2019 because they will be in their final year of effective life. This recommendation follows advice from the manufacturer that electrodes be replaced every 5 years.*

***Recommendation 6:** Regardless of what instrument or lab is used for pH measurement, field technicians must ensure there is no air space in sample bottles to ensure minimal drift of pH in sample bottles caused by gas exchange at the water – air interface, samples are kept cool, and pH measurement occurs as soon as possible after collection.*

Independent research project

The results from Dr. Weidman's research are not yet available for review.

7.1.3.2.8 Kitimat River water quality

The results of the water quality sampling at the Rio Tinto intake on the Kitimat River are shown in Appendix H. None of the results showed exceedances of the BC water quality objectives. The maximum measured sulphate concentration was less than 1% of the BC Drinking Water Guideline.

7.1.3.2.9 Results from previously reported analyses

As discussed in Section 7.1.2.8, other sampling and analyses have been conducted during the EEM program beyond the core water chemistry sampling. Those additional elements of the Program have been previously reported in Annual Reports and their appendices, and other technical memos. This section only summarizes some of the key results.

Fish sampling

Fish presence/absence surveys were conducted in in some of the sensitive lakes (LAK006, LAK012, LAK023, LAK044, LAK028) and some of the less sensitive lakes (LAK007, LAK016, LAK034) during the monitoring campaigns of 2013, 2015 and 2017. Each of the lakes was sampled once. Key findings include:

a) The 2013 fish survey in four acid-sensitive lakes (i.e., LAK023, LAK006, LAK012 and LAK044) found no fish in LAK044 (which has no inlets or outlets). Three-spine stickleback (*Gasterosteus aculeatus*) was present in three of the lakes (i.e., LAK023, LAK006 and LAK012). Lakes LAK006 and LAK012 had also coastal cutthroat trout (*Oncorhynchus clarkii*), coho salmon (*Oncorhynchus kisutch*) and dolly varden char (*Salvelinus malma*). LAK023 had residualized coho (discussed under point "c" below) as confirmed by DNA analysis of the fish tissue.

b) The 2015 survey of the three less sensitive lakes found coastal cutthroat trout to be common in all three lakes. Both LAK007 and LAK016 also had coastal coho salmon and dolly varden char. LAK034 only had coastal cutthroat trout and threespine stickleback.

c) Both LAK023 (sampled in 2013) and LAK016 (sampled in 2015) had mature coho showing freshwater residualism (i.e., remaining in freshwater for all of their life history rather than migrating to the sea), apparently due to ephemeral outlets which leave adults trapped in the lake (Parkinson et al. 2016).

d) The 2017 survey of LAK028 found no fish, due to physical features of the channel which prevent upstream fish migration.

e) Given small fish populations in small lakes, future gill netting presents a risk of depleting the fish population in one or more lakes due to mortalities caused by gill netting (C. Perrin, pers. comm.). Discretion will be needed in cooperation with ENV on deciding whether fish sampling using gill netting is needed in future cases, or whether other less intrusive methods of sampling (e.g., eDNA) could be used.

Additional details are documented and discussed in the relevant technical reports from Limnotek – i.e., Perrin et al. 2013, Limnotek 2016, Bennett and Perrin 2018.

Regional amphibians and potential risks of aquatic acidification

Based on the literature review conducted in 2017, we identified that at least 7 amphibian species occur within the overall study area. Six of these species require aquatic breeding habitats in low-lying areas; i.e, within the isopleth of 10 kg/ha/yr. Two of the seven species identified (Coastal Tailed Frog – *Ascaphus truei* – and Western Toad – *Anaxyrus boreas*) are listed as 'Special Concern' federally.

The observation data collected indicate that 6 of the amphibian species have been observed within the zone of highest deposition close to the smelter, indicating tolerance to historic and current levels of deposition and their effects on soils and aquatic environments.

Two critical knowledge gaps remain:

1. Acid sensitivity of the smaller ponds (< 1 ha) and wetlands occupied by amphibians in the Kitimat area is unknown. Smaller bodies of water are expected to have a wider range of acid sensitivity than larger lakes (i.e., both more acid sensitive and less acid sensitive).
2. Sensitivity of local amphibians to acidification is partially known. Literature available only for the two observed species: Wood Frog and Western Toad. It is not possible to confidently extrapolate acid-sensitivity from studies of species with similar life histories and habitats to the seven species or populations found in the Kitimat Valley.

Lake level monitoring

Water level was measured in 2018 using sensors and data loggers in the acid-sensitive lakes called LAK006, LAK012, LAK023 in May through October, and in acid-sensitive LAK028 during September and October. Observations of surface water level (in cm) were registered every 30 minutes and mean daily values were derived from these data.

It was observed in both 2017 and 2018 that water surface elevation declined over the summer in all lakes and increased in October corresponding with increasing rainfall during the autumn. The timing of change in water surface elevation was similar among the four lakes (Figure 7.25). Magnitude and rate of change differed because of differences in drainage area, lake morphometry, and other hydrological attributes.

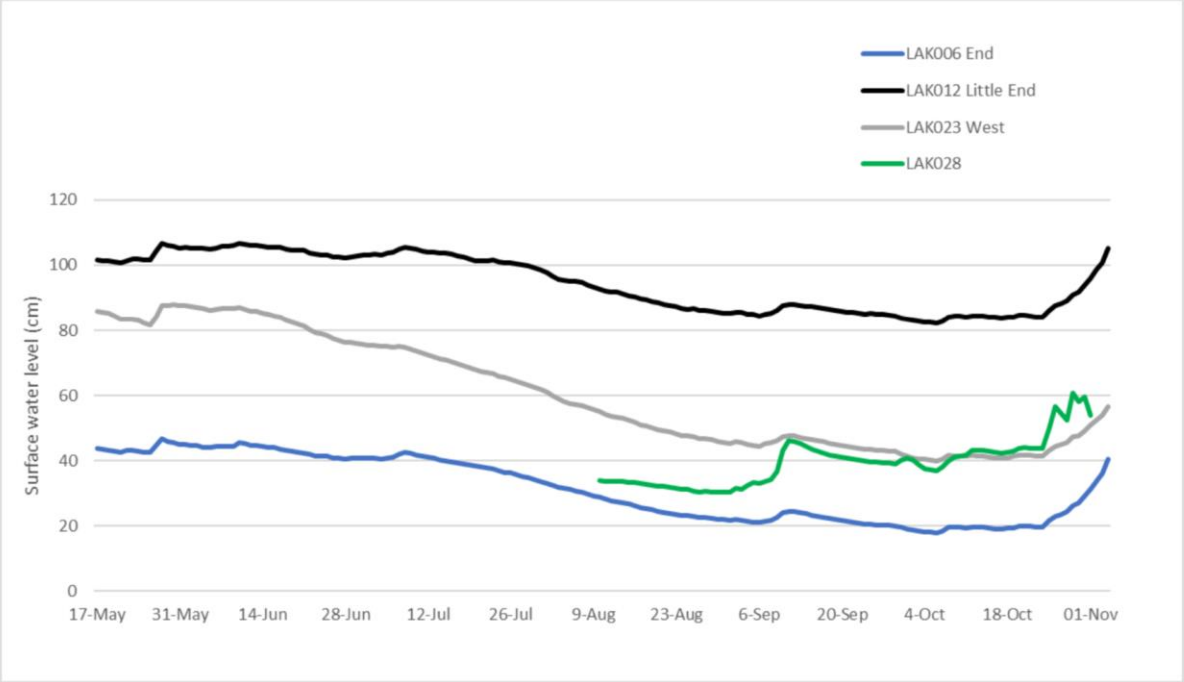

Figure 7.25. Mean daily surface water levels as measured in 2018 in End Lake (LAK006), Little End Lake (LAK012), West Lake (LAK023) and LAK028. Note that water level is relative to a benchmark at each lake and not to a common benchmark (Source: Limnotek 2019).

<u>Bathymetric analyses</u>

Bathymetric surveys were conducted for LAK006, LAK012 and LAK023 in 2015, and then for LAK028 in 2018. The purpose of the surveys were to assist with interpretation of lake biogeochemistry by improving the calculation of lake water residence time.

As an example of this work, Figure 7.26 shows the bathymetric map of LAK028, colour-coded by depth interval. At full pool, the volume of LAK028 is 105,840 m^3 with an error of ±4.0% (details in Limnotek 2019). Volume calculations showed that lake volume declines linearly with elevation over the top 1m of water depth.

Full details on collection and analysis of the bathymetry data are reported in specific technical memos associated with the work.

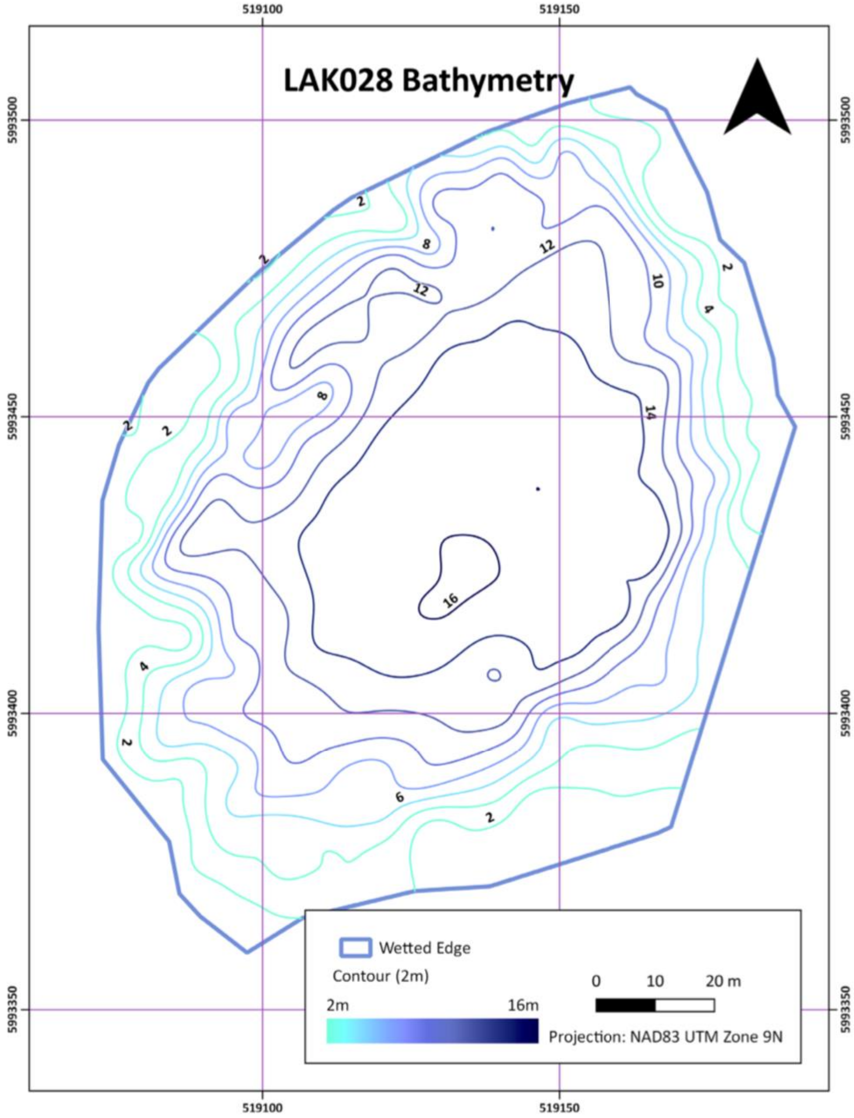

Figure 7.26. Bathymetric map of LAK028 (Source: Limnotek 2019).

Water residence time for lakes

Table 7.19 shows the estimated water residence time for each of the seven EEM sensitive lakes. Initial estimates were presented in Table 25 of the EEM Plan but these estimates have been improved by additional data on lake depths, a revision to the calculation used in the EEM Plan, and/or more precise estimates of lake volume from bathymetric analyses conducted as part of the EEM Program. The results show that five of the seven EEM sensitive lakes have estimated water residence times of less than one year. LAK006 has an estimated residence time of 1.4 years and LAK044 has an estimated residence time of 2.1 years. Overall this indicates that for all of the sensitive lakes, lake chemistry properties would be expected to respond to changes in deposition and/or other changes in the watershed within essentially 1-2 years.

Table 7.19. Estimates of water residence time for the EEM sensitive lakes. The estimates from the EEM Plan (Table 25) are shown, versions of those estimates based on additional depth information and revised calculation, and the results from the bathymetric analyses of lake volume for four of the lakes. The orange cells indicate the best available estimate of water residence time for each lake.

				Initial Estimate from 2012 Data (Table 25 in EEM Plan)			Revised Estimates			Bathymetric Analysis	
Lake	Lake Area (ha)	Watershed Area (ha)	Runoff (m)	Depth at sampling point (m)	Estimated Midrange Lake Volume (m^3)[1]	Estimated Midrange Residence Time (yr)	Depth at sampling point (m)[2]	Estimated Lake Volume (m^3)[3]	Estimated Water Residence Time (yr)	Lake Volume (m^3)	Calculated Water Residence Time (yr)
LAK006	10.25	91.2	0.88	5.7	584,232	0.7	20.1	1,029,613	1.3	1,129,350	1.4
LAK012	2.30	90.1	0.86	3.5	80,538	0.1	6.7	76,820	0.1	94,455	0.1
LAK022	5.74	39.9	0.83	10.1	580,128	1.7	7.6	218,120	0.7		
LAK023	6.77	40.3	0.90	2.7	182,857	0.5	8.5	288,741	0.8	185,064	0.5
LAK028	1.02	11.9	1.58	15.5	158,726	0.8	15.2	77,520	0.4	105,840	0.6
LAK042	1.46	37.2	0.60	12.0	175,186	0.8	13.5	98,842	0.4		
LAK044	2.01	9.9	0.64	15.0	300,832	4.8	13.4	134,871	2.1		

[1] Lake volume estimated as [lake area] * [mean depth], where mean depth is assumed to be depth at the sampling point

[2] Average depth at sampling point across all samples taken from 2012 to 2018

[3] Lake volume estimated as [lake area] * [mean depth], where mean depth is assumed to be *half* of the depth at the sampling point

Depth profile, water column chemistry, and deep water sampling for LAK028

The 2017 water column sampling from LAK028 strongly suggested the presence of meromixis (i.e., surface and bottom waters do not mix), which was also implied by the small surface area relative to lake depth. The results of the water column sampling (see Bennett and Perrin 2018) show that thermal and chemical conditions change significantly at depths >9 m.

The surface mixed layer (<9 m) had water temperature typical of north coast lakes in the fall, high dissolved oxygen that could support fish, conductivity and inorganic nitrogen concentrations typical of nutrient deficient lakes, and a surface pH (~ 5) at the low end of tolerances for aquatic organisms. The bottom water layer was anoxic and would not support fish, with higher pH, higher conductivity, a warming thermocline, an odour of H_2S, and other evidence of sulphur-reducing green and/or purple bacteria.

In 2018, the deep water sampling of LAK028 confirmed earlier observations of stable chemical stratification, consistent with meromixis. Mean sulphate concentrations were 5.0 mg·L-1 in the epilimnion (surface layer), 4.1 mg·L-1 in the chemocline (transition layer), and close to nil in the hypolimnion, which showed high availability of sulphate and presence of oxygen at the surface and reduction to sulphide, given the sample odor, in the bottom waters.

Limnotek (2019) concluded:

> *The surface mixed layer contained oxygen which favoured sulphate compared to sulphides that were present in the bottom mixed layer. Due to the chemically reduced environment, fish are not be expected to survive in the bottom mixed layer. The reducing conditions also favour release of solutes from the sediments and potential growth of cyanobacteria or purple sulphur bacteria in the bottom mixed layer.*

Non-EEM sites

Table 7.20 provides a summary of the "non-EEM" sites sampled during the course of the EEM Program to date and the associated recommendations. Additional details and sample data are reported in the annual reports and technical memos associated with each year of the program.

Lakes MOE3 and MOE6 were sampled in 2013 and 2014, respectively. MOE expressed concern that lakes MOE3 and MOE6 could potentially be sensitive to increased emissions and thus requested that they should be sampled. It was determined that neither lake is sensitive to the predicted increases in acidic deposition (based on MOE3 having a very high critical load, and MOE6 having high base cations and high Gran ANC[13]). The final recommendation was not to add these lakes to the EEM Program. Similarly, Cecil Creek was sampled at three sites in 2013 because it receives drainage from one the EEM lakes (i.e., LAK023 or West Lake). The sampling data showed that Cecil Creek also has a high critical load and therefore it was not added to the EEM Program for further monitoring.

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[13] A critical load was not calculated for MOE6 because it was sampled only in 2014. Critical loads were calculated for the one-off additional locations sampled in 2013 (i.e., MOE3 and Cecil Creek) but not for those sampled in 2014. The calculation of critical loads requires modeled deposition that is relevant to the year of sampling (for the modeled estimate of pre-industrial SO_4^{2-} and by 2014, we concluded that the emissions had changed to significantly from the "pre-KMP" conditions for which deposition had been modeled. Even in 2013, when critical loads were re-estimated for the EEM lakes (to compare the effect of changing the sampling season), emissions had already decreased from 2012, but it was decided that critical loads should not be calculated again with the 2014 sampling data.. The high Gran ANC and high base cations indicate that the estimated critical load for MOE6 would be high. As part of the SSWC modeling in the present work, a critical load was estimated for MOE6 (despite the flaws previously identified) in order to be able to use MOE6 in the full data set of all the lakes. The estimated critical load is very high (>400 meq/m^2/yr).

Goose Creek constitutes a network of streams draining the acid-sensitive lake LAK028. A reconnaissance of water chemistry of these streams started in 2013 following a request by MOE to obtain water quality information to assist with understanding conditions of cutthroat trout (*Oncorhynchus clarkii*) spawning habitat in lower Goose Creek. Multiple sites within the drainage were sampled in 2014 and 2015. This initial assessment concluded that the Goose Creek drainage is not sensitive to acidic deposition and should not be added as a regular component of the EEM Program. In 2018, several of these sites were resampled and additional samples were collected from a region of the watershed that had not been previously sampled. These new data did not change the original conclusion.

In 2014, a continuous pH monitor was established Anderson Creek as a Rio Tinto voluntary initiative. The results of the STAR showed that Anderson Creek has a high critical load and was predicted to have no change in pH with increased deposition. However, Rio Tinto decided to install the monitor as a source of additional information because of the proximity of the stream to the smelter (immediately north). Monitoring was continued through 2018, although some years had substantial technical difficulties with the instrument (as described in annual reports). Each year, the recommendation was to continue monitoring. However, the recommendation presently is to discontinue monitoring at this location because it is not providing information that is critical to the EEM Program.

7.1.3.3 Modifications to the EEM Program

The following subsections describe modifications that *have occurred* during the first six years of the EEM program (i.e., not prospective proposals).

7.1.3.3.1 Adjustments to sampling program

Adjustments to the sampling program

- After not being included in the initial EEM design for 2013 (due to its high ANC and lack of sensitivity to acidification), LAK024 (Lakelse Lake) was added into the Program in 2014 because of its high public value.
- Three control lakes were added to the program in 2015 to provide the ability to discriminate smelter effects from general regional patterns of change in water chemistry caused by environmental variability.
- Additional intra-annual sampling was added to 3 sensitive lakes in 2014 and 3 more sensitive lakes in 2016, to provide higher statistical power to detect changes.
- Continuous pH monitors were added to 3 sensitive lakes in 2014 and 1 additional lake in 2018 to assess the seasonal and diurnal variability in pH.
- Water level monitoring was added to the lakes with continuous pH monitors to detect when storm events occurred that might affect chemical conditions.
- Bathymetric data was collected and analyzed for 4 lakes in order to develop accurate estimates of lake volume for better estimates of residence time, and therefore how long it will take lake chemistry to respond to changes in emissions.
- A depth profile was developed for LAK028, plus additional sampling of the chemistry at depth, to explore the location and potential effects of hypolimnetic sulphate reduction.

Modification of methods

- Applied the improved methodology for defining watershed area that was applied in the KAA
- When the additional within-season sampling was first added (2014), the inter-annual changes in water chemistry were calculated using only the sample taken on the "annual sampling" day and the other samples were used to explore variability separate from the reporting of inter-annual change. We moved to reporting mean values and standard errors for lakes with multiple samples within the index period in the 2016 Annual Report.
- Various minor corrections to calculations and/or computational errors, as needed.
- Exploration of variable organic charge density (as explained elsewhere in this appendix).
- In 2013, the use of a commercial laboratory for additional measurement of pH from lake samples was added to the program.

Refining how we interpret the results

As explored and discussed in multiple places through the aquatic chapter and appendices, the results of the initial couple years of sampling indicated that the pH of the EEM lakes has much greater natural variability (in addition to measurement uncertainty) than was understood during the development of the EEM program. This has resulted in a critical change in perspective – that pH is highly variable with low power to detect changes of the defined effect size of concern. This change in how the data are interpreted directly lead to many if not most of the changes in the sampling program described above, additional emphasis on the importance of taking a multi-metric view as defined in the evidentiary framework, as well as providing the rationale for conducting the rigorous statistical analysis of changes in water chemistry within a probabilistic framework (see Appendix F).

7.1.3.4 Comprehensive synthesis ('pulling all the pieces together')

NOTE: The content of this section exists solely in the Aquatic Ecosystems chapter of the main report.

7.1.3.5 Conclusions

NOTE: The content of this section exists solely in the Aquatic Ecosystems chapter of the main report.

7.1.4 What Do We Recommend for the EEM Program Going Forward?

7.1.4.1 Recommendations regarding EEM lakes

NOTE: The content of this section exists solely in the Aquatic Ecosystems chapter of the main report.

7.1.4.2 Recommendations regarding non-EEM lakes and stream sites

During the course of the EEM Program, water chemistry samples were also collected and analyzed at the following “non-EEM” sites to assess concerns that there were additional sites outside of the EEM lakes that could potentially be sensitive to increases in deposition. These sites included several sites in Cecil Creek, lakes MOE3 and MOE6, and multiple sites within the Goose Creek drainage. In all cases these sites have been determined to have low to very low sensitivity and our recommendations have been that further sampling is not required and they do not need to be added to the EEM Program.

Table 7.20. Summary of monitoring actions taken and recommendations for non-EEM sites through the 2013-2018 period

Year	Actions at non-EEM sites	Recommendations for non-EEM sites
2013	• Lake **MOE3** was sampled • **Cecil Creek** receives drainage from West Lake (LAK023) and was sampled in three locations	• The non-EEM sites MOE3, MOE6 and Cecil Creek were considered insensitive to increased deposition (based on high critical loads and/or high base cations and Gran ANC) and not added to the annual EEM sampling. • Calculate critical loads for Goose Creek sites[14]
2014	• Additional sampling of non-EEM lakes and stream identified as being potentially sensitive to increased emissions, including Lake **MOE6** and six sites within the **Goose Creek** watershed • Continuous monitoring of stream pH was initiated in **Anderson Creek** in the fall of 2014 for a 10-day trial period (November 19-28), and was restarted on March 31, 2015 • Critical loads and exceedances were calculated for the MOE3 and Cecil Creek in order to determine if they are sensitive to increased emissions of SO_2. For MOE6, sensitivity was assessed based on Gran ANC and the concentration of base cations[15]. • A preliminary assessment of the sensitivity of the Goose Creek sites was conducted based on the water chemistry samples collected and analyzed in 2014	
2015	• Sampling of two additional sites within the **Goose Creek** watershed, previously identified as being potentially sensitive to increased emissions. • A preliminary assessment of the sensitivity of the **additional Goose Creek** sites was conducted based on the water chemistry samples collected and analyzed in 2015. • Continuous monitoring of stream pH was continued in **Anderson Creek**	• The preliminary assessment of water chemistry at Goose Creek sites suggests that these sites are insensitive to potential increases in acid deposition. No further action required.
2016	• Maintained continuous pH monitoring in **Anderson Creek** • Terms of reference were drafted for reviewing the literature and available regional data to understand the potential risks to **amphibians** in the Kitimat Valley	• Continue continuous pH monitoring at Anderson Creek.

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[14] Subsequent to this recommendation in the 2013/2014 Annual EEM Report, we chose not to do this work because the high values for base cations and Gran ANC indicated that these stream sites were not sensitive.

[15] As per earlier footnote, the critical load for MOE6 was estimated for the purposes of the present Comprehensive Review.

Year	Actions at non-EEM sites	Recommendations for non-EEM sites
2017	• Maintained continuous pH monitoring in Anderson Creek • Literature review on potential effects of acidification on amphibians in the Kitimat Valley was completed	• No additional changes to the lake sampling program were recommended at this time. • Continue continuous pH monitoring at Anderson Creek. • It was recommended to re-sample for water chemistry the eight tributaries of Goose Creek that were previously sampled in 2014 and 2015, in order to determine if there have been any significant changes. It was also recommended to assess the benthic community of Goose Creek and compare its composition with that of similar streams.
2018	• Water chemistry measurements were done in 7 stream sites from the Goose Creek network • Potential stream sites were ranked for bioassessment but not sampled in 2018 • Continuous monitoring of pH in Anderson Creek	• Continue continuous pH monitoring at Anderson Creek as part of the episodic acidification study sub-component.

7.2 Aquatic Appendix B: Acid neutralizing capacity (ANC) as a biological indicator of the effects of freshwater acidification

7.2.1 Definitions of ANC and related terms

Acid neutralizing capacity (ANC) is a measure of the sensitivity of surface waters to acidification. ANC can be defined in several different ways, and it is closely related to the term *alkalinity* (various definitions in Hemond 1990). *Gran ANC* has been the primary measure of ANC for all the analyses in the STAR and EEM. ANC is a measure of the capacity of a solution to neutralize strong acids and is determined by titration to the inflection point of the pH-alkalinity titration curve. **Gran ANC** includes the buffering effect of organic anions. Another commonly used metric is Charge Balance ANC or Charge Balance Alkalinity (CBANC or CBALK), hereafter referred to as **CBANC**. CBANC is generally calculated as the equivalent sum of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) minus the equivalent sum of strong acid anions (SO_4^{2-}, NO_3-, Cl^-). CBANC does not take into account the buffering effect of organic anions.

In surface waters with organic anions, Gran ANC will be lower than CBANC. The relationship between Gran ANC and CBANC depends on the nature of the organic anions present in the sample. Hemond (1990) notes that for organic anions which follow the model developed by Oliver et al. (1983), CBANC = Gran ANC + 4.6 * DOC, where Gran ANC and CBANC are measured in μeq/l , DOC (Dissolved Organic Carbon) is measured in mg/l, and 4.6 is the assumed charge density of organic anions (CD = μeq of organic anions per mg of DOC). For example, using the above formula, a water sample with CBANC = 23 μeq/l and DOC = 5 mg/l (roughly the average DOC in the seven sensitive lakes included in the EEM program), would have a GranANC of 0 μeq/l. Charge densities reported in the literature are generally in the range of 4-6 μeq per mg DOC (Hemond 1990), but can range from 2 to 10 μeq per mg DOC (Table 3 in Marmorek et al. 1996). The more general formula relating CBANC and Gran ANC is: CBANC = Gran ANC + CD * DOC, where CD is the charge density.

Measurements of pH and ANC can be substantially influenced by dissolved organic carbon (DOC). In recognition of this dynamic, Base Cation Saturation (**BCS**, Lawrence et al. 2007), previously described in Europe as Organic Acid Adjusted ANC (ANC_{OAA}, Lyderson et al. 2004), was developed as an alternative measure of ANC taking into consideration that only a subset of organic anions are strongly acidic. BCS (or ANC_{OAA}) is equal to CBANC minus strongly acidic organic anions (Lawrence et al. 2007, 2013, Lyderson et al. 2004). A distinct threshold for inorganic aluminum (Al) mobilization occurs at a BCS value that closely approximates 0, regardless of the DOC (Lawrence et al. 2007). Values of BCS < 0 would indicate that acid-neutralization within the watershed is not sufficient to buffer acidic deposition without mobilization of toxic inorganic Al (Baldigo et al. 2009). Though the definitions of BCS and ANC_{OAA} are identical, the methods of calculating these metrics differ slightly among the above authors. In citing results from a given author, we use whatever metric they used. Figure 7.27 compares the three ANC metrics, assuming that BCS and ANC_{OAA} are estimated as CBANC – 1/3 * [CD * DOC].

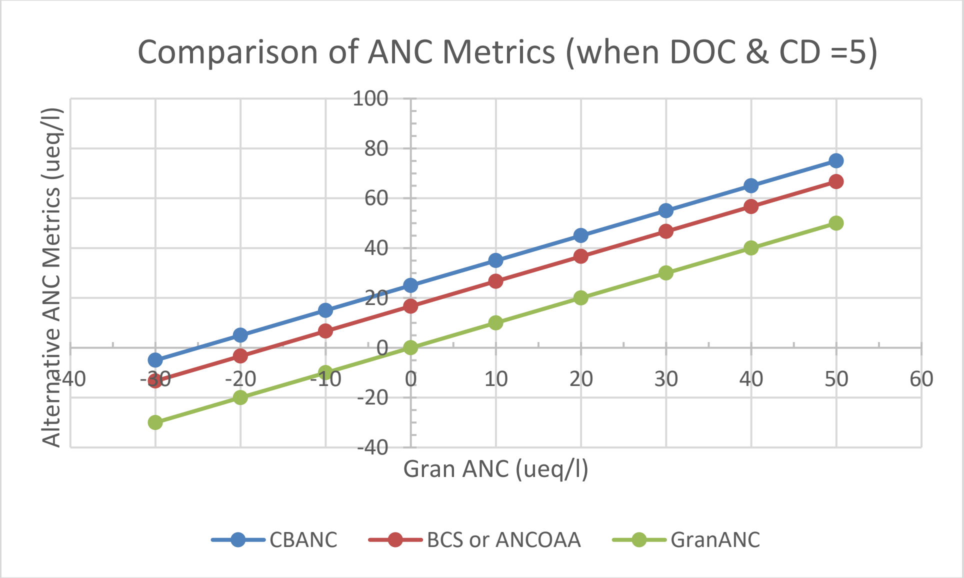

Figure 7.27. Comparison of Gran ANC, CBANC and ANC_{OAA} for a water sample with a charge density (CD) of 5 μeq per mg DOC, and a DOC level of 5 mg/L.

7.2.2 ANC and acidification of surface waters

Acidification of surface waters, accompanied by high concentrations of H+ and elevated levels of inorganic Al, impoverishes fish communities due to negative biological effects, including damage to the tissues by aluminum accumulation on fish gills (Baker et al. 1990, Section 3.5.5 of the STAR, ESSA et al. 2013).

Water bodies with Gran ANC values below 0 are considered acidic (Baker et al. 1991). Low ANC values make lakes and streams more susceptible to episodic acidification (Baron et al. 2011) following strong hydrological events (e.g., storms and snowmelt).

While pH was historically the dominant variable used to predict effects of acidification on biota, either independently or together with calcium and inorganic aluminum concentrations (Baker et al. 1990), ANC has also been extensively used as a predictive variable (Driscoll et al. 2001, Posch et al. 2007, Solheim et al. 2008). Driscoll et al. (2001) studied water chemistry in lakes in the Northeastern United States during summer (low flow) conditions, which likely represent the highest ANC values throughout the year. Lakes with ANC values below 0 μeq/l during low flow conditions are considered chronically acidic (i.e., they are likely to remain acidic throughout the year). Lakes with ANC within the 0-50 μeq/l range are considered susceptible to episodic acidification (i.e., ANC might decrease below 0 during high flow events such as storms or spring freshets). Finally, lakes with ANC values greater than 50 μeq/l are considered relatively insensitive to inputs of acidic deposition.

7.2.3 ANC values and aquatic biota in the KMP study area

In the STAR, an ANC limit of 26 μeq/L[16] was applied in the Steady State Water Chemistry model that estimated critical loads of acidity for the 41 lakes and 20 streams sampled. Eight of the 41 sampled lakes had a Gran ANC value less than the defined ANC limit of 26 μeq/L. Another 4 lakes and 1 stream had an ANC between 26 and 50 μeq/L and therefore could potentially experience acidic episodes during storm and snowmelt events (Driscoll et al. 2001). The remaining 70% of the sampled lakes and 95% of the sampled streams had an ANC >50 μeq/L and therefore are relatively insensitive to acidic deposition. The distribution of Gran ANC values across the STAR lakes and streams is shown in Figure 7.28.

In general, little is known about the aquatic biota in the lakes within the study area, except for Lakelse Lake. The Kitimat River supports runs of all five species of Pacific salmon (i.e., Chinook, Sockeye, Coho, Pink and Chum), anadromous steelhead (*Oncorhynchus mykiss*), Dolly Varden char (*Salvelinus malma*), and coastal cutthroat trout (*Oncorhynchus clarkii*); the lower 10 km of the river is a major salmon migration route (ESSA et al. 2013). Non-salmonids include coastrange sculpin (*Cottus aleuticus*), slimy sculpin (*C. cognatus*), Pacific lamprey (*Entosphenus tridentatu*), and three-spine stickleback (*Gasterosteus aculeatus*). Freshwater fish species of special conservation status, as identified on provincial red and blue lists, include cutthroat trout, bull trout, and Dolly Varden char. Eulachon were abundant historically in the Kitimat River, but began to decline in the mid-1970's and are now virtually extirpated; fishing for eulachon was halted in 1972 due to contamination from pulp mill effluent (Olson et al. 2015).

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[16] Recall: The ANC limit applied in the STAR was developed by starting with a pH threshold of 6.0 pH units (as supported in the research literature as a threshold for avoiding adverse impacts on aquatic ecosystems). The threshold of 6.0 pH units was equated to a comparable ANC threshold by using a regional pH-ANC relationship fit to all the sample data. See ESSA et al., 2013.

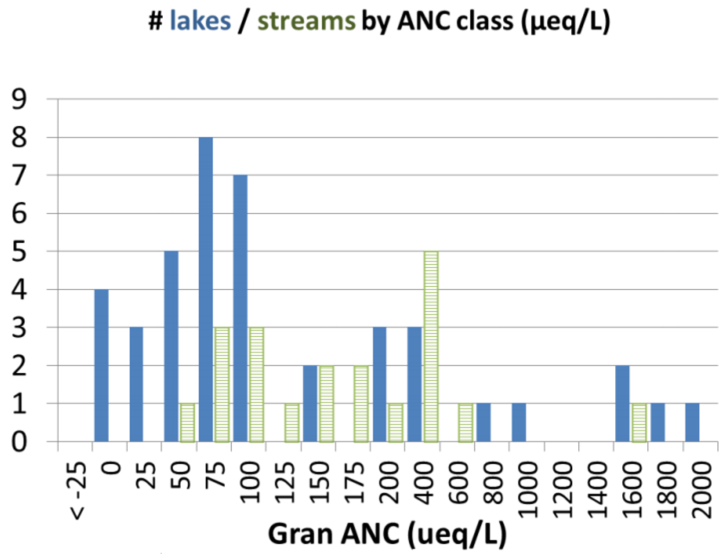

Figure 7.28: Distribution of Gran Acid Neutralizing Capacity amongst lakes (blue solid bars) and streams (green cross-hatched bars) sampled as part of the STAR program in 2012 . The number on the x-axis shows the maximum value of the ANC interval (e.g., "25" indicates waters with ANC between 0 and 25 µeq/L). Note that the ANC interval is 25 µeq/L up to 200 µeq/L, and then increases to 200 µeq/L. Source: ESSA et al. 2013

Fish sampling was conducted in 2013, 2015 and 2017 as part of the EEM program to confirm presence/absence of fish in some of the sensitive lakes (LAK006, LAK012, LAK023, LAK044, LAK028) and some of the less sensitive lakes (LAK007, LAK016, LAK034). Each of the above lakes was only sampled once; details are in Perrin et al. 2013, Limnotek 2016, Bennett and Perrin 2018. Key findings were as follows:

a) The 2013 fish survey in four acid-sensitive lakes (i.e., LAK023, LAK006, LAK012 and LAK044) found no fish in LAK044, as well as presence of stickleback in three of the lakes (i.e., LAK023, LAK006 and LAK012). Lakes LAK006 and LAK012 also had coastal cutthroat trout, coho salmon and dolly varden char. LAK023 had residualized coho (discussed under point c) below).
b) The 2015 survey of the three less sensitive lakes found coastal cutthroat trout to be common in all three lakes. Both LAK007 and LAK016 also had coastal coho salmon (*Oncorhynchus kisutch*) and dolly varden char. LAK034 only had coastal cutthroat trout and threespine stickleback (*Gasterosteus aculeatus*).
c) Both LAK023 (sampled in 2013) and LAK016 (sampled in 2015) had mature coho showing freshwater residualism (i.e., remaining in freshwater for all of their life history rather than migrating to the sea), apparently due to ephemeral outlets which leave adults trapped in the lake (Parkinson et al. 2016).
d) The 2017 survey of LAK028 found no fish, due to physical features of the channel which prevent upstream fish migration.

7.2.4 Use of ANC as indicator of impacts of acidification on aquatic biota

Fish, and other aquatic species, exhibit complex responses to changes in water chemistry and their susceptibility to acidification varies depending on their life stage and local adaptation, as well as on the duration, frequency and magnitude of exposure to acidic conditions (Kernan et al. 2010).

Multiple studies have identified ANC critical levels for specific fish species (Lien et al. 1996, Laudon et al. 2005, Kernan et al. 2010), invertebrates (Raddum and Skjelkvåle 1995) or for broader categories of aquatic biota (Wright et al. 2005, Posch et al. 2007). A CBANC threshold of 20 μeq/L has been widely used in Europe as a water quality indicator protective of most key indicator organisms (Wright et al. 2005). Most of these studies have been conducted in Northern Europe.

Setting thresholds is complicated by the nonlinear dynamics involved in the relation between water chemistry and physiological responses and by the influence of multiple factors that operate at diverse spatial and temporal scales (Groffman et al. 2006).

Most of the studies conducted on the relationships between ANC values and the biological response of aquatic biota have been conducted in Northern Europe (Lien et al. 1996, Laudon et al. 2005), especially for brown trout (*Salmo trutta*). In North America, research on chemical thresholds as indicators for the impacts of acidification on freshwater biota has focused on Eastern North America (Driscoll et al. 2001, Baldigo and Lawrence 2007, Baldigo et al. 2019), especially on fish populations and communities in parts of the Adirondack Mountains of northern New York (Baldigo and Lawrence 2001, Baldigo et al. 2009); an area with soils of low buffering capacity that was severely affected by acid rain in the late 1980s.

7.2.4.1 Generic ANC thresholds for aquatic biota

As an example of a generic ANC threshold, Posch et al. (2007), in their assessment of critical loads of acidity for alpine lakes in Switzerland, adopted a critical CBANC value of 20 μeq/L as critical ANC value for the Steady-State Water Quality (SSWC) model, assuming this value to be generally protective of fish and invertebrates. This CBANC threshold follows the recommendations from the manual for modeling and mapping critical loads and air pollution in Europe (UNECE 2004).

A CBANC of 20 μeq/L has been widely used in Europe as a water quality threshold sufficient for protecting most key indicator organisms (Wright et al. 2005, Kernan et al. 2010). According to a study in Norway by Lien et al. (1996), this ANC value corresponds to a 10% probability of damaged brown trout populations (Kernan et al. 2010). In the UK, a lower CBANC value of 0 μeq/L, which corresponds to a damage probability of 50% for brown trout populations, has been used for naturally acidic sites (Kernan et al. 2010).

In their study on the recovery and evolution of acidified surface waters in Europe, Wright et al. (2005) established three CBANC ranges based on expected impact on brown trout and other aquatic biota: surface waters with CBANC < 0 μeq/L would be eventually be barren of fish; CBANC 0–20 would indicated sparse fish populations and CBANC > 20 would not have a detrimental effect on fish populations.

In North America, Baldigo et al. (2009) sampled 36 Adirondack streams as part of the Western Adirondack Stream Survey (WASS). They found a strong ($R^2 = 0.69$) relationship between BCS and an index of benthic community structure (acidBAP, acid Biological Assessment Profile, derived from percent mayfly richness and percent acid-tolerant taxa, Burns et al., 2008). Based on these results, the authors derived four biologically relevant ranges of BCS thresholds (Figure 8 in Baldigo et al. 2009):

1) above 50 μeq/L of BCS, there would be no biological impacts;
2) between BCS values of 0 and 50 μeq/L, biota would be exposed to background toxic levels of Al with a *slight* biological impact;
3) BCS values between -35 and 0 μeq/L would indicate chronic toxicity and a *moderate* biological impact; and
4) BCS below -35 μeq/L would point to acutely toxic waters and a *severe* biological impact.

Baldigo et al. (2009) concluded that acidBAP and BCS were useful indicators of ecosystem effects and potential recovery at the local and regional scale.

Baldigo et al. (2019), in their study on long-term effects of acidification on streams in in the Western Adirondacks (New York state, United States), found a non-linear asymptotic relationship between Gran ANC and biological effects on aquatic biota (Figure 7.29); i.e., the biomass of all fish communities is generally zero at or below a Gran ANC of 0 μeq/L and typically increases with ANC to a maximum of about 2,500 g/0.1 ha at and above a Gran ANC of 250–300 μeq/L. They also found that chronic and acute Al_i thresholds (1.0–2.0 μmol/L) correspond to Gran ANC values of approximately 20 to -10 μeq/L.

Decreased pH leads to complexation of DOC with inorganic Al to form nontoxic organic aluminum (Al_o). Thus, low pH and low DOC levels can increase the concentrations of biologically labile Al_i and increase toxicity to resident biota (Baldigo et al. 2019).

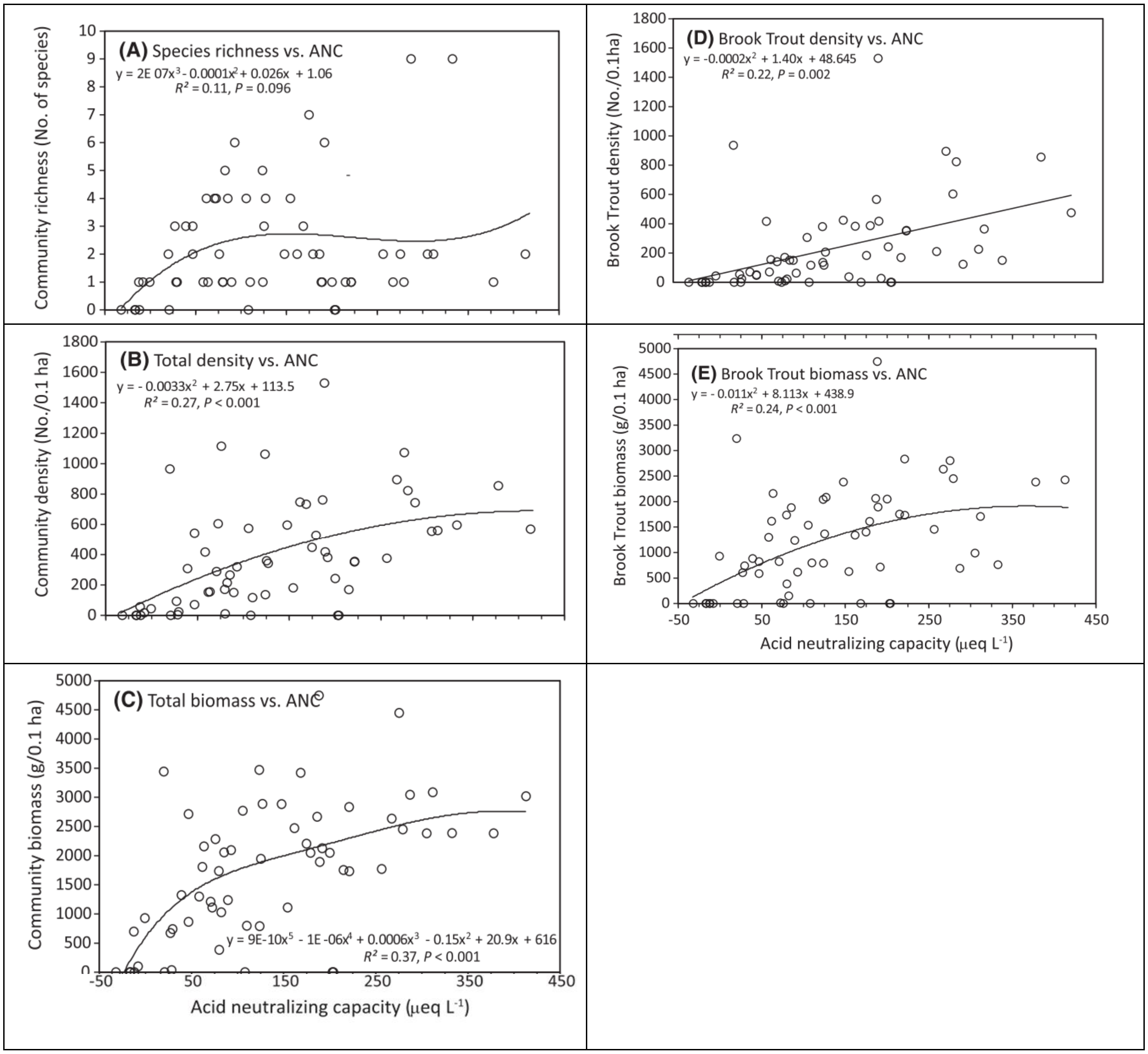

Figure 7.29: Relationships between acid-neutralizing capacity (ANC; μeq/L) and (A) fish community richness, (B) total fish community density, (C) total fish community biomass, (D) density of Brook Trout, and (E) biomass of Brook Trout. Source: Baldigo et al., 2019.

7.2.4.2 Species-specific ANC thresholds for fish

Lien et al. (1996) analyzed the empirical correlation between observed CBANC and the status of various fish species populations (fish data obtained from interview surveys) in 1095 lakes and Atlantic salmon (*Salmo salar*) populations in 30 rivers in Norway. While most of these lakes had sufficient water chemistry data to estimate CBANC, in some lakes with more limited data they used a modified estimate of ANC (based on measured bicarbonate, hydrogen ion, dissolved aluminum and estimated organic anions). They found a strong relationship between fish status and CBANC values, and derived CBANC thresholds for various species (Table 7.21). Atlantic salmon was the fish species most sensitive to low ANC concentrations. According to this study, perch tolerated the lowest ANC –in lakes where perch had disappeared all the other species were also lost.

In general, the results from Lien et al. (1996) showed that lakes with healthy fish populations had higher mean pH, positive calculated CBANC, higher Ca and lower labile Al. Overall, results indicated that in lakes with CBANC < -40 μeq/L, very few fish communities had survived. Lakes with CBANC > 40 μeq/L showed no evidence of reduced fish population levels. At CBANC = 10 μeq/L, several of the species studied showed reductions in their populations of about 25%. The results for Atlantic salmon in the surveyed rivers suggest that no population was affected when the mean CBANC exceeded 20 μeq/L. To put that CBANC value in context, a CBANC of 20 μeq/L would be equivalent to a Gran ANC of -3 μeq/L for an example lake with a charge density of 4.6 μeq/mg of DOC, and a DOC level of 5 mg/L – see definitions in Section 7.2.1. Some Atlantic Salmon populations became extinct at positive ANC, and at CBANC = 0 μeq/L (≈GranANC of -23 μeq/L for the above-described example lake) nearly 50% of the populations had been lost. CBANC values lower than -20 μeq/L (≈GranANC of -43 μeq/L for the above-described example lake)were associated with the extinction of Atlantic salmon in nearly all the rivers.

Table 7.21: Thresholds of CBANC concentration (μeq/l) for different fish species where 25% and 50% of the lakes showed reduced or extinct populations (Source: Lien et al. 1996). The values in parentheses are approximate values due to low sample size.

Fish species	CBANC (μeq/l) at which 25 or 50% of lakes show reduced populations		CBANC (μeq/l) at which 25 or 50% of lakes show extinct populations	
	25%	50%	25%	50%
Atlantic salmon (*Salmo salar*)	10	5	5	0
Brown trout (*Salmo trutta*)	10	0	-10	-20
Arctic char (*Salvelinus alpinus*)	10	-5	-10	-15
Pike (*Esox lucius*)	10	-5	(-15)	(-30)
Minnow (*Phoxinus phoxinus*)	5	-5	-5	-15
Whitefish (*Coregonus lavaretus*)	(-5)	(-10)	(-15)	(-20)
Perch (*Perca fluviatilis*)	-5	-15	-30	-35

The authors proposed Atlantic salmon status as a good indicator of acidification of rivers, and brown trout (the most common fish species found in lakes in Norway) as an indicator for acidification in lakes.

Laudon et al. (2005) also studied the biological effects of acidification on brown trout by experimentally analyzing the effects of spring snow melt events on six streams in northern Sweden that differed in their concentrations of dissolved organic carbon (DOC). The authors studied mortality and physiological responses to declines in pH and found that the index that best separated the response classes in the brown trout populations was the ratio **ANC/H$^+$**. Based on their results, Laudon et al. (2005) identified two ANC/H$^+$ thresholds (Figure 7.30): *ANC/H$^+$ = 5* as a limit for *high* mortality and *ANC/H$^+$ = 20* as a limit for *some* mortality. However, the large of variability in this ratio (note that the y-axis is on a log scale) suggests that it is preferable to use a fixed threshold rather than a ratio for ANC or BCS. As summarized below in Section 7.2.5, most literature recommends a fixed value rather than a ratio for an ANC or BCS threshold.

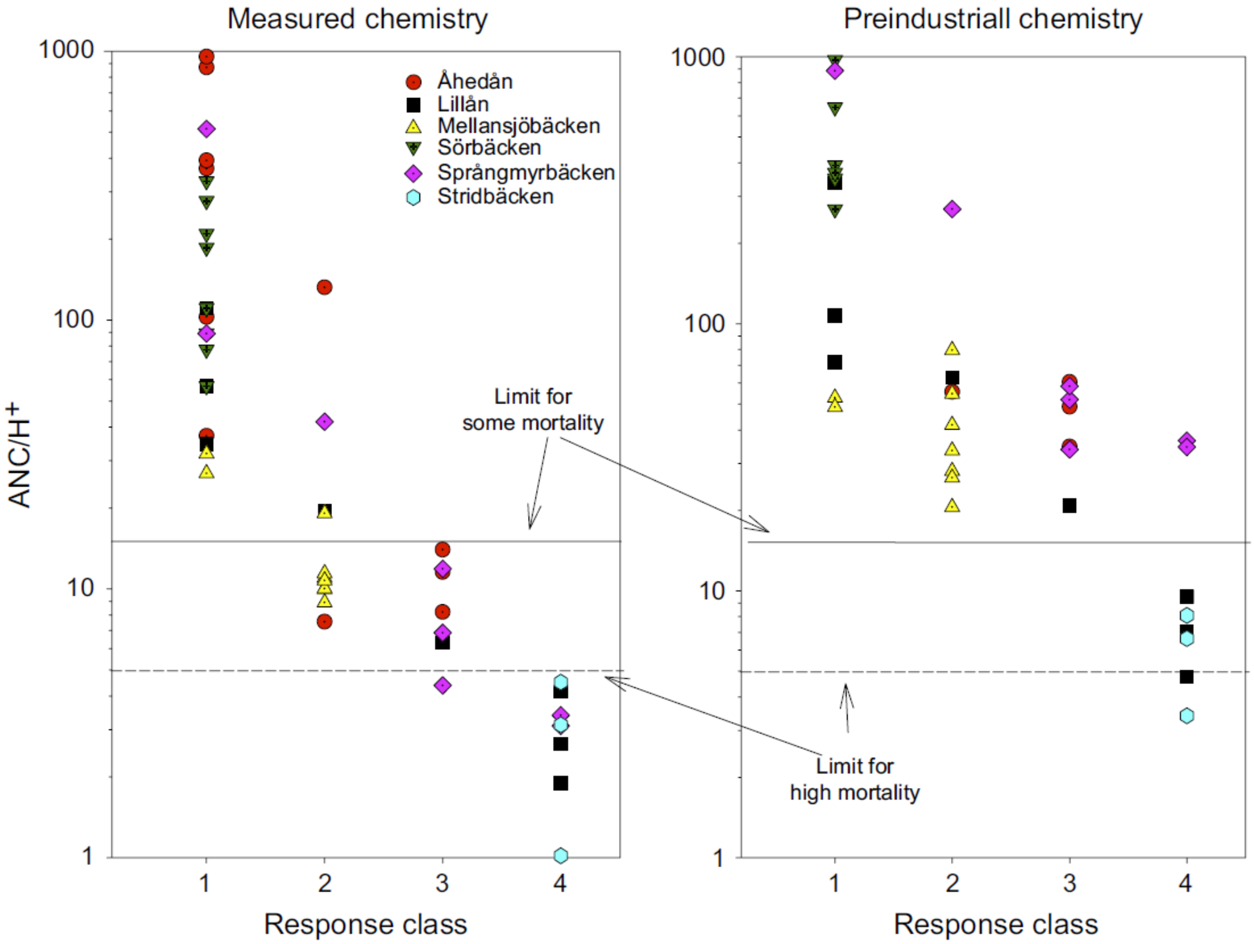

Figure 7.30: Relationship between the response pattern of the experimental fish and the ANC/H$^+$ ratio during spring flood as observed in six study streams (left pane) and predicted for pre-industrial water chemistry at the same locations. The response classes are: 1) no significant response; 2) physiological response without mortality; 3) physiological response with some mortality and 4) high mortality. Each point represents a sample location. Source: Laudon et al. 2005

The results from Laudon et al. (2005) suggest that fish in DOC-rich streams can tolerate higher acidity and inorganic aluminium levels than fish in low DOC streams. These findings are aligned with other studies (Solheim et al. 2008) documenting that fish in humic waters can tolerate higher acidity (lower pH) than fish in clear waters, mostly due to lower toxicity of Al in humic waters. The review on acidification studies by Solheim et al. (2008) found that humic content had a positive effect for most acid-sensitive indicators.

When considering ANC as a predictive variable for the biological effects of acidification, Solheim et al. (2008) highlighted the need to consider that the correlation between ANC and pH is dependent on the TOC level, as acidified humic lakes have lower pH than clear water lakes at the same value of ANC.

A later Norwegian study connecting ANC$_{OAA}$[17] with acidification effects on brown trout populations was conducted by Hesthagen et al. (2016) in the Vikedal watershed, which is recovering from acidification and has seen an increase in brown trout population since the late 1990s. The authors performed a principal component analysis of nine selected chemical variables considered to affect the survival of young brown trout. They found a significant ($R^2 = 0.61$) correlation between ANC$_{OAA}$ and densities of young of year (YoY) brown trout in the streams (Figure 7.31a), and also a significant relationship ($R^2 = 0.55$) between ANC$_{OAA}$ and older parr (Figure 7.31b).

They identified three ranges of BCS values corresponding to three stages in the process of recovery from acidification (Hesthagen et al. 2016): (i) low density with 10-20 specimens per 100 m^2 at an ANC$_{OAA}$ of -18 to -5 μeq/L; (ii) medium and unstable density with 20-30 specimens per 100 m^2 at an ANC$_{OAA}$ of -5 to 10 μeq/L; and (iii) increasing density to 40-50 specimens per 100 m^2 at an ANC$_{OAA}$ of 10-25 μeq/L.

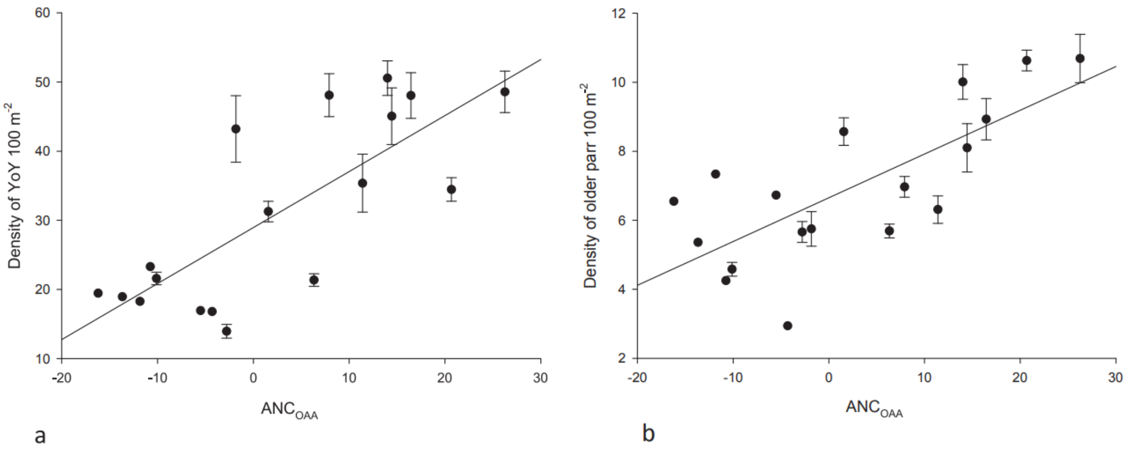

Figure 7.31: Densities 100 m2 ± 95% CL of YoY (a) and older parr (b) of brown trout in the study streams in River Vikedal watershed in relation to ANC$_{OAA}$ between 1987 and 2010. CL limits for 1987-1992 are not available due to one sampling run. Source: Hesthagen et al. 2016

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[17] North American research and literature often uses the term Base Cation Surplus, whereas the convention in European research and literature (which is generally more extensive) has been to apply the term “organic anion adjusted ANC” or ANC$_{OAA}$. These are different terms for the same metric, though the methods of calculation differ slightly among different authors.

In North America, there have been several studies on the effects of acidification on fish species (Baldigo and Lawrence 2001, 2007) in streams in the Adirondack Mountains; an area which was affected by acid rain, especially in the late 1980s, and has been recovering since the late 1990s.

Baldigo and Lawrence (2001) analyzed water quality, physical habitat, and population (density and biomass) data for various fish species from the Neversink River Basin for the period 1991–95. They conducted a regression analysis between population variables and environmental factors and found a strong relation between fish population and acid-related parameters. Specifically, slimy sculpin (*Cottus cognatus*) density ($r^2 = 0.83$; $p \leq 0.1$) and biomass ($r^2 = 0.74$; $p \leq 0.1$) was strongly related to Gran ANC.

This study (Baldigo and Lawrence 2001) did not identify ANC thresholds but found reference pH values for the various fish species: brook trout (*Salvelinus fontinalis*) were observed only at sites where mean pH exceeded 4.77, slimy sculpin at sites where mean pH exceeded 5.26, brown trout (*Salmo trutta*) and longnose dace (*Rhinichthys cataractae*) at sites where mean pH exceeded 5.69, and blacknose dace (*Rhinichthys atratulus*) and Atlantic salmon (*Salmo salar*) at sites where mean pH exceeded 6.36.

A later study by Baldigo et al. (2007) empirically explored the effects of exposure of caged brook trout (*Salvelinus fontinalis*), a member of the char genus *Salvelinus* native to Eastern North America, to acidified streams in the southwestern Adirondack Mountains of New York. This is an area that is geologically susceptible to acidification and has received some of the most acidic deposition in North America. Following the enactment of the Clean Air Act Amendments of 1990, there were significant ANC increases in two of the local streams over the period from 1991 to 2001. This study aimed at comparing the biological responses of brook trout to stream water chemistry in 2001-03, with the responses observed during similar tests conducted in 1984–1985, 1988–1990, and 1997 (Baldigo et al. 2007).

Baldigo et al. (2007) documented daily cumulative mortality of brook trout in six headwater streams, as well as 15-min stream discharge and water chemistry data (pH, Gran ANC, and inorganic monomeric aluminum Al_{im}). . Based on these results, the authors developed regression equations between brook trout mortality at the end of each test and median Al_{im} concentrations during each test. Concentrations of Al_{im} greater than 2.0 and 4.0 µmol/L were closely correlated with low and high mortality rates, respectively, and accounted for 83% of the variation in mortality. Despite reductions in acidic deposition and increases in ANC, they found little difference in stream toxicity to brook trout between the later period and the earlier period. Two to four days of exposure to Al_{im} concentrations greater than 4.0 µmol/L resulted in 50–100% mortality. Critical values of ANC were not identified in this study.

7.2.4.3 Other studies using ANC as an indicator for aquatic biota

In Norway, Raddum and Skjelkvåle (1995) analyzed water quality and aquatic invertebrates from 108 localities. They observed that sensitive species/taxa are associated with high ANC and pH, while tolerant species/taxa are associated with low pH and ANC. The authors also found that in oligotrophic water bodies, such as those found in Norway, sensitive fauna can tolerate lower ANC (CBANC) than in areas with originally high ionic strength and high pH, as in

Central Europe. Raddum and Skjelkvåle (1995) suggest a CBANC threshold of 20 μeq/l for oligotrophic waters with low ionic strength and a critical level of a critical level of 50 μeq/l for waters with higher ionic strength. Further studies based on 10 years of chemical and biological data from various localities in Norway, UK and Ireland confirmed this CBANC critical range from 20 to 50 μeq/l, depending on the type of water chemistry, type of invertebrate fauna and their adaptation to native water chemistry (Raddum and Skjelkvåle 2001).

Another regional study on acidification and its effects on aquatic biota in Norwegian lakes and rivers (Lien et al. 1996) explored the status of invertebrate communities (i.e., zooplankton and benthic invertebrates) from 165 sites in relation to water chemistry. Results from this study indicate that sites with CBANC <10 μeq/L had less diverse invertebrate assemblages than sites with higher ANC values. A CBANC value of -*30 μ*eq/L seems to be a critical threshold for severe impacts since water bodies with CBANC below this value showed a very restricted invertebrate faunal assemblage. No effects on invertebrate diversity were detected at CBANC >*30 μeq/l*. Lien et al. (1996) also observed that, at sites with pH >5.5, invertebrate fauna varied considerably as a function of Ca concentration, but that Ca concentrations had little or no influence on the diversity of fauna at pH < 5.0.

While European countries have quite different assemblages of fish species than Western North America, there's a somewhat greater similarity in invertebrate species, and similar patterns of changes in zooplankton species richness with acidification (Marmorek and Korman 1993). Therefore, thresholds derived in Europe for invertebrate assemblages may be more directly transferable to lakes in the Kitimat Valley than are thresholds derived for fish species. Work by Holt et al. (2003) identified pH 6.0 as a threshold for significant changes in the structure of zooplankton communities in Ontario lakes, which in the STAR was found to correspond to a critical GranANC of 26 μeq/L (calculations of critical ANC to be redone with a larger dataset as part of the Comprehensive Review).

Vinebrooke and Graham 1997explored the use of **periphyton** assemblages as indicators of acidification recovery in acidified Canadian Shield lakes. () They found that DIC (Dissolved Inorganic Carbon), DOC and Al explained more of the variation in periphyton metrics than did ANC; periphyton metrics included rates of biomass accrual (total, filamentous greens, desmids), and species richness. ANC was however helpful in discriminating three species from other clusters of periphyton (Figure 5 in Vinebrooke and Graham 1997). ANC was measured in the field, so likely this was neither GranANC nor CBANC. This study therefore has little relevance to developing ANC thresholds for the EEM program.

7.2.5 Summary of ANC thresholds found in the literature

The ANC thresholds discussed in this literature review correspond to various measurements of ANC (i.e., CBANC, Gran ANC, BCS), different levels of impact (e.g., good population status, some damage to populations, or extinction of population) and different aquatic receptors, from specific fish species to broader taxonomic groups (e.g., invertebrates, general fish population). Table 7.22 shows the range of ANC critical values found in the literature for all these different cases.

The most common ANC measurement reported in the studies is the charge balance or **CBANC** (Figure 7.32). In general, CBANC values over 20 µeq/l are expected to support most aquatic biota. Lien et al. (1996) derived species-specific CBANC critical values for fish species found in Norway and found Atlantic salmon to be the most sensitive species. Because the species analyzed in Lien et al. (1996) are not found in the Kitimat Valley, these thresholds can provide relevant guidance for developing appropriate regional ANC thresholds but do not offer prescriptive thresholds that are directly transferable.

Base Cation Saturation (**BCS**) has also been used as a biological indicator for the effects of acidification. In their study in acidified streams in Northeast America, Baldigo et al. (2009) identified three BCS related to levels of aluminum toxicity (Figure 7.33).

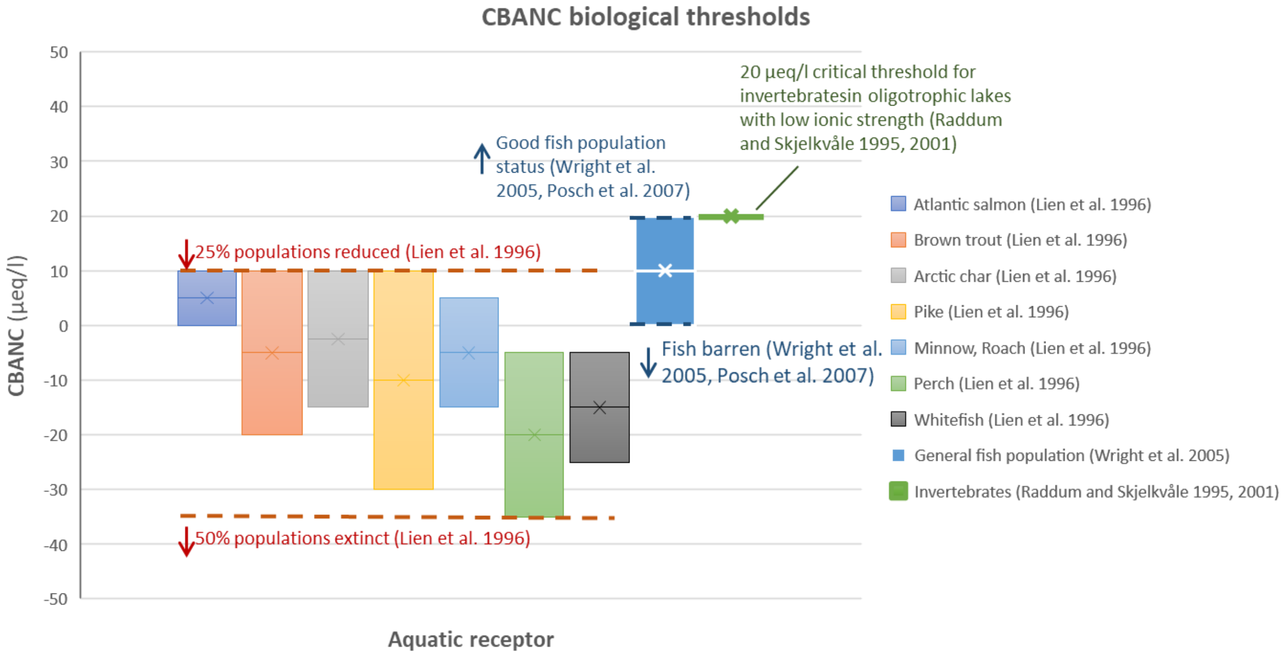


Figure 7.32: CBANC biological thresholds found in the literature

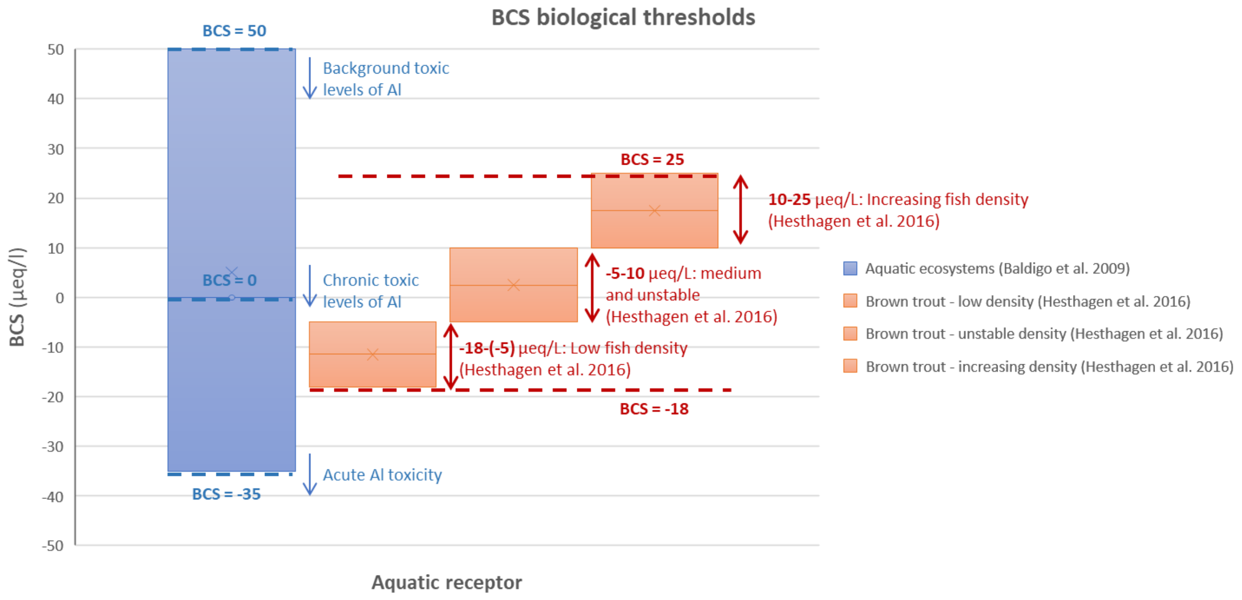


Figure 7.33: Biological thresholds for BCS / ANC_{OAA} found in the literature

Baldigo et al. (2019) recently studied fish communities from 48 streams in the western Adirondacks (NY, USA) in order to assess present-day effects of acidification on fish assemblages and identify biological targets and chemical effect thresholds. They identified ANC biological thresholds in relation to fish biomass density and inorganic Al toxicity levels (Figure 7.34).

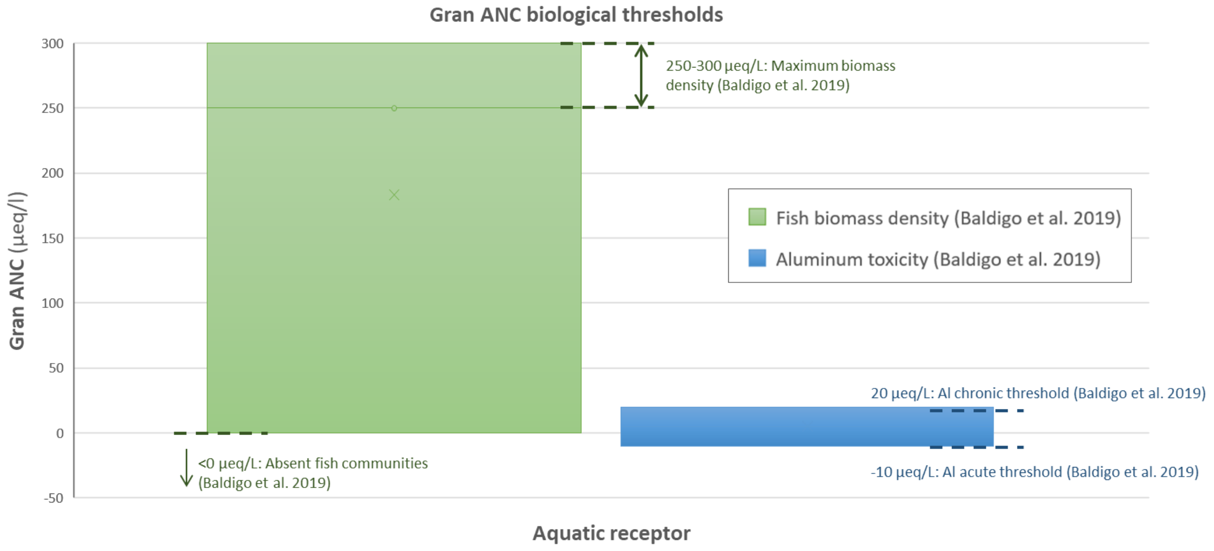


Figure 7.34: Gran ANC biological thresholds for fish biomass and inorganic aluminum toxicity (Source: Baldigo et al. 2019)

Table 7.22: Overview of ANC thresholds found in the literature

Source	Study Location	Indicator of Biological Effect	Chemistry metric	Threshold
Baldigo et al. 2007	Adirondack Mountains (New York, **North America**) – streams	Brook trout - mortality	Inorganic monomeric aluminium (**Al_{im}**) µmol/l	Concentrations of Al_{im} greater than **2.0** and **4.0** µmol/L were closely correlated with low and high mortality rates
Baldigo et al. 2009	Adirondack Mountains (New York, **North America**) – streams	(General) aquatic ecosystems – toxicity due to mobilization of inorganic Al Macroinvertebrate community structure – - **acidBAP**	**BCS** (µeq/l)	BCS values corresponding to Al concentrations • no impact when BCS ≥ 50 • **50**: background toxic level • *slight* impact at BCS between 50 and 0 • **0**: chronic toxic • *moderate* impact at BCS between 0 and -35 • **-35**: acutely toxic • *severe* impact at BCS below -35
Baldigo et al. 2019	Adirondack Mountains (New York, **North America**)	Fish community - biomass	**Gran ANC** (µeq/l)	**0**: no fish **250 – 300**: maximum biomass **-10 to – 20**: acute to chronic Al toxicity
Wright et al. (2005), Kernan et al. (2010)	Europe – lakes and streams	Fish (brown trout but applies to aquatic biota in general) – population status (presence and abundance)	**CBANC** (µeq/l)	CBANC < 0: barren of fish CBANC 0–20: sparse fish population CBANC > 20: good population status
Posch et al. (2007)	Europe - lakes	Fish and invertebrates – damage threshold	**CBANC** (µeq/l)	**20**
Raddum and Skjelkvåle (1995, 2001)	Norway – surface water	Invertebrates - Abundance	**CBANC** (µeq/l)	**20**: oligotrophic waters (Norway) **50**: waters with high ionic strength (Central Europe)
Lien et al. (1996)	Norway – 1095 lakes and 30 rivers	Atlantic salmon, brown trout, Arctic char, pike, minnow, whitefish and perch - Fish population status (reduced and extinct)	**CBANC** (µeq/l)	Atlantic salmon[1]: **5/0** Brown trout: **0/-20** Arctic char: **-5/-15** Pike: **-5/-30** Minnow: **-5/-15** Whitefish: **-10/-20** Perch: **-15/-35**
Laudon et al. (2005)	Sweden – streams (effect of spring melt)	Brown trout – Physiological responses and mortality (4 classes from no response to high mortality)	**ANC/H+**	**5**: high mortality **20**: some mortality
Hesthagen et al. 2016	Norway	Brown trout – Population density; YoY (age 0+) and older parr (age ≥1+)	**ANC_{OAA}** (µeq/l)	**-18** to **-5**: low density **-5** to **10**: medium and unstable density **10** to **25**: increasing density

7.2.6 Recommendations for ANC Thresholds

The recommendations resulting from this literature review are described and discussed in the Aquatic Ecosystems chapter (i.e., Section 7 of the SO_2 EEM 2019 Comprehensive Review report).

7.2.7 Literature cited

Baker, J.P., D.P. Bernard, S.W. Christensen, M.J. Sale, J. Freda, K. Heltcher, D. Marmorek, L. Rowe, P. Scanlon, G. Suter, W. Warren-Hicks, and P. Welbourn. 1990. Biological Effects of changes in surface water acid-base chemistry. NAPAP Report 13. In: National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology. Volume II, 1990.

Baldigo B.P. and G.B. Lawrence. 2001. Effects of stream acidification and habitat on fish populations of a North American river. *Aquat.sci.* 63: 196–222

Baldigo B.P., G.B. Lawrence and H. Simonin. 2007. Persistent Mortality of Brook Trout in Episodically Acidified Streams of the Southwestern Adirondack Mountains, New York. *Transactions of the American Fisheries Society* 136: 121–134

Baldigo B.P., G.B. Lawrence, R.W. Bode, H.A. Simonin, K.M. Roy, A.J. Smith. 2009. Impacts of acidification on macroinvertebrate communities in streams of the western Adirondack Mountains, New York, USA. *Ecological Indicators* 9: 226–239

Baldigo B.P., S.D. George, G.B. Lawrence, and E.A. Paul. 2019. Acidification Impacts and Goals for Gauging Recovery of Brook Trout Populations and Fish Communities in Streams of the Western Adirondack Mountains, New York, USA. *Transactions of the American Fisheries Society* 148: 373–392

Baron J.S, C.T. Driscoll, J.L. Stoddard, and E.E. Richer. 2011. Empirical Critical Loads of Atmospheric Nitrogen Deposition for Nutrient Enrichment and Acidification of Sensitive US Lakes. *BioScience* 61: 602–613

Bennett, S. and C.J. Perrin. 2018. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lakes in 2017. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 49pp. plus appendices.

Burns, D.A., Riva-Murray, K., Bode, R.W., Passy, S., 2008. Changes in stream chemistry and biology in response to reduced levels of acid deposition during 1987–2003 in the Neversink River Basin Catskill Mountains. Ecological Indicators 8 (3), 191–203.

Driscoll, C.T., M.D. Kehtinen and T.J. Sullivan. 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. *Water Res. Research*. 30 (2): 297-306.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants, and University of Illinois. 2013. Sulphur Dioxide Technical

Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Volume 2: Final Technical Report. Prepared for Rio Tinto Alcan, Kitimat, B.C. pp.

Groffman P.M, J.S. Baron, T. Blett, A.J. Gold, I. Goodman, L.H. Gunderson, B.M. Levinson, M.A. Palmer, H.W. Paerl, G.D. Peterson, N. LeRoy Poff, D.W. Rejeski, J.F. Reynolds, M.G. Turner, K.C. Weathers, and J. Wiens. 2006. Ecological Thresholds: The Key to Successful Environmental Management or an Important Concept with No Practical Application? *Ecosystems* 9: 1–13

Hemond, H.F. 1990. Acid neutralizing capacity, alkalinity, and acid.base status of natural waters containing organic acids. Environ. Sci. Technol. 24: 1486.1489.

Henriksen A, Skjelkvåle BL, Mannio J, Wilander A, Harriman R, Curtis C, Jensen JP, Fjeld E, Moiseenko T. 1998. Northern European lake survey, 1995. Finland, Norway, Sweden, Denmark, Russian Kola, Russian Karelia, Scotland and Wales. *Ambio* 27:80–91

Hesthagen T., P. Fiske, and R. Saksgård. 2016. Recovery of young brown trout (Salmo trutta) in acidified streams: What are the critical values for acid-neutralizing capacity? *Atmospheric Environment* 146: 236-244

Holt, C.A., N.D. Yan, and K.M. Somers. 2003. pH 6 as the threshold to use in critical load modeling for zooplankton community change with acidification in lakes of south-central Ontario: accounting for morphometry and geography. Canadian Journal of Fisheries and Aquatic Sciences 60:151-158.

Kernan, M., R.W. Battarbee, C.J. Curtis, D.T. Monteith and E.M. Shilland (Eds.). 2010. Recovery of lakes and streams in the UK from the effects of acid rain. UK Acid Waters Monitoring Network 20 Year Interpretative Report.

Laudon H, Antonio B.S. Poleo, L.A. Vøllestad, and K. Bishop. 2005. Survival of brown trout during spring flood in DOC-rich streams in northern Sweden: the effect of present acid deposition and modelled pre-industrial water quality. *Environmental Pollution* 135: 121–130

Lawrence, G. B.; Sutherland, J. W.; Boylen, C. W.; Nierzwicki-Bauer, S. A.; Momen, B.; Baldigo, B. P.; Simonin, H. A. Acid rain effects on aluminum mobilization clarified by inclusion of strong organic acids. Environ. Sci. Technol. 2007, 41 (1), 93−98.

Lawrence, G.B., J. E. Dukett, N. Houck, P. Snyder, and S. Capone. 2013. Increases in dissolved organic carbon accelerate loss of toxic Al in Adirondack lakes recovering from acidification. Environ. Sci. Technol. 2013, 47, 7095−7100. Dx.doi.org/10.1021/es4004763

Lien L., G.G. Raddum, A. Fjellheim, and A. Henriksen. 1996. A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. *The Science of the Total Environment* 177: 173-193

Limnotek. 2016. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of water and aquatic Biota in 2015. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 66p.

Lydersen, E., T. Larssen, E. Fjeld. 2004. The influence of total organic carbon (TOC) on the relationship between acid neutralizing capacity (ANC) and fish status in Norwegian lakes. *Science of the Total Environment* 326 (2004) 63–69. Doi:10.1016/j.scitotenv.2003.12.005

Marmorek, D.R. and J. Korman. 1993. The use of zooplankton in a biomonitoring program to detect lake acidification and recovery. Water, Air, and Soil Pollution 69: 223-241.

Marmorek, D.R., R.M. MacQueen, C.H.R. Wedeles, J. Korman, P.J. Blancher, and D.K. McNicol. 1996. Improving pH and alkalinity estimates for regional-scale acidification models: incorporation of dissolved organic carbon. Canadian Journal of Fisheries and Aquatic Sciences 53: 1602-1608.

Oliver, B.G., E.M. Thurman, and R.L., Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim*. Acta 47, 2031.

Olson, E.L., C.L. Murray, D.M. Abraham, D.R. Marmorek, and A.W. Hall. 2015. Eulachon in the Kemano River and Nearby Rivers: A Literature Review. Prepared for Rio Tinto Alcan (Kitimat, BC) and Haisla Nation Council (Kitamaat Village, BC). Prepared by ESSA Technologies Ltd. (Vancouver, BC). pp.

Parkinson, Eric A., Chris J. Perrin, Daniel Ramos-Espinoza, and Eric B. Taylor. 2016. Evidence for freshwater residualism in Coho Salmon, Oncorhynchus kisutch, from a watershed on the north coast of British Columbia. Canadian Field-Naturalist 130(4): 336–343.

Perrin, C.J., E. Parkinson and S. Bennett 2013. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of water and aquatic Biota in 2013. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 41p.

Posch M., Eggenberger U., Kurz D., Rihm B. 2007: Critical Loads of Acidity for Alpine Lakes. A weathering rate calculation model and the generalized First-order Acidity Balance (FAB) model applied to Alpine lake catchments. Environmental studies no. 0709. Federal Office for the Environment, Berne. 69 S.

Raddum, G. G.; Skjelkvåle, B. L. Critical limits of acidification to invertebrates in different regions of Europe. Water, Air, Soil Pollut. 1995, 85, 475–480.

Solheim A.L., S. Rekolainen, S.J. Moe, L. Carvalho, G. Phillips, R. Ptacnik, W.E. Penning, L.G. Toth, C. O'Toole, A.L. Schartau and T. Hesthagen. 2008. Ecological threshold responses in European lakes and their applicability for the Water Framework Directive (WFD) implementation: synthesis of lakes results from the REBECCA project. *Aquat Ecol* 42:317–334

Vinebrooke R.D and M.D. Graham. 1997. Periphyton assemblages as indicators of recovery in acidified Canadian Shield lakes. *Can. J. Fish. Aquat. Sci*. 54: 1557–1568

Richard F. Wright, Thorjørn Larssen, Lluis Camarero, Bernard J. Cosby, Robert C. Ferrier, Rachel Helliwell, Martin Forsius, Alan Jenkins, Jiri Kopáěek, Vladimir Majer, Filip Moldan, Maximilian Posch, Michela Rogora, and Wolfgang Schöpp. 2005. Recovery of Acidified European Surface Waters. *Environ. Sci. Technol*. 2005 393: 64A-72A

UNECE (ed). 2004. Manual on methodologies and criteria for Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends. Convention on Long-range Transboundary Air Pollution. Umweltbundesamt Berlin, UBA Texte 52/04, distributed at http://www.icpmapping.org

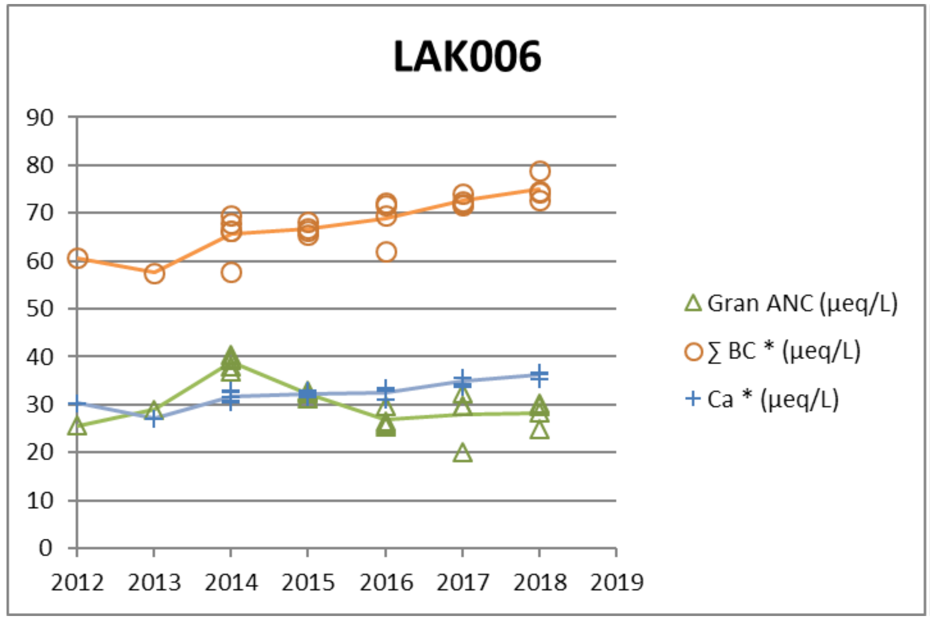
7.2.8 Articles overview

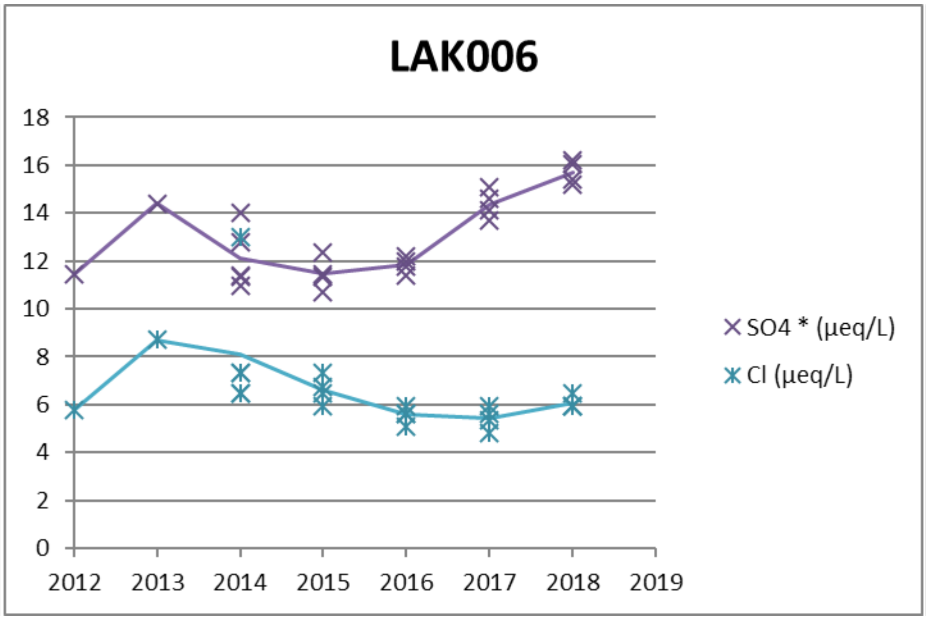
Citation	Summary	Relevance
Lien et al. 1996	Analysis of status of fish and invertebrate populations in Norway in the context of surface water acidification. Critical levels of ANC are proposed for various species.	High
Baron et al. 2011	Determination of critical for N deposition for headwater lakes in regions of the United States where the primary environmental impacts come from N deposition and climate change.	Medium
Vinebrooke and Graham 1997	Survey of acidified shield lakes (Canada) to assess periphyton assemblages as indicators of natural recovery. Regression analyses showed that DIC (dissolved inorganic carbon) and DOC (dissolved organic carbon) were the only significant predictors of periphyton abundance (biomass)	Low
Hesthagen et al. 2016	Studied the recovery of recovery of young allopatric brown trout (*Salmo trutta*) in acid-sensitive streams in a Norwegian watershed. Their densities correlated significantly with ANC_{OAA}, and at least three stages in the recovery process were recognised.	Medium
Houle et al. 2006	ANC is highly predictable ($r^2 = 0.75$) based on the size of the exchangeable Ca^{2+} reservoir in soil in 21 catchments representative of soil and lake conditions encountered in northeastern North America (Quebec)	Low
Burns et al. 2008	Study to document the extent of biological recovery within the Neversink River watershed since the 1980s. Statistical comparisons of data on stream chemistry and an acid biological assessment profile (Acid BAP) derived from invertebrate data showed no significant differences between the two years (1987 and 2003)	Low
Driscoll et al. 2001	Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. This paper analyzes the state of knowledge on acidification and ecosystems recovery in response to emissions reduction.	Medium
Groffman et al. 2006	This paper discusses methods for identifying and investigating thresholds using a variety of examples from terrestrial and aquatic environments, at ecosystem, landscape and regional scales.	Low
Laudon et al. 2005	Mortality and physiological responses in brown trout (*Salmo trutta*) were studied during spring snow melt in six streams in northern Sweden that differed in concentrations of dissolved organic carbon (DOC) and pH declines. The results suggest that fish in these systems can tolerate higher acidity and inorganic aluminium levels than fish in low DOC streams.	Medium
Solheim et al. 2008	This paper presents the main conclusions from the work on lakes in the REBECCA project. Reports on previous work on the use of ANC as threshold for aquatic organisms	Medium
Lydersen et al. 2004	The authors propose a propose a modified ANC calculation where the permanent anionic charge of the organic acids is assumed as a part of the strong acid anions.	High
Baldigo and Lawrence 2001	Study of water quality, physical habitat, and fisheries at sixteen reaches in the Neversink River Basin (1991–95) to identify the effects of acidic precipitation. Regression analyses revealed strong relations ($r^2 \pm 0.41$ to 0.99; $p \leq 0.05$) between characteristics of the two most common species (brook trout and slimy sculpin) populations and ANC, among other water chemistry parameters.	High
Baldigo and Lawrence 2007	Water chemistry, discharge, and mortality of caged brook trout Salvelinus fontinalis were characterized in six headwater streams in the southwestern Adirondack Mountains of New York during spring 2001–2003. Results were compared with mortality recorded during similar tests during 1984–1985, 1988–1990, and 1997. Concentrations of Alim greater than 2.0 and 4.0 lmol/L were closely correlated with low and high mortality rates, respectively, and accounted for 83% of the variation in mortality. Two to four days of exposure to Alim concentrations greater than 4.0 lmol/L resulted in 50–100% mortality.	High
Baldigo et al. 2009	As part of the Western Adirondack Stream Survey, water chemistry from 200 streams was sampled five times and macroinvertebrate communities were surveyed once from a subset of 36 streams in the Oswegatchie and Black River Basins during 2003–2005 and evaluated to: (a) document the effects that chronic and episodic acidification have on macroinvertebrate communities across the region, (b) define the relations between acidification and the health of affected species assemblages, and (c) assess indicators and thresholds of biological effects.	High
Baldigo et al. 2019	The authors characterized fish communities at 48 streams in the western Adirondacks (NY, USA) to assess present-day effects of acidification on fish assemblages, refine important relations, and identify biological targets and chemical effect thresholds that could help gauge biological recovery across the region	High

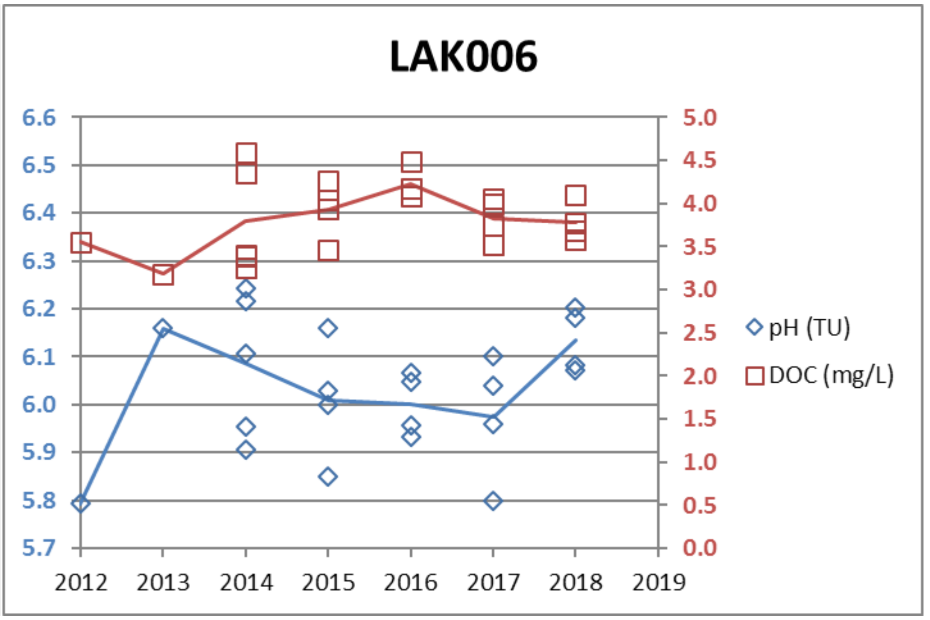
7.3 Aquatic Appendix C: Changes in Ion Concentrations from 2012 to 2018

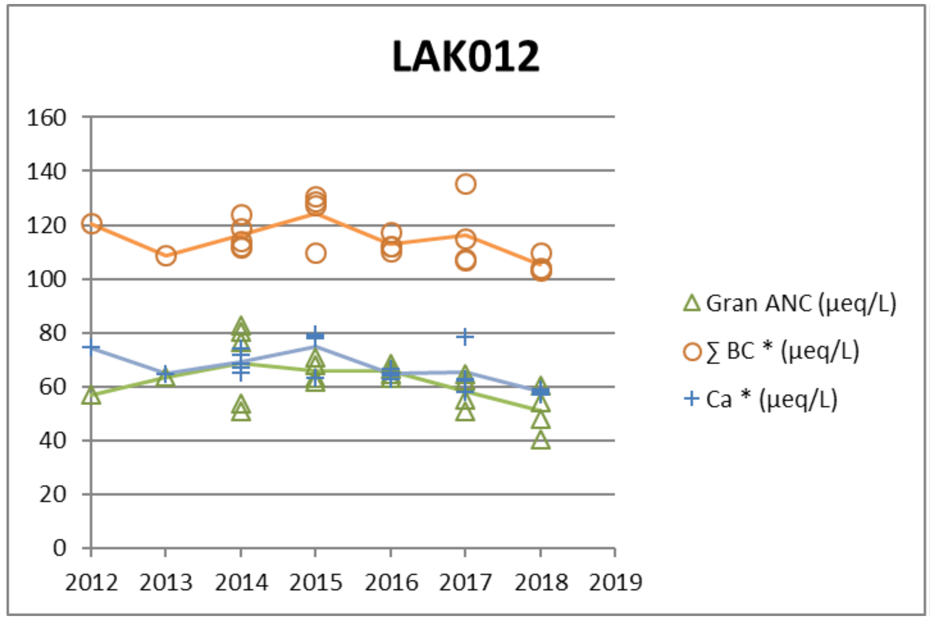
For each of the EEM lakes, the figures in this appendix show the inter-annual changes in six major water chemistry metrics from 2012 to 2018: Gran ANC, base cations and calcium (left panel), sulfate and chloride (centre panel), and pH and dissolved organic carbon (right panel). The selection of each pair of metrics is solely based on optimizing graphical representation across all metrics and lakes (i.e., metrics with somewhat similar numeric ranges are shown together). The right panel has two Y-axes, neither of which start at zero – be aware that this can make relatively minor changes appear to be much more substantial than they are. Due to large variation among the lakes for some of the metrics, the Y-axis is not consistent across the lakes, therefore extra caution is required for making comparisons among lakes with respect to the magnitude of changes. However, these graphs are especially useful for looking at the patterns of changes across the sampling record and determining whether similar patterns are observed across lakes and/or metrics.

7.3.1 Sensitive Lakes





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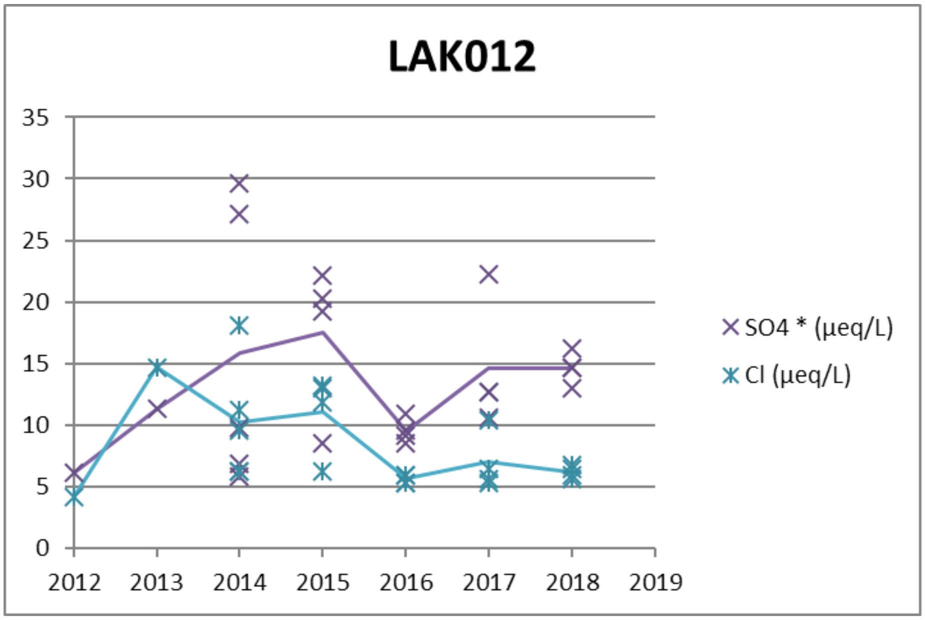
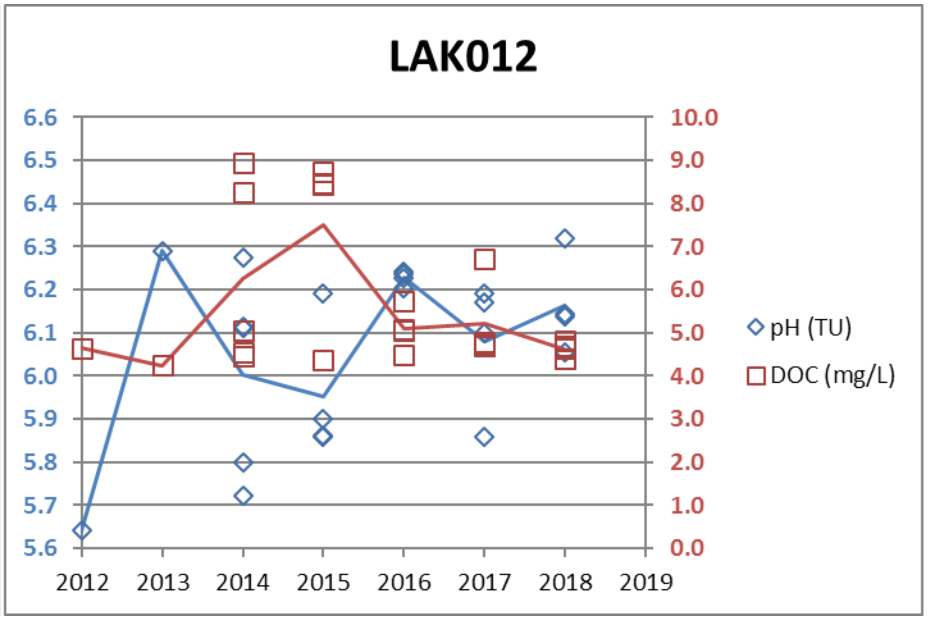
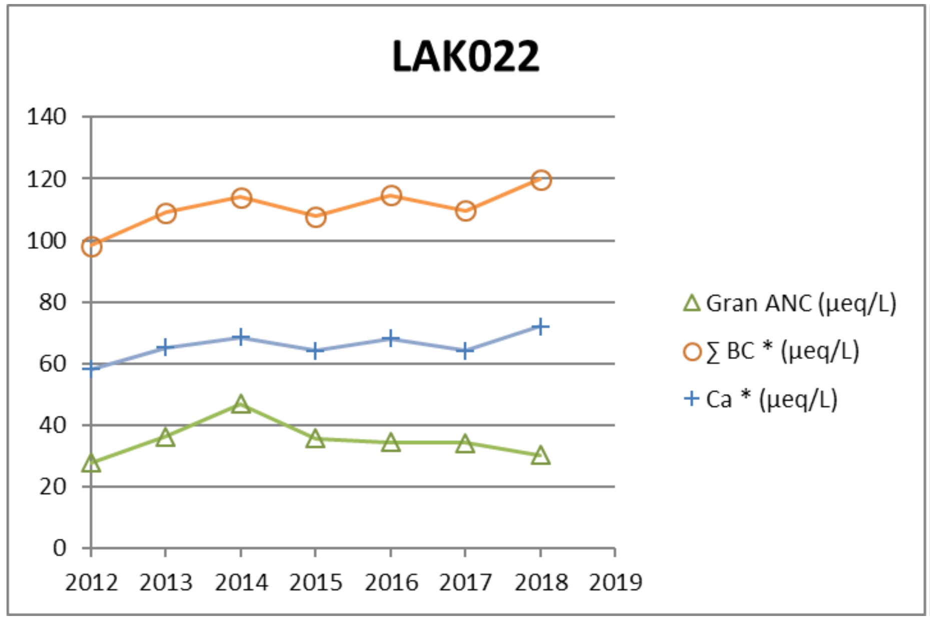
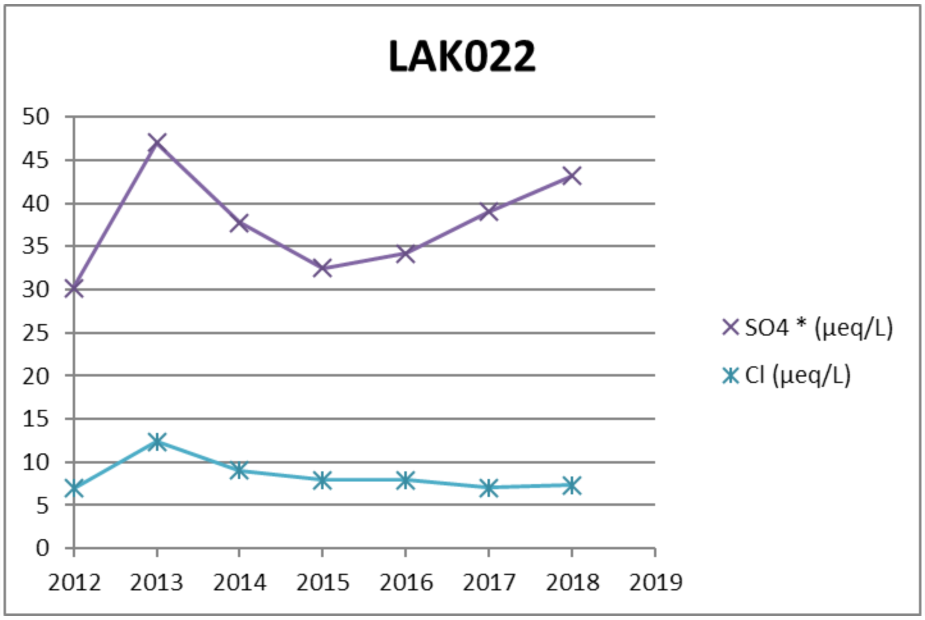
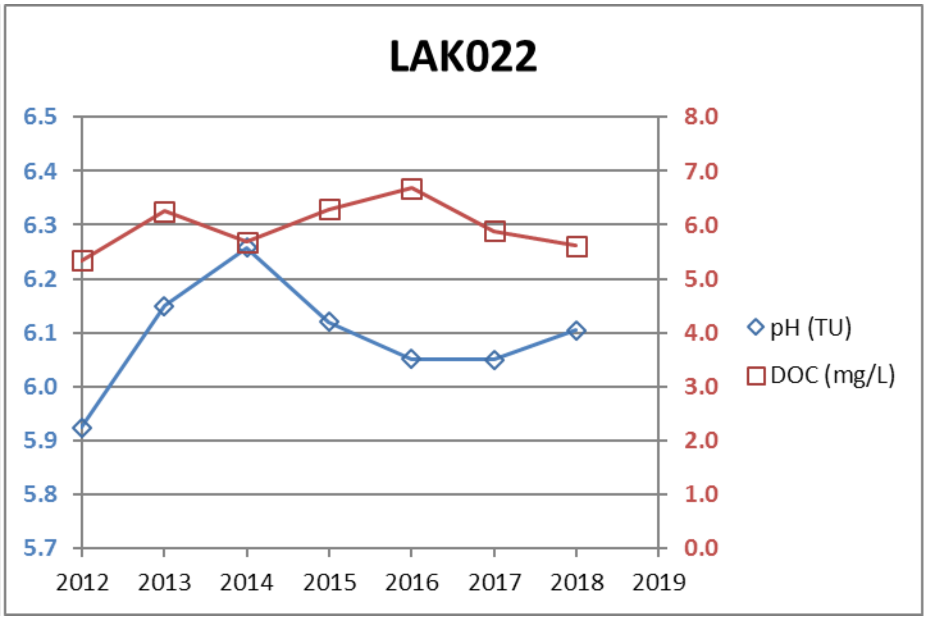
80
60
40
20
0
2012 2013 2014 2015 2016 2017 2018 2019
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

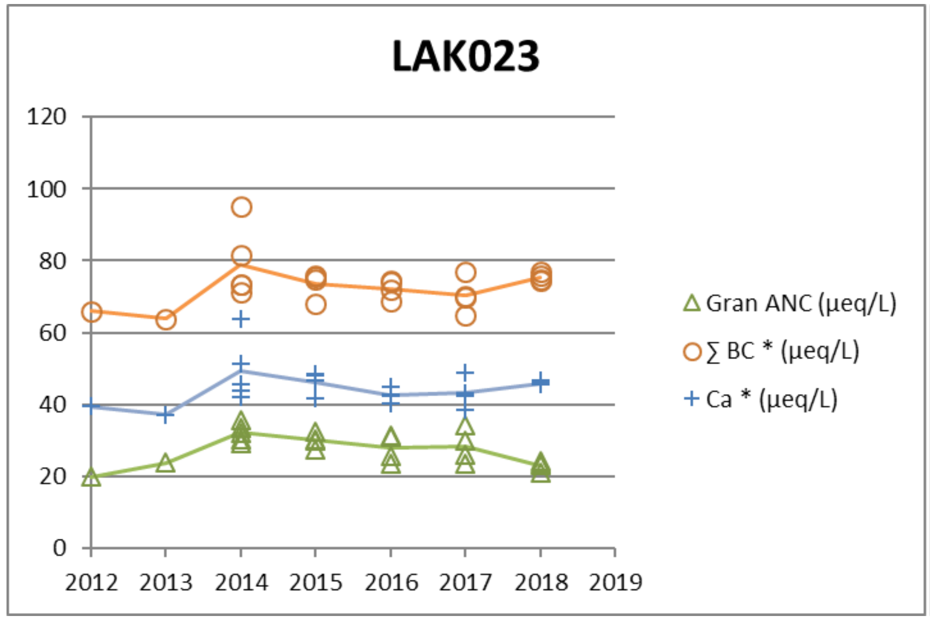

LAK012
35
30
25
20
15
10
5
0
2012 2013 2014 2015 2016 2017 2018 2019
× SO4 * (µeq/L)
✳ Cl (µeq/L)

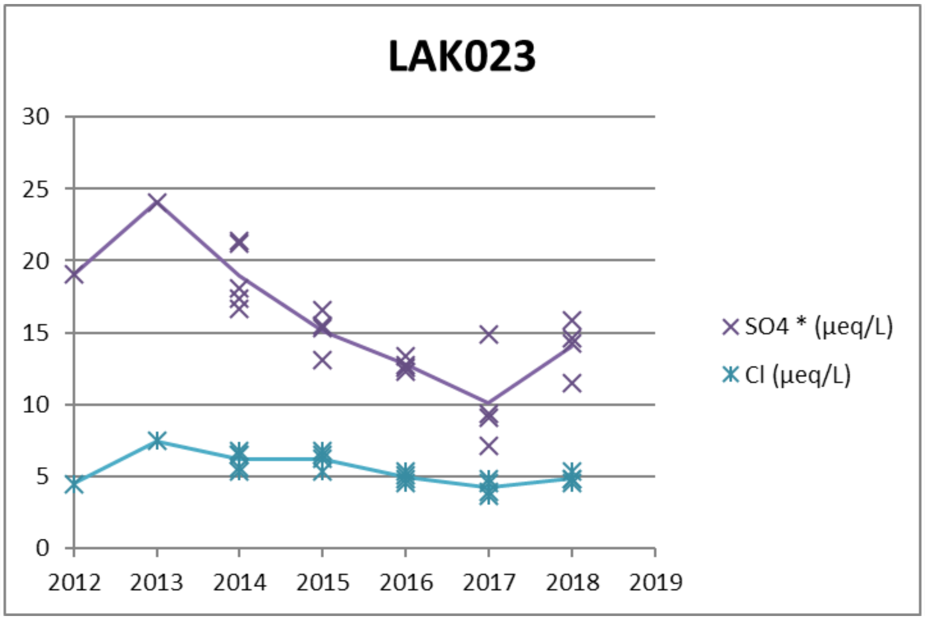

LAK012
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012 2013 2014 2015 2016 2017 2018 2019
◇ pH (TU)
□ DOC (mg/L)

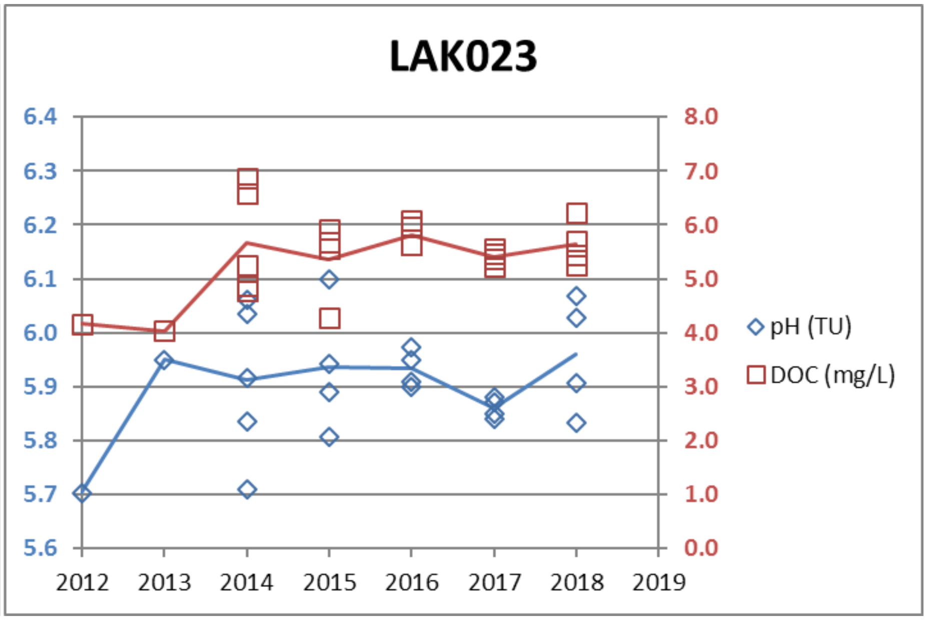

LAK022
140
120
100
80
60
40
20
0
2012 2013 2014 2015 2016 2017 2018 2019
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

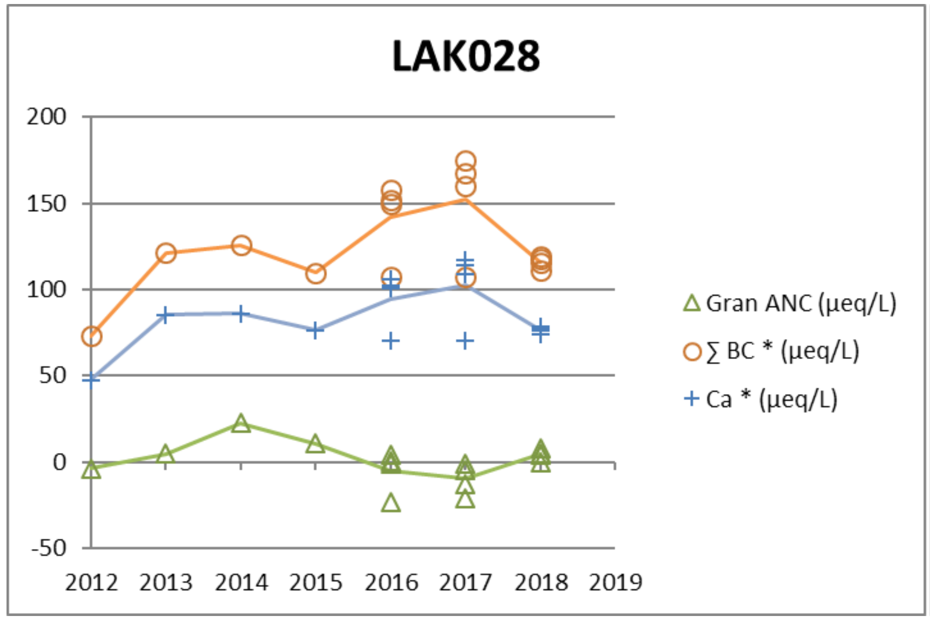

LAK022
50
45
40
35
30
25
20
15
10
5
0
2012 2013 2014 2015 2016 2017 2018 2019
× SO4 * (µeq/L)
✳ Cl (µeq/L)

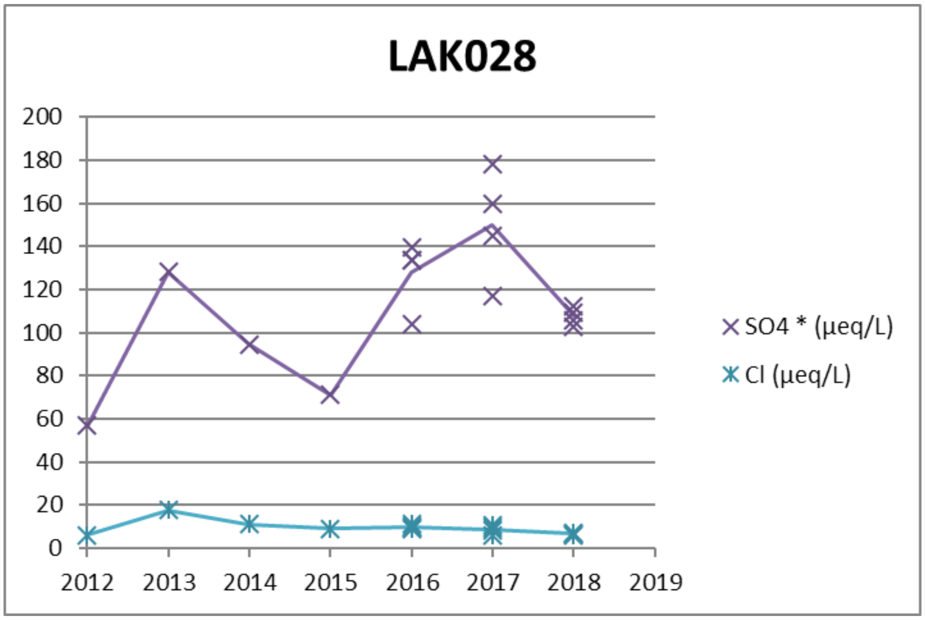

LAK022
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012 2013 2014 2015 2016 2017 2018 2019
◇ pH (TU)
□ DOC (mg/L)

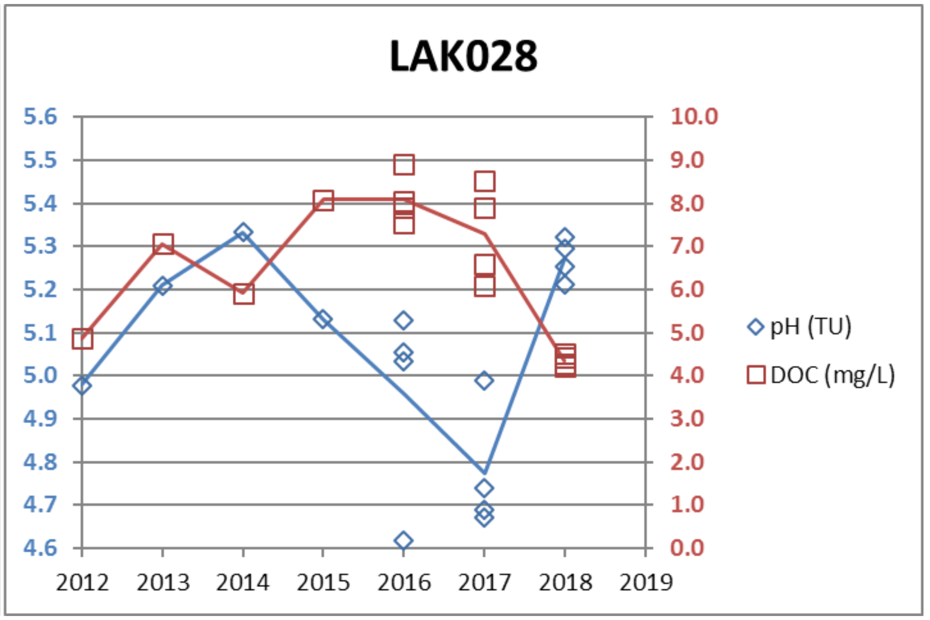

LAK023
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
2018
2019
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

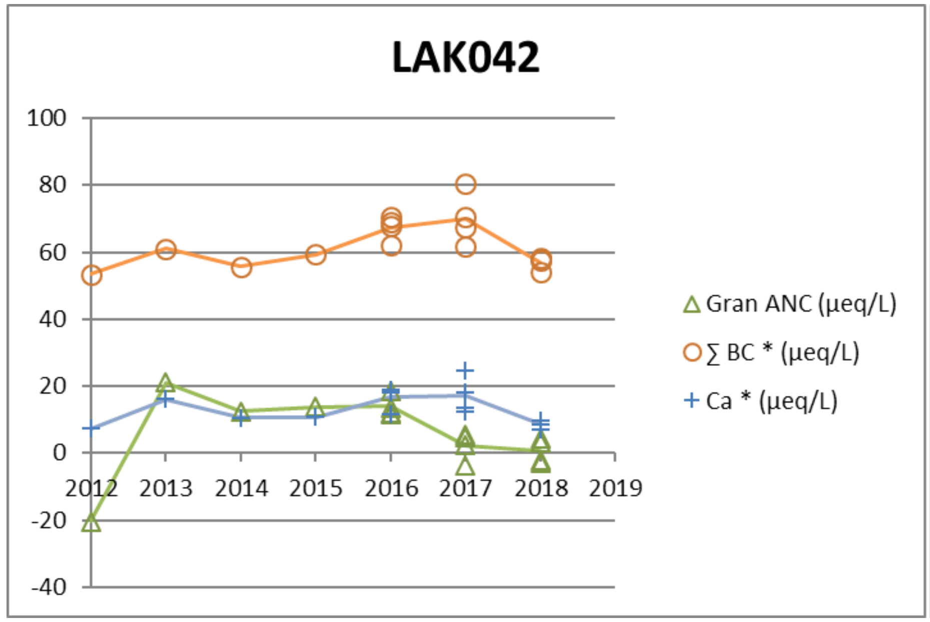

LAK023
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
2018
2019
× SO4 * (µeq/L)
✳ Cl (µeq/L)

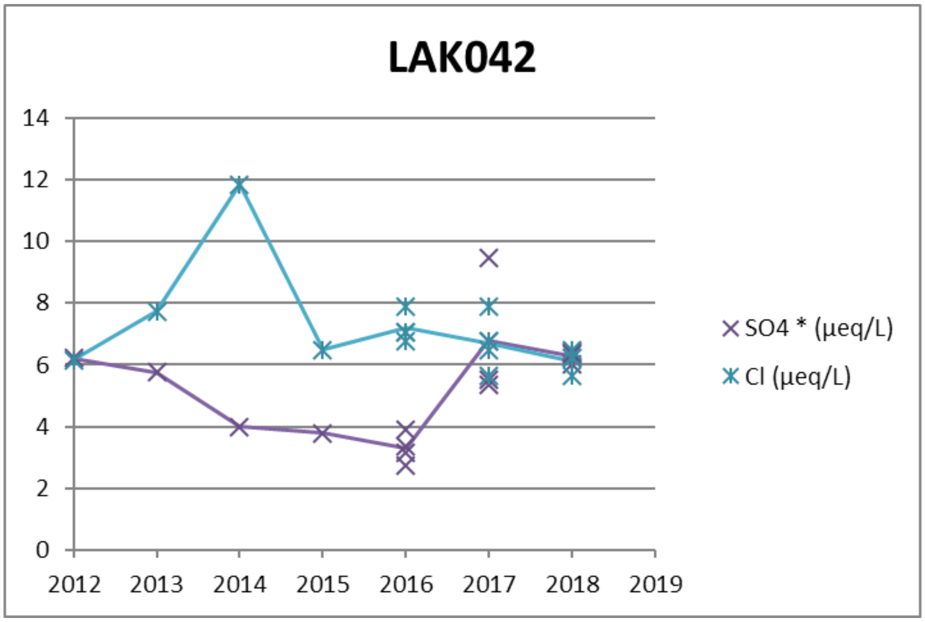

LAK023
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
2018
2019
◇ pH (TU)
□ DOC (mg/L)

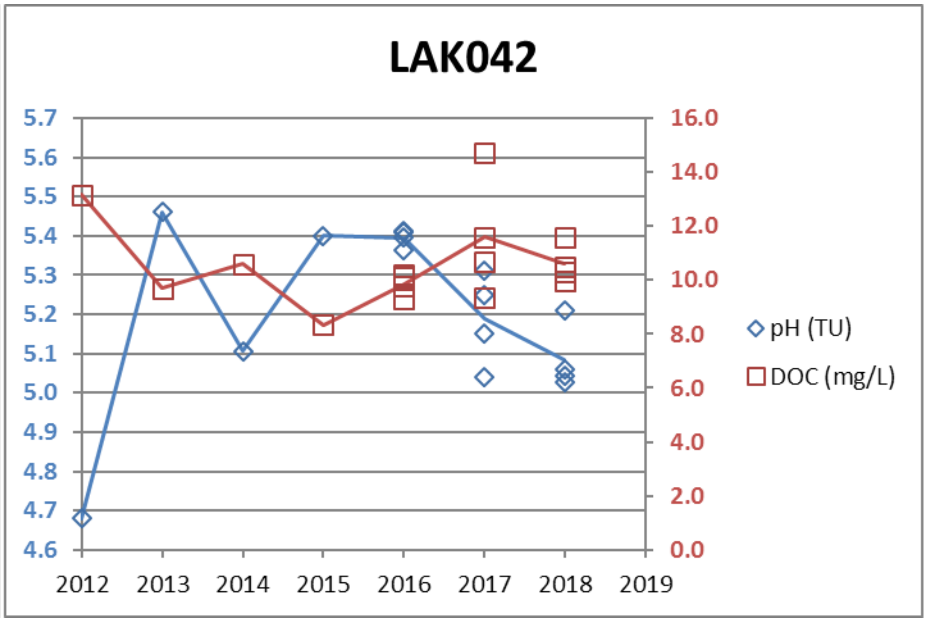

LAK028
200
150
100
50
0
-50
2012
2013
2014
2015
2016
2017
2018
2019
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

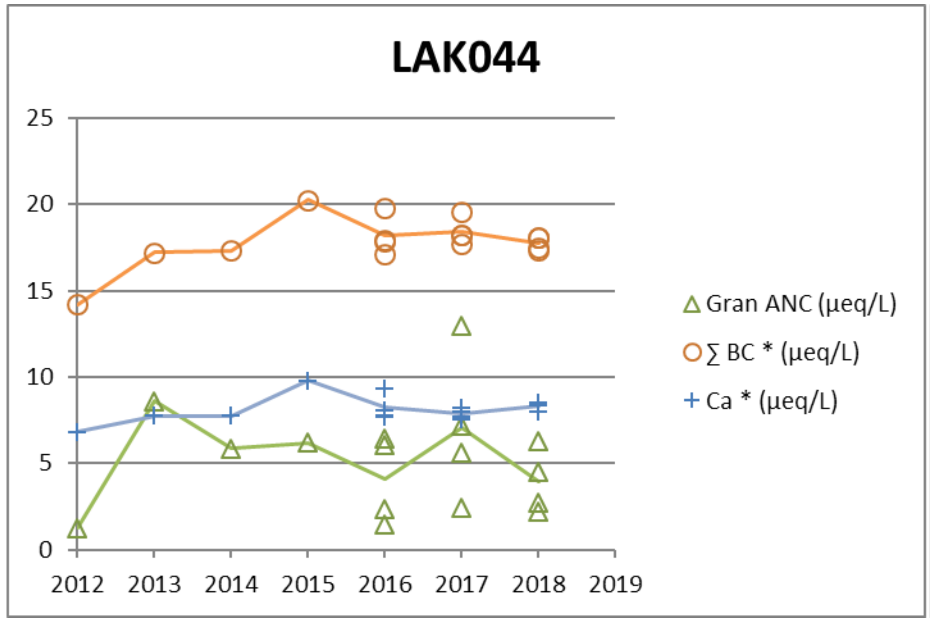

LAK028
200
180
160
140
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
2018
2019
× SO4 * (µeq/L)
✳ Cl (µeq/L)

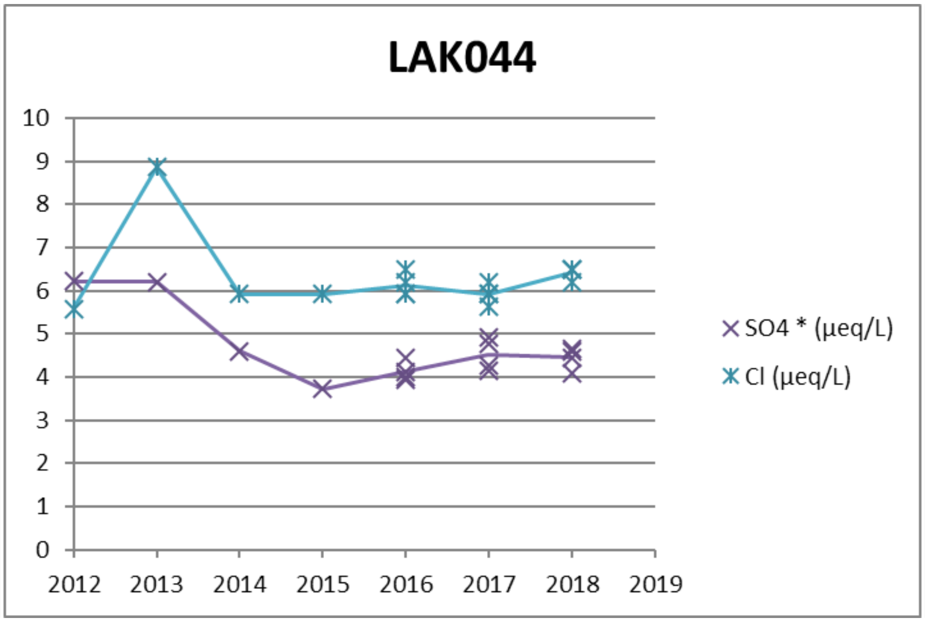

LAK028
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
2018
2019
◇ pH (TU)
□ DOC (mg/L)

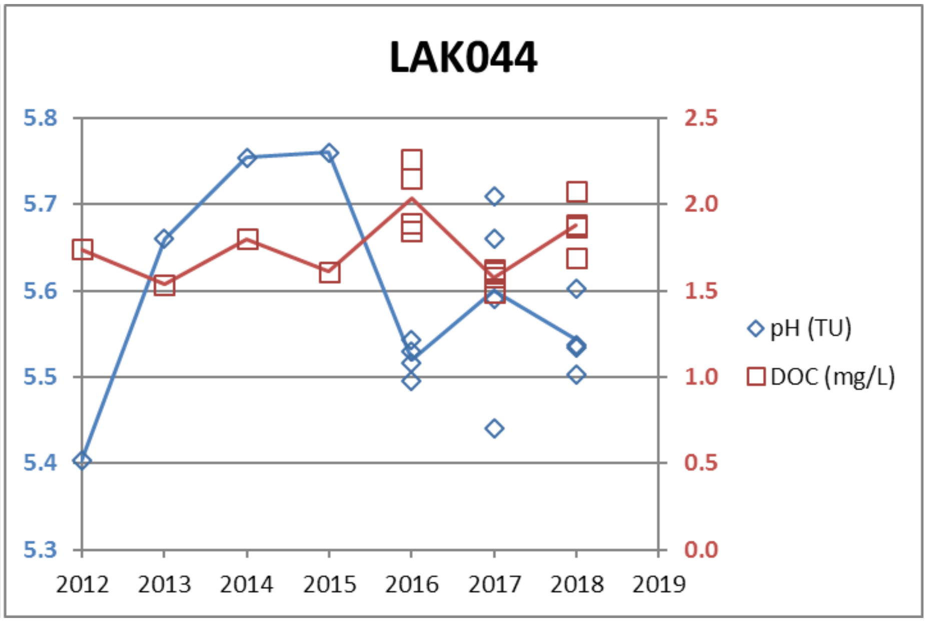

LAK042
100
80
60
40
20
0
-20
-40
2012
2013
2014
2015
2016
2017
2018
2019
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)


LAK042
14
12
10
8
6
4
2
0
2012
2013
2014
2015
2016
2017
2018
2019
× SO4 * (µeq/L)
⋇ Cl (µeq/L)

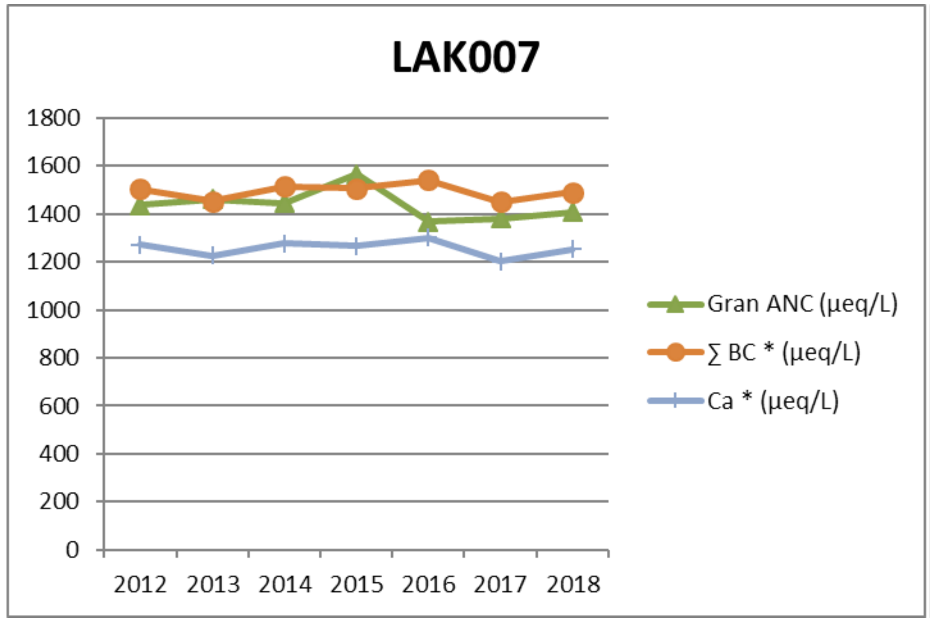

LAK042
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2012
2013
2014
2015
2016
2017
2018
2019
◇ pH (TU)
□ DOC (mg/L)

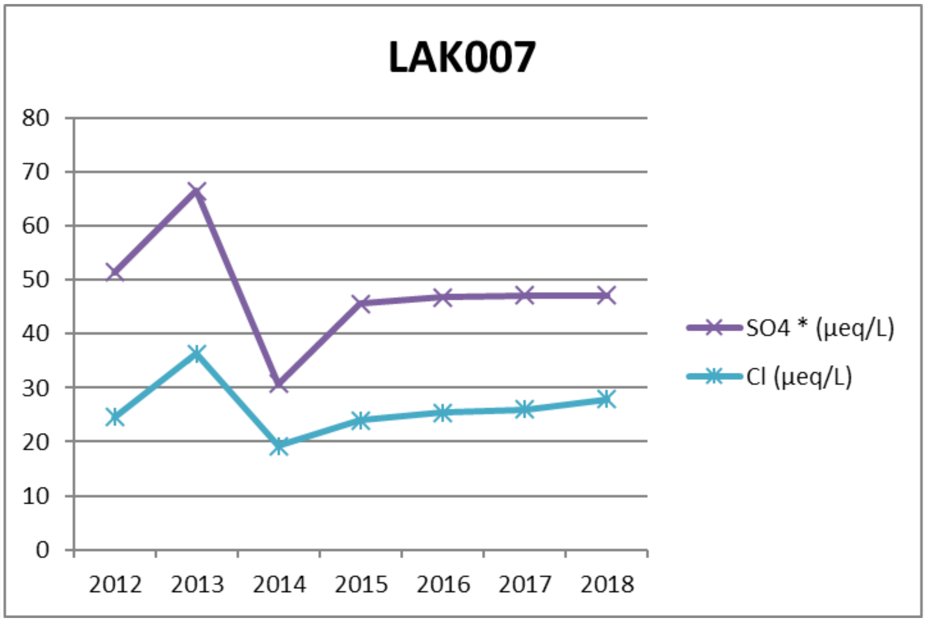

LAK044
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
2018
2019
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

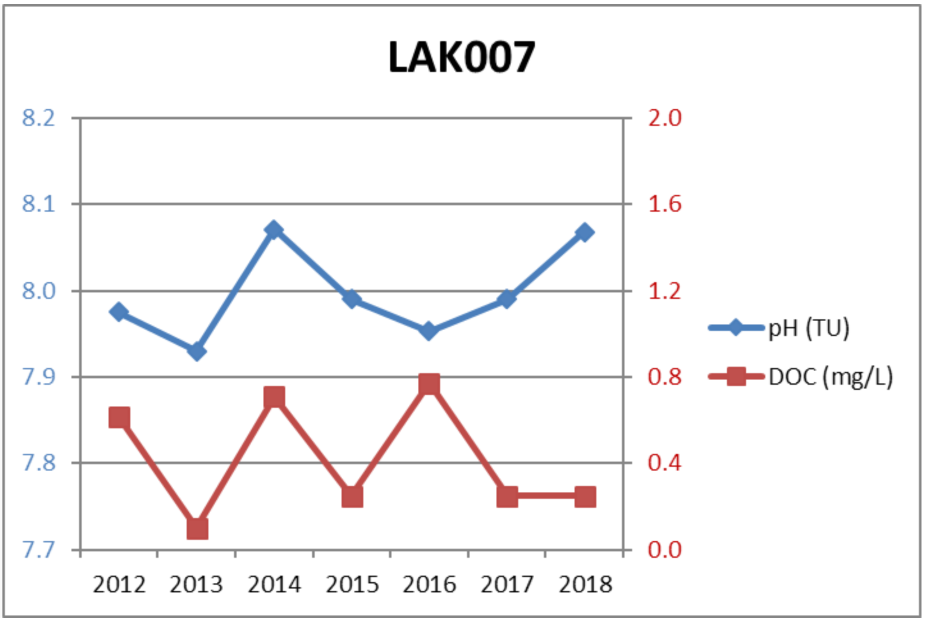

LAK044
10
9
8
7
6
5
4
3
2
1
0
2012
2013
2014
2015
2016
2017
2018
2019
× SO4 * (µeq/L)
⋇ Cl (µeq/L)

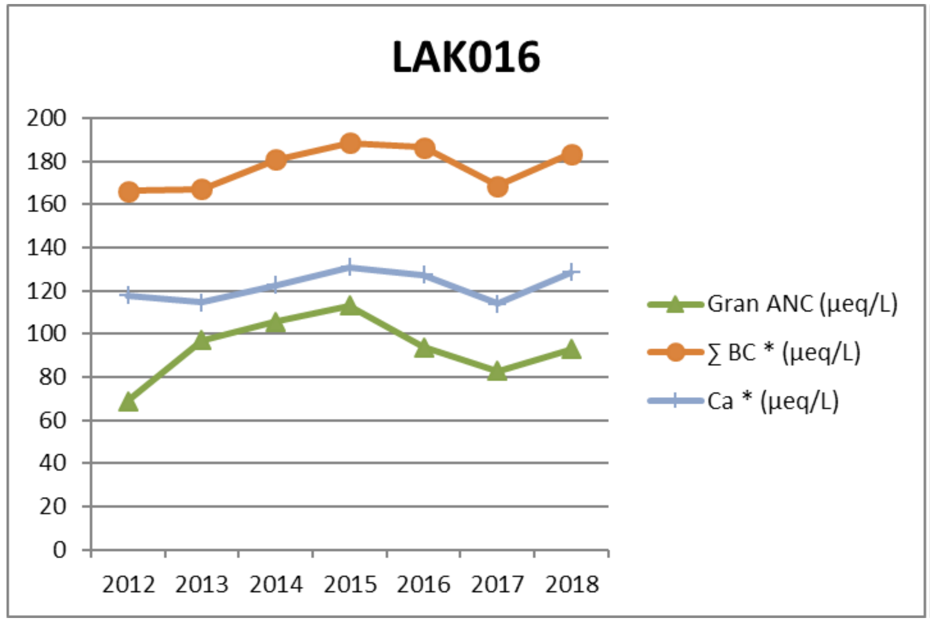

LAK044
5.8
5.7
5.6
5.5
5.4
5.3
2.5
2.0
1.5
1.0
0.5
0.0
2012
2013
2014
2015
2016
2017
2018
2019
◇ pH (TU)
□ DOC (mg/L)

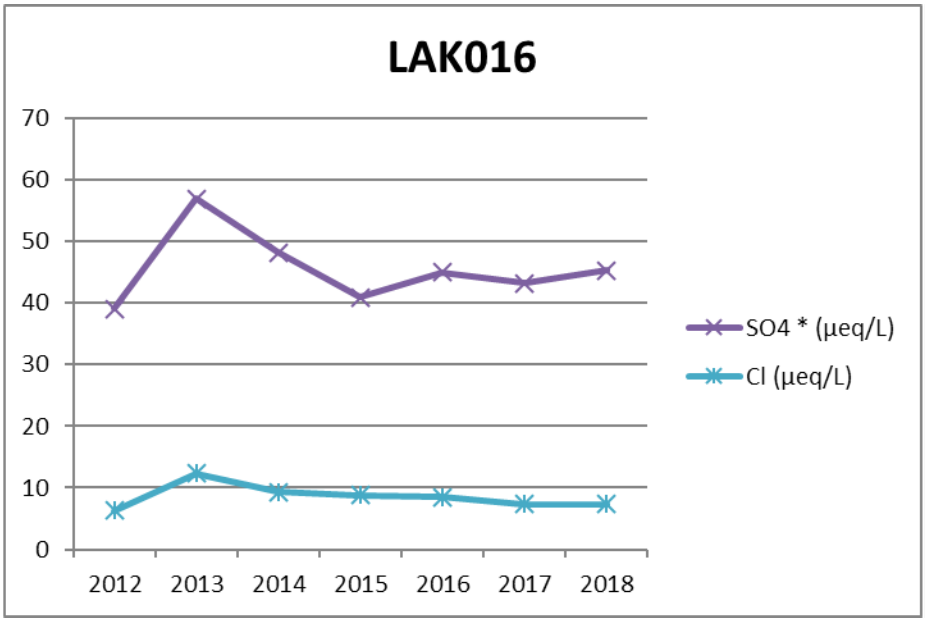
7.3.2 Less Sensitive Lakes

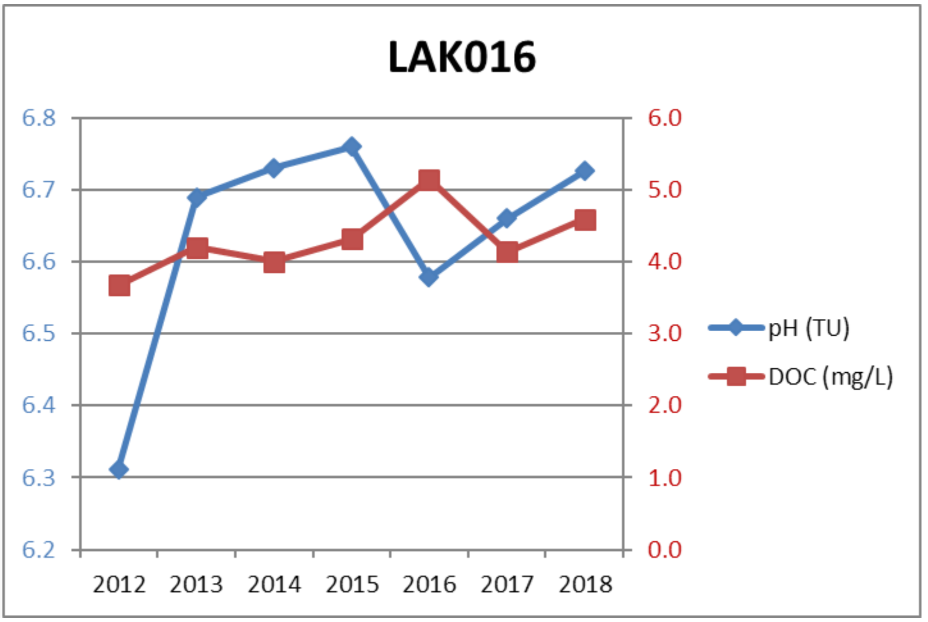


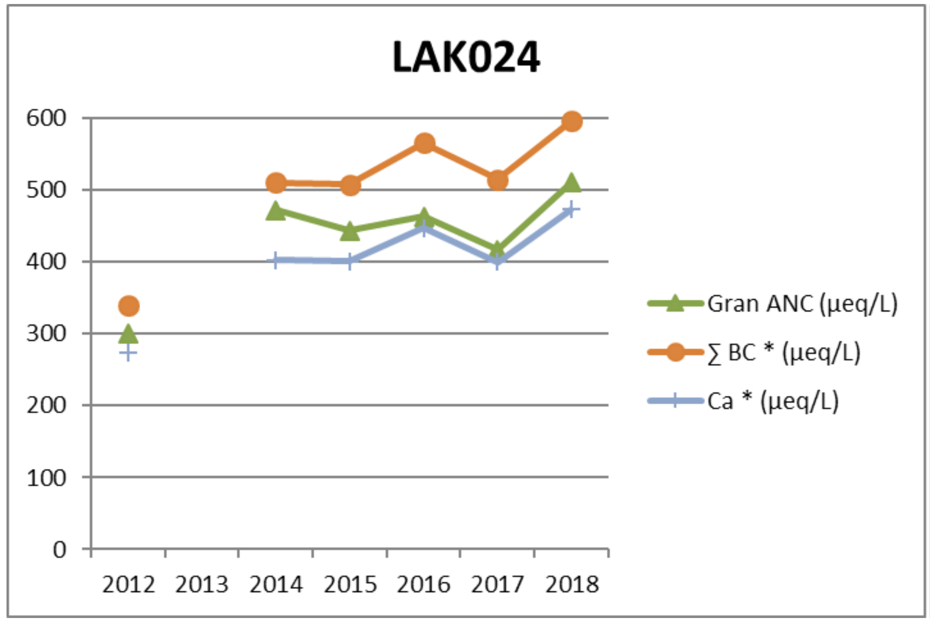


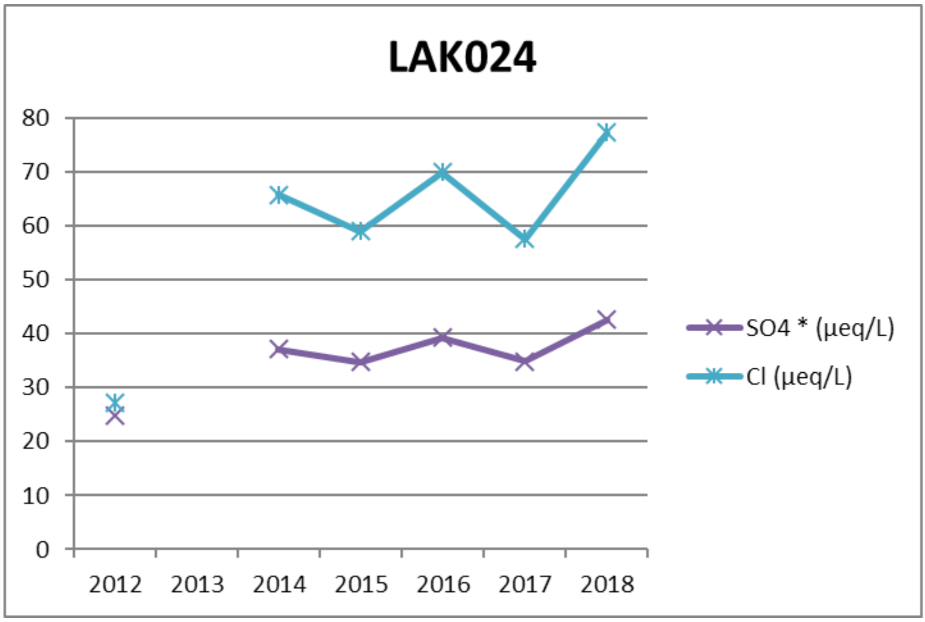


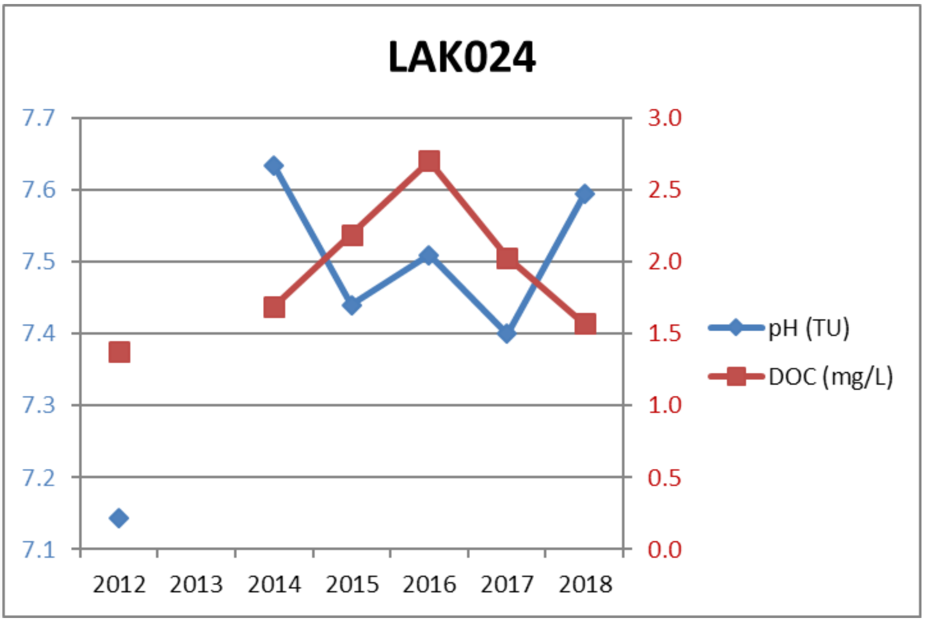


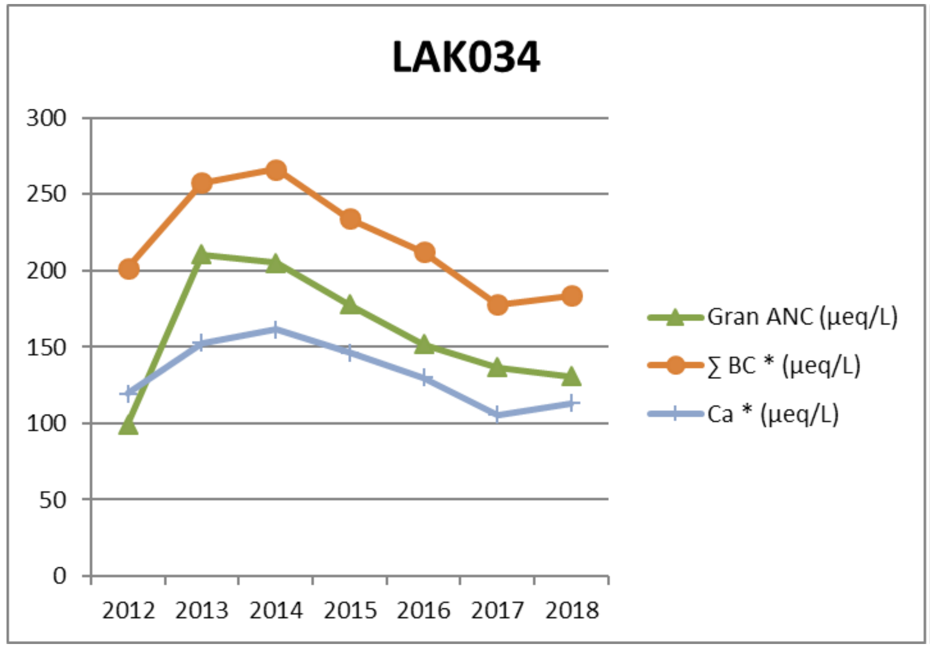


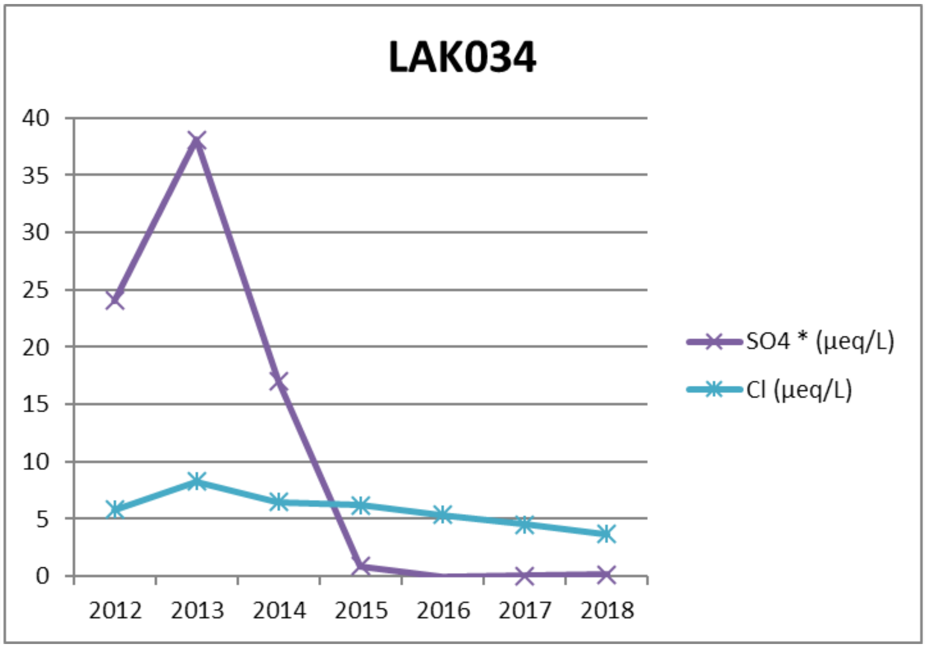


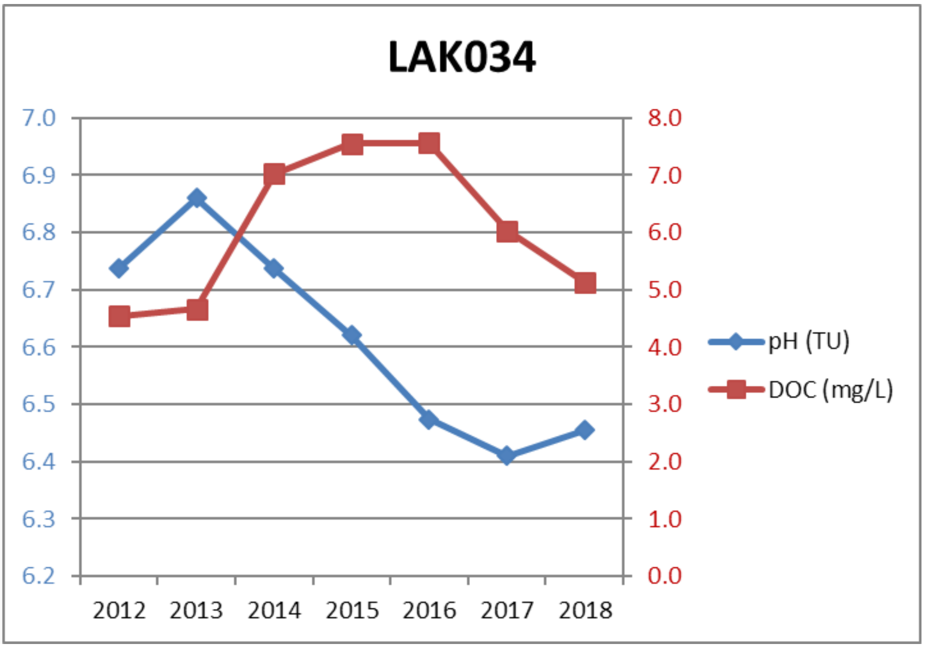

LAK024
600
500
400
300
200
100
0
2012
2013
2014
2015
2016
2017
2018
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)


LAK024
80
70
60
50
40
30
20
10
0
2012
2013
2014
2015
2016
2017
2018
SO4 * (µeq/L)
Cl (µeq/L)

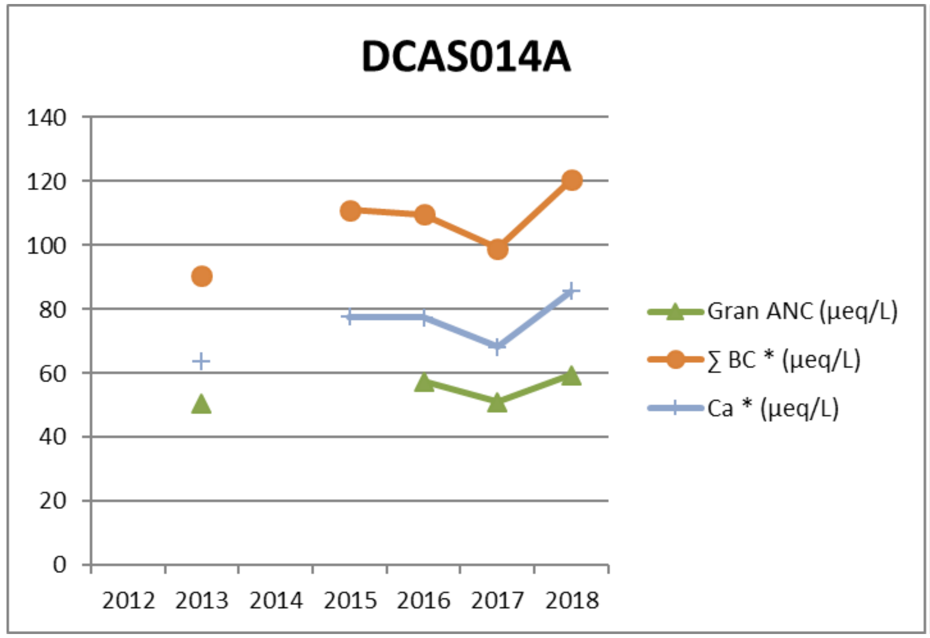

LAK024
7.7
7.6
7.5
7.4
7.3
7.2
7.1
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2012
2013
2014
2015
2016
2017
2018
pH (TU)
DOC (mg/L)

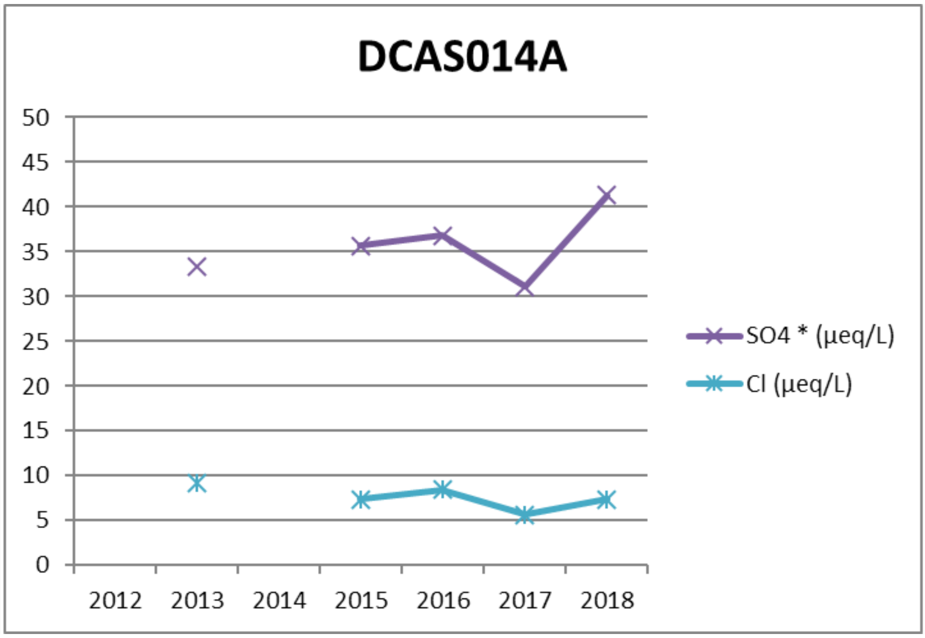

LAK034
300
250
200
150
100
50
0
2012
2013
2014
2015
2016
2017
2018
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)

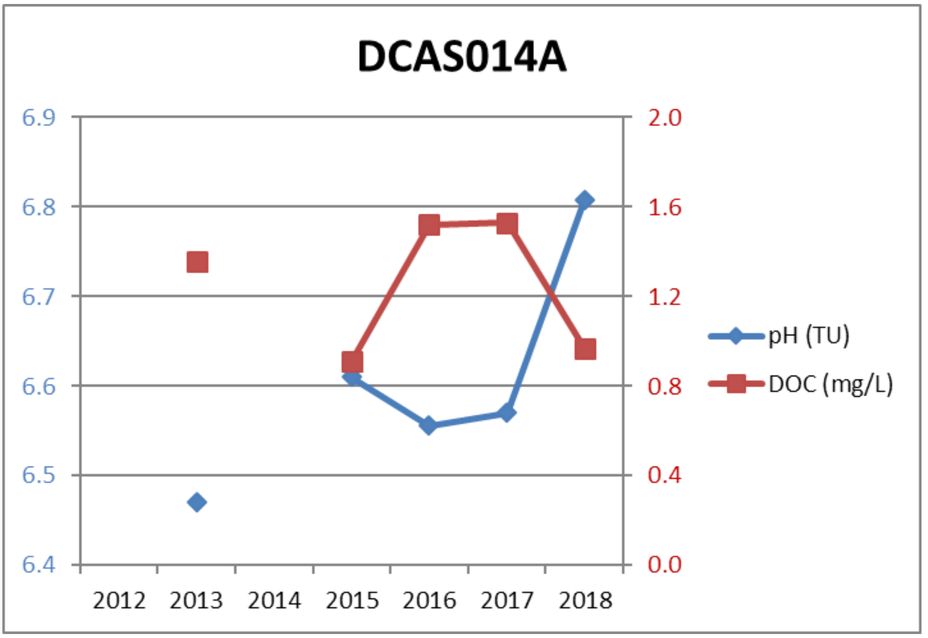

LAK034
40
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
2018
SO4 * (µeq/L)
Cl (µeq/L)

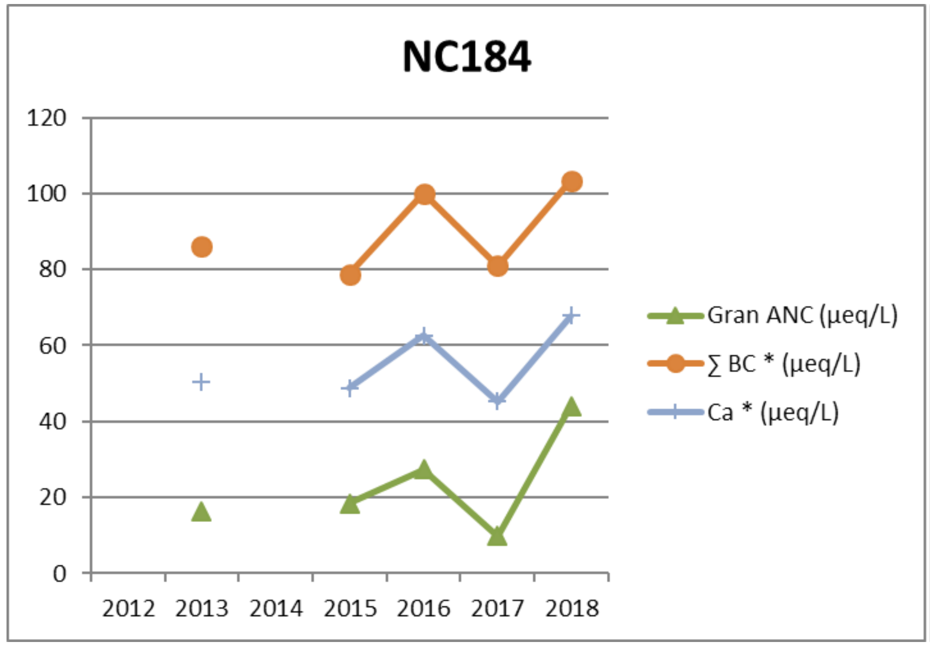

LAK034
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
2018
pH (TU)
DOC (mg/L)

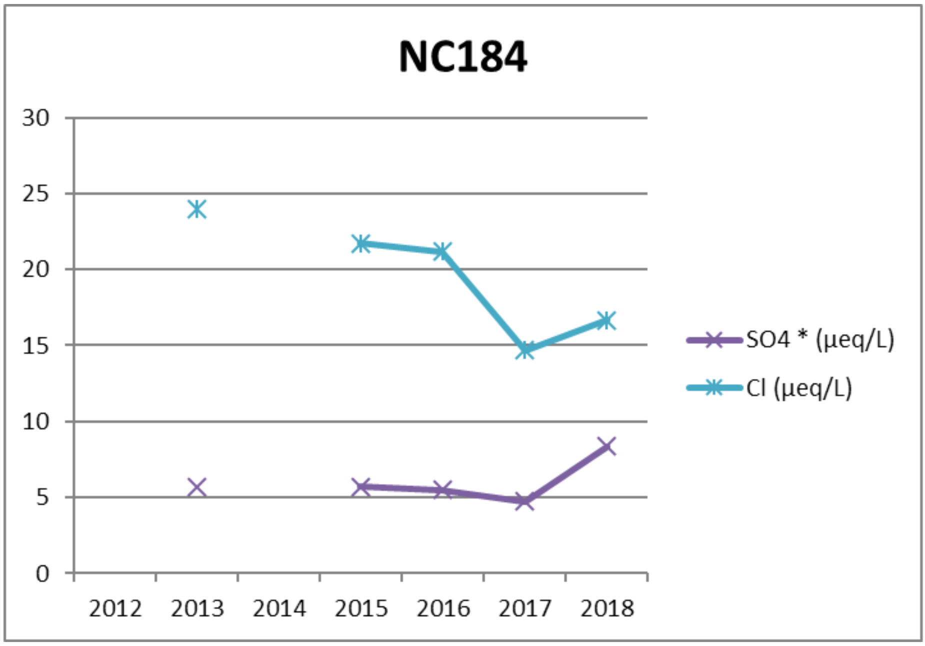
7.3.3 Control Lakes

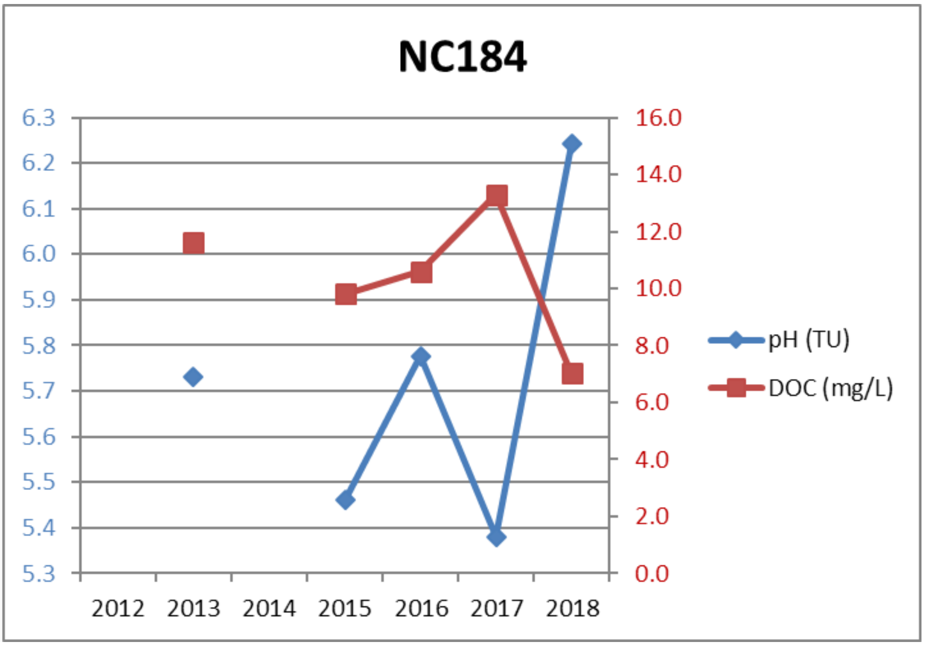


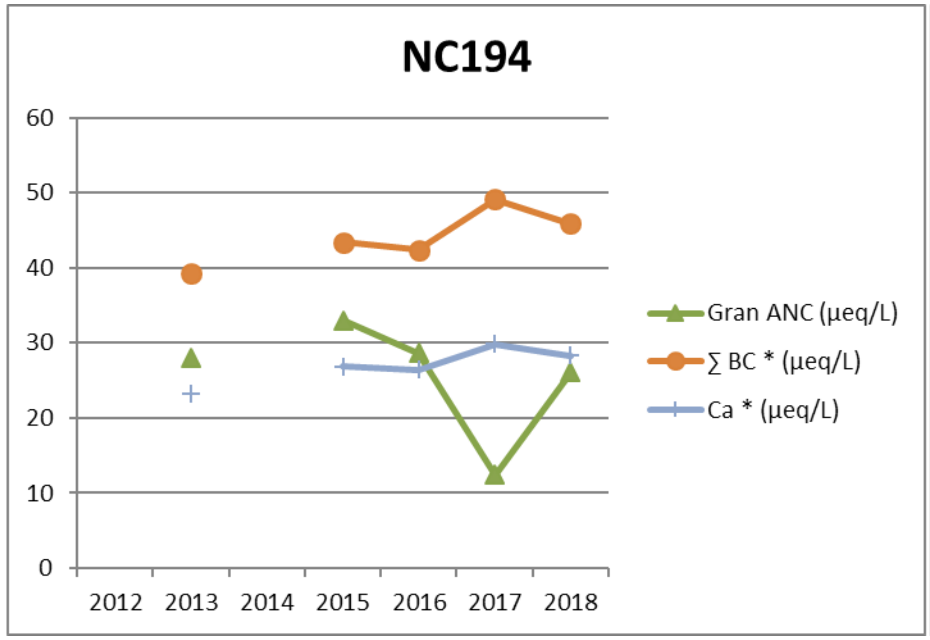


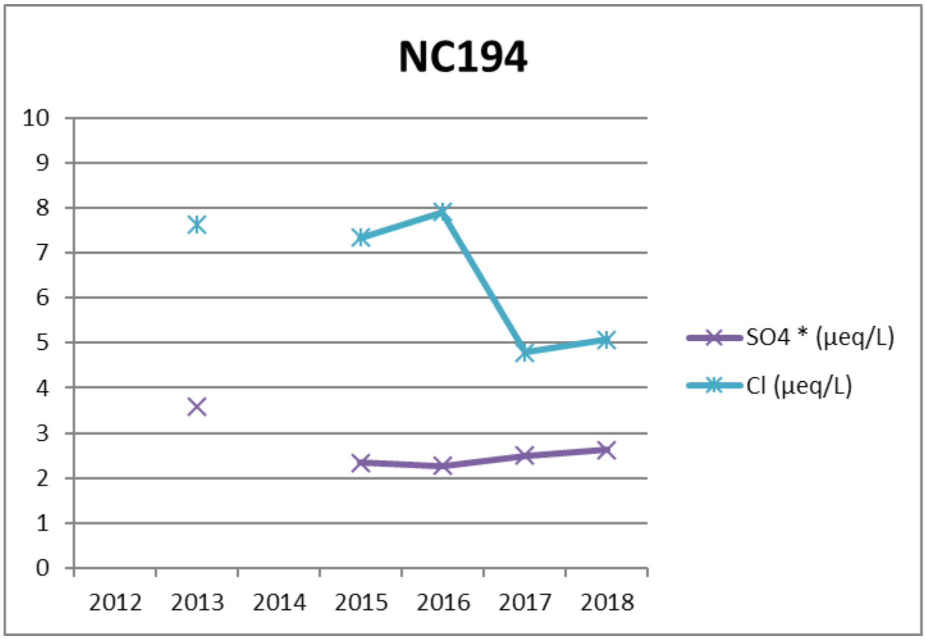


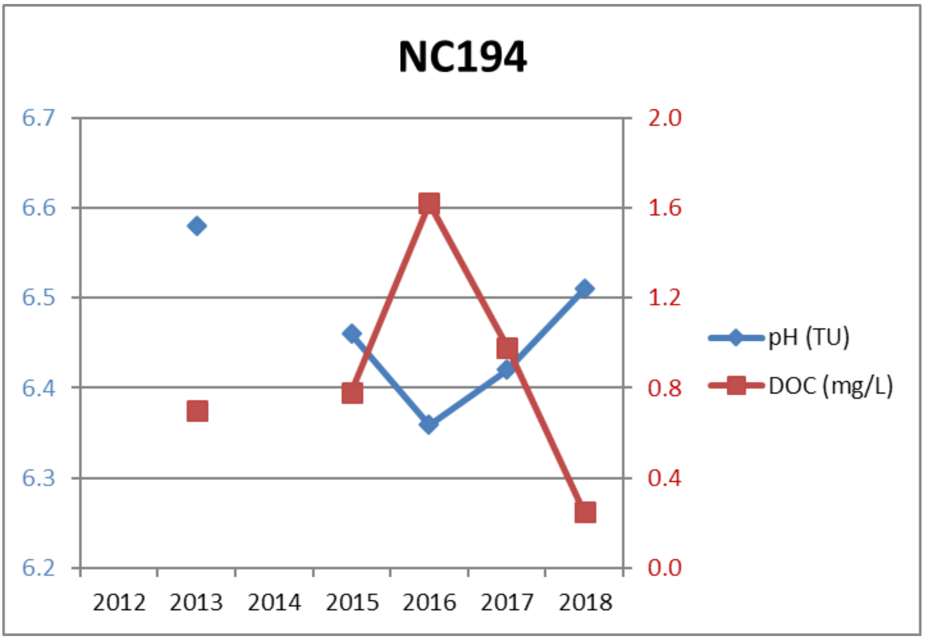







NC194
60
50
40
30
20
10
0
2012
2013
2014
2015
2016
2017
2018
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)


NC194
10
9
8
7
6
5
4
3
2
1
0
2012
2013
2014
2015
2016
2017
2018
SO4 * (µeq/L)
Cl (µeq/L)


NC194
6.7
6.6
6.5
6.4
6.3
6.2
2.0
1.6
1.2
0.8
0.4
0.0
2012
2013
2014
2015
2016
2017
2018
pH (TU)
DOC (mg/L)

7.4 Aquatic Appendix D: Water Chemistry Data from Annual Sampling (2012-2018)

The two tables below shows the sample results for each of the EEM lakes and control lakes from annual monitoring conducted from 2012 to 2018, including pH, dissolved organic carbon (DOC), Gran ANC, and the concentration of major anions and cations, as well as the sum of all base cations (BC). In 2013-2016, the pH of the water samples was measured by two different laboratories (Trent University and ALS). The first table provides the mean annual value and standard error for each metric for lakes with multiple within-season samples, as calculated from all the within-season samples. The second table presents the sampling data in its “raw” units, as measured, without converting concentration values to charge equivalents. Although acidification studies require converting measured concentrations to charge equivalents, these unconverted values may be more familiar and therefore easier to interpret for some audiences.

Note: these tables provide the original, unadjusted values for base cations and sulphate (i.e., not corrected for marine influence, as done prior to the analyses and explorations presented throughout the Comprehensive Review).

Mean Annual Values

The mean annual values and standard deviation have been calculated for all lakes with multiple within-season samples. Sample values with no standard deviation indicate that only a single annual sample was taken for that particular lake in that particular year.

Lake	Year	pH TU	SE[1]	pH ALS	SE	DOC mg/L	SE	Gran ANC µeq/L	SE	SO_4 µeq/L	SE	Cl µeq/L	SE	F µeq/L	SE	Ca µeq/L	SE	Mg µeq/L	SE	K µeq/L	SE	Na µeq/L	SE	∑ BC µeq/L
Lak006	2012	5.8				3.6		25.7		11.4		5.8		4.5		30.3		12.5		2.9		14.9		60.6
LAK007	2012	8.0				0.6		1437.6		51.4		24.6		2.8		1272.2		157.0		19.3		55.4		1503.9
LAK012	2012	5.6				4.6		57.0		6.1		4.2		5.0		74.5		20.8		5.2		20.0		120.6
LAK016	2012	6.3				3.7		68.7		39.0		6.3		7.8		117.7		20.5		7.3		20.8		166.3
LAK022	2012	5.9				5.3		27.8		30.2		6.9		6.1		58.1		16.0		3.2		20.8		98.1
LAK023	2012	5.7				4.2		19.8		19.0		4.5		5.6		39.4		12.0		3.7		10.8		65.9
LAK024	2012	7.1				1.4		299.5		24.8		27.3		1.6		273.2		33.0		4.2		29.6		340.0
LAK028	2012	5.0				4.9		-4.0		56.9		6.1		20.7		47.5		9.5		3.1		12.8		72.9
LAK034	2012	6.7				4.5		99.4		24.1		5.8		5.8		119.3		31.6		5.8		44.9		201.7
LAK042	2012	4.7				13.2		-20.4		6.2		6.1		3.2		7.4		22.7		3.1		20.3		53.4
LAK044	2012	5.4				1.7		1.3		6.2		5.6		2.9		6.8		3.2		4.1		0.0		14.2
Lak006	2013	6.2		6.1		3.2		29.0		14.4		8.7		5.6		27.1		13.0		5.3		12.2		57.6
LAK007	2013	7.9		8.1		0.1		1462.1		66.5		36.3		3.7		1226.0		156.5		21.9		47.6		1452.0
LAK012	2013	6.3		6.1		4.2		63.5		11.3		14.7		8.2		64.8		20.3		9.2		14.6		108.9
LAK016	2013	6.7		7.2		4.2		96.9		56.9		12.3		11.5		114.4		23.9		11.2		17.6		167.1
LAK022	2013	6.2		6.1		6.2		36.4		47.1		12.4		8.7		65.1		19.2		6.0		18.8		109.1
LAK023	2013	6.0		6.0		4.0		23.8		24.1		7.5		7.4		37.1		13.3		5.1		8.3		63.9
LAK024	2013																							
LAK028	2013	5.2		5.5		7.1		4.8		128.1		17.7		32.0		85.1		18.3		5.0		13.0		121.3
LAK034	2013	6.9		7.4		4.7		210.4		38.1		8.2		10.0		152.7		41.7		9.2		54.1		257.7
LAK042	2013	5.5		5.4		9.7		21.0		5.7		7.7		3.2		16.0		22.3		3.4		19.3		61.0
LAK044	2013	5.7		6.0		1.5		8.6		6.2		8.9		3.8		7.8		3.6		5.9		-2.0		15.3
Lak006	2014	6.1	*0.1*	6.6	*0.2*	3.8	*0.3*	38.8	*0.6*	12.1	*0.6*	8.1	*1.2*	4.8	*0.1*	31.7	*0.5*	14.6	*0.4*	4.7	*0.3*	14.5	*1.2*	65.5
LAK007	2014	8.1		8.0		0.7		1445.7		30.7		19.2		1.9		1276.8		156.7		20.2		61.8		1515.5
LAK012	2014	6.0	*0.1*	6.7	*0.2*	6.3	*1.0*	68.8	*6.8*	15.8	*5.2*	10.3	*2.2*	5.2	*0.2*	69.3	*1.6*	21.3	*0.6*	7.3	*0.5*	18.3	*1.6*	116.1
LAK016	2014	6.7		6.7		4.0		105.7		48.2		9.3		9.5		122.4		25.0		10.1		23.3		180.8
LAK022	2014	6.3		6.4		5.7		46.9		37.8		9.0		6.9		68.5		18.9		5.2		21.4		114.0
LAK023	2014	5.9	*0.1*	6.7	*0.3*	5.7	*0.4*	32.1	*1.1*	18.9	*1.0*	6.1	*0.3*	6.2	*0.2*	49.3	*3.9*	14.9	*0.4*	4.0	*0.1*	10.8	*0.3*	79.0
LAK024	2014	7.6		7.5		1.7		472.1		37.2		65.7		2.3		402.3		50.1		7.8		50.2		510.4
LAK028	2014	5.3		5.7		5.9		22.6		94.4		11.0		23.3		85.9		17.7		4.4		17.6		125.7
LAK034	2014	6.7		7.0		7.0		205.0		17.0		6.5		7.7		161.4		43.6		9.4		51.9		266.3
LAK042	2014	5.1		5.4		10.6		12.5		4.0		11.8		2.6		10.5		23.6		3.7		17.9		55.7

Lake	Year	pH TU	SE[1]	pH ALS	SE	DOC mg/L	SE	Gran ANC µeq/L	SE	SO_4 µeq/L	SE	Cl µeq/L	SE	F µeq/L	SE	Ca µeq/L	SE	Mg µeq/L	SE	K µeq/L	SE	Na µeq/L	SE	∑ BC µeq/L
LAK044	2014	5.8		5.6		1.8		5.9		4.6		5.9		2.8		7.8		3.9		5.3		0.4		17.3
Lak006	2015	6.0	*0.1*	6.4	*0.3*	3.9	*0.2*	32.4	*0.4*	11.5	*0.3*	6.6	*0.3*	4.4	*0.1*	32.3	*0.3*	14.8	*0.2*	3.9	*0.1*	15.7	*0.3*	66.7
LAK007	2015	8.0		7.9		0.3		1565.6		45.6		24.0		2.6		1266.6		161.5		21.0		58.6		1507.7
LAK012	2015	6.0	*0.1*	6.3	*0.2*	7.5	*1.0*	65.9	*2.1*	17.6	*3.1*	11.1	*1.7*	4.7	*0.1*	74.8	*3.9*	23.2	*0.9*	8.1	*0.8*	18.0	*0.8*	124.2
LAK016	2015	6.8		6.9		4.3		113.1		40.9		8.7		8.6		130.9		25.0		9.8		22.9		188.6
LAK022	2015	6.1		6.2		6.3		35.6		32.5		7.9		5.9		64.1		18.1		4.4		21.2		107.8
LAK023	2015	5.9	*0.1*	6.2	*0.1*	5.4	*0.4*	30.0	*1.0*	15.1	*0.7*	6.2	*0.3*	5.2	*0.2*	46.1	*1.5*	13.9	*0.3*	3.8	*0.1*	9.7	*0.1*	73.5
LAK024	2015	7.4		7.5		2.2		443.0		34.7		59.0		2.1		400.5		49.3		8.7		49.0		507.6
LAK028	2015	5.1		5.3		8.1		10.8		71.1		9.0		20.5		76.5		15.7		3.2		14.4		109.8
LAK034	2015	6.6		6.7		7.6		177.8		0.9		6.2		4.7		146.5		37.1		5.3		45.1		234.0
LAK042	2015	5.4		5.5		8.3		13.8		3.8		6.5		2.3		10.7		23.1		2.5		23.0		59.3
LAK044	2015	5.8		5.8		1.6		6.2		3.7		5.9		2.7		9.8		4.4		5.5		0.5		20.3
Lak006	2016	6.0	*0.0*	6.3	*0.1*	4.2	*0.1*	26.9	*1.0*	11.8	*0.2*	5.6	*0.2*	4.2	*0.1*	32.6	*0.5*	14.8	*0.7*	4.2	*0.6*	17.2	*0.9*	68.8
LAK007	2016	8.0		8.1		0.8		1368.6		46.7		25.4		2.6		1301.5		162.8		20.2		58.3		1542.8
LAK012	2016	6.2	*0.0*	6.5	*0.1*	5.1	*0.3*	65.8	*1.2*	9.5	*0.5*	5.6	*0.2*	4.6	*0.1*	64.7	*0.8*	20.8	*0.6*	6.0	*0.6*	21.6	*0.8*	113.0
LAK016	2016	6.6		6.9		5.2		93.9		44.9		8.5		8.2		127.4		26.4		8.9		23.7		186.5
LAK022	2016	6.1		6.4		6.7		34.4		34.2		7.9		5.8		68.1		19.2		4.2		23.1		114.6
LAK023	2016	5.9	*0.0*	6.2	*0.1*	5.8	*0.1*	27.9	*1.9*	12.7	*0.2*	4.9	*0.2*	5.1	*0.1*	42.5	*0.9*	14.1	*0.4*	4.7	*0.5*	11.0	*0.8*	72.3
LAK024	2016	7.5		7.6		2.7		463.1		39.2		70.0		2.3		446.5		55.3		9.5		53.9		565.3
LAK028	2016	5.0	*0.1*	5.1	*0.1*	8.1	*0.3*	-4.9	*6.2*	127.8	*8.1*	10.0	*0.5*	26.8	*0.8*	94.7	*8.3*	23.8	*1.7*	3.7	*0.2*	19.5	*1.6*	141.6
LAK034	2016	6.5		7.1		7.6		151.6		0.0		5.4		4.4		130.0		34.3		3.8		44.1		212.3
LAK042	2016	5.4	*0.0*	5.7	*0.0*	9.8	*0.2*	14.0	*1.5*	3.3	*0.2*	7.2	*0.2*	2.2	*0.1*	16.7	*1.7*	24.7	*0.4*	2.7	*0.2*	23.3	*0.2*	67.4
LAK044	2016	5.5	*0.0*	6.0	*0.1*	2.0	*0.1*	4.1	*1.3*	4.1	*0.1*	6.1	*0.1*	2.3	*0.1*	8.2	*0.4*	4.1	*0.0*	5.5	*0.1*	0.3	*0.2*	18.2
Lak006	2017	6.0	*0.1*	6.4	*0.1*	3.8	*0.1*	27.9	*2.7*	14.4	*0.3*	5.4	*0.2*	4.2	*0.0*	34.8	*0.5*	15.6	*0.2*	4.1	*0.1*	18.0	*0.4*	72.5
LAK007	2017	8.0		8.0		0.3		1381.6		47.1		25.9		2.4		1201.7		165.2		19.9		62.6		1449.4
LAK012	2017	6.1	*0.1*	6.5	*0.1*	5.2	*0.5*	58.2	*3.2*	14.6	*2.6*	7.0	*1.2*	4.4	*0.1*	65.4	*4.5*	21.7	*1.2*	7.7	*1.0*	21.5	*0.9*	116.3
LAK016	2017	6.7		6.8		4.1		82.7		43.2		7.3		7.7		114.0		24.7		6.9		22.9		168.6
LAK022	2017	6.1		6.3		5.9		34.2		39.0		7.1		5.4		64.1		19.5		3.8		22.2		109.6
LAK023	2017	5.9	*0.0*	6.2	*0.0*	5.4	*0.1*	28.5	*2.4*	10.1	*1.7*	4.2	*0.3*	4.6	*0.0*	43.2	*2.1*	13.8	*0.3*	2.3	*0.2*	11.2	*0.3*	70.5
LAK024	2017	7.4		7.6		2.0		416.6		34.9		57.5		2.0		399.6		52.2		8.5		54.2		514.4
LAK028	2017	4.8	*0.1*	5.1	*0.1*	7.3	*0.6*	-9.9	*4.5*	150.0	*13.0*	8.7	*1.0*	27.2	*1.7*	102.5	*11.0*	26.5	*2.5*	3.5	*0.4*	19.9	*1.6*	152.4
LAK034	2017	6.4		6.8		6.0		136.5		0.1		4.5		3.4		105.6		30.3		2.7		39.1		177.8
LAK042	2017	5.2	*0.1*	5.4	*0.1*	11.6	*1.1*	2.3	*2.1*	6.8	*0.9*	6.7	*0.5*	2.4	*0.0*	17.1	*2.7*	26.9	*1.1*	2.8	*0.3*	23.2	*0.5*	70.0
LAK044	2017	5.6	*0.1*	6.0	*0.1*	1.6	*0.0*	7.0	*2.2*	4.5	*0.2*	5.9	*0.1*	2.2	*0.0*	7.9	*0.1*	4.2	*0.1*	5.6	*0.1*	0.7	*0.2*	18.4

Lake	Year	pH		pH		DOC		Gran ANC		SO_4		Cl		F		Ca		Mg		K		Na		∑ BC
		TU	*SE*[1]	ALS	*SE*	mg/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L	*SE*	µeq/L
Lak006	2018	6.1	*0.0*	6.4	*0.0*	3.8	*0.1*	28.3	*1.2*	15.7	*0.2*	6.1	*0.1*	4.2	*0.1*	36.2	*0.3*	16.1	*0.5*	4.3	*0.3*	18.5	*0.6*	75.1
LAK007	2018	8.1		8.1		0.3		1407.6		47.1		27.9		2.6		1251.5		157.4		20.6		61.3		1490.8
LAK012	2018	6.2	*0.1*	6.6	*0.1*	4.6	*0.1*	50.9	*4.3*	14.6	*0.7*	6.2	*0.3*	4.6	*0.1*	58.3	*0.4*	19.7	*0.6*	6.2	*0.3*	21.1	*0.8*	105.2
LAK016	2018	6.7		6.9		4.6		92.8		45.3		7.3		8.1		128.5		23.3		7.3		24.3		183.5
LAK022	2018	6.1		6.3		5.6		30.3		43.2		7.3		5.8		72.1		19.3		4.2		24.4		119.9
LAK023	2018	6.0	*0.1*	6.4	*0.1*	5.6	*0.2*	23.0	*0.7*	14.1	*0.9*	4.9	*0.2*	4.9	*0.1*	45.9	*0.3*	15.0	*0.3*	3.3	*0.2*	11.4	*0.4*	75.5
LAK024	2018	7.6		7.6		1.6		509.9		42.6		77.3		2.4		472.7		56.4		9.4		57.2		595.7
LAK028	2018	5.3	*0.0*	5.5	*0.0*	4.4	*0.1*	4.2	*1.6*	107.5	*2.0*	6.6	*0.2*	20.9	*0.3*	76.4	*0.9*	19.0	*0.5*	2.8	*0.1*	17.9	*0.7*	116.0
LAK034	2018	6.5		6.6		5.1		130.6		0.1		3.7		3.7		113.1		27.7		2.1		40.8		183.7
LAK042	2018	5.1	*0.0*	5.3	*0.0*	10.6	*0.4*	0.6	*1.9*	6.3	*0.1*	6.1	*0.2*	2.3	*0.1*	8.8	*0.6*	23.9	*0.5*	2.3	*0.1*	21.8	*0.1*	56.8
LAK044	2018	5.5	*0.0*	5.9	*0.0*	1.9	*0.1*	3.9	*0.9*	4.5	*0.1*	6.4	*0.1*	2.2	*0.0*	8.3	*0.1*	4.1	*0.2*	5.5	*0.1*	-0.2	*0.3*	17.7
NC184	2012																							
NC194	2012																							
DCAS14A	2012																							
NC184	2013	5.7				11.6		16.2		5.7		24.0		0.3		50.5		17.5		4.4		13.8		86.2
NC194	2013	6.6				0.7		28.0		3.6		7.6		0.3		23.2		3.4		5.2		7.4		39.2
DCAS14A	2013	6.5				1.4		50.6		33.4		9.2		0.6		63.9		10.3		10.3		6.1		90.6
NC184	2014																							
NC194	2014																							
DCAS14A	2014																							
NC184	2015	5.5		5.6		9.8		18.4		5.7		21.7		0.5		48.8		16.1		2.9		10.8		78.7
NC194	2015	6.5		6.5		0.8		33.0		2.3		7.3		0.5		26.9		4.4		4.3		7.9		43.4
DCAS14A	2015	6.6		6.7		0.9				35.7		7.3		0.5		77.6		12.4		11.2		9.9		111.0
NC184	2016	5.8		6.2		10.6		27.3		5.5		21.2		0.5		62.6		19.3		2.7		15.5		100.1
NC194	2016	6.4		6.6		1.6		28.7		2.3		7.9		0.5		26.4		4.3		3.8		7.9		42.4
DCAS14A	2016	6.6		6.8		1.5		57.5		36.8		8.5		0.5		77.5		11.8		10.5		9.7		109.6
NC184	2017	5.4		6.0		13.3		9.8		4.7		14.7		0.5		45.2		17.4		2.5		15.9		81.0
NC194	2017	6.4		6.4		1.0		12.4		2.5		4.8		0.5		29.9		5.7		3.6		9.9		49.1
DCAS14A	2017	6.6		6.7		1.5		51.0		31.1		5.6		0.5		68.2		11.8		9.1		9.9		99.0
NC184	2018	6.2		6.4		7.0		44.0		8.3		16.6		0.5		67.8		17.3		3.1		15.3		103.4
NC194	2018	6.5		6.7		0.3		26.1		2.6		5.1		0.5		28.3		4.3		4.1		9.1		45.8
DCAS14A	2018	6.8		6.8		1.0		59.3		41.3		7.3		0.5		85.6		12.6		11.5		10.7		120.4

[1] SE = standard error

Sampling Data in “Raw” Units

The annual or mean annual values (depending on whether the lake had multiple within-season samples) are presented in their “raw” units, as measured, without converting concentration values to charge equivalents.

Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (µS/s)	SO_4 (mg/L)	Cl (mg/L)	F (mg/L)	NO3 (µg/L)	NH4 (µg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
Lak006	2012	5.8		3.6	1.3	6.7	0.6	0.2	0.1	0.1	3.0	0.6	0.2	0.1	0.5	0.0	0.1	0.0
Lak007	2012	8.0		0.6	71.9	148.9	2.6	0.9	0.1	4.7	1.8	25.5	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2012	5.6		4.6	2.9	12.7	0.3	0.1	0.1	0.7	3.4	1.5	0.3	0.2	0.5	0.7	0.1	0.2
LAK016	2012	6.3		3.7	3.4	17.9	1.9	0.2	0.1	0.8	3.9	2.4	0.3	0.3	0.6	0.0	0.1	0.0
LAK022	2012	5.9		5.3	1.4	10.7	1.5	0.2	0.1	0.7	3.7	1.2	0.2	0.1	0.6	0.0	0.1	0.0
LAK023	2012	5.7		4.2	1.0	7.5	0.9	0.2	0.1	0.3	3.3	0.8	0.2	0.1	0.3	0.0	0.1	0.0
LAK024	2012	7.1		1.4	15.0	40.0	1.3	1.0	0.0	0.4	2.4	5.5	0.5	0.2	1.2	0.0	0.0	0.0
LAK028	2012	5.0		4.9	-0.2	12.2	2.8	0.2	0.4	1.5	3.4	1.0	0.1	0.1	0.4	0.1	0.4	0.0
LAK034	2012	6.7		4.5	5.0	22.4	1.2	0.2	0.1	1.6	4.9	2.4	0.4	0.2	1.1	0.0	0.0	0.0
LAK042	2012	4.7		13.2	-1.0	11.9	0.3	0.2	0.1	0.7	8.5	0.2	0.3	0.1	0.6	0.6	0.4	0.0
LAK044	2012	5.4		1.7	0.1	3.1	0.3	0.2	0.1	0.4	3.0	0.1	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2013	6.2	6.1	3.2	1.5	7.0	0.7	0.3	0.1	2.5	2.5	0.5	0.2	0.2	0.5	0.0	0.0	0.0
Lak007	2013	7.9	8.1	0.1	73.2	147.0	3.4	1.3	0.1	2.5	2.5	24.6	2.0	0.9	1.8	0.0	0.0	0.0
LAK012	2013	6.3	6.1	4.2	3.2	12.8	0.6	0.5	0.2	2.5	2.5	1.3	0.3	0.4	0.6	0.4	0.1	0.0
LAK016	2013	6.7	7.2	4.2	4.9	20.3	2.8	0.4	0.2	22.7	7.1	2.3	0.3	0.4	0.6	0.0	0.0	0.0
LAK022	2013	6.2	6.1	6.2	1.8	13.8	2.3	0.4	0.2	2.5	2.5	1.3	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	2013	6.0	6.0	4.0	1.2	9.6	1.2	0.3	0.1	30.1	2.5	0.7	0.2	0.2	0.3	0.0	0.1	0.0
LAK024	2013																	
LAK028	2013	5.2	5.5	7.1	0.2	20.3	6.2	0.6	0.6	20.4	2.5	1.7	0.3	0.2	0.6	0.2	0.6	0.0
LAK034	2013	6.9	7.4	4.7	10.5	28.3	1.9	0.3	0.2	2.5	2.5	3.1	0.5	0.4	1.4	0.0	0.0	0.0
LAK042	2013	5.5	5.4	9.7	1.1	8.0	0.3	0.3	0.1	2.5	2.5	0.3	0.3	0.1	0.6	0.3	0.3	0.0
LAK044	2013	5.7	6.0	1.5	0.4	3.3	0.3	0.3	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2014	6.1	6.6	3.8	1.9	8.5	0.6	0.3	0.1	7.7	40.5	0.6	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2014	8.1	8.0	0.7	72.4	154.2	1.6	0.7	0.0	2.5	2.5	25.6	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2014	6.0	6.7	6.3	3.4	13.9	0.8	0.4	0.1	7.6	5.3	1.4	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	2014	6.7	6.7	4.0	5.3	21.5	2.4	0.3	0.2	2.5	6.7	2.5	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2014	6.3	6.4	5.7	2.3	14.4	1.9	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	2014	5.9	6.7	5.7	1.6	9.3	0.9	0.2	0.1	10.9	5.3	1.0	0.2	0.2	0.4	0.0	0.1	0.0
LAK024	2014	7.6	7.5	1.7	23.6	63.1	2.1	2.3	0.0	5.1	2.5	8.1	0.8	0.4	2.5	0.0	0.0	0.0
LAK028	2014	5.3	5.7	5.9	1.1	20.2	4.6	0.4	0.4	2.5	2.5	1.7	0.2	0.2	0.6	0.1	0.5	0.0
LAK034	2014	6.7	7.0	7.0	10.3	27.5	0.9	0.2	0.1	2.5	2.5	3.2	0.5	0.4	1.3	0.1	0.0	0.0
LAK042	2014	5.1	5.4	10.6	0.6	10.8	0.3	0.4	0.1	2.5	2.5	0.2	0.3	0.2	0.6	0.4	0.3	0.0

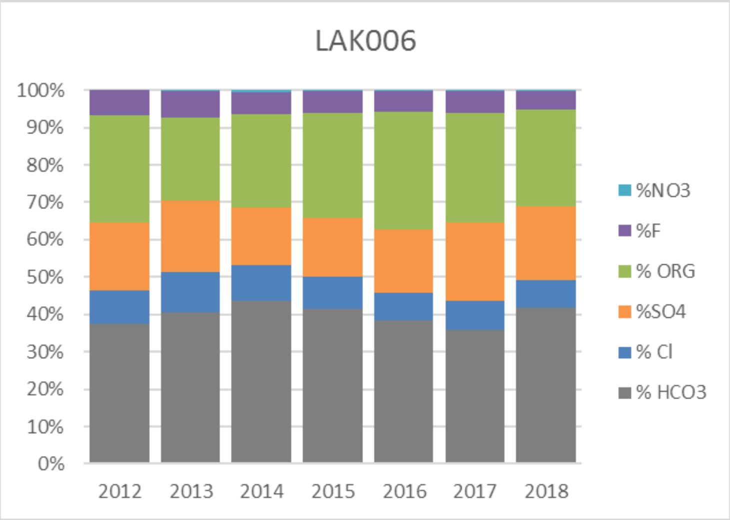
Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (µS/s)	SO_4 (mg/L)	Cl (mg/L)	F (mg/L)	NO3 (µg/L)	NH4 (µg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
LAK044	2014	5.8	5.6	1.8	0.3	3.6	0.3	0.2	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2015	6.0	6.4	3.9	1.6	5.6	0.6	0.2	0.1	3.4	5.4	0.7	0.2	0.2	0.5	0.1	0.1	0.0
Lak007	2015	8.0	7.9	0.3	78.4	151.2	2.3	0.9	0.0	5.6	2.5	25.4	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2015	6.0	6.3	7.5	3.3	10.1	0.9	0.4	0.1	8.3	8.0	1.5	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	2015	6.8	6.9	4.3	5.7	20.7	2.0	0.3	0.2	7.9	2.5	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2015	6.1	6.2	6.3	1.8	12.8	1.6	0.3	0.1	2.5	2.5	1.3	0.2	0.2	0.6	0.1	0.1	0.0
LAK023	2015	5.9	6.2	5.4	1.5	5.9	0.8	0.2	0.1	6.3	2.5	0.9	0.2	0.2	0.3	0.0	0.1	0.0
LAK024	2015	7.4	7.5	2.2	22.2	58.7	2.0	2.1	0.0	8.1	2.5	8.1	0.7	0.4	2.3	0.1	0.0	0.0
LAK028	2015	5.1	5.3	8.1	0.5	17.8	3.5	0.3	0.4	2.5	2.5	1.5	0.2	0.1	0.5	0.2	0.6	0.0
LAK034	2015	6.6	6.7	7.6	8.9	22.3	0.1	0.2	0.1	2.5	2.5	2.9	0.5	0.2	1.2	0.1	0.0	0.0
LAK042	2015	5.4	5.5	8.3	0.7	8.1	0.2	0.2	0.0	2.5	2.5	0.2	0.3	0.1	0.7	0.2	0.3	0.0
LAK044	2015	5.8	5.8	1.6	0.3	3.5	0.2	0.2	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2016	6.0	6.3	4.2	1.3	7.8	0.6	0.2	0.1	2.5	2.5	0.7	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2016	8.0	8.1	0.8	68.5	153.7	2.4	0.9	0.1	6.5	2.5	26.1	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2016	6.2	6.5	5.1	3.3	12.4	0.5	0.2	0.1	5.0	4.7	1.3	0.3	0.2	0.6	0.3	0.1	0.0
LAK016	2016	6.6	6.9	5.2	4.7	20.8	2.2	0.3	0.2	10.9	2.5	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2016	6.1	6.4	6.7	1.7	13.7	1.7	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	2016	5.9	6.2	5.8	1.4	9.1	0.6	0.2	0.1	2.5	5.1	0.9	0.2	0.2	0.4	0.0	0.1	0.0
LAK024	2016	7.5	7.6	2.7	23.2	66.3	2.2	2.5	0.0	20.7	2.5	9.0	0.8	0.4	2.6	0.1	0.0	0.0
LAK028	2016	5.0	5.1	8.1	-0.2	23.7	6.2	0.4	0.5	21.5	2.5	1.9	0.3	0.2	0.6	0.1	0.7	0.0
LAK034	2016	6.5	7.1	7.6	7.6	22.1	0.0	0.2	0.1	2.5	2.5	2.6	0.4	0.2	1.1	0.1	0.0	0.0
LAK042	2016	5.4	5.7	9.8	0.7	8.8	0.2	0.3	0.0	2.5	3.7	0.3	0.3	0.1	0.7	0.2	0.3	0.0
LAK044	2016	5.5	6.0	2.0	0.2	3.9	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2017	6.0	6.4	3.8	1.4	8.8	0.7	0.2	0.1	2.5	2.5	0.7	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2017	8.0	8.0	0.3	69.1	149.0	2.4	0.9	0.0	2.5	2.5	24.1	2.1	0.8	2.0	0.0	0.0	0.0
LAK012	2017	6.1	6.5	5.2	2.9	12.9	0.7	0.2	0.1	9.7	5.6	1.3	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	2017	6.7	6.8	4.1	4.1	18.5	2.1	0.3	0.1	2.5	2.5	2.3	0.3	0.3	0.7	0.0	0.1	0.0
LAK022	2017	6.1	6.3	5.9	1.7	12.8	1.9	0.3	0.1	2.5	2.5	1.3	0.3	0.2	0.6	0.0	0.1	0.0
LAK023	2017	5.9	6.2	5.4	1.4	7.9	0.5	0.2	0.1	7.7	2.5	0.9	0.2	0.1	0.3	0.0	0.1	0.0
LAK024	2017	7.4	7.6	2.0	20.9	57.4	2.0	2.0	0.0	11.2	2.5	8.1	0.8	0.4	2.4	0.1	0.0	0.0
LAK028	2017	4.8	5.1	7.3	-0.5	26.9	7.2	0.3	0.5	25.3	3.3	2.1	0.3	0.1	0.6	0.1	0.7	0.0
LAK034	2017	6.4	6.8	6.0	6.8	17.6	0.0	0.2	0.1	2.5	2.5	2.1	0.4	0.1	1.0	0.1	0.0	0.0
LAK042	2017	5.2	5.4	11.6	0.1	9.8	0.4	0.2	0.0	2.5	5.4	0.3	0.3	0.1	0.7	0.3	0.4	0.0
LAK044	2017	5.6	6.0	1.6	0.4	4.4	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0

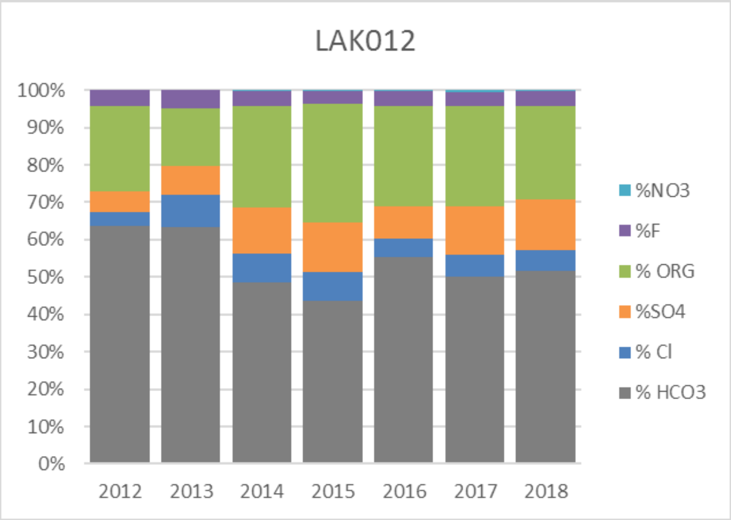
Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (µS/s)	SO_4 (mg/L)	Cl (mg/L)	F (mg/L)	NO3 (µg/L)	NH4 (µg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
Lak006	2018	6.1	6.4	3.8	1.4	8.8	0.8	0.2	0.1	2.5	2.5	0.7	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2018	8.1	8.1	0.3	70.4	147.4	2.4	1.0	0.0	2.5	2.5	25.1	2.0	0.8	2.0	0.0	0.0	0.0
LAK012	2018	6.2	6.6	4.6	2.5	11.5	0.7	0.2	0.1	2.5	2.5	1.2	0.3	0.2	0.6	0.3	0.1	0.0
LAK016	2018	6.7	6.9	4.6	4.6	20.0	2.2	0.3	0.2	2.5	2.5	2.6	0.3	0.3	0.7	0.0	0.1	0.0
LAK022	2018	6.1	6.3	5.6	1.5	13.4	2.1	0.3	0.1	2.5	2.5	1.5	0.3	0.2	0.7	0.0	0.1	0.0
LAK023	2018	6.0	6.4	5.6	1.1	9.4	0.7	0.2	0.1	2.5	2.5	0.9	0.2	0.1	0.4	0.0	0.1	0.0
LAK024	2018	7.6	7.6	1.6	25.5	70.2	2.4	2.7	0.0	2.5	2.5	9.5	0.9	0.4	2.8	0.0	0.0	0.0
LAK028	2018	5.3	5.5	4.4	0.2	17.7	5.2	0.2	0.4	2.5	3.3	1.5	0.2	0.1	0.5	0.1	0.5	0.0
LAK034	2018	6.5	6.6	5.1	6.5	17.8	0.0	0.1	0.1	2.5	2.5	2.3	0.3	0.1	1.0	0.0	0.0	0.0
LAK042	2018	5.1	5.3	10.6	0.0	8.6	0.3	0.2	0.0	2.5	2.5	0.2	0.3	0.1	0.6	0.3	0.4	0.0
LAK044	2018	5.5	5.9	1.9	0.2	3.6	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
NC184	2012																	
NC194	2012																	
DCAS14A	2012																	
NC184	2013	5.7		11.6	0.8	10.0	0.4	0.9	0.0	5.0	1.0	1.0	0.3	0.2	0.8			
NC194	2013	6.6		0.7	1.4	3.9	0.2	0.3	0.0	1.0	1.0	0.5	0.1	0.2	0.3			
DCAS14A	2013	6.5		1.4	2.5	10.6	1.7	0.3	0.0	52.6	2.5	1.3	0.1	0.4	0.3	0.0	0.0	0.0
NC184	2014																	
NC194	2014																	
DCAS14A	2014																	
NC184	2015	5.5	5.6	9.8	0.9	11.6	0.4	0.8	0.0	2.5	2.5	1.0	0.2	0.1	0.7	0.2	0.3	0.0
NC194	2015	6.5	6.5	0.8	1.7	5.4	0.1	0.3	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	2015	6.6	6.7	0.9		14.0	1.8	0.3	0.0	6.8	2.5	1.6	0.2	0.4	0.4	0.0	0.0	0.0
NC184	2016	5.8	6.2	10.6	1.4	12.8	0.4	0.8	0.0	2.5	2.5	1.3	0.3	0.1	0.8	0.1	0.3	0.0
NC194	2016	6.4	6.6	1.6	1.4	5.9	0.1	0.3	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	2016	6.6	6.8	1.5	2.9	14.8	1.8	0.3	0.0	2.5	2.5	1.6	0.2	0.4	0.4	0.0	0.0	0.0
NC184	2017	5.4	6.0	13.3	0.5	11.4	0.3	0.5	0.0	2.5	2.5	0.9	0.2	0.1	0.7	0.2	0.3	0.0
NC194	2017	6.4	6.4	1.0	0.6	4.9	0.1	0.2	0.0	2.5	2.5	0.6	0.1	0.1	0.3	0.0	0.0	0.0
DCAS14A	2017	6.6	6.7	1.5	2.6	11.7	1.5	0.2	0.0	2.5	2.5	1.4	0.2	0.4	0.3	0.0	0.0	0.0
NC184	2018	6.2	6.4	7.0	2.2	12.3	0.5	0.6	0.0	2.5	2.5	1.4	0.3	0.1	0.7	0.1	0.2	0.0
NC194	2018	6.5	6.7	0.3	1.3	5.4	0.2	0.2	0.0	2.5	2.5	0.6	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	2018	6.8	6.8	1.0	3.0	14.7	2.0	0.3	0.0	2.5	2.5	1.7	0.2	0.5	0.4	0.0	0.0	0.0

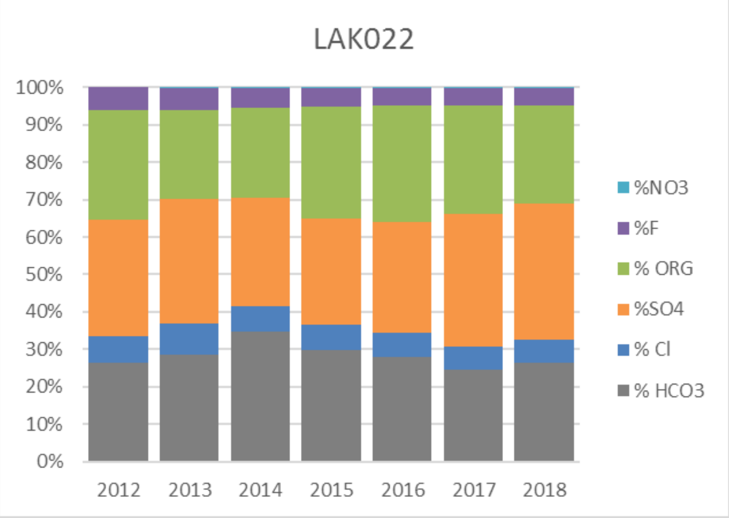
7.5 Aquatic Appendix E: Anion Composition

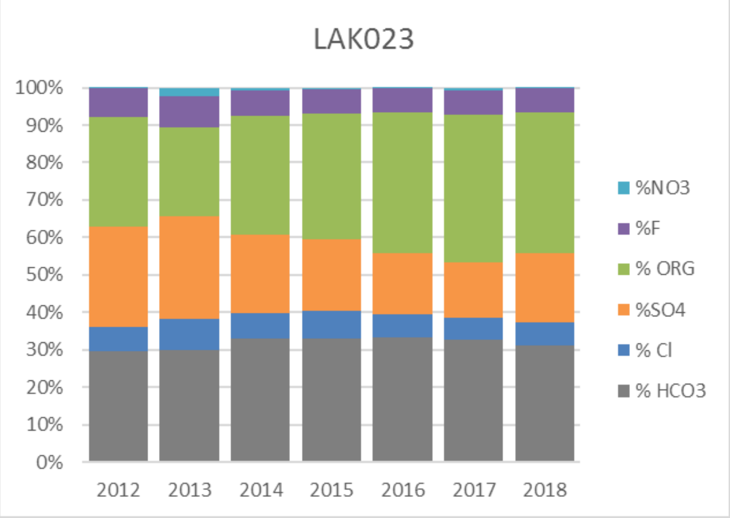
For each of the EEM lakes, the figures in this appendix show the inter-annual changes in the composition of major anions (HCO_3^-, SO_4^{2-}, F^-, Cl^-, NO_3^-, and organic anions) from 2012 to 2018. Composition is expressed in terms of the percent of total anions.

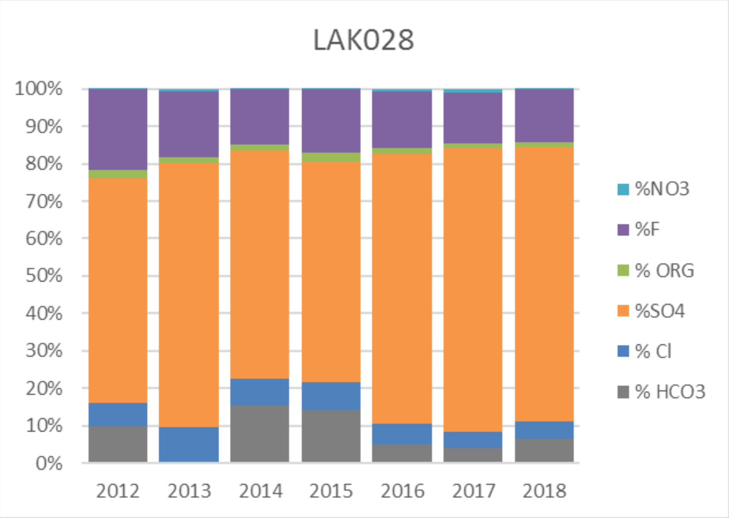
7.5.1 Sensitive Lakes

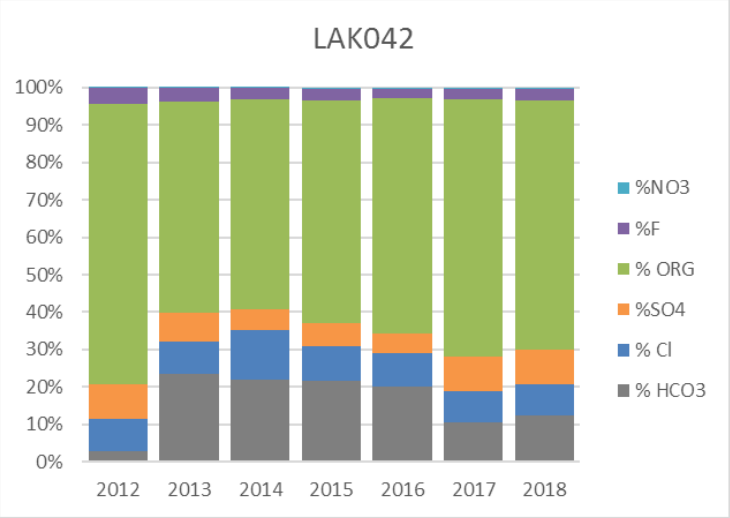


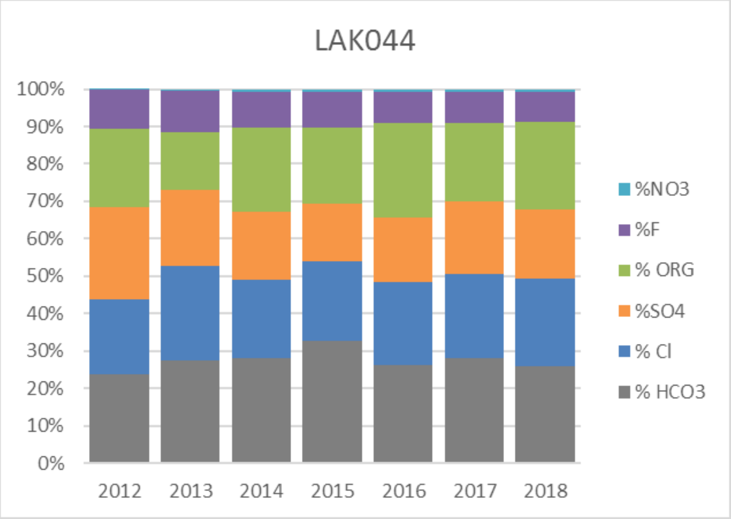



LAK022
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2012
2013
2014
2015
2016
2017
2018
%NO3
%F
% ORG
%SO4
% Cl
% HCO3

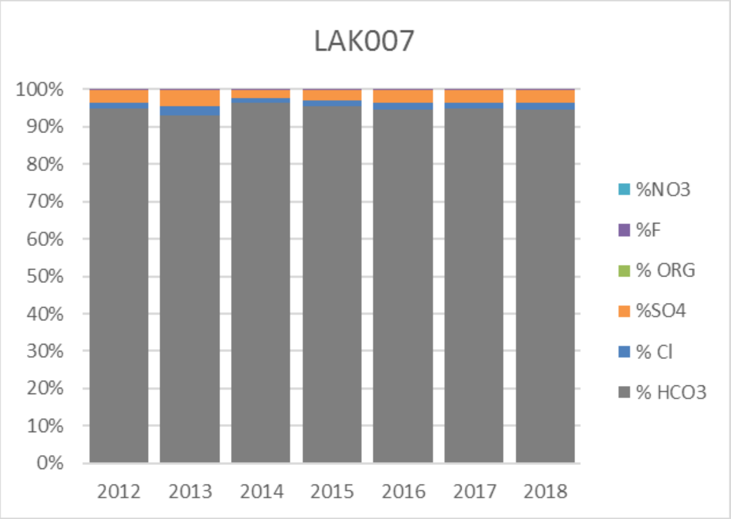

LAK023
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2012
2013
2014
2015
2016
2017
2018
%NO3
%F
% ORG
%SO4
% Cl
% HCO3

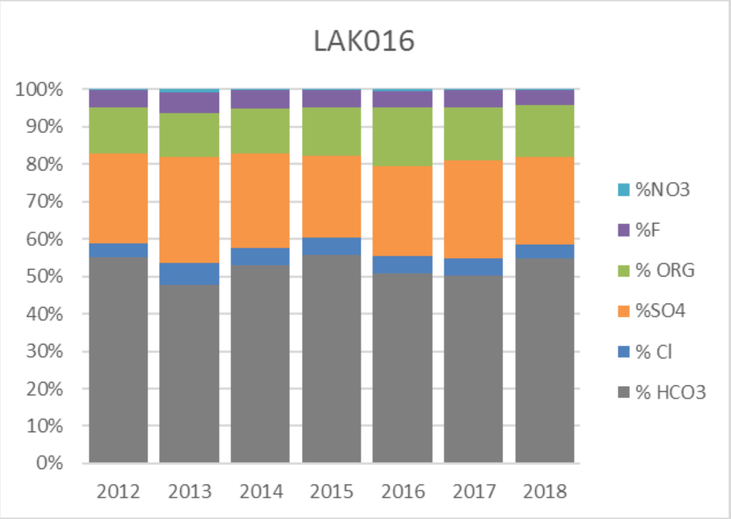

LAK028
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2012
2013
2014
2015
2016
2017
2018
%NO3
%F
% ORG
%SO4
% Cl
% HCO3

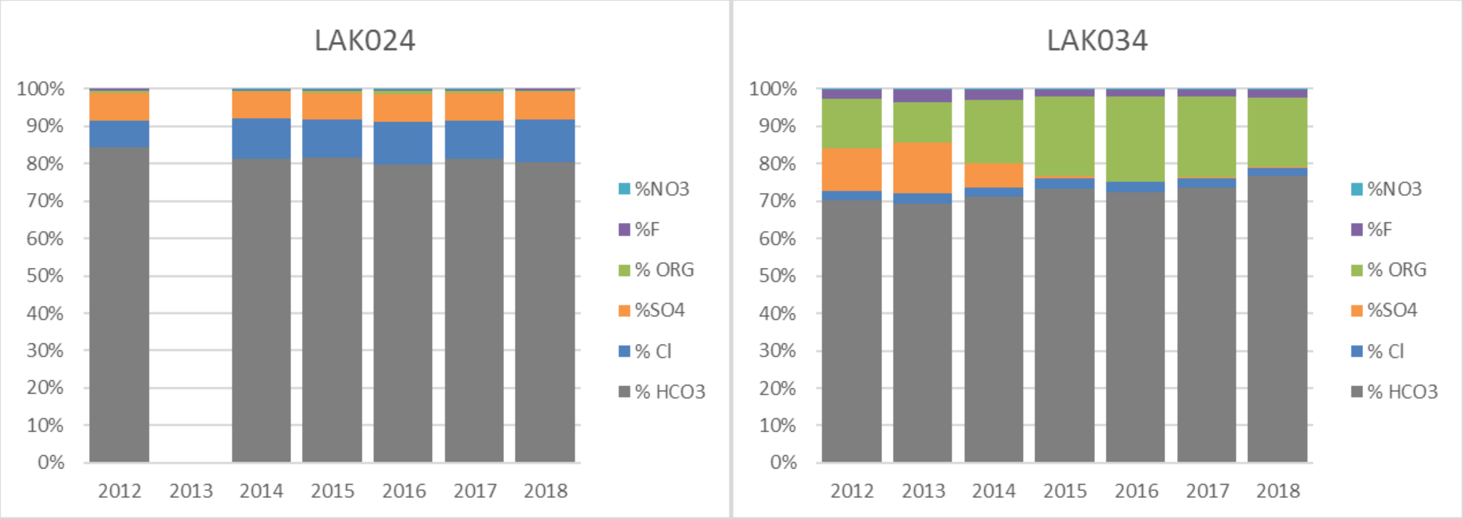

LAK042
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2012
2013
2014
2015
2016
2017
2018
%NO3
%F
% ORG
%SO4
% Cl
% HCO3



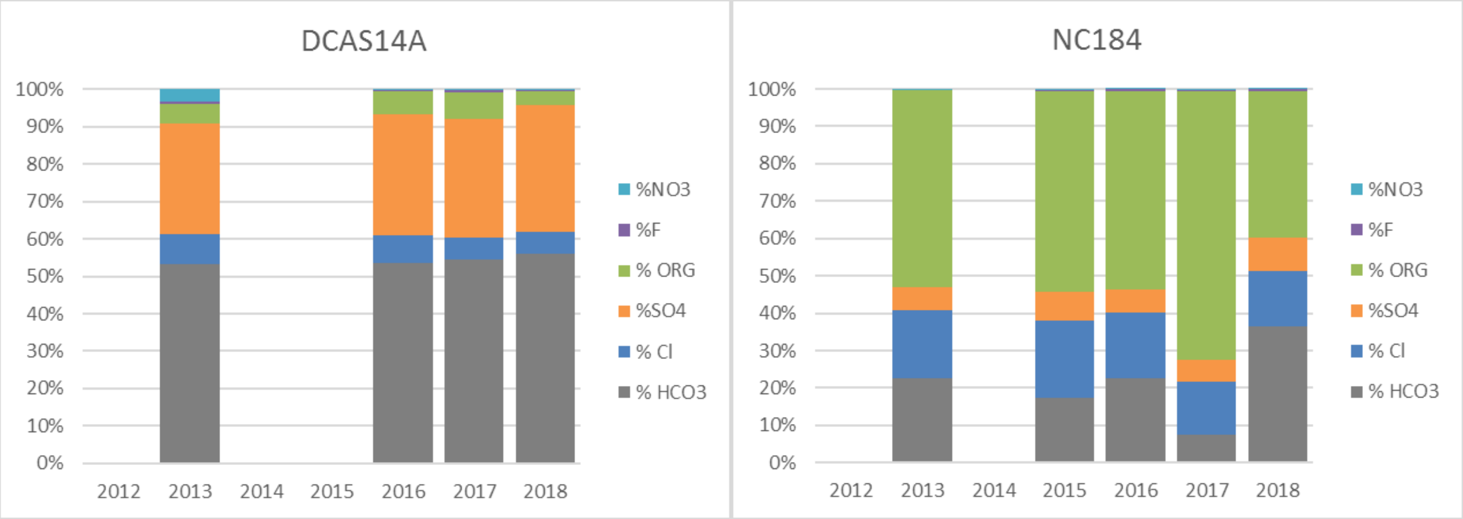
7.5.2 Less Sensitive Lakes

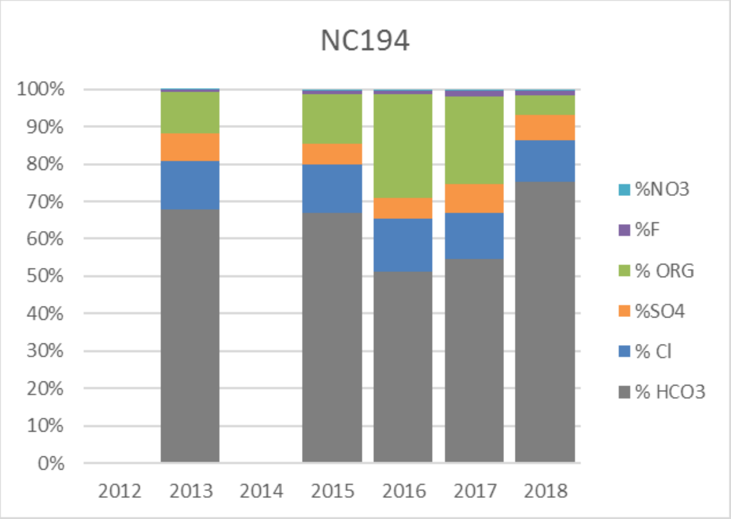






7.5.3 Control Lakes




NC194
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2012
2013
2014
2015
2016
2017
2018
%NO3
%F
% ORG
%SO4
% Cl
% HCO3

7.6 Aquatic Appendix F: Statistical Analysis of Water Chemistry Data

7.6.1 Introduction

The EEM Plan (ESSA et al. 2014; chapter 7) described an evidentiary framework for assessing whether or not changes in lake chemistry could be causally attributed to emissions from the Kitimat smelter. Figure 7.35 is a simplified representation of the evidentiary framework, helpful for providing context for the analyses which follow. Section 7.6.2 is a reference section, providing graphs of the patterns of change in water chemistry within each lake, both over time and in relation to precipitation and emissions. In Section 7.6.3 we provide an overview of the statistical power analyses completed in 2016. Section 7.6.4 is the core of this Appendix, with statistical analyses of changes in water chemistry in support of the evidentiary framework. Building on Figure 7.35, we focus first on changes in lake sulphate (Section 7.6.4.2, where statistical methods are described), and then examine pH (Section 7.6.4.3) and Gran ANC (Section 7.6.4.4), using the data collected from fall samples. In Section 7.6.4.5, we consider the data collected from three intensively monitored lakes. Section 7.6.4.6 summarizes all of the changes in the three primary variables by lake. It is worth emphasizing that the goal of these analyses is to determine whether or not the smelter has caused lake acidification, and if so, whether the magnitude of acidification exceeds thresholds for biological effects. While it may be of scientific interest to understand the causes of all chemical changes in each lake, that is beyond the scope of the EEM, the Comprehensive Report and this analysis.

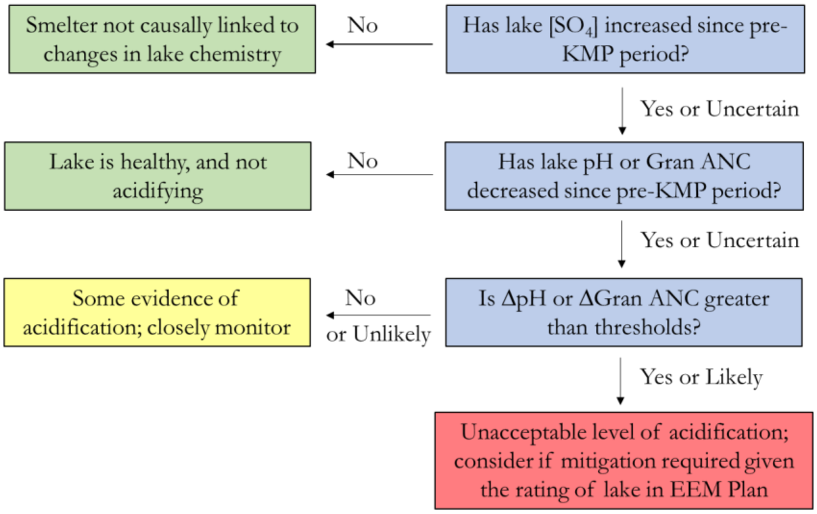


Figure 7.35: Simplification of the evidentiary framework presented in chapter 7 of the SO_2 EEM Plan.

7.6.2 General Patterns of Variability and Change

7.6.2.1 Water Chemistry Time Series

Description of Analyses:

- Time series of lake chemistry data

Purpose of Analyses:

- To first understand patterns of change in water chemistry over space and time, prior to exploring possible reasons for these patterns
- The patterns of interest include variability across and within years within each lake, differences in the magnitude of variability across different lakes, and differences in water chemistry between different groups of lakes (e.g., sensitive, less sensitive, control)
- These graphs are meant to simply display general patterns of changes over time or relationships between variables, independent of any statistical analysis, assignment of causality or application of the evidentiary framework.

7.6.2.1.1 SO_4 over time

- See Section 7.6.4.2 for statistical analyses of changes in sulphate
- See Section 7.6.4.6 for an integration of analyses of changes in sulphate, pH and ANC by lake

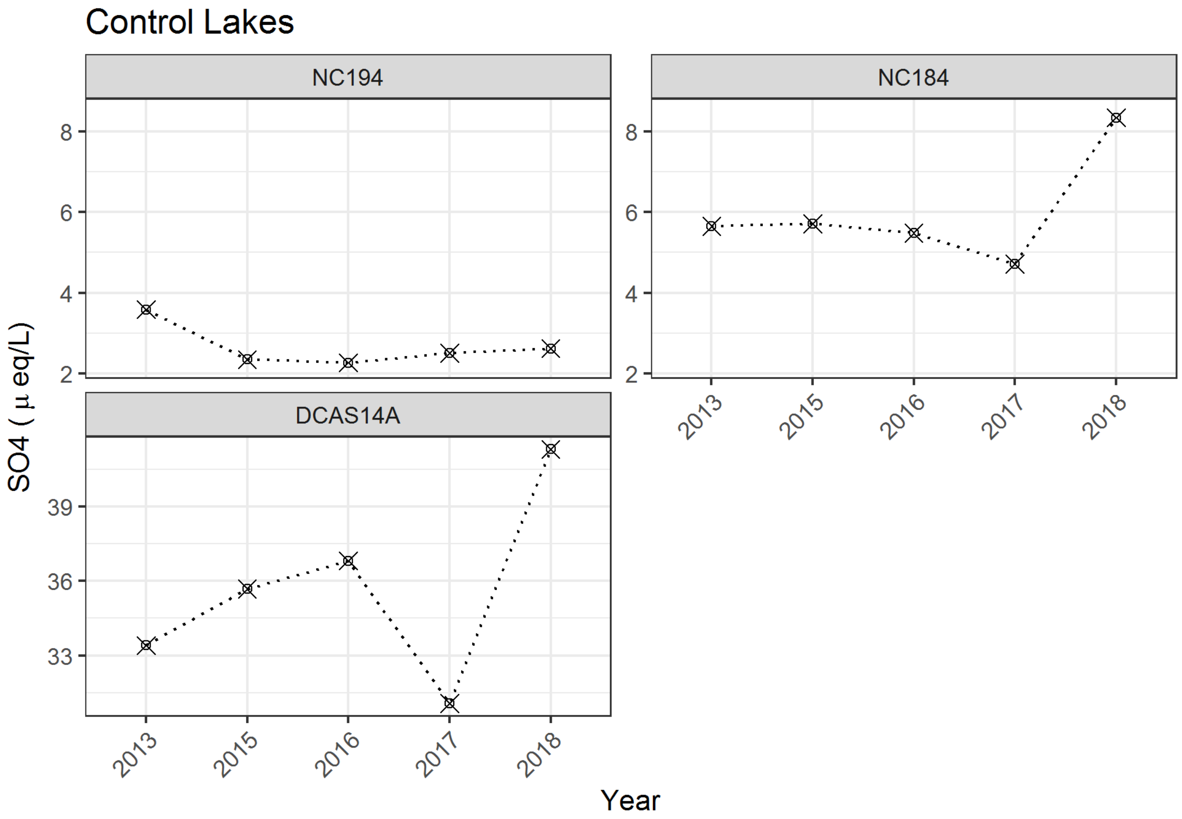


Figure 7.36: Annual trend of SO_4 concentrations for the control lakes (DCAS14A, NC184, NC194) for the years 2013-2018. Note that the scales are different on the y-axes. Graphs use the minimum and maximum concentrations for each lakes to make the relative patterns comparable. The magnitude of change in DCAS14A (Alastair Lake) is much larger than in the other two control lakes.

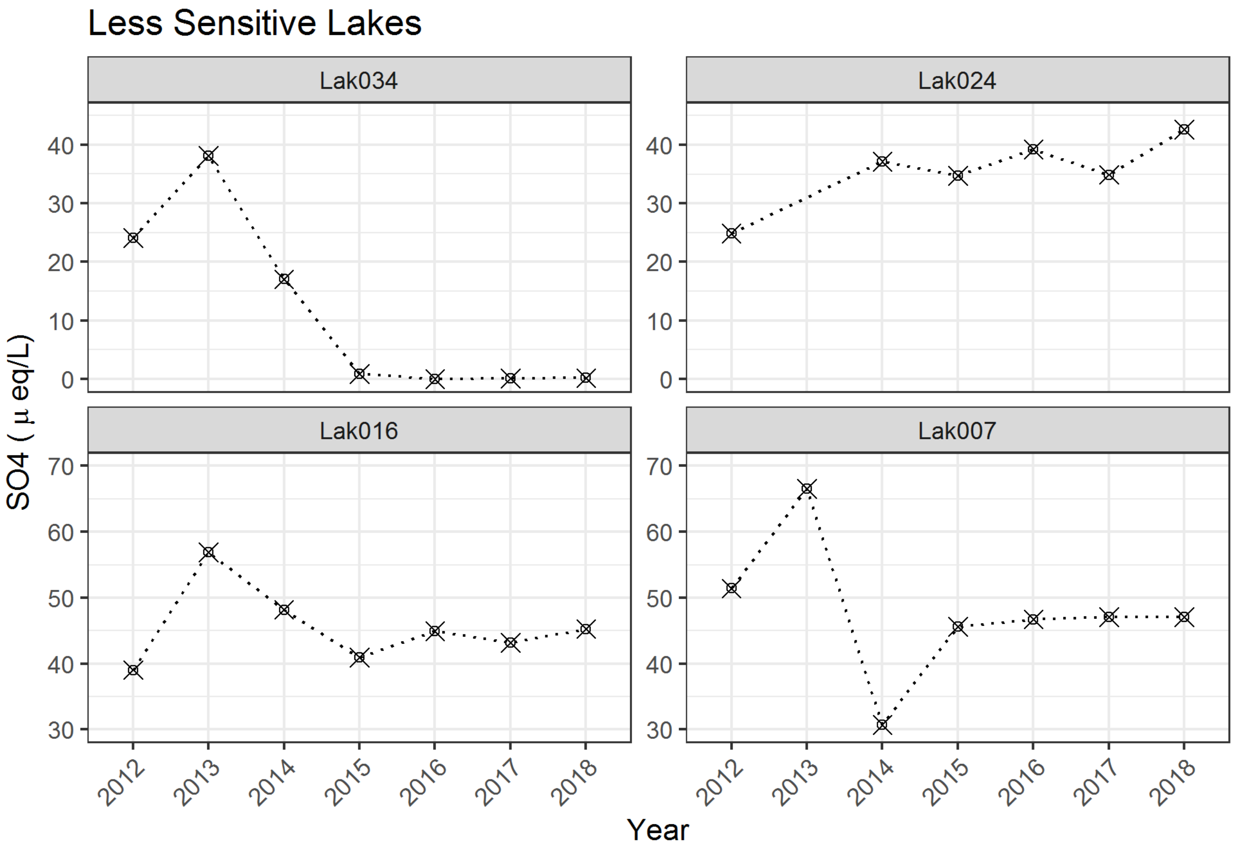


Figure 7.37: Annual trend of SO_4 concentrations for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034) for the years 2012-2018. Note that the scales are different on the y-axes.

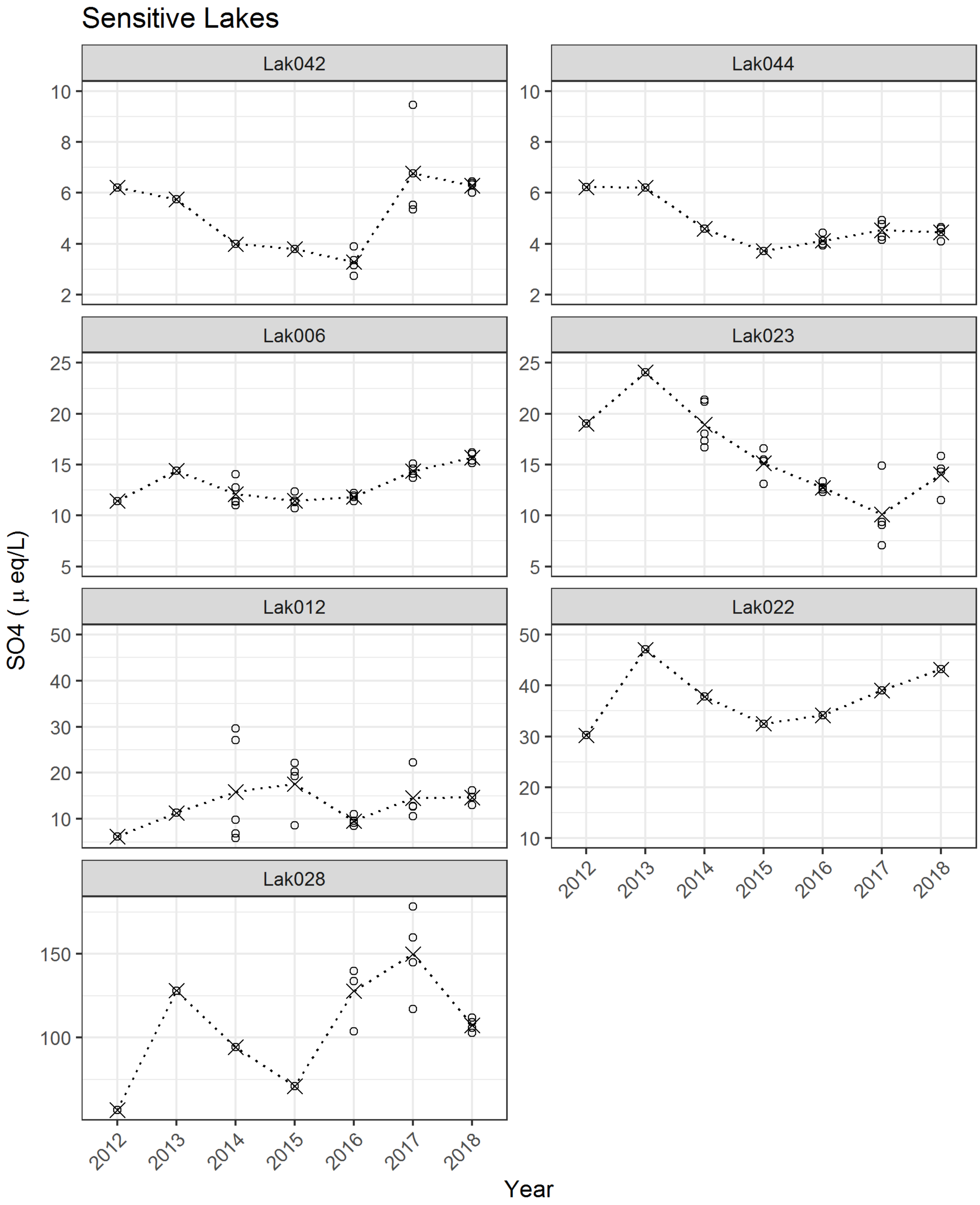


Figure 7.38: Annual trend of SO_4 for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) for the years 2012-2018. Note that the scales are different on the y-axes.

7.6.2.1.2 Gran ANC over time

- See Section 7.6.4.4 for statistical analyses of changes in Gran ANC
- See Section 7.6.4.6 for an integration of analyses of changes in sulphate, pH and ANC by lake

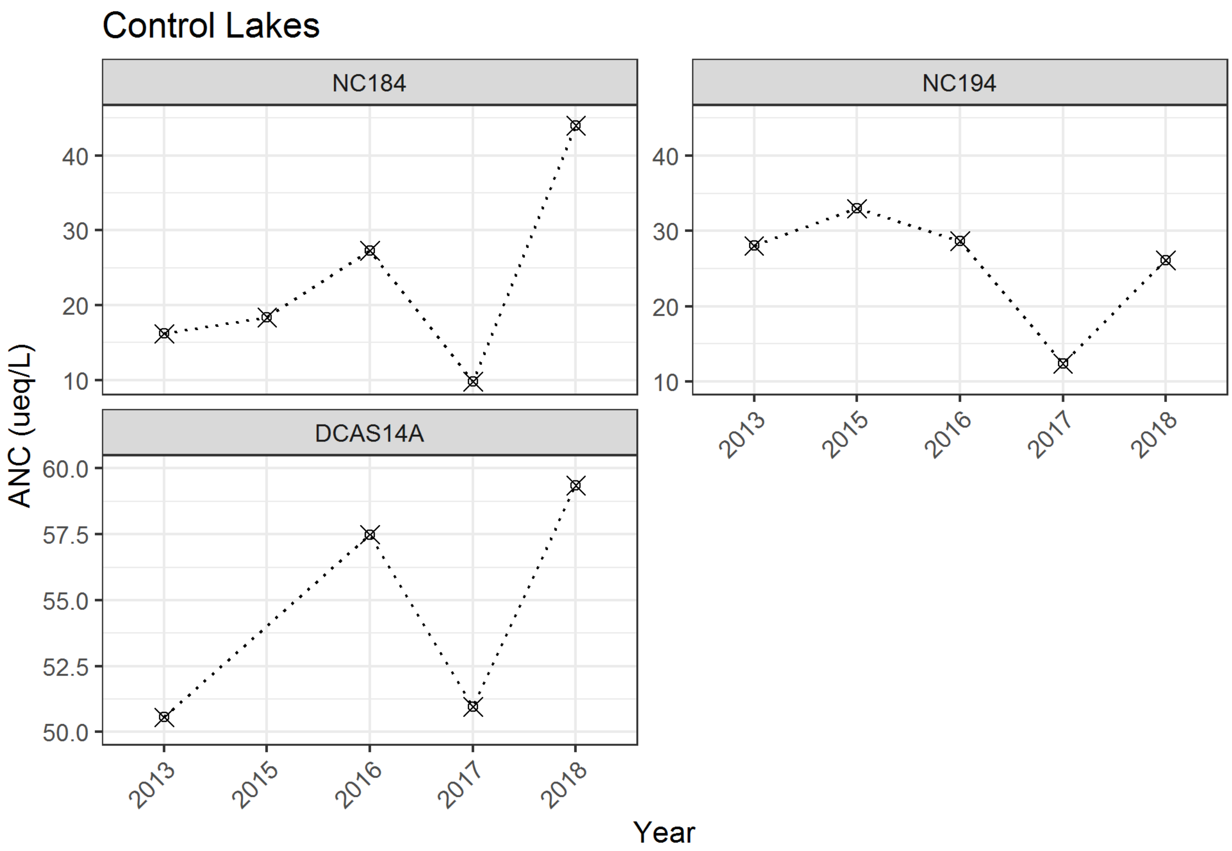


Figure 7.39: Annual trend in Gran ANC (μeq/L) for the control lakes (DCAS14A, NC184, NC194) for the years 2013-2018.

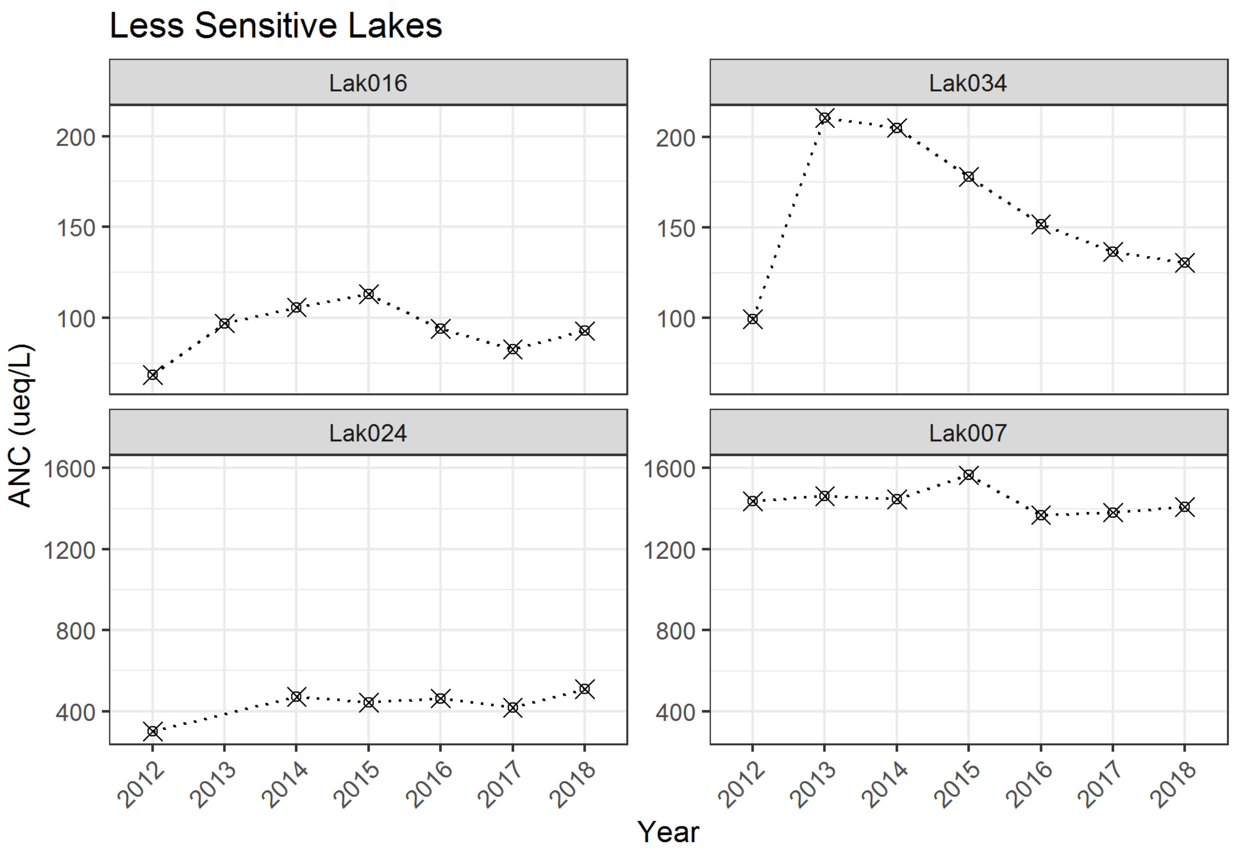


Figure 7.40: Annual trend in Gran ANC (μeq/L) for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034) for the years 2012-2018. Note that the scales are different on the y-axes.

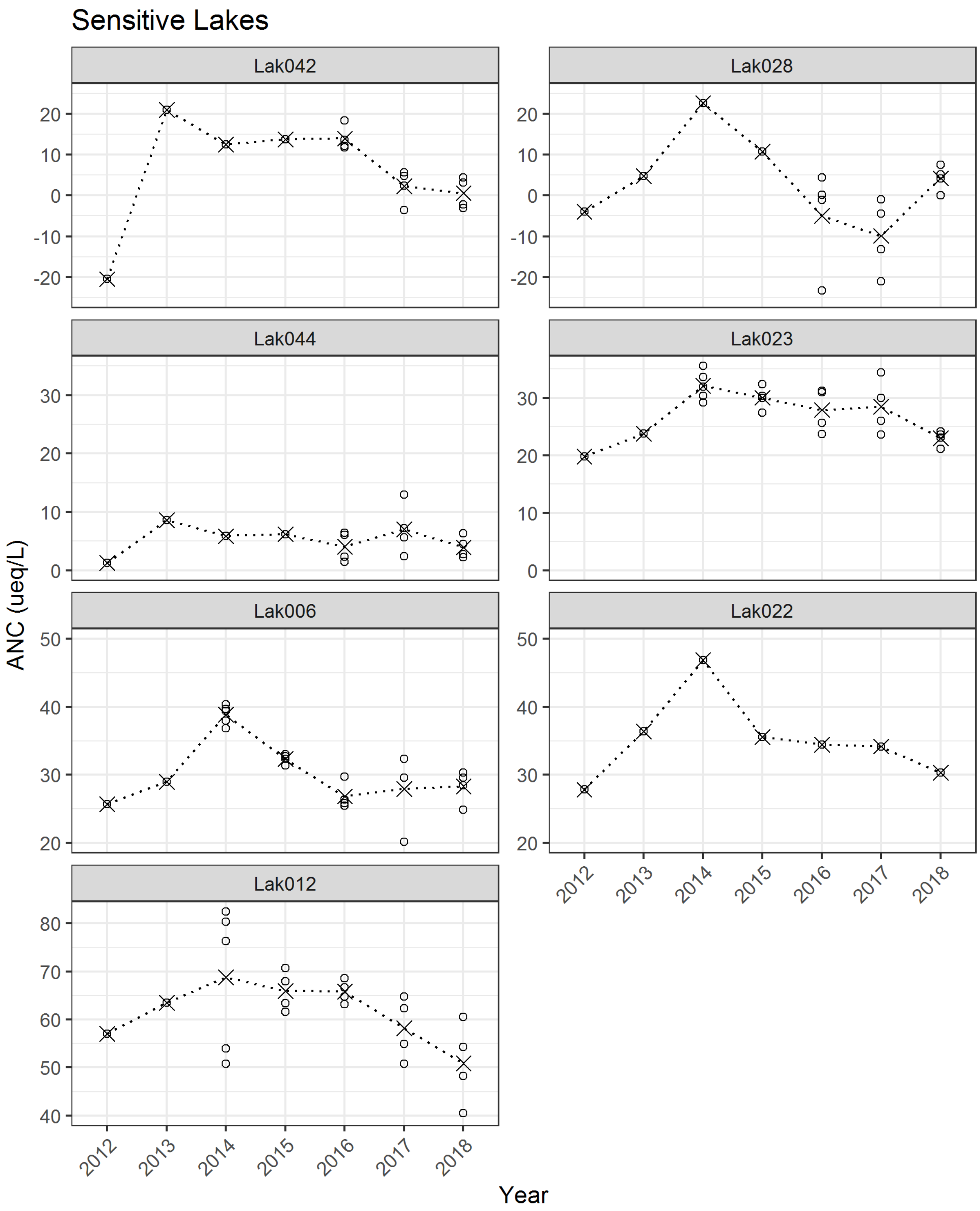


Figure 7.41: Annual trend of Gran ANC (μeq/L) for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) for the years 2012-2018. Note that the scales are different on the y-axes.

7.6.2.1.3 pH over time

- See Section 7.6.4.3 for statistical analyses of changes in pH
- See Section 7.6.4.6 for an integration of analyses of changes in sulphate, pH and ANC by lake

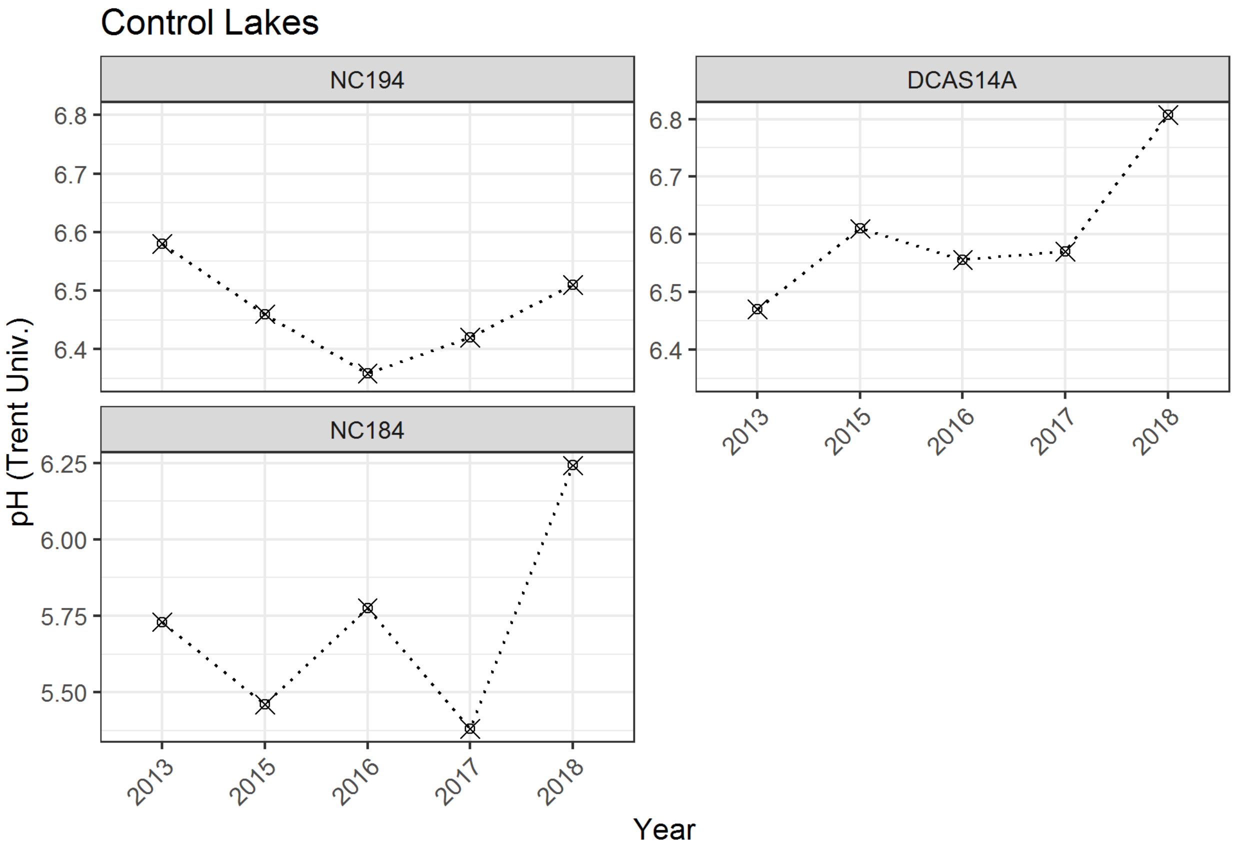


Figure 7.42: Annual trend of pH for the control lakes (DCAS14A, NC184, NC194) for the years 2013-2018. Note that the scales are different on the y-axes.

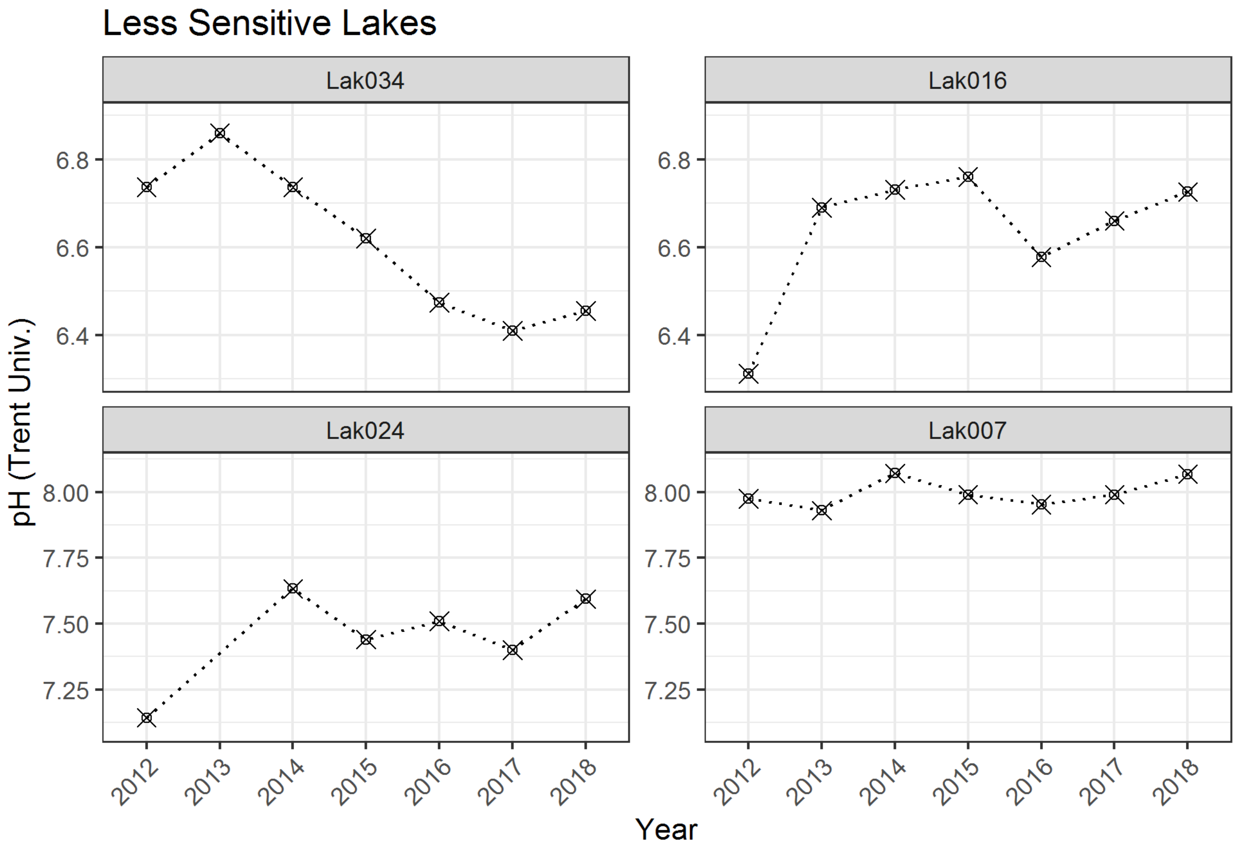


Figure 7.43: Annual trend of pH for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034) for the years 2012-2018. Note that the scales are different on the y-axes.

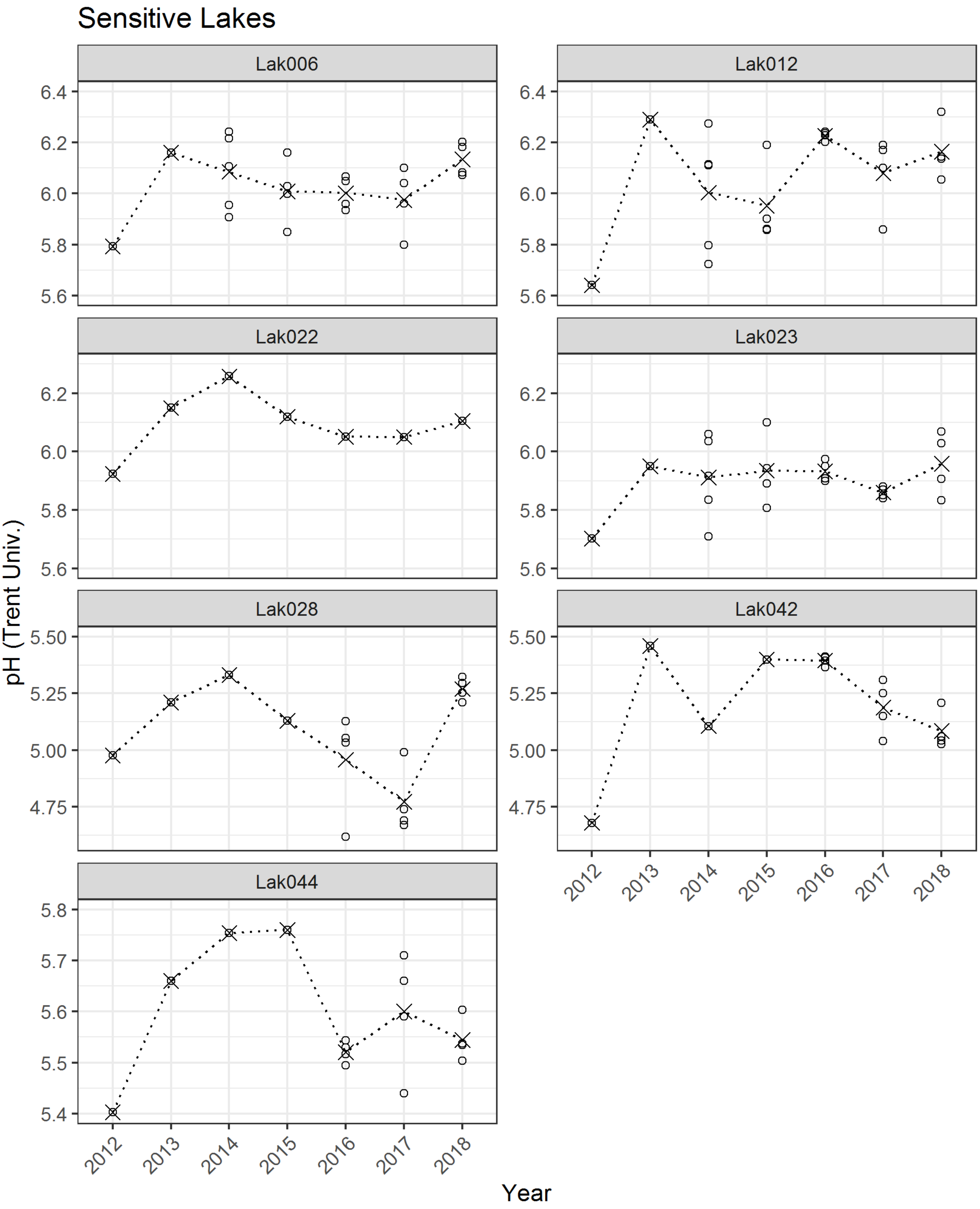


Figure 7.44. Annual trend of pH for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) for the years 2012-2018.

7.6.2.1.4 DOC over time

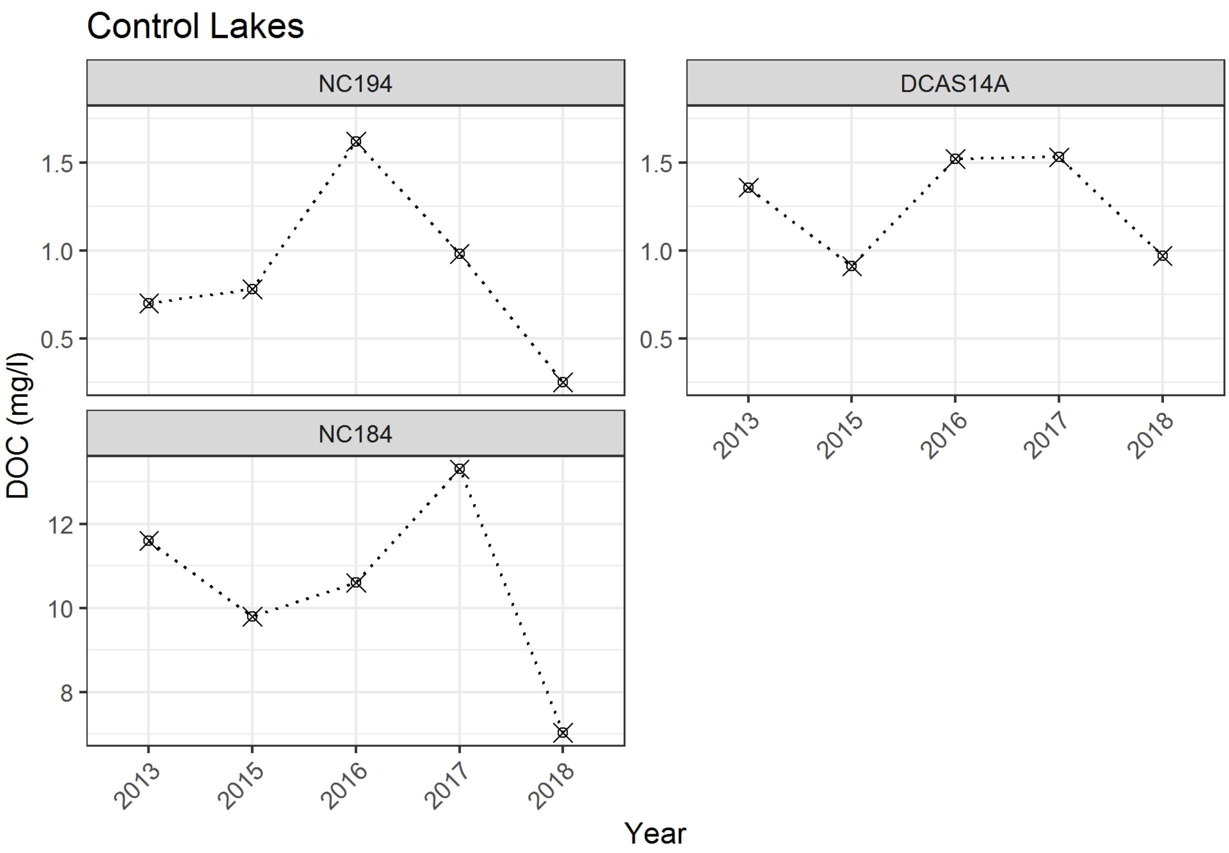


Figure 7.45: Annual trend in DOC (mg/L) for the control lakes (DCAS14A, NC184, NC194) for the years 2013-2018.

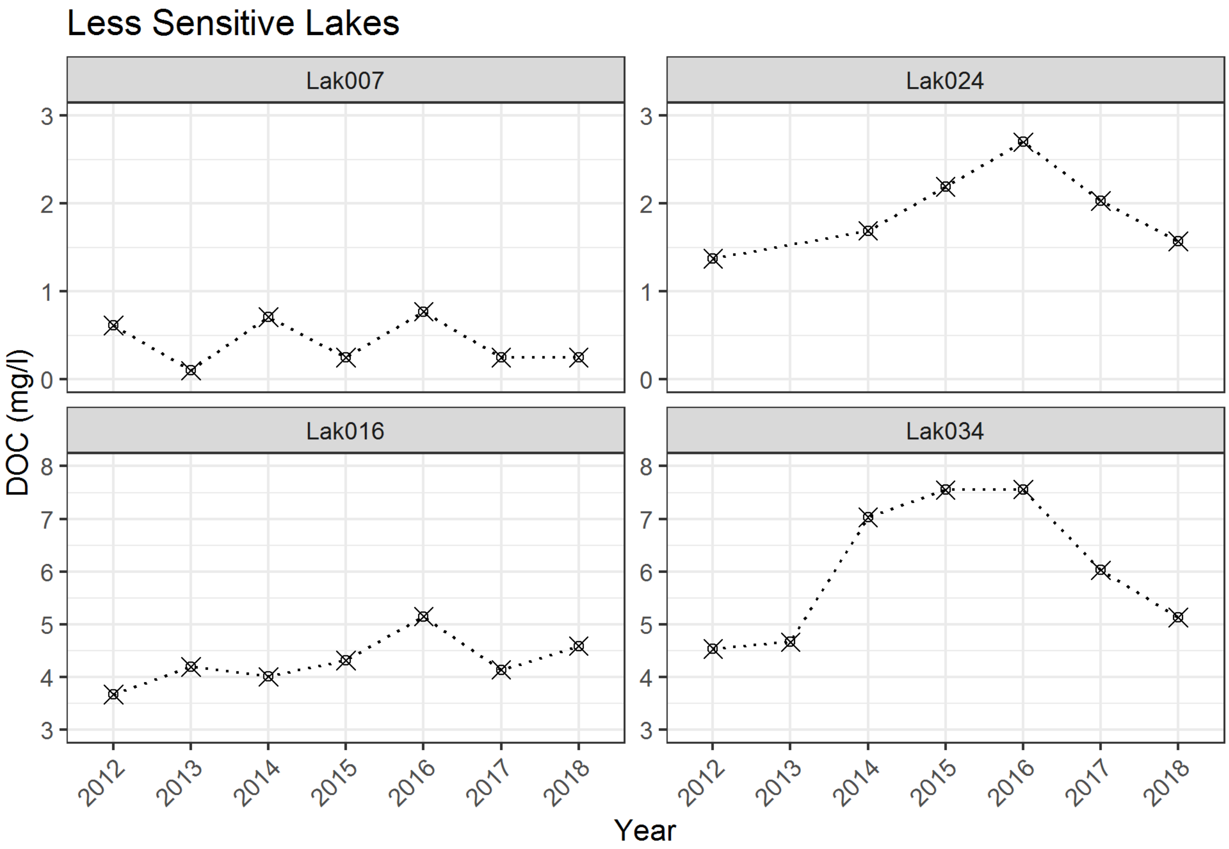


Figure 7.46: Annual trend in DOC (mg/L) for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034) for the years 2012-2018.

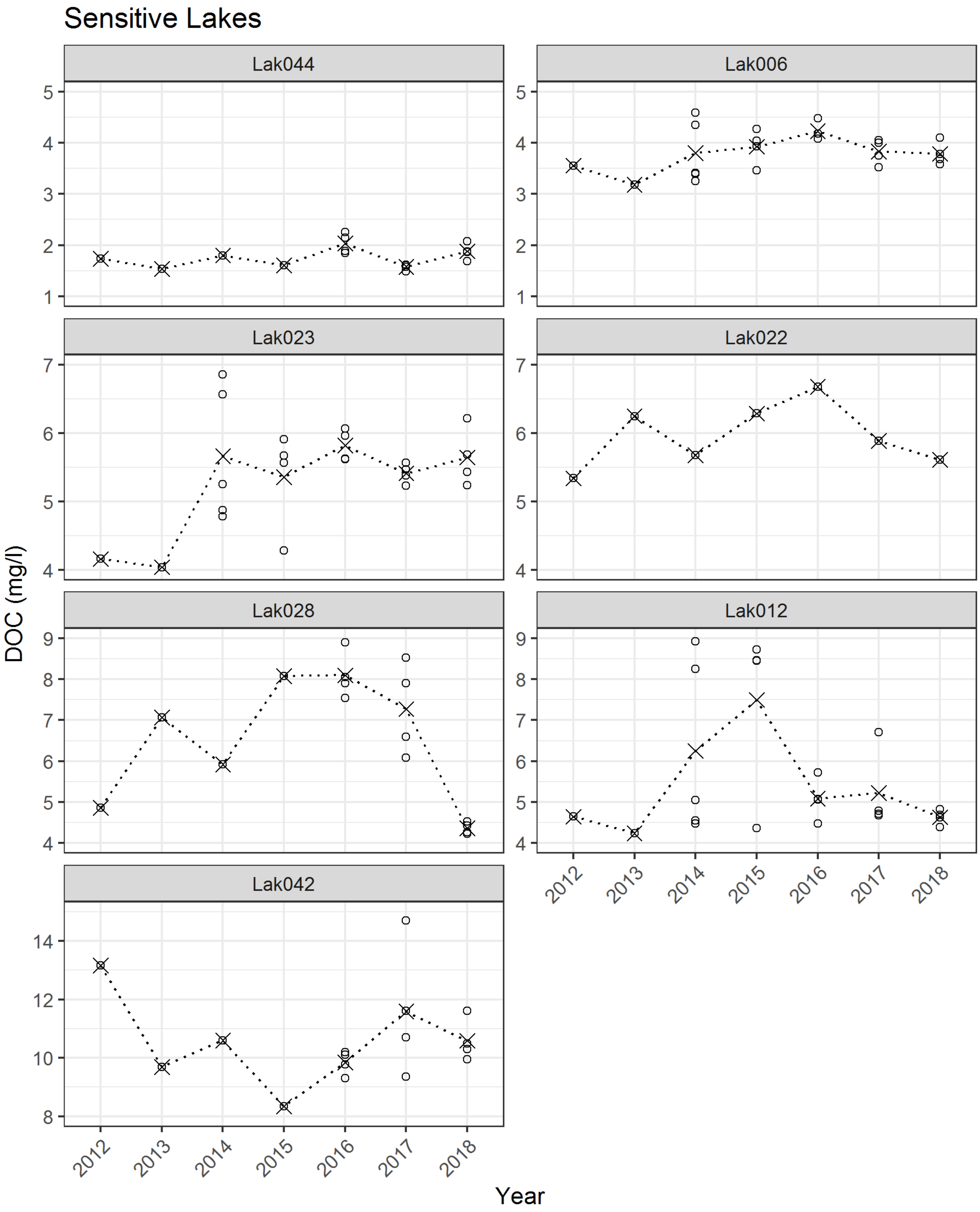


Figure 7.47: Annual trend of DOC (mg/L) for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) for the years 2012-2018.

7.6.2.1.5 Base cations over time

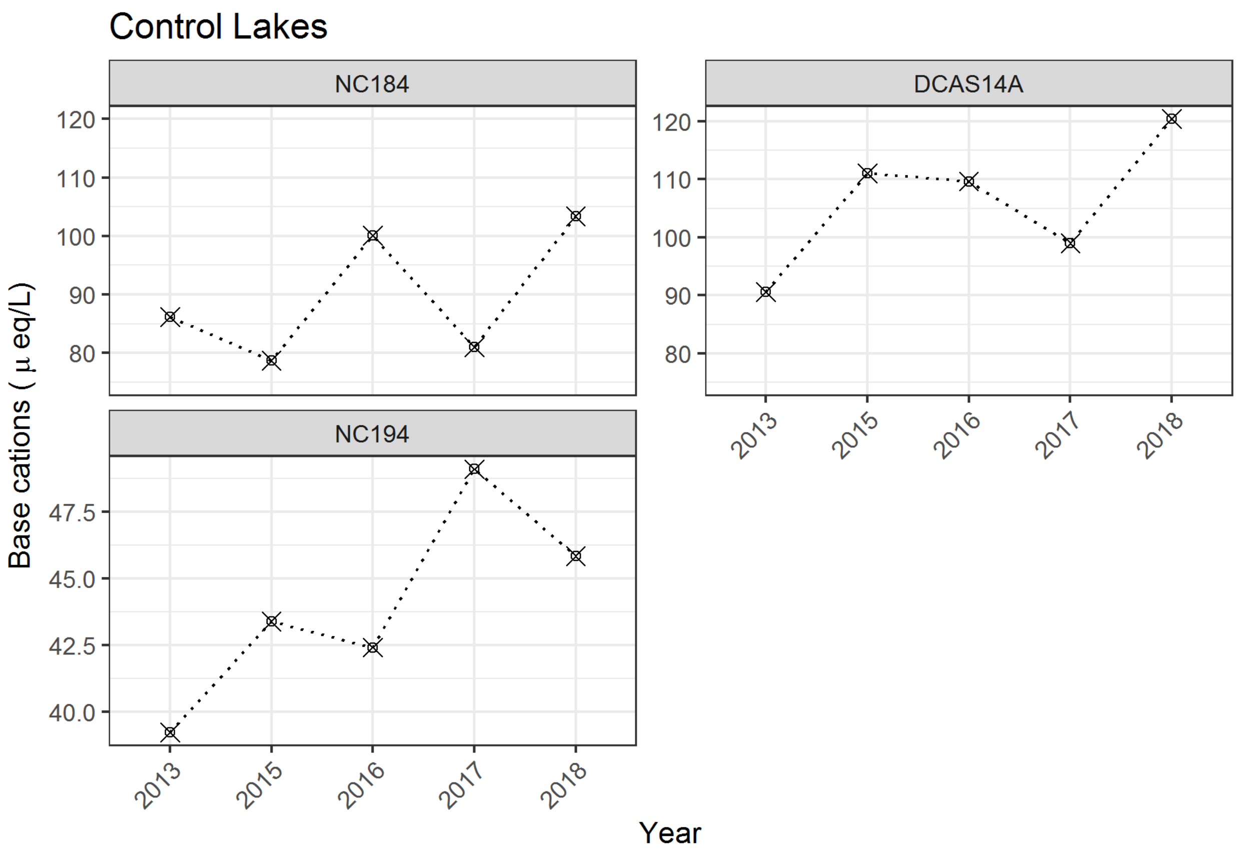


Figure 7.48: Annual trend in Base cations for the control lakes (DCAS14A, NC184, NC194) for the years 2013-2018.

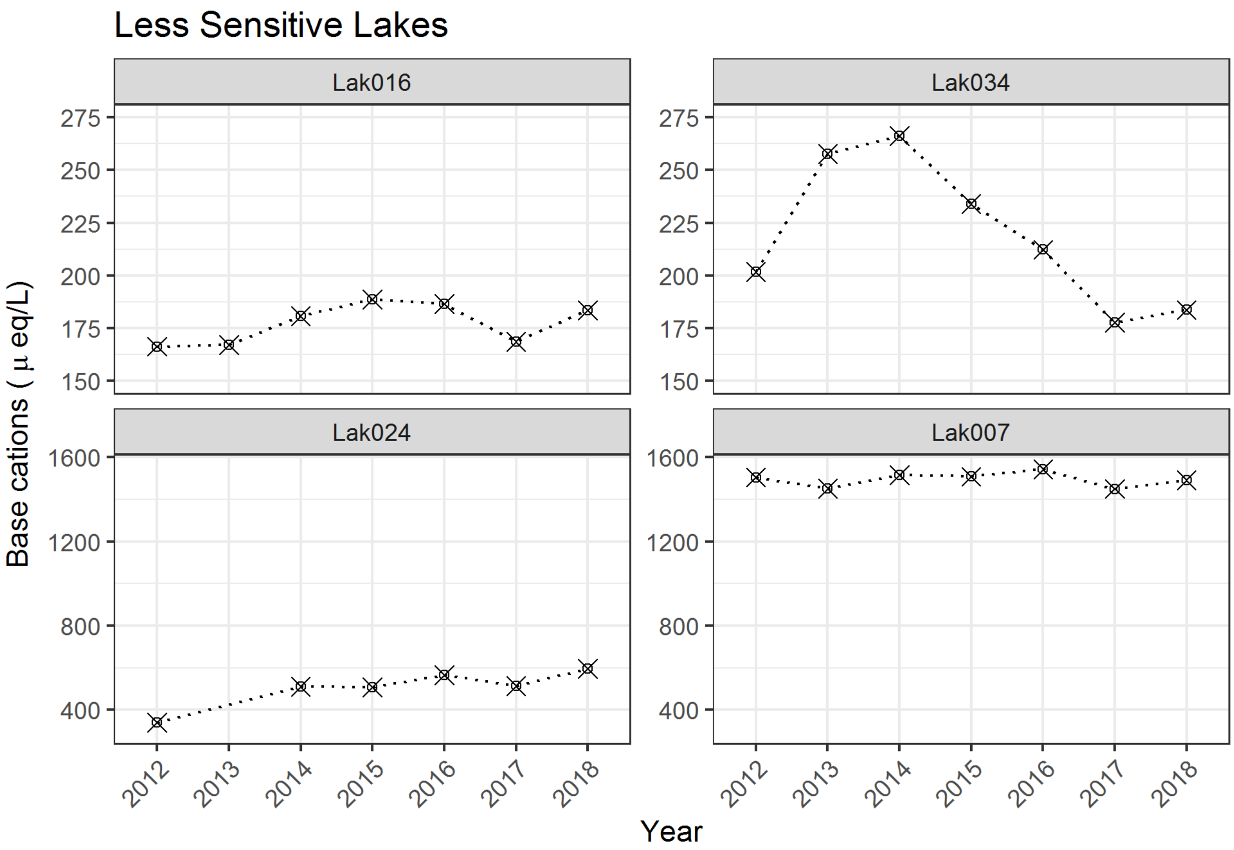


Figure 7.49: Annual trend in Base Cations for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034) for the years 2012-2018.

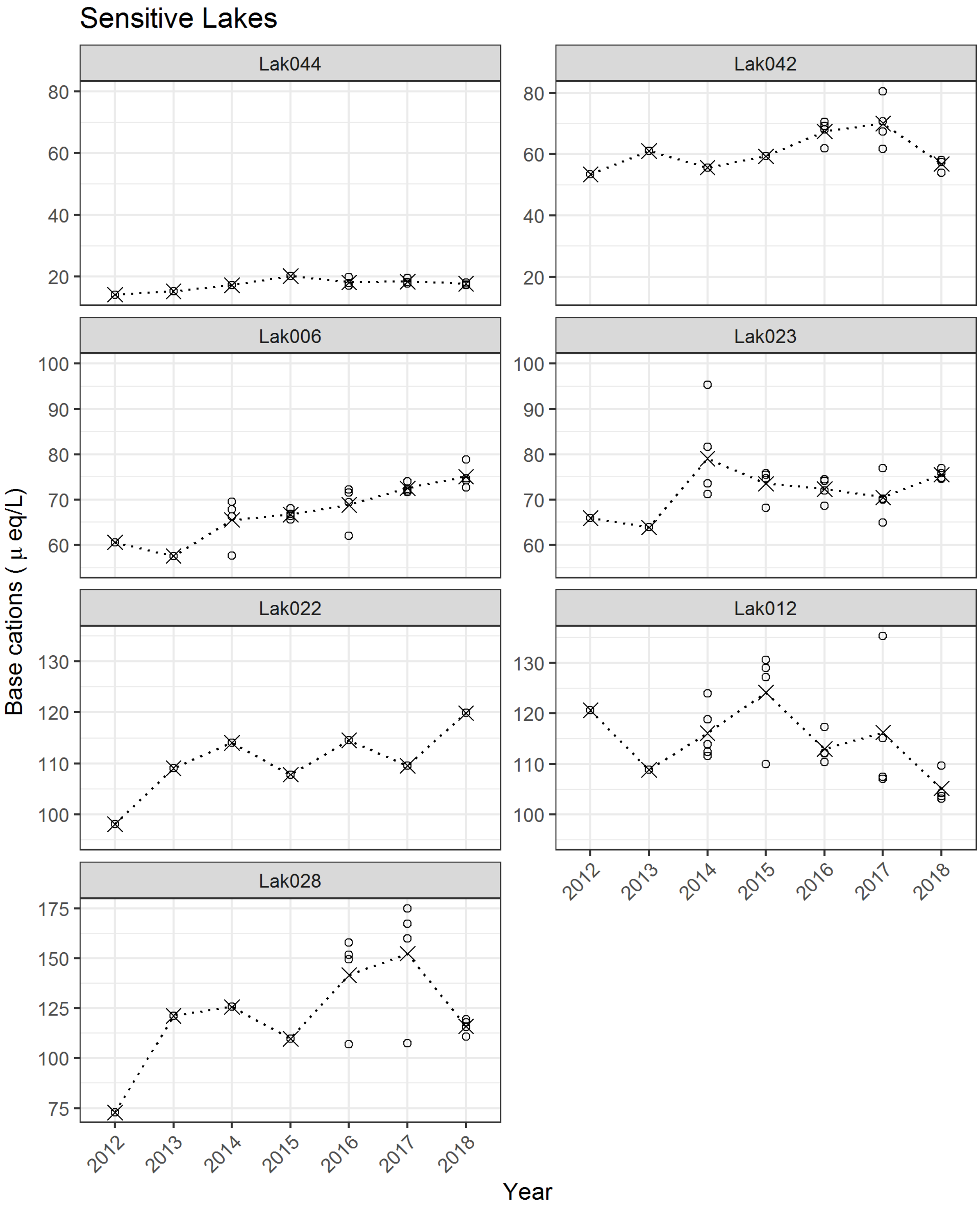


Figure 7.50: Annual trend of Base Cations for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) for the years 2012-2018.

7.6.2.1.6 Calcium over time

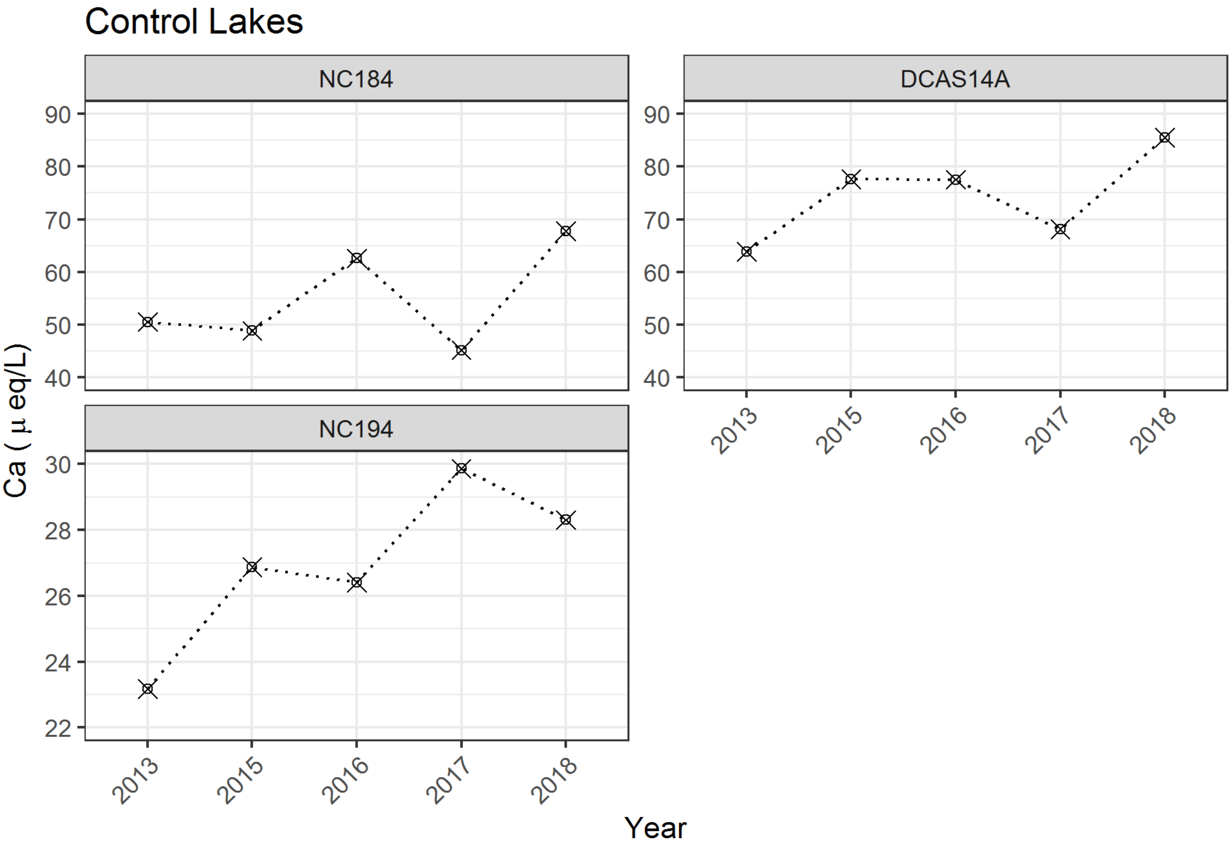


Figure 7.51: Annual trend in Calcium for the control lakes (DCAS14A, NC184, NC194) for the years 2013-2018.

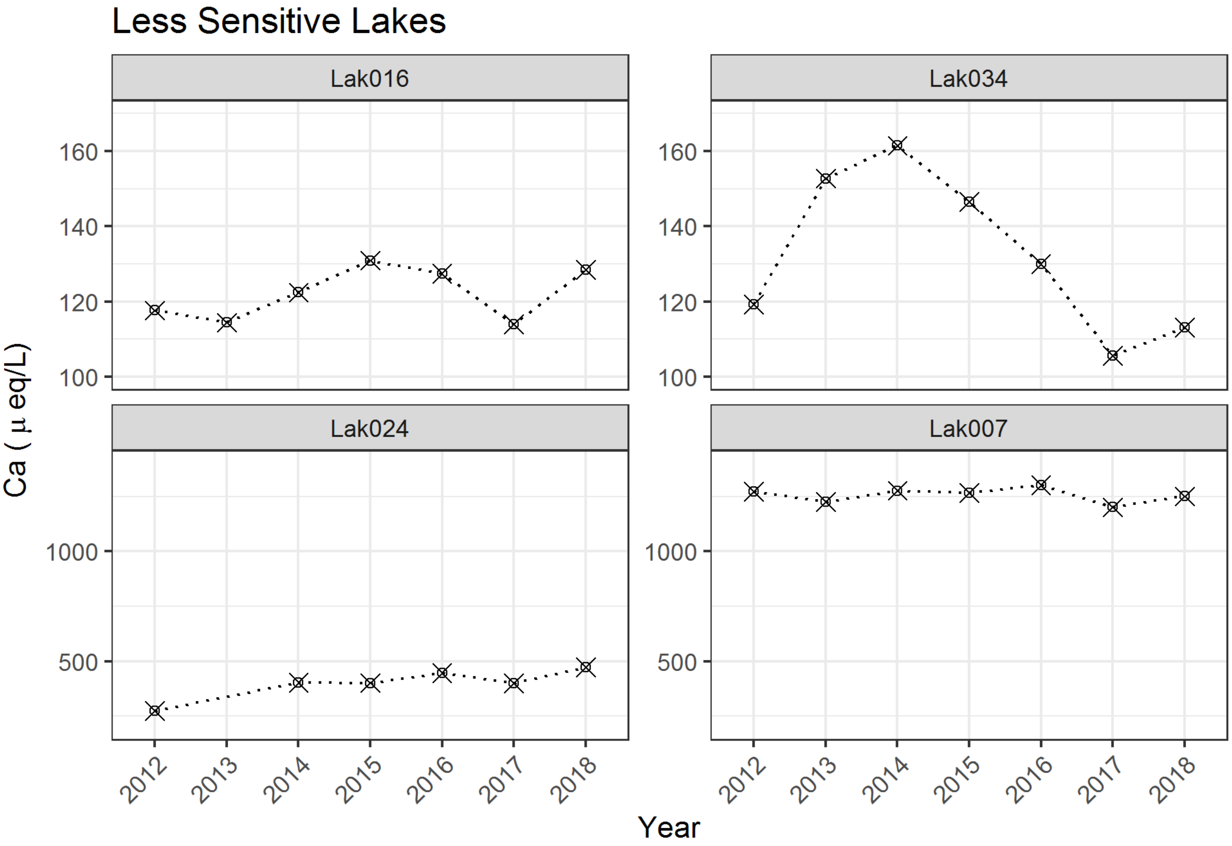


Figure 7.52: Annual trend in Calcium for the less sensitive lakes (LAK007, LAK016, LAK024, LAK034) for the years 2012-2018.

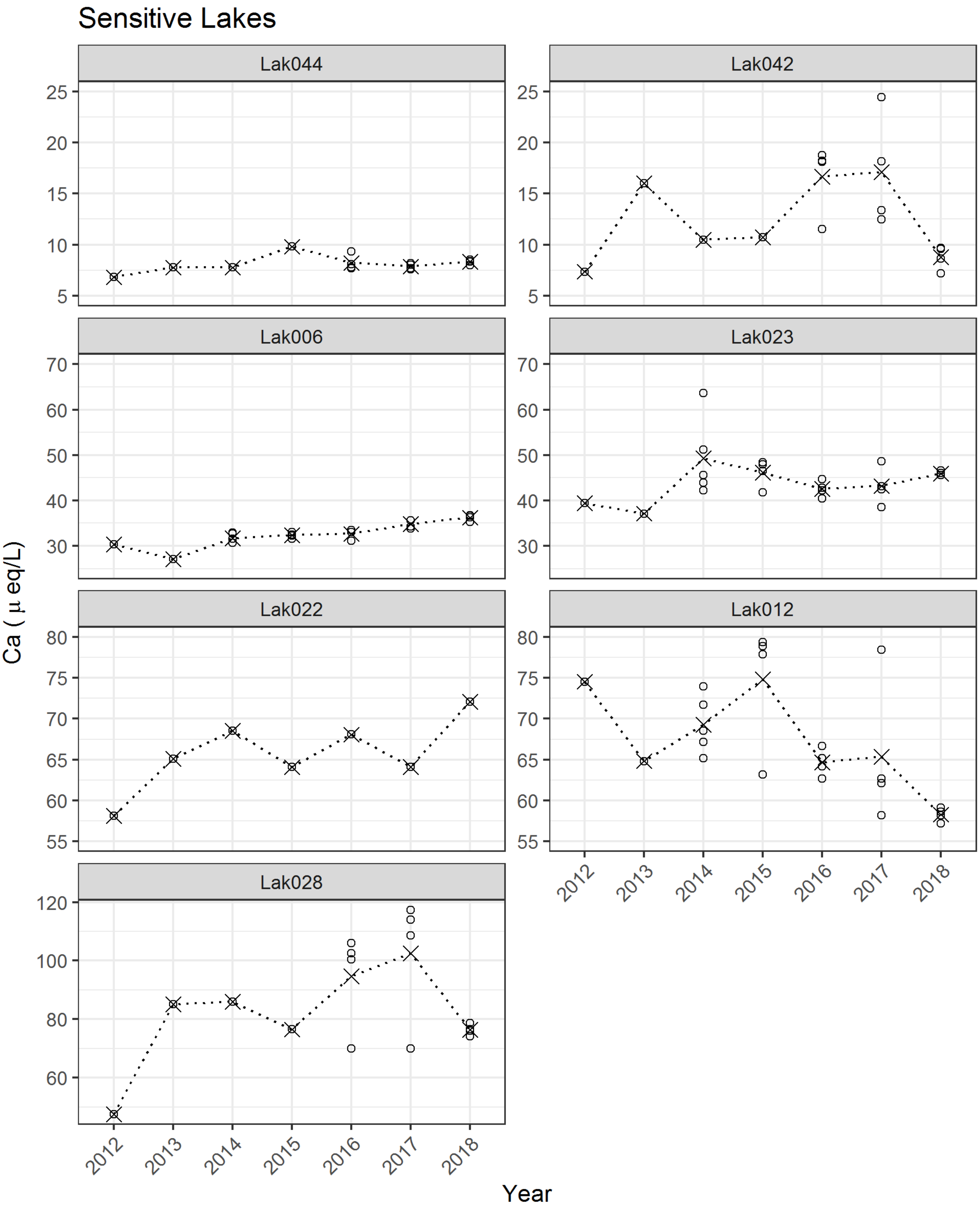


Figure 7.53: Annual trend of Calcium for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044) for the years 2012-2018.

7.6.2.2 Lake Chemistry Relative to Recent Precipitation

The EEM is designed to detect long term trends, not episodic changes in water chemistry. Eight lakes are sampled annually during the fall index period, while six lakes are sampled four times during this period. We are however interested in understanding the extent to which late summer and fall storms may affect lake chemistry, and the apparent trends over multiple years. Snowmelt and rainstorms may affect water chemistry through a number of natural and anthropogenic mechanisms, summarized succinctly by Wiggington et al. 1996:

> "Four major natural processes can produce [acidic] episodes: (1) dilution, (2) nitrification, (3) organic acid production, and (4) the sea salt effect (Galloway et al. 1987, Peters and Driscoll 1987, Turner et al. 1990, Heath et al. 1992, Kahl et al. 1992). Atmospheric deposition can contribute to episodic acidification by (1) providing direct inputs of acidic water to surface waters, (2) conditioning watersheds via the accumulation of $S042^-$, $NO3^-$, $NH4^+$, and H^+ from atmospheric de- position in the upper layers of watershed soils during relatively dry periods, and (3) lowering the chronic ANC of some systems and subsequently lowering the minimum ANC values attained during episodes (Galloway et al. 1987)."

Intensive studies of acidic episodes require very frequent sampling (i.e., hourly) before, during and after a storm event to detect ANC and pH declines and deduce the most likely causes of these declines. Such fine scale examinations are beyond the scope of the EEM. Looking at the patterns of change in water chemistry vs. total precipitation over 3-day and 14-day intervals is the best that we can do with the data that we have. We cannot detect effects which occur on finer time scales than our sampling frequency.

7.6.2.2.1 SO_4 vs. Precipitation

Purpose of analysis: These graphs are intended to explore whether SO_4 is associated with the magnitude of recent precipitation, which could create a spurious long-term trend. For example, if big storms occurred prior to the annual sampling later in the 7-year time series (i.e., 2017 or 2018), and increased SO_4, due to washout of atmospheric or watershed SO_4, this might generate a false long-term pattern of increasing SO_4 over multiple years. Conversely, if major storms occurred prior to annual sampling early in the time series (i.e., 2012 or 2013), and increased concentrations of SO_4, this might generate a false long-term pattern of decreasing SO_4 over multiple years. Since most of the sensitive lakes were sampled four times in the fall (beginning in 2014), averaging over a range of weather conditions in October, there is a lower risk that the mean of these four values will generate a false pattern of SO_4 concentrations confounded by storm events. Storm events which carry smelter-origin sulphate into the lakes would however represent a real effect of the smelter on lake chemistry.

Explanation of the graphs: We used two explanatory variables: the total amount of precipitation in the 3 days prior to sampling (i.e., prior week's precipitation, estimated from the Haul Road site); and the total amount of precipitation in the 14 days (2 weeks) prior to sampling.

- See Section 7.6.4.2.6 for statistical analyses of the ability of covariates describing recent precipitation to explain observed patterns of changes over time in sulphate, beyond those patterns observed in control lakes.

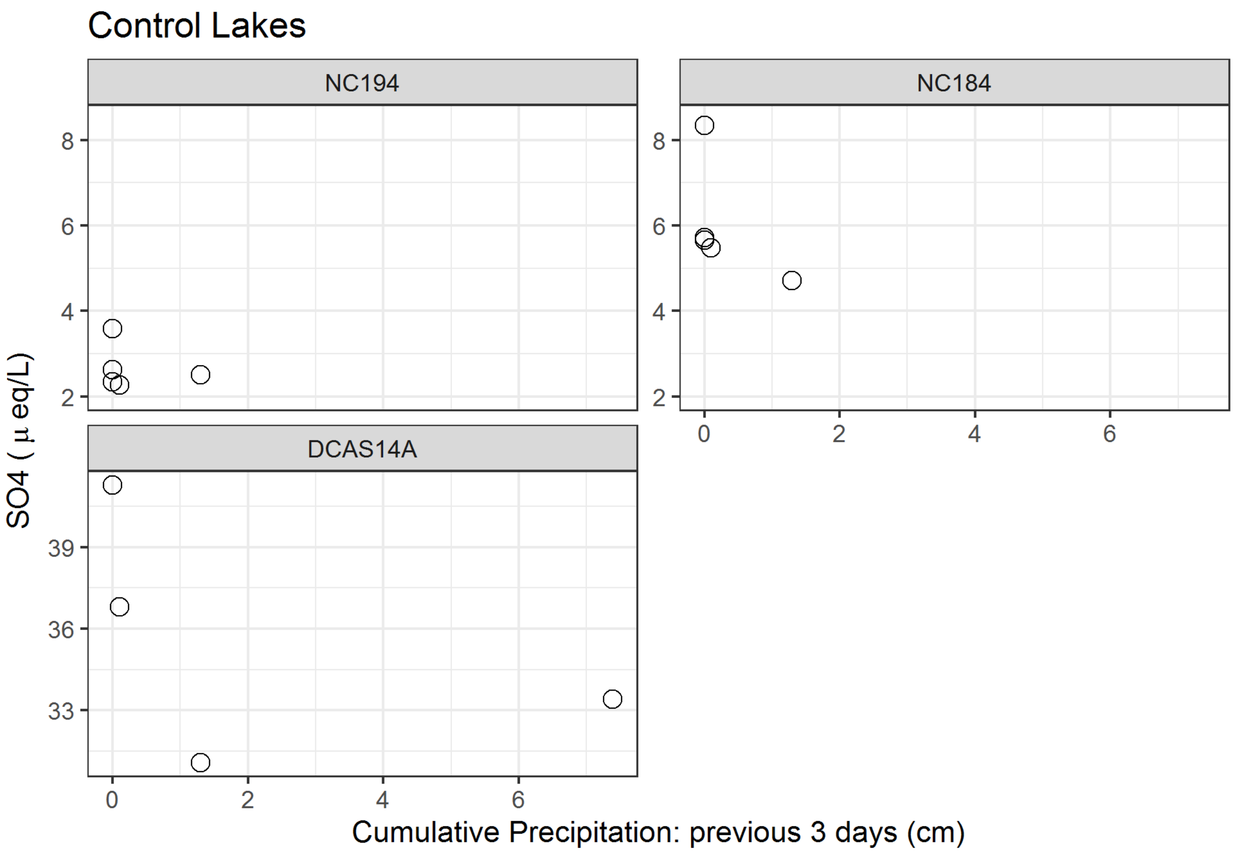


Figure 7.54: Concentration of SO_4 vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

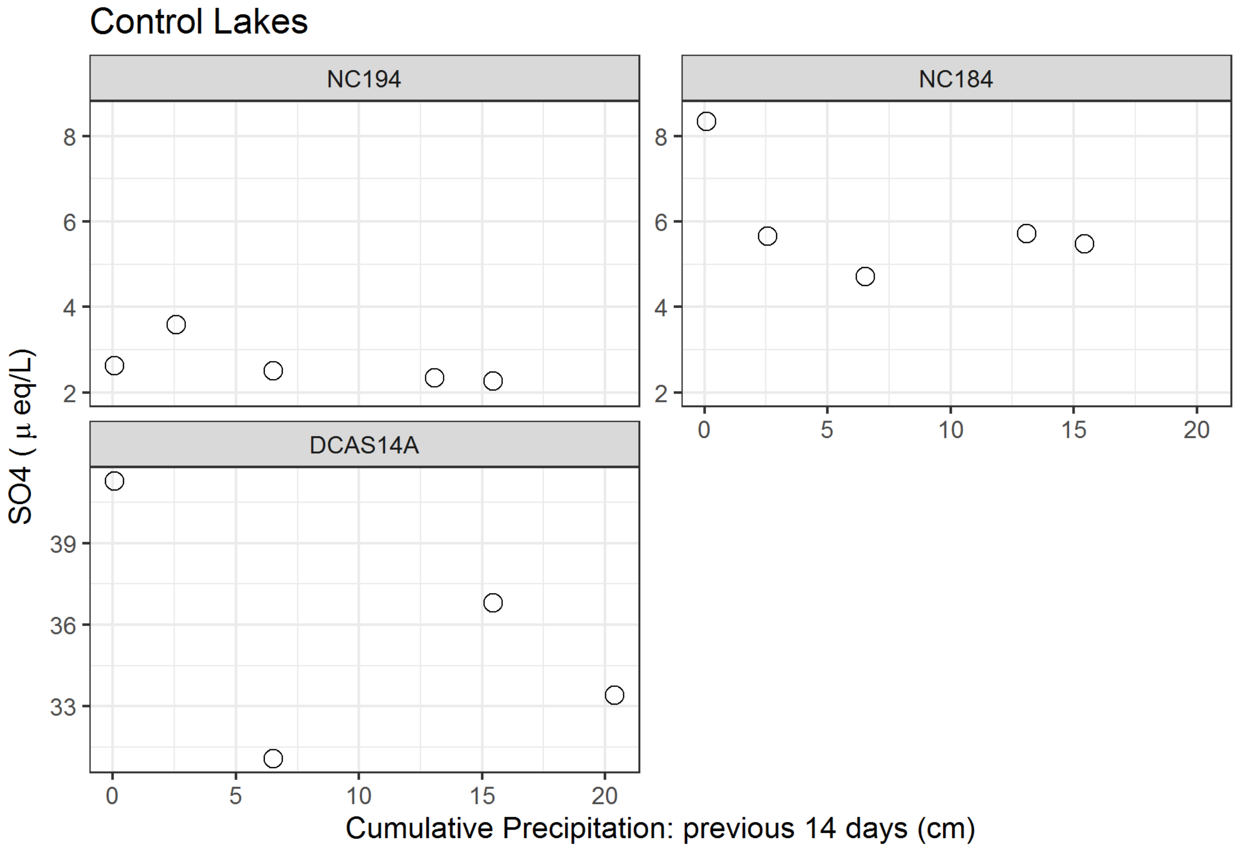


Figure 7.55: Concentration of SO_4 vs. cumulative precipitation (cm) over the previous 14 days for the control lakes (DCAS14A, NC184, NC194).

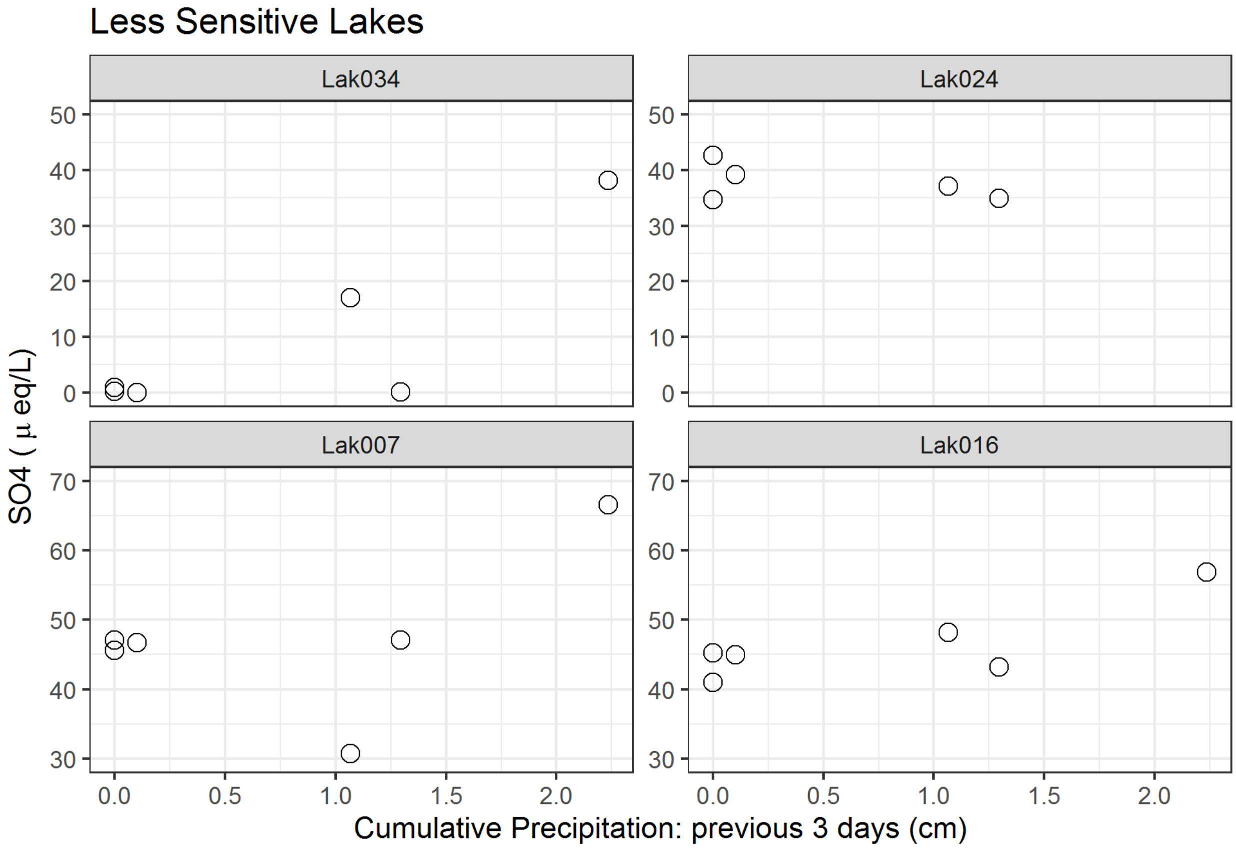


Figure 7.56: Concentration of SO_4 vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

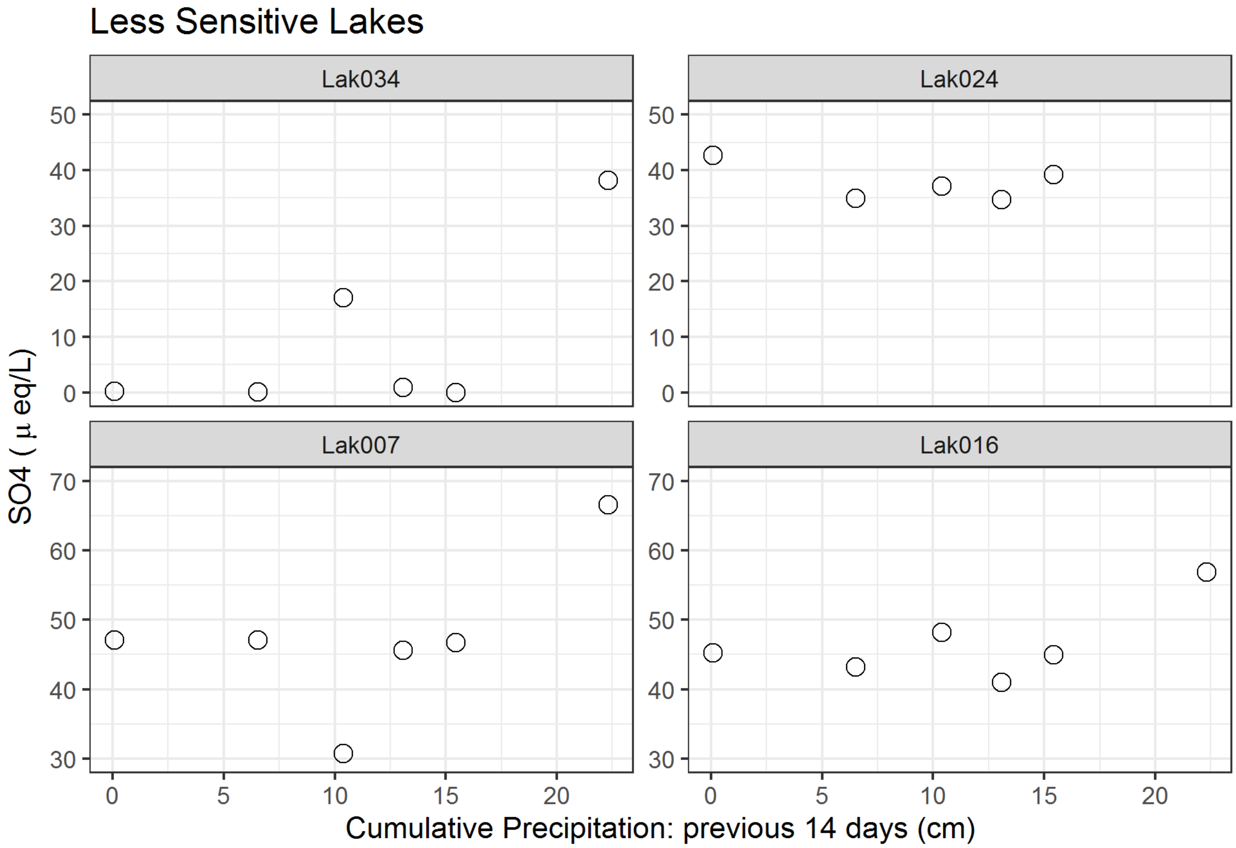


Figure 7.57: Concentration of SO_4 vs. cumulative precipitation (cm) over the previous 14 days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

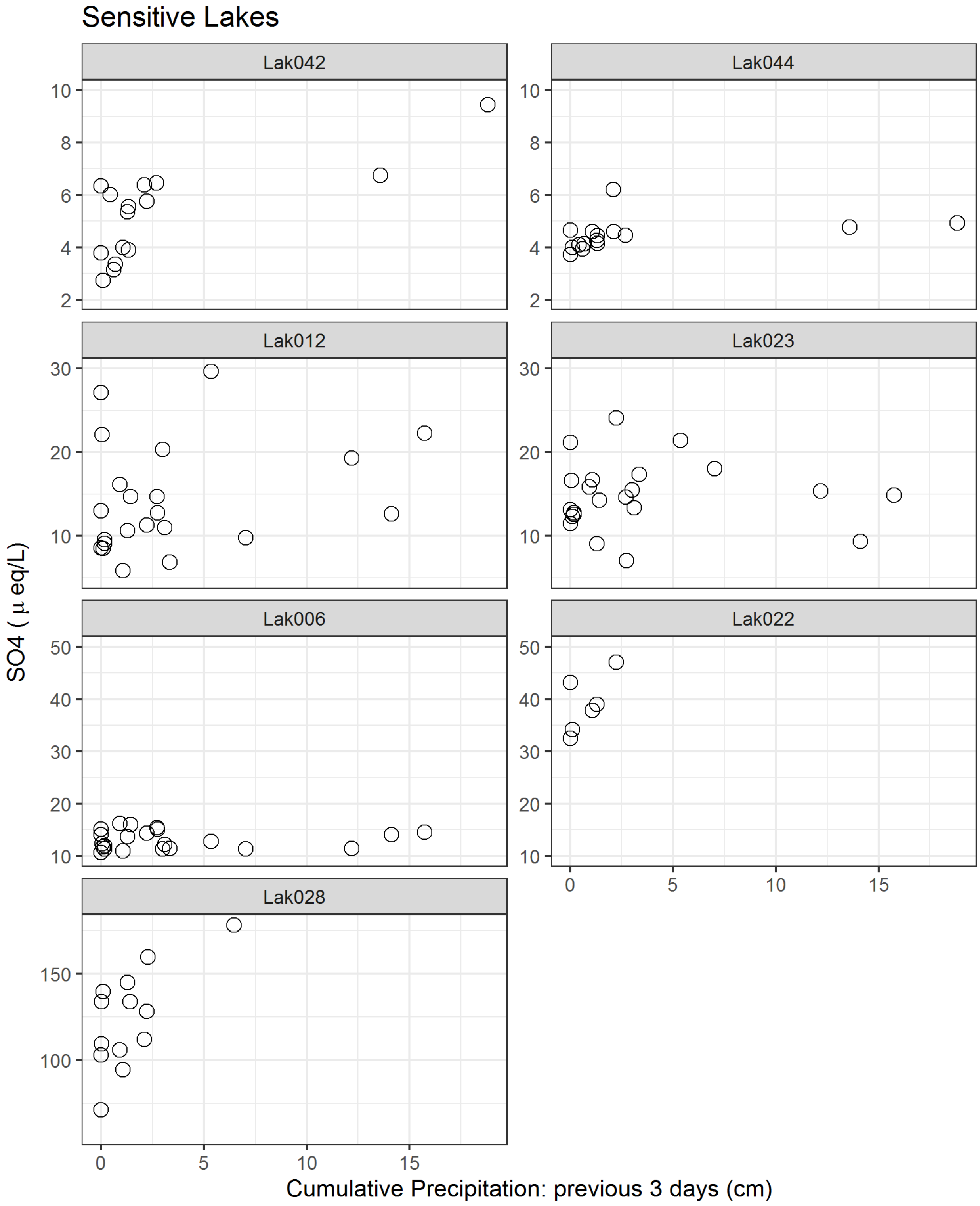


Figure 7.58: Concentration of SO_4 vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

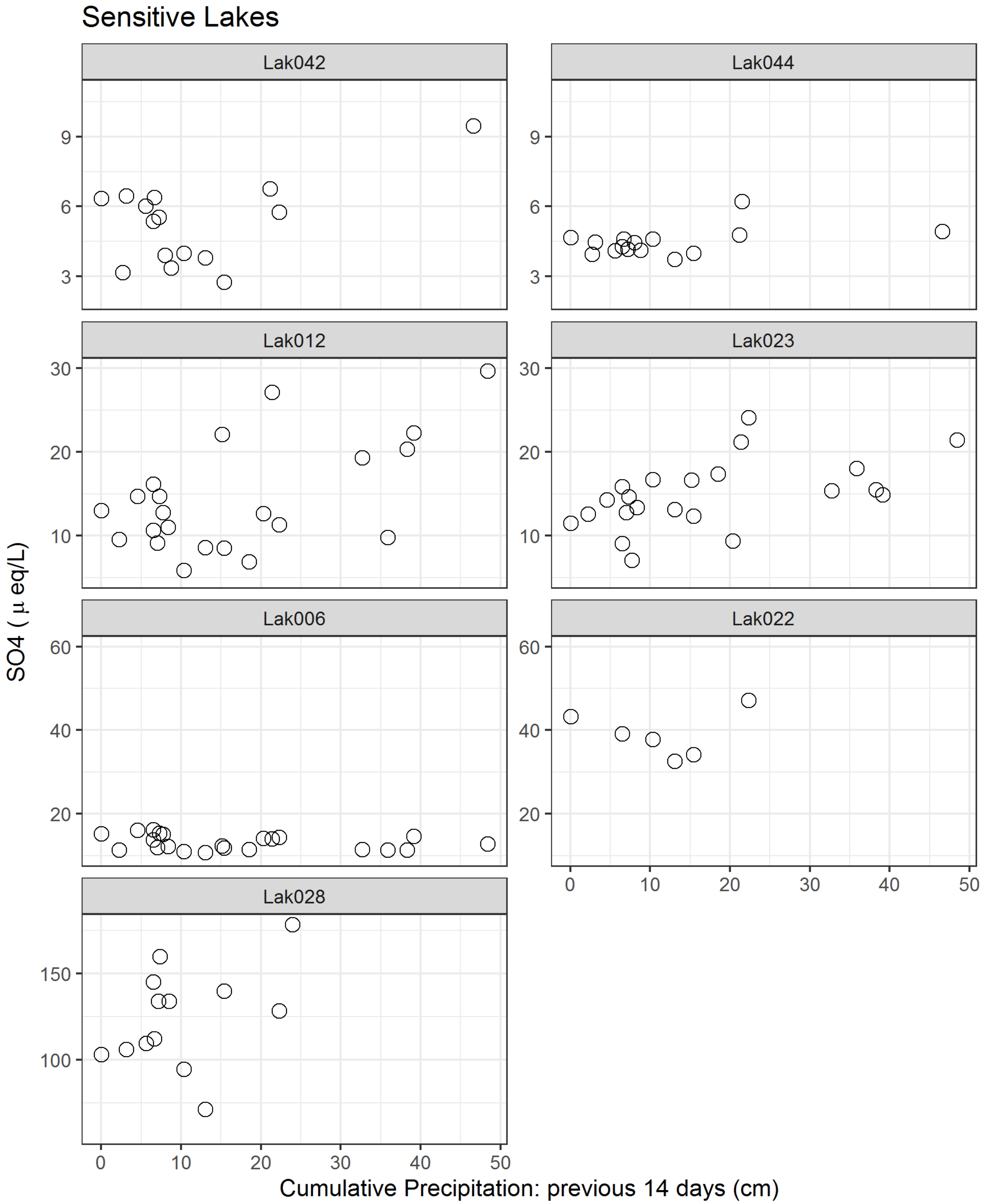


Figure 7.59: Concentration of SO_4 vs. cumulative precipitation (cm) over the previous 14 days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.2.2 Gran ANC vs. Precipitation

Purpose of analysis: Similar to what is described above, but unlike for SO_4 (where a positive correlation with precipitation is hypothesized), these graphs are intended to explore whether Gran ANC is *inversely* associated with the magnitude of recent precipitation, which could create a spurious long-term trend. For example, if big storms occurred prior to the annual sampling later in the 7-year time series (i.e., 2017 or 2018), and depressed Gran ANC, this might generate a false long-term pattern of declining Gran ANC over multiple years. Conversely, if major storms occurred prior to annual sampling early in the time series (i.e., 2012 or 2013), and depressed Gran ANC, this might generate a false long-term pattern of increasing Gran ANC over multiple years. Since most of the sensitive lakes were sampled four times in the fall (beginning in 2014), averaging over a range of weather conditions in October, there is a lower risk that the mean of these four values will generate a false pattern of Gran ANC declines due to confounding with storm events. Storm events which carry smelter-origin sulphate and hydrogen into the lakes (and cause a decline in a lake's Gran ANC) would however represent a real effect of the smelter on lake chemistry.

Explanation of the graphs: We used the same two explanatory variables explained above – precipitation over the week prior to sampling, and over the previous 4 weeks, as measured at Haul Road.

- See Section 7.6.4.4.6 for statistical analyses of the ability of covariates describing recent precipitation to explain patterns of changes over time in Gran ANC, beyond those patterns observed in control lakes.

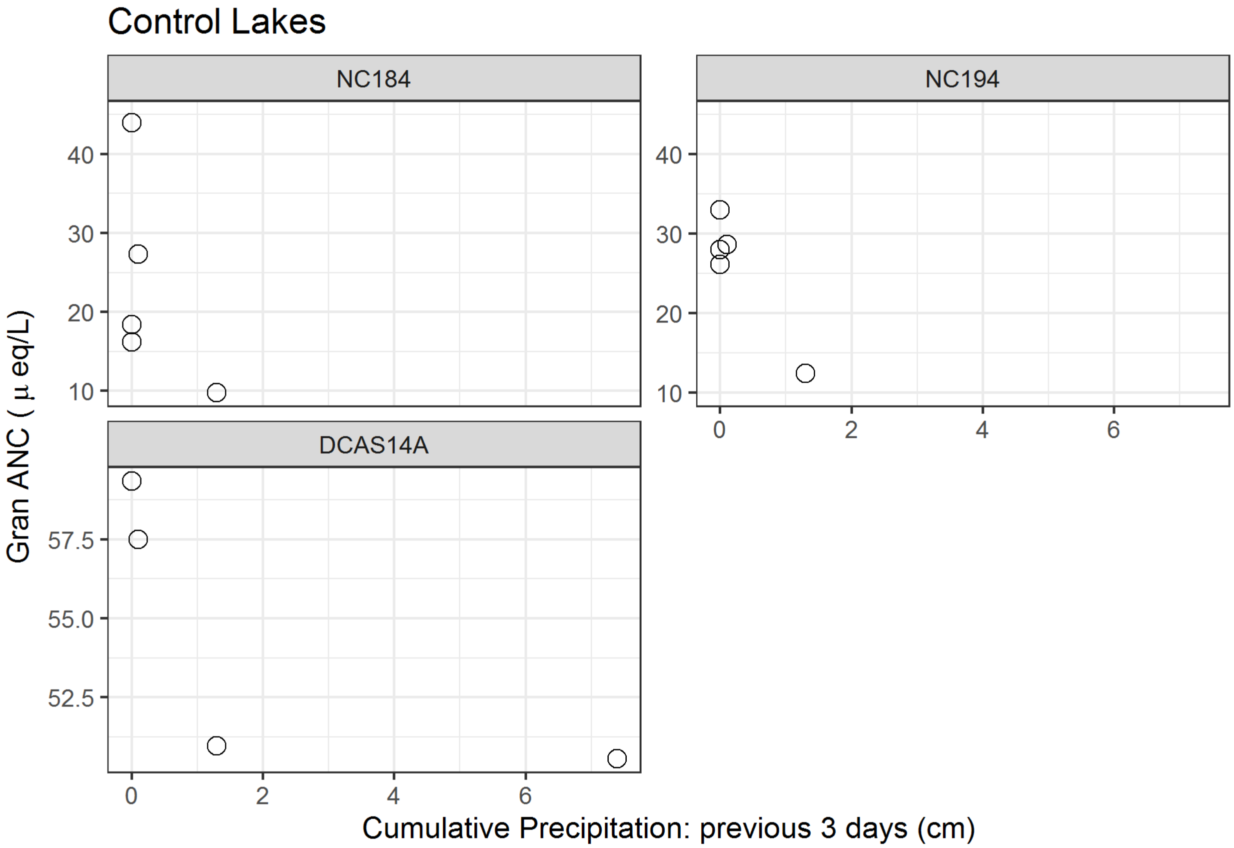


Figure 7.60: Gran ANC (μeq/L) vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

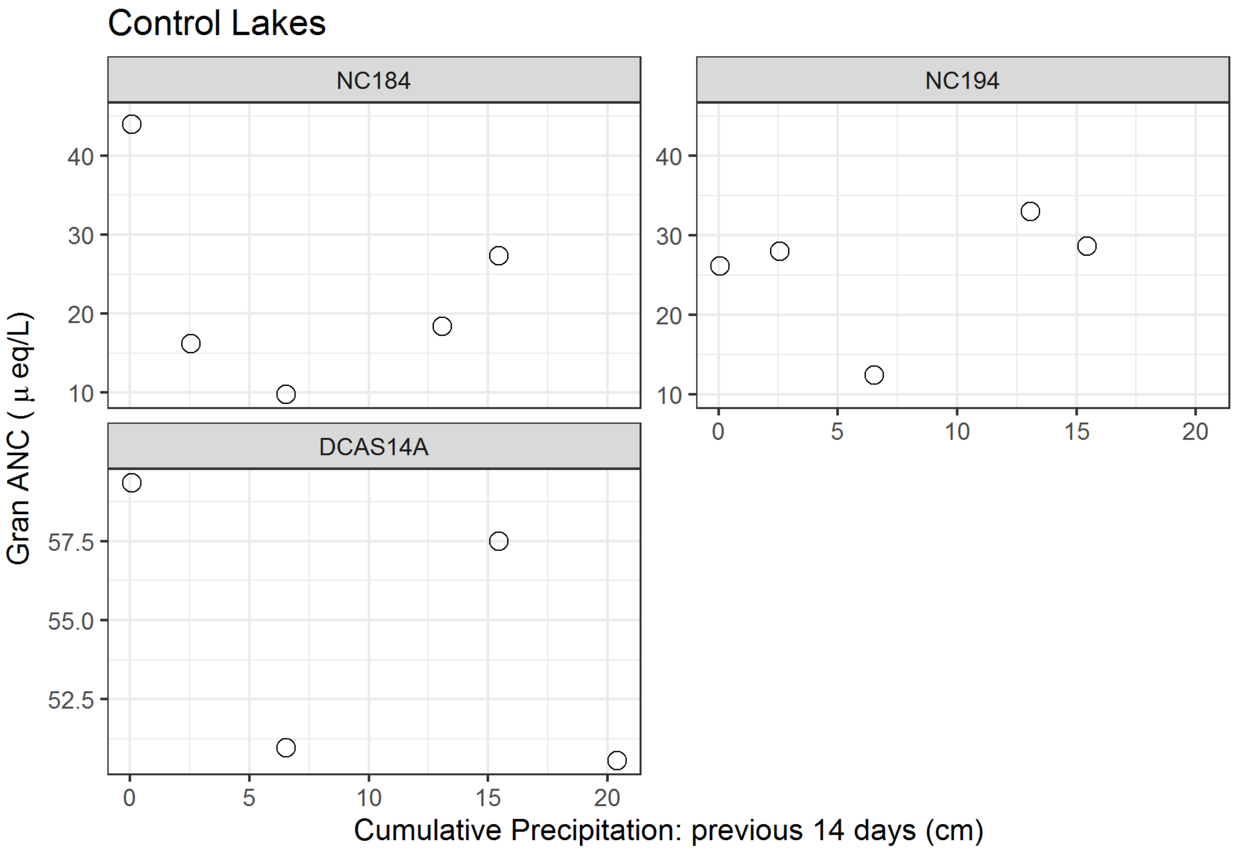


Figure 7.61: Gran ANC (μeq/L) vs. cumulative precipitation (cm) over the previous 14 days for the control lakes (DCAS14A, NC184, NC194).

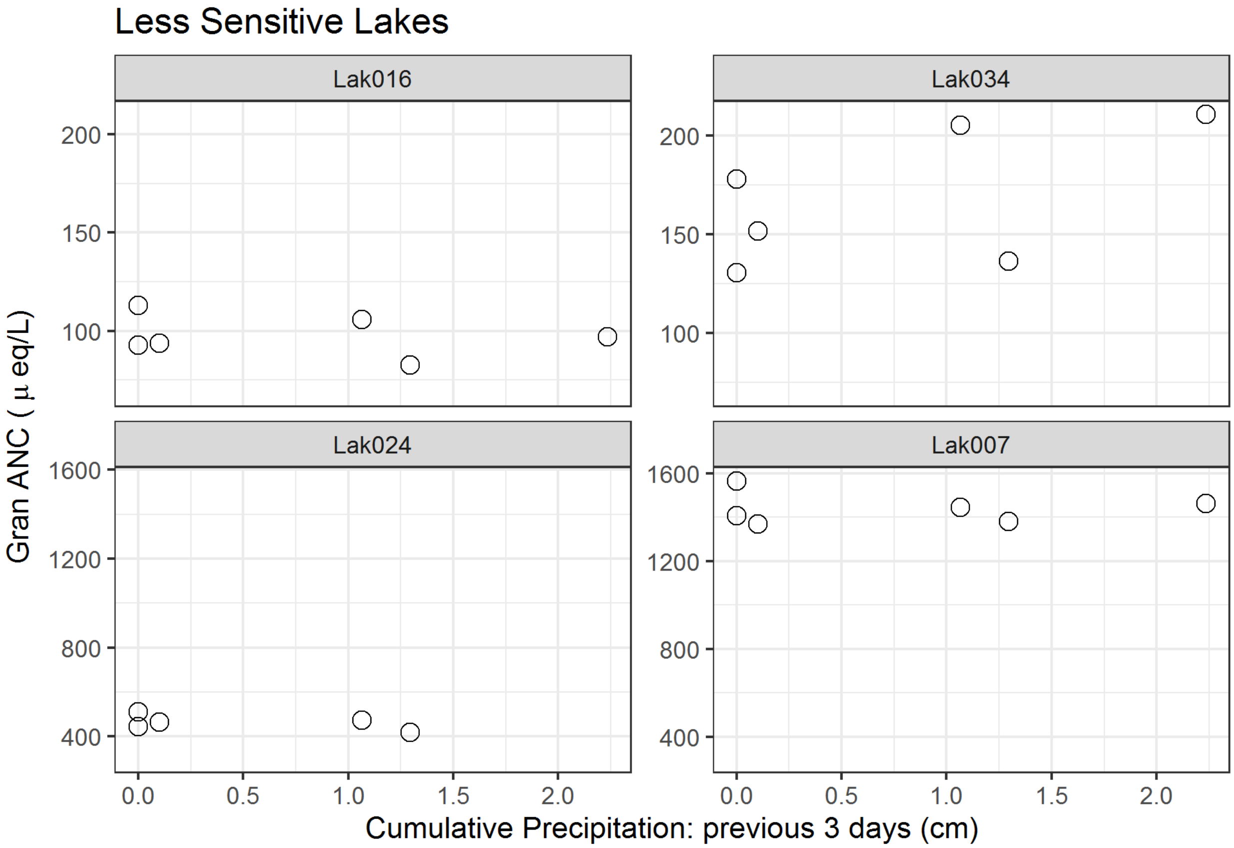


Figure 7.62: Gran ANC (μeq/L) vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

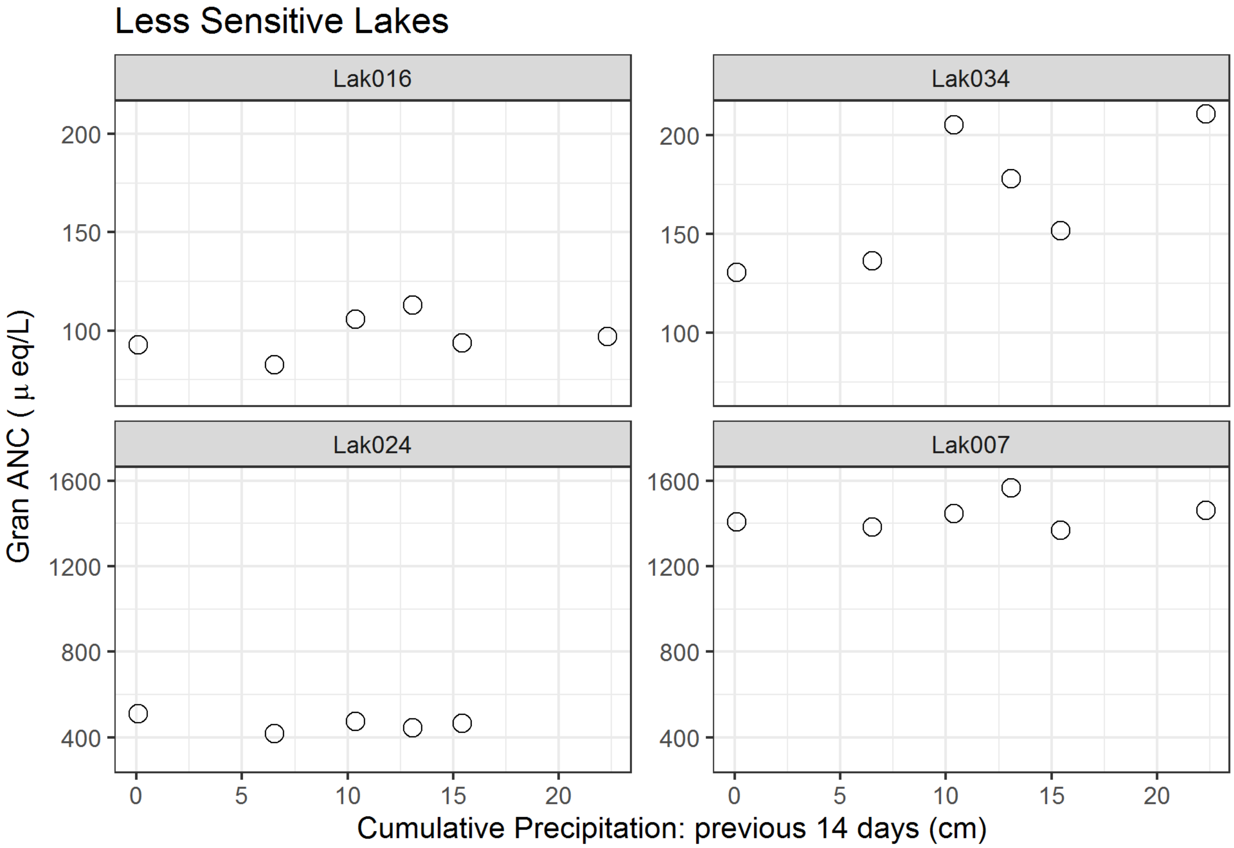


Figure 7.63: Gran ANC (µeq/L) vs. cumulative precipitation (cm) over the previous 14 days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

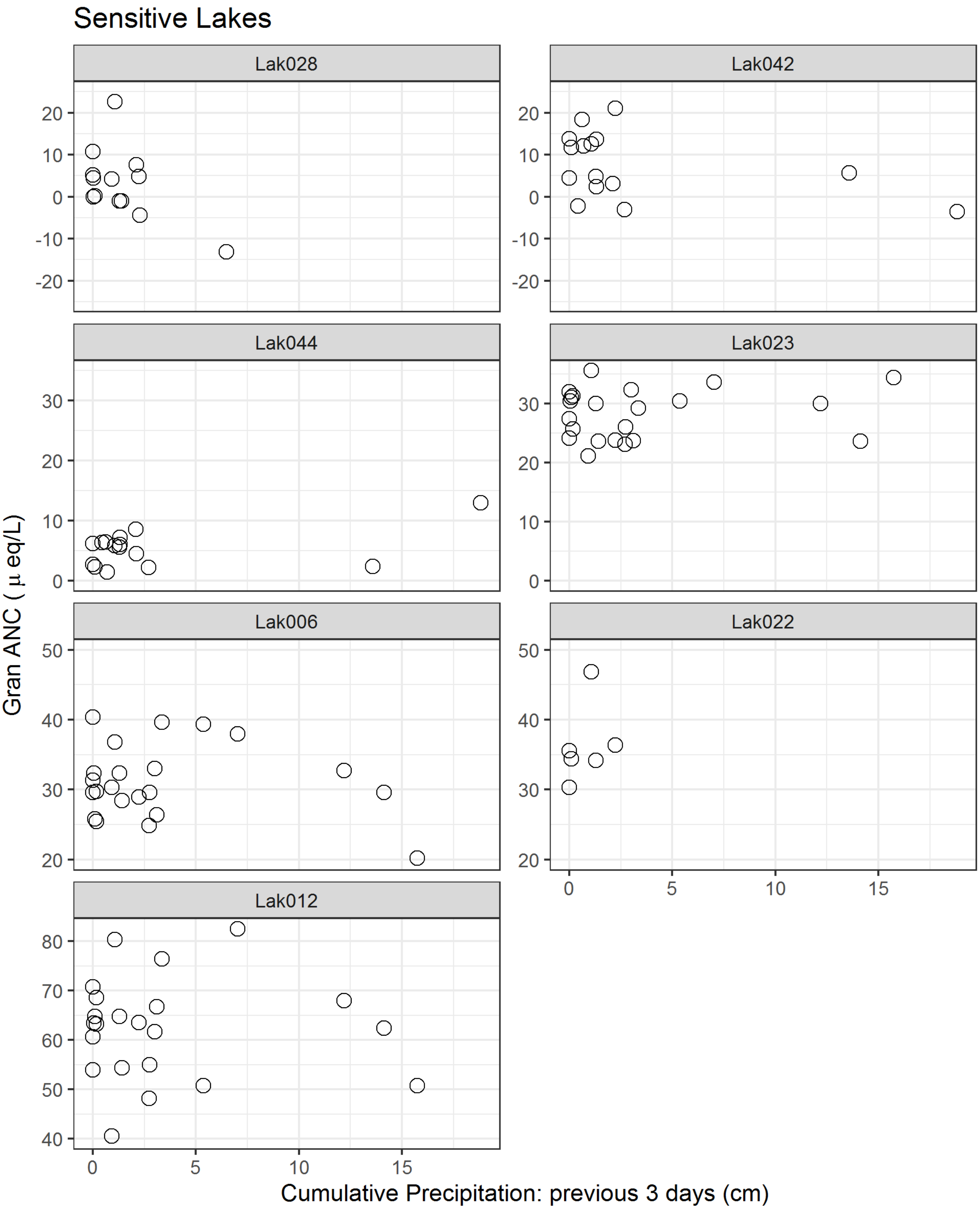


Figure 7.64: Gran ANC (μeq/L) vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

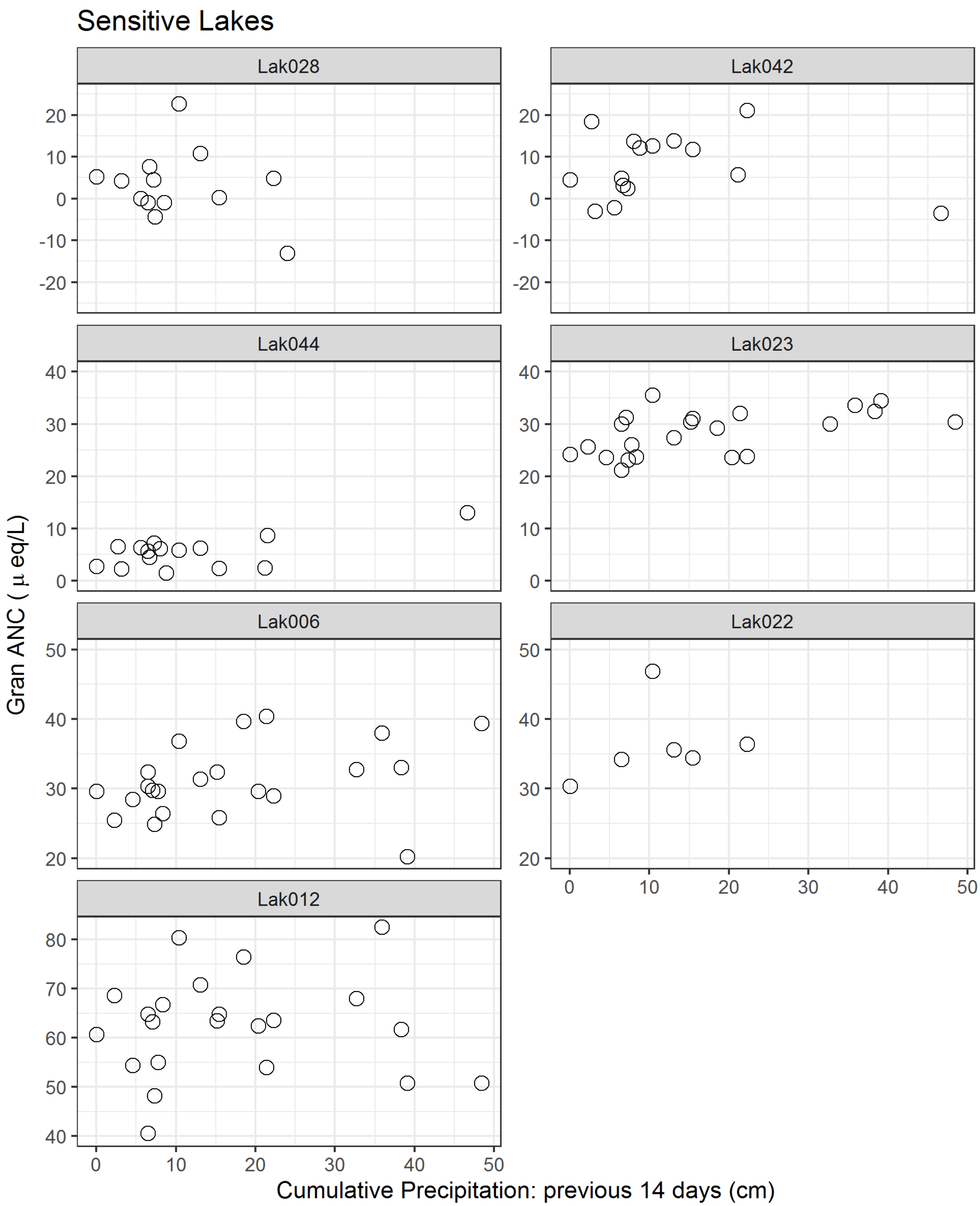


Figure 7.65: Gran ANC (μeq/L) vs. cumulative precipitation (cm) over the previous 14days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.2.3 pH vs. Precipitation

Purpose of analysis: As for Gran ANC, described above.

Explanation of the graphs: We used the same two explanatory variables explained above – precipitation over the 3-days prior to sampling, and over the previous 2 weeks, as measured at Haul Road.

- See Section 7.6.4.3.6 for statistical analyses of the ability of covariates describing recent precipitation to explain patterns of changes over time in pH, beyond those patterns observed in control lakes.

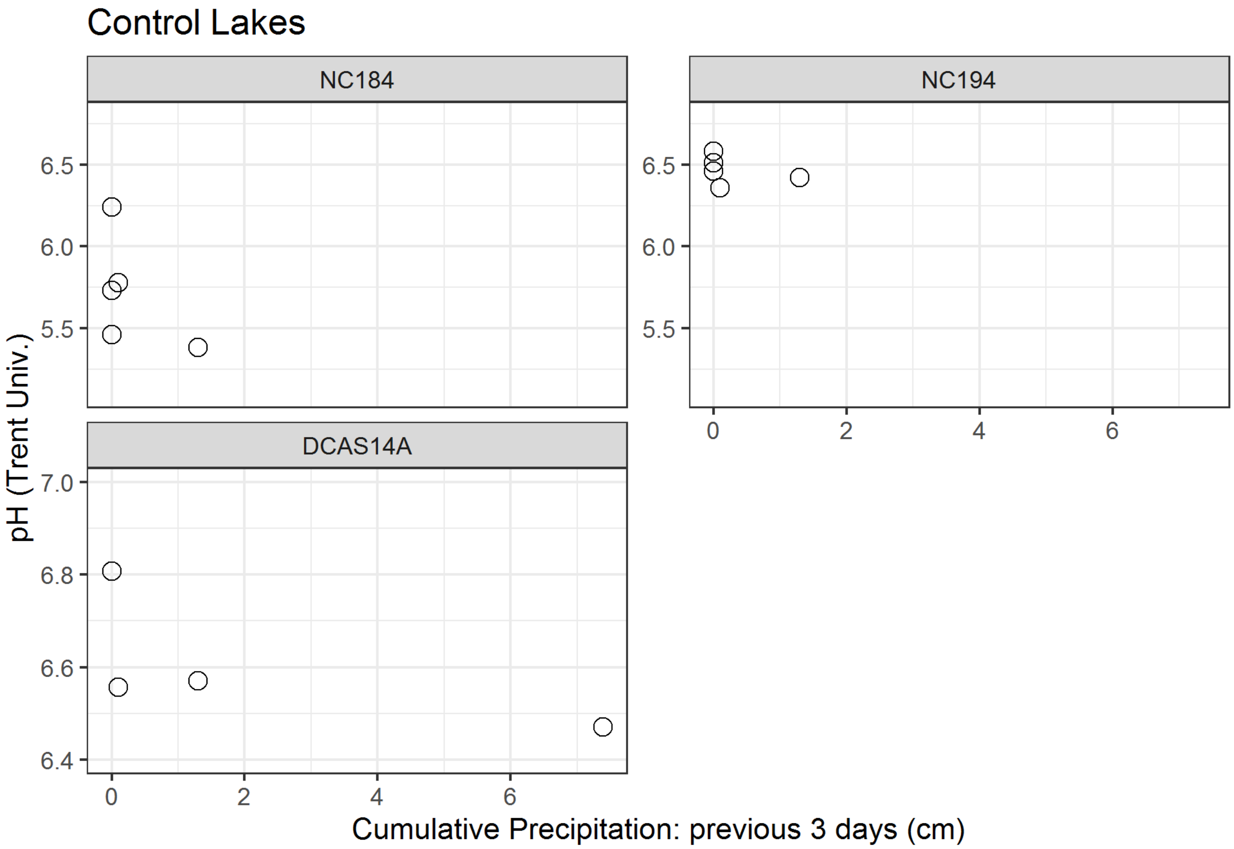


Figure 7.66: pH (+/-0.2) vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

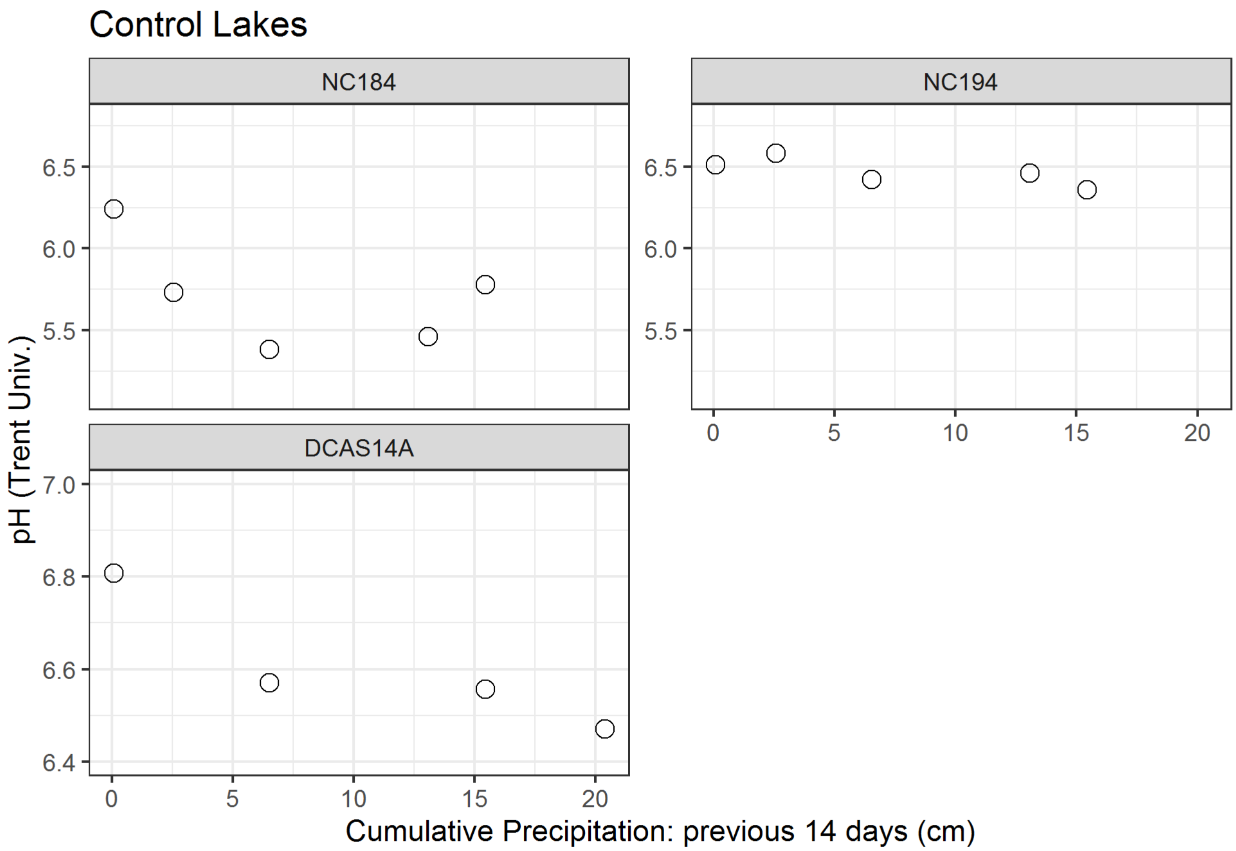


Figure 7.67: pH (+/-0.2) vs. cumulative precipitation (cm) over the previous 14 days for the control lakes (DCAS14A, NC184, NC194).

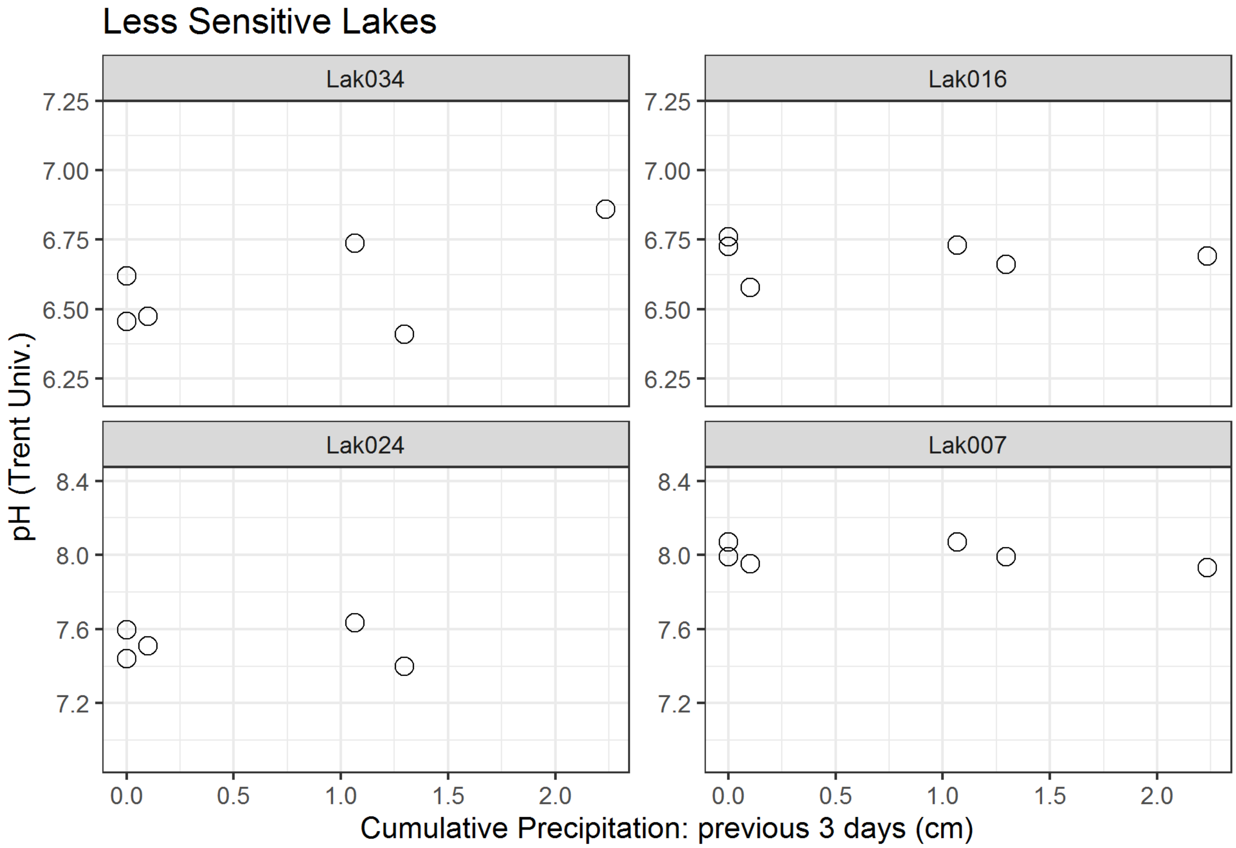


Figure 7.68: pH (+/-0.2) vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

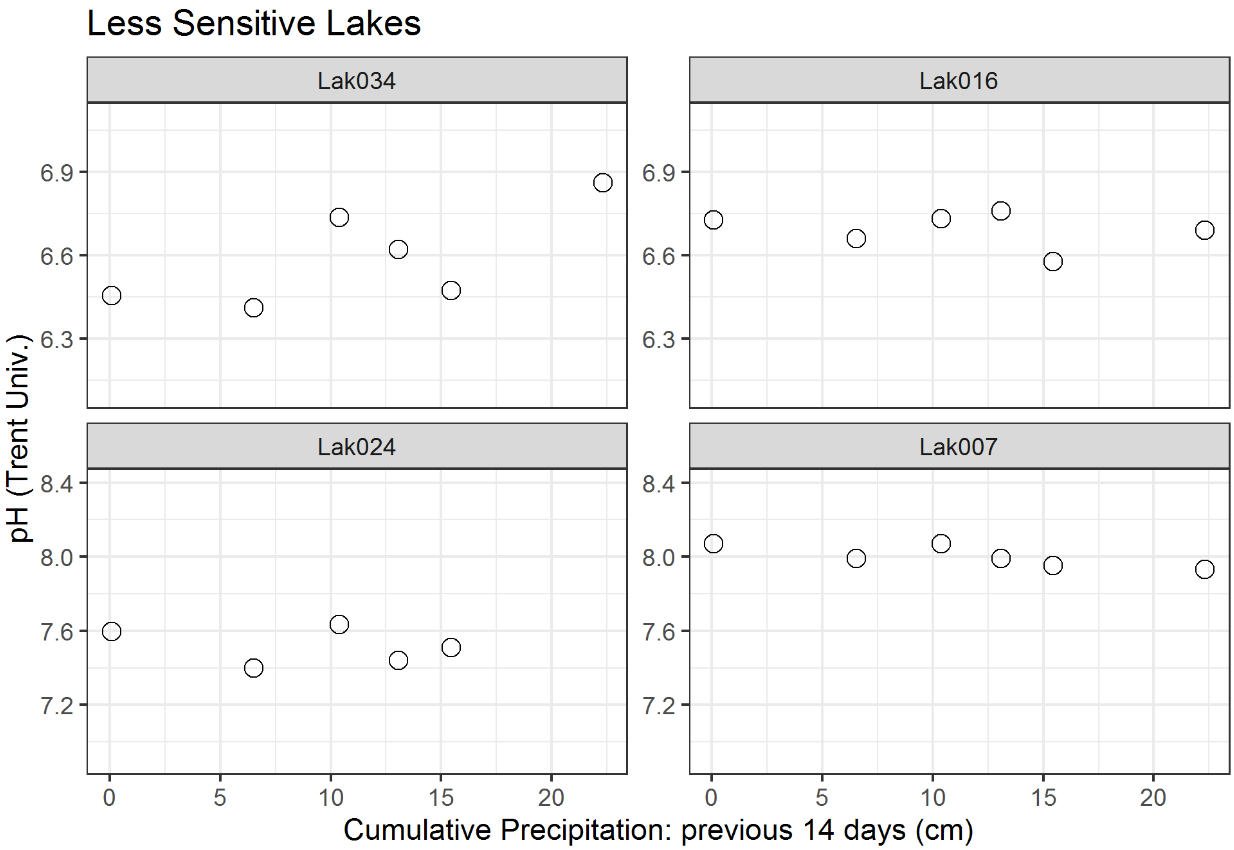


Figure 7.69: pH (+/-0.2) vs. cumulative precipitation (cm) over the previous 14 days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

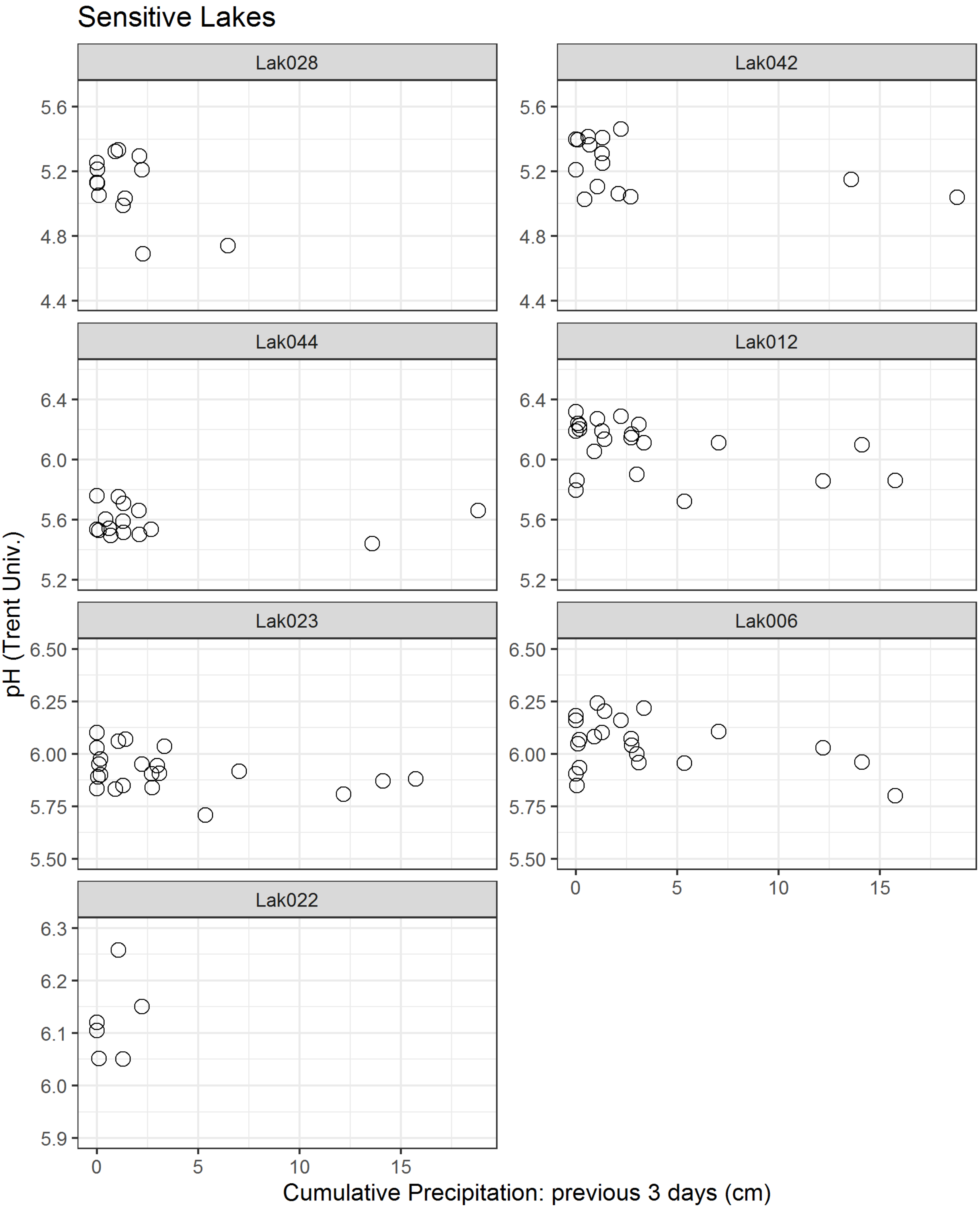


Figure 7.70: pH (+/-0.2) vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

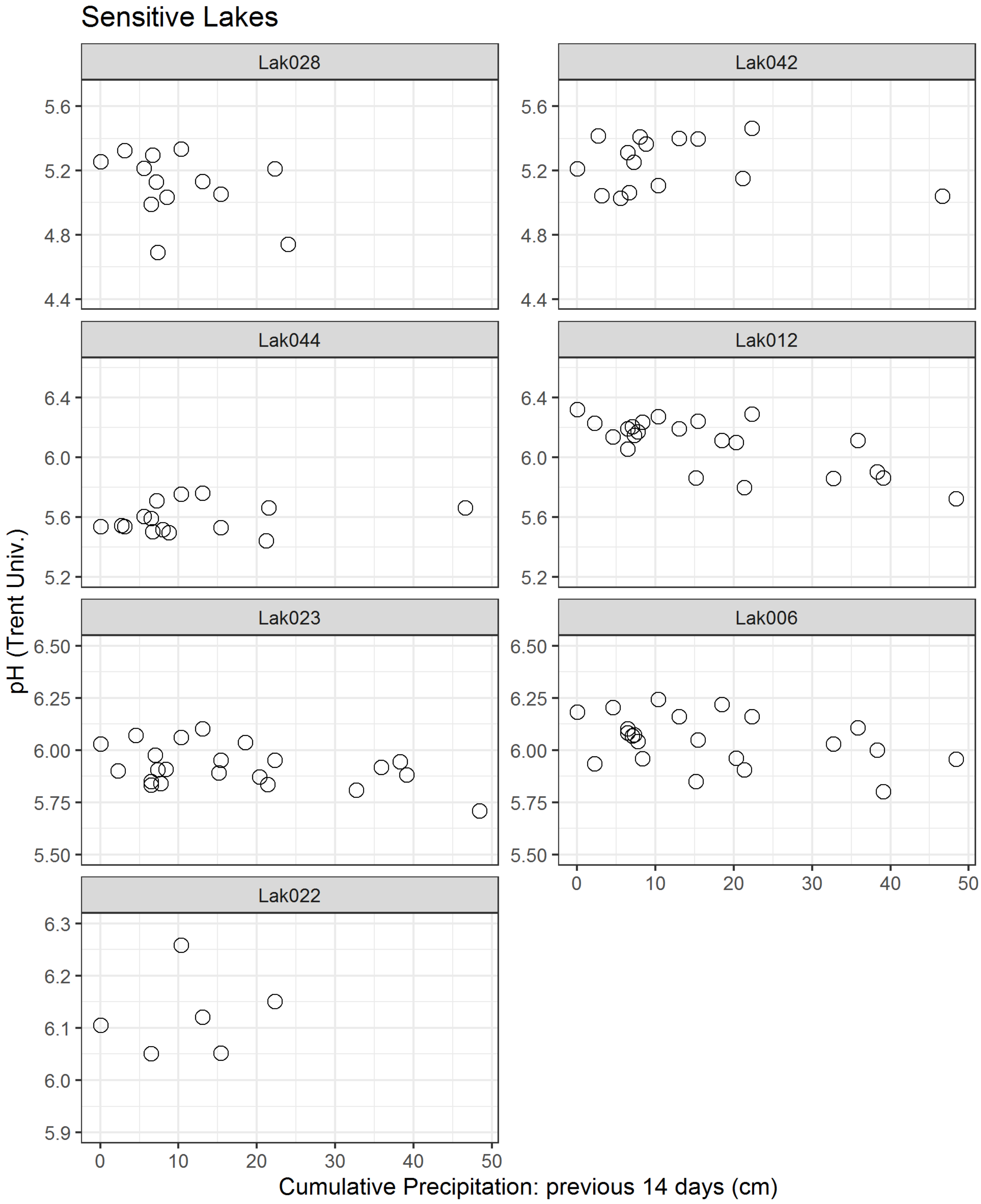


Figure 7.71: pH (+/-0.2) vs. cumulative precipitation (cm) over the previous 14 days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.2.4 Other Lake Chemistry Metrics vs. Precipitation

- Other metrics explored
- Only against recent precipitation

Purpose of analyses: Base cation dilution can be one of the most frequent causes of declines in ANC and pH during and following storm events (Wiggington et al. 1996). We are therefore interested to see if there is any pattern of declining base cation concentrations following periods of higher levels of precipitation. As noted above, intensive studies of acidic episodes require very frequent sampling during a storm event to deduce the most likely causes of ANC and pH declines. Looking at broad patterns between base cations and total precipitation is the best that we can do with the data that we have, but misses effects which occur on finer time scales.

Dissolved Al tends to increase as pH declines, particularly at lower pH levels. We are therefore interested to see if there is any pattern of increasing Al associated with storm events.

Marine storms can in theory bring pulses of chloride to lakes in the Kitimat Valley (concentrations of Ca, Mg, Na and K are decremented for sea-salt contributions based on the ratios of these cations to chloride). Pulses of chloride could potentially cause a seasalt effect, as sodium is exchanged for other ions in the soil, including H+ and Al, which is one of the mechanisms of natural acidification noted by Wiggington et al. (1996), and explained further in the references they cite. We are therefore interested to see if chloride is positively associated with precipitation, as this is another possible confounding factor affecting long term trends in pH and ANC.

We have only performed statistical analyses of changes over time for sulphate, pH and Gran ANC, as these are the primary metrics in the evidentiary framework. If the primary metrics show evidence of changes that are of concern for a given lake, we can then do quantitative analyses of other chemical parameters to better understand the full picture of chemical changes with the subject lake.

Explanation of the graphs and tables of results: We used the same two explanatory variables explained above – precipitation over the 3-days prior to sampling, and over the previous 2 weeks, as measured at Haul Road.

7.6.2.2.5 Base cations vs. Precipitation

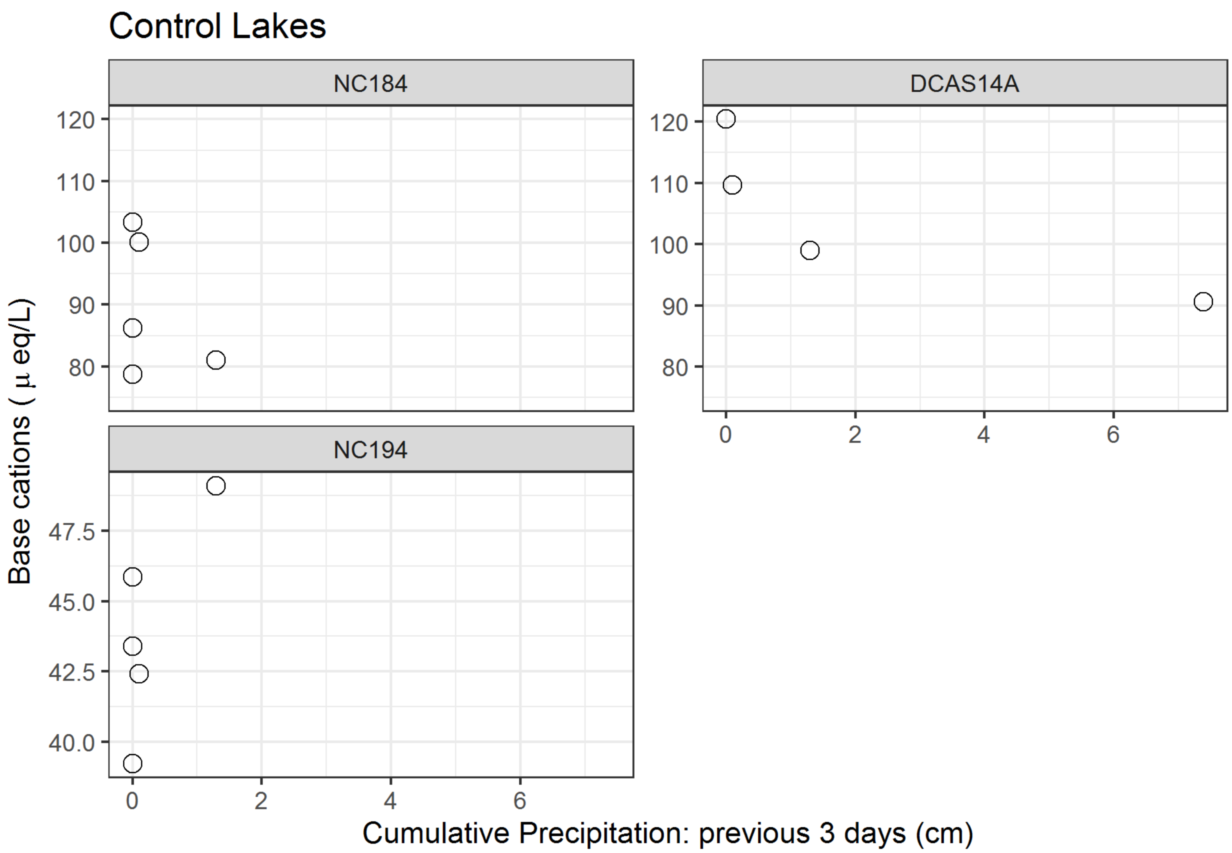


Figure 7.72: Base Cations (Ca + Na + Mg + K) vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

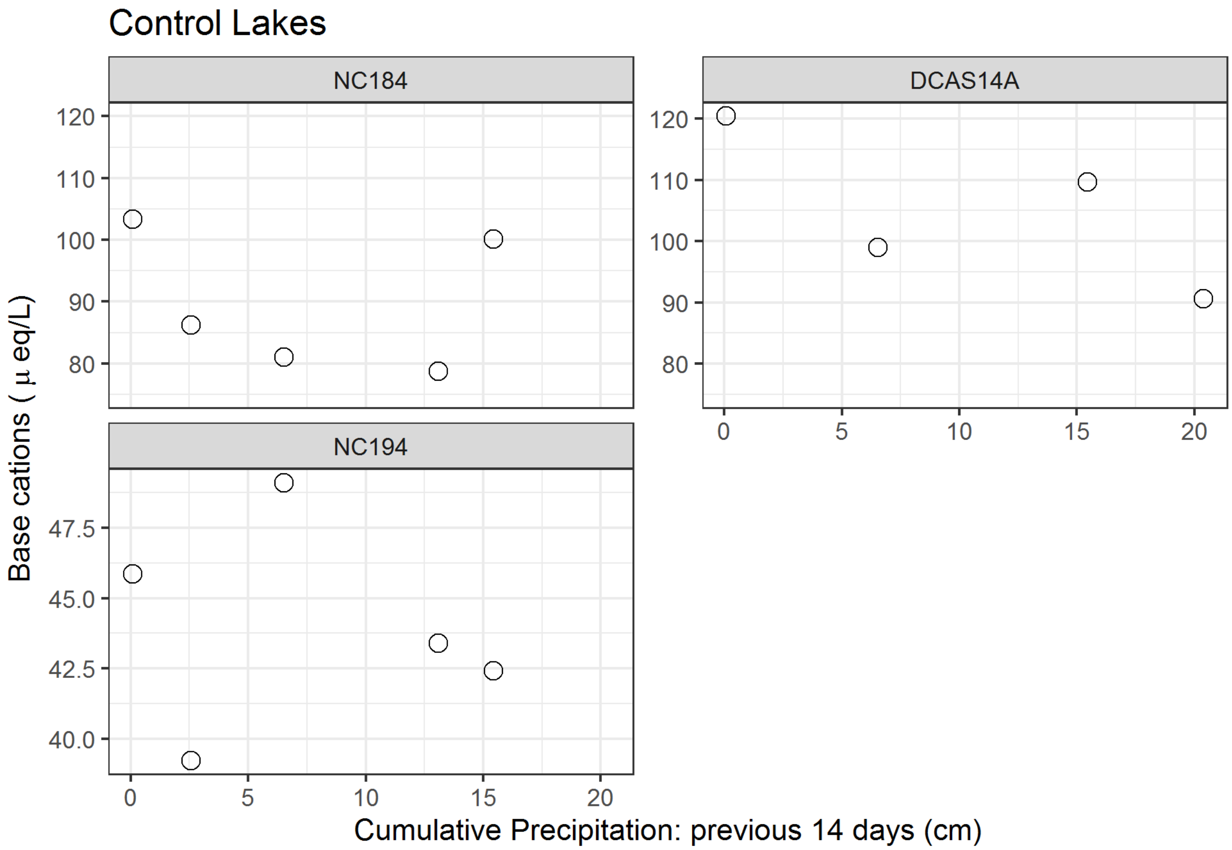


Figure 7.73: Base Cations (Ca + Na + Mg + K) vs. cumulative precipitation (cm) over the previous fourteen days for the control lakes (DCAS14A, NC184, NC194).

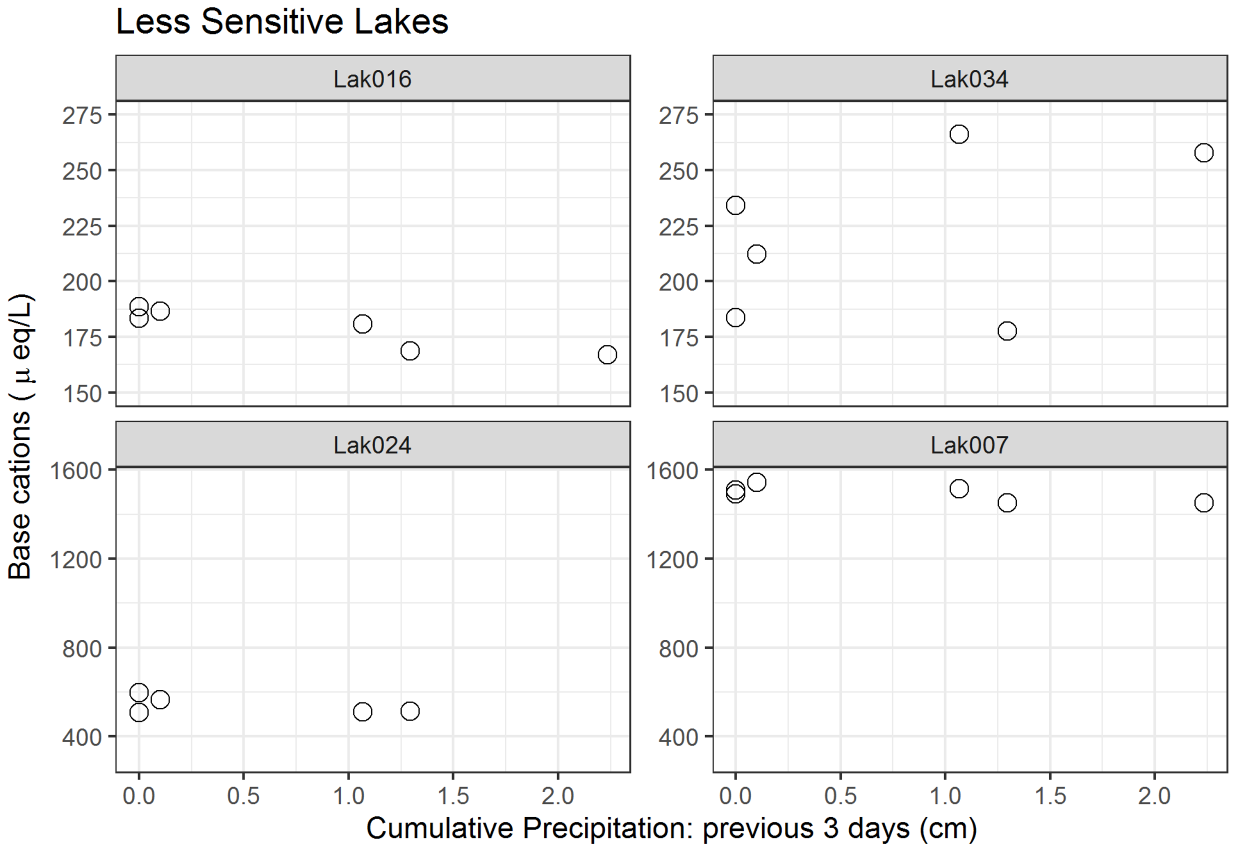


Figure 7.74: Base Cations (Ca + Na + Mg + K) vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

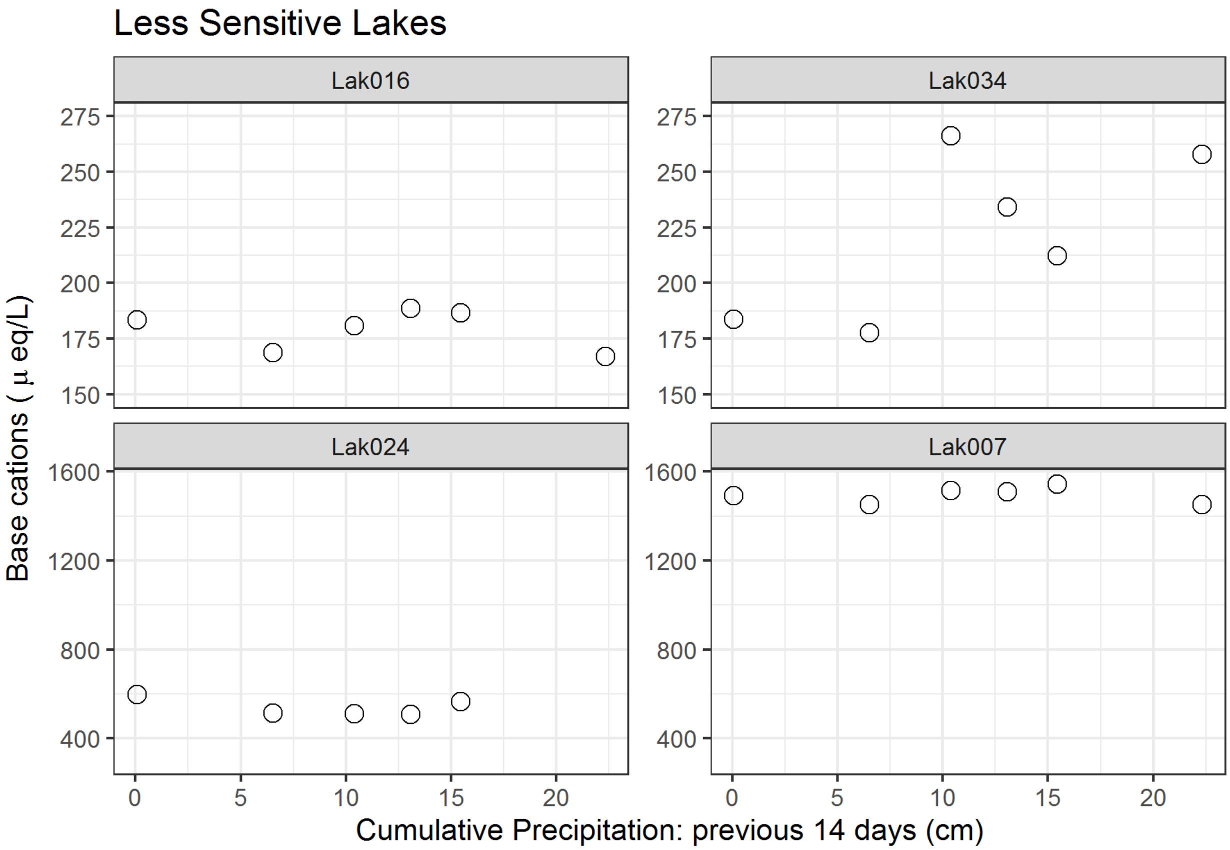


Figure 7.75: Base Cations (Ca + Na + Mg + K) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

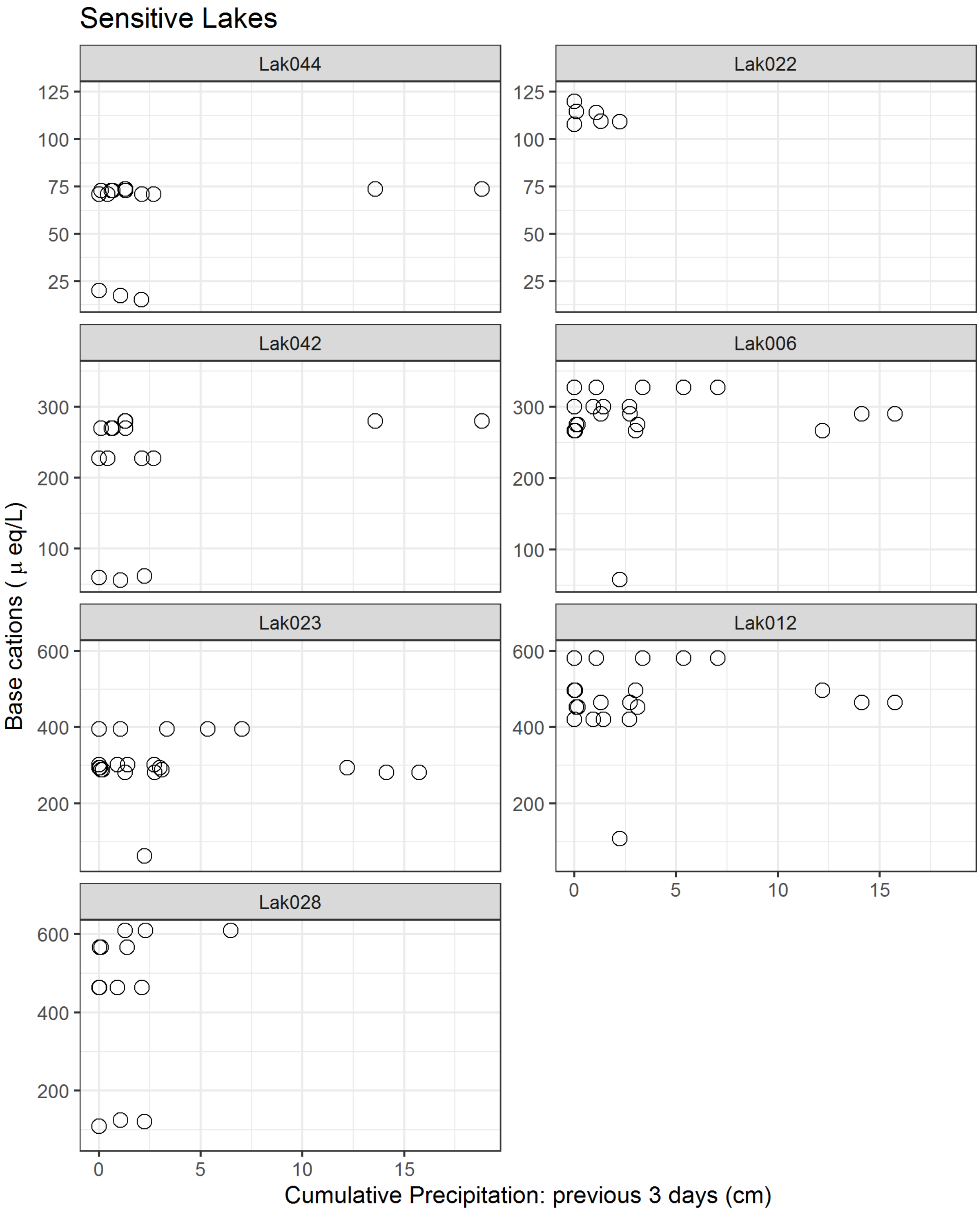


Figure 7.76: Base Cations (Ca + Na + Mg + K) vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

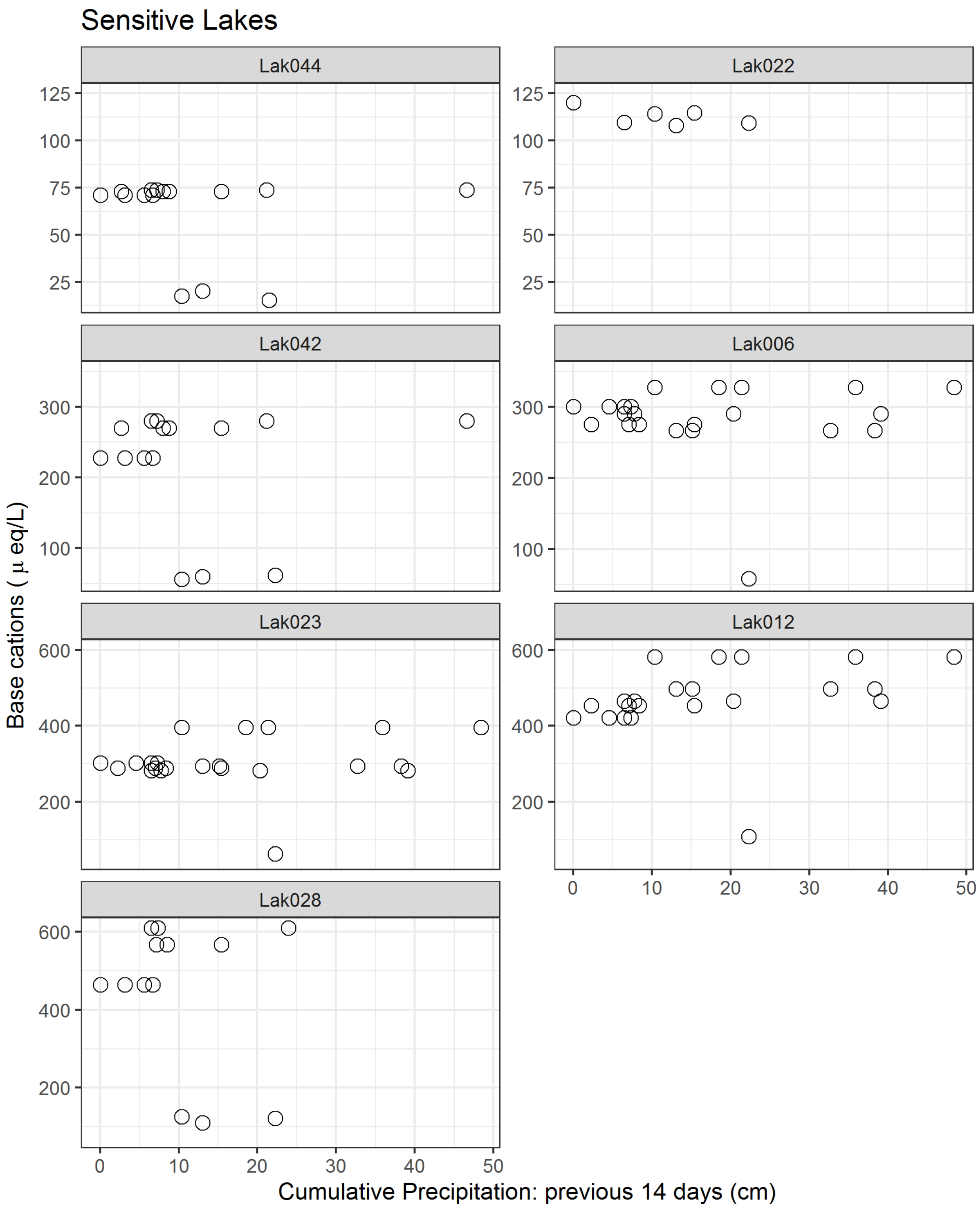


Figure 7.77: Base Cations (Ca + Na + Mg + K) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.2.6 Aluminum vs. Precipitation

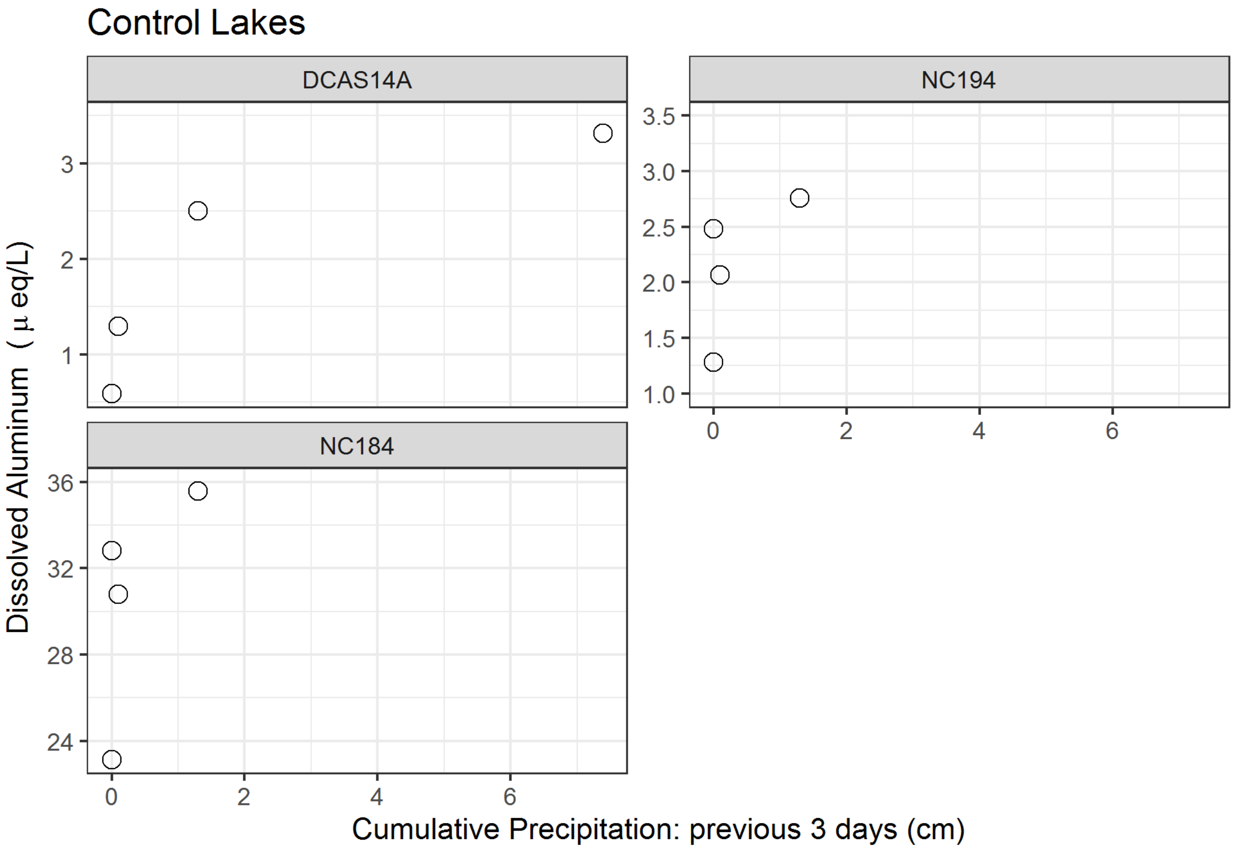


Figure 7.78: Dissolved Aluminum (μeq/l) vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

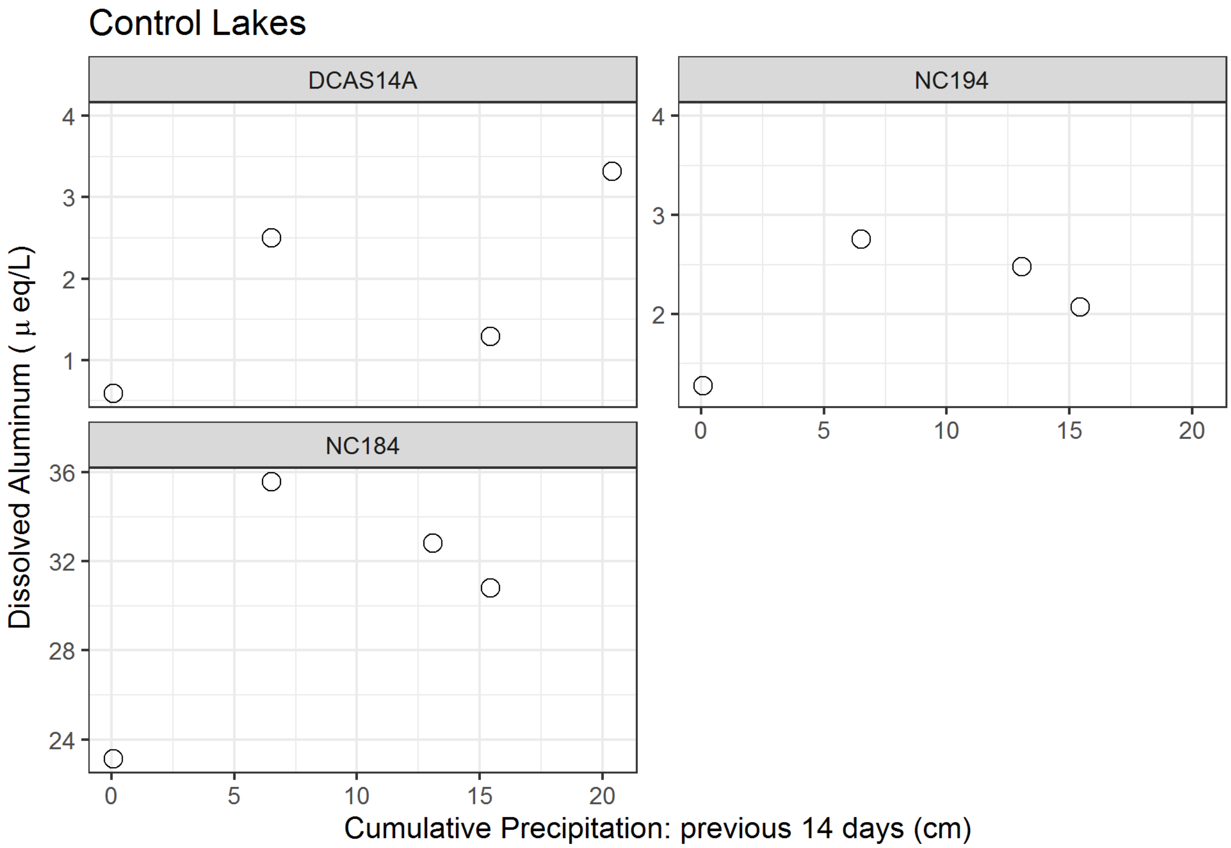


Figure 7.79: Dissolved Aluminum (μeq/l) vs. cumulative precipitation (cm) over the previous fourteen days for the control lakes (DCAS14A, NC184, NC194).

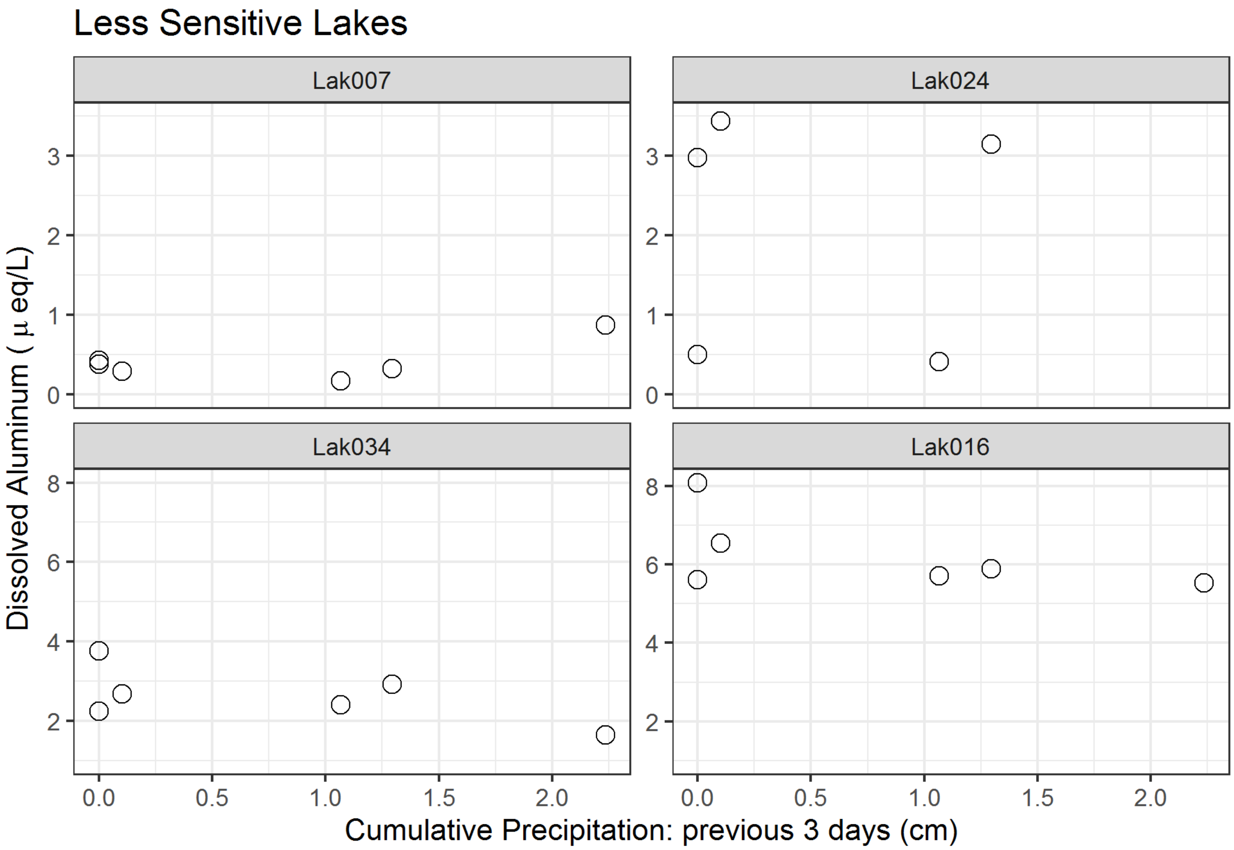


Figure 7.80: Dissolved Aluminum (μeq/l) vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

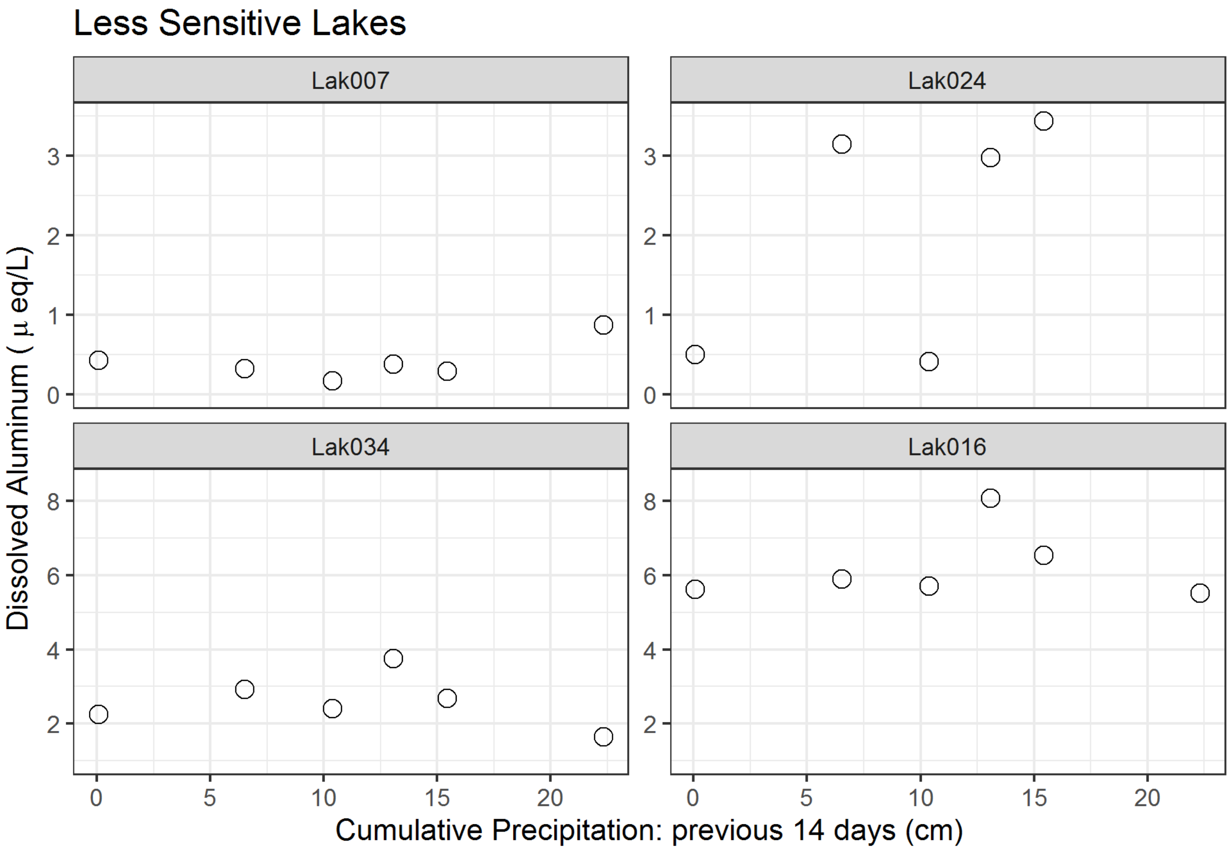


Figure 7.81: Dissolved Aluminum (μeq/l) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

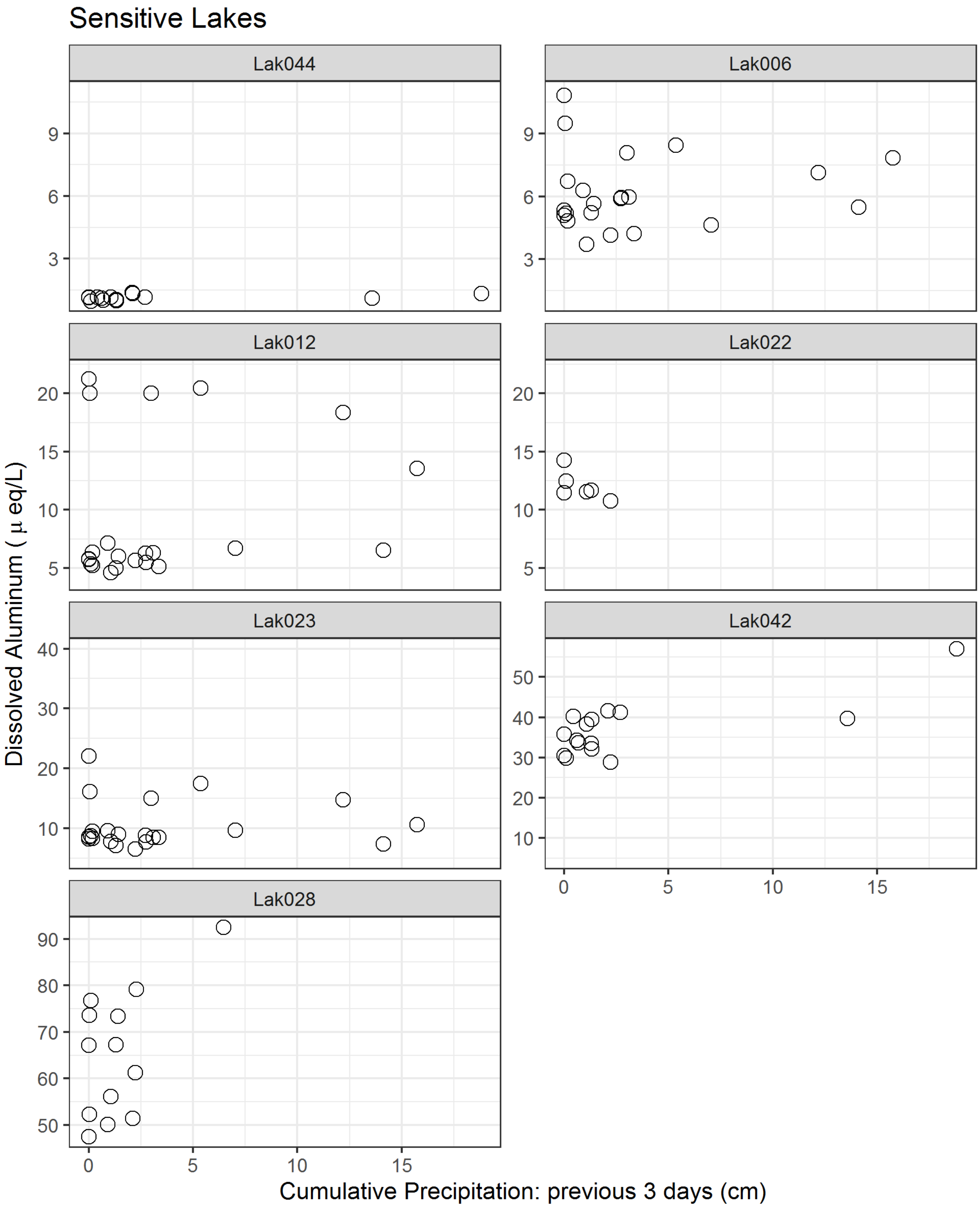


Figure 7.82: Dissolved Aluminum (μeq/l) vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

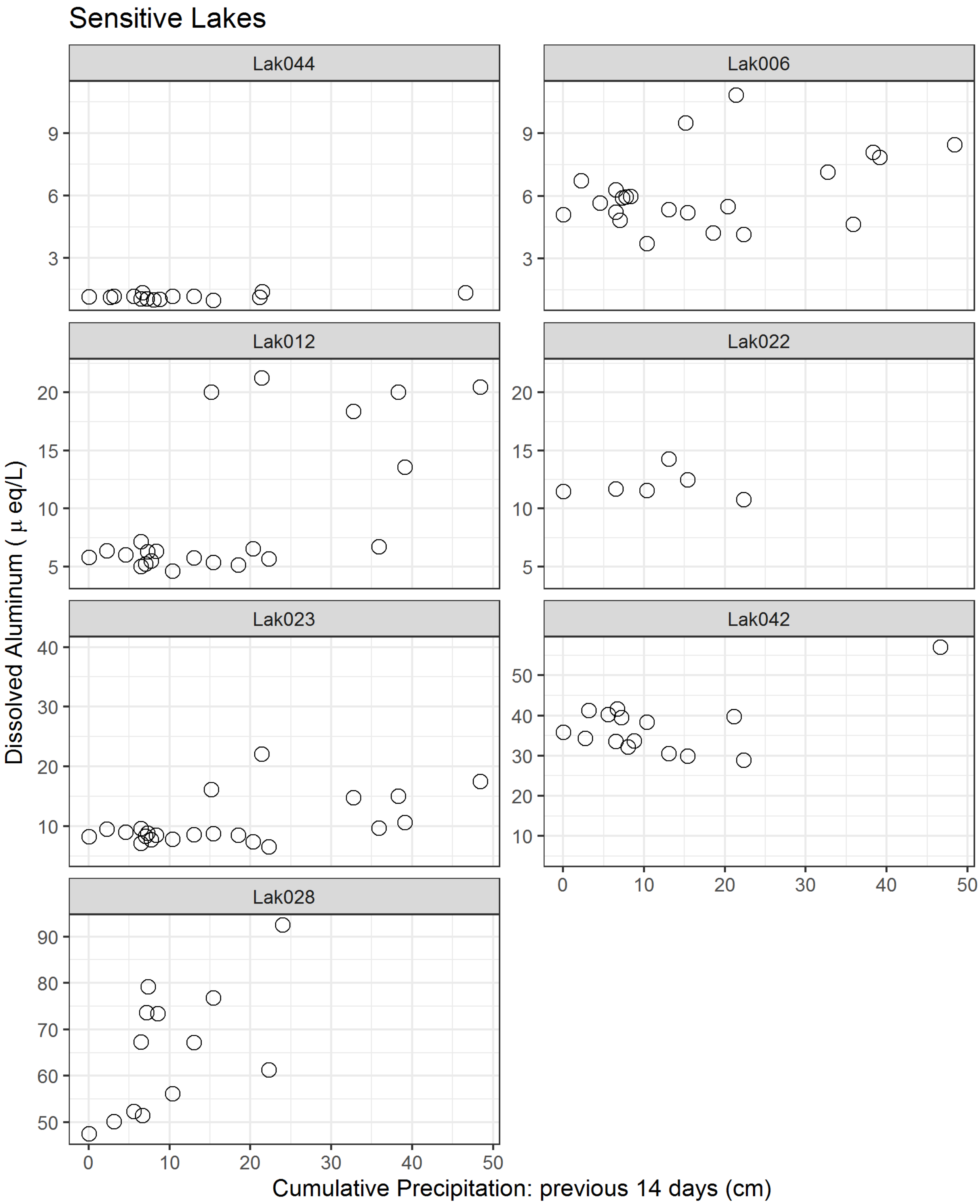


Figure 7.83: Dissolved Aluminum (μeq/l) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.2.7 Chloride vs. Precipitation

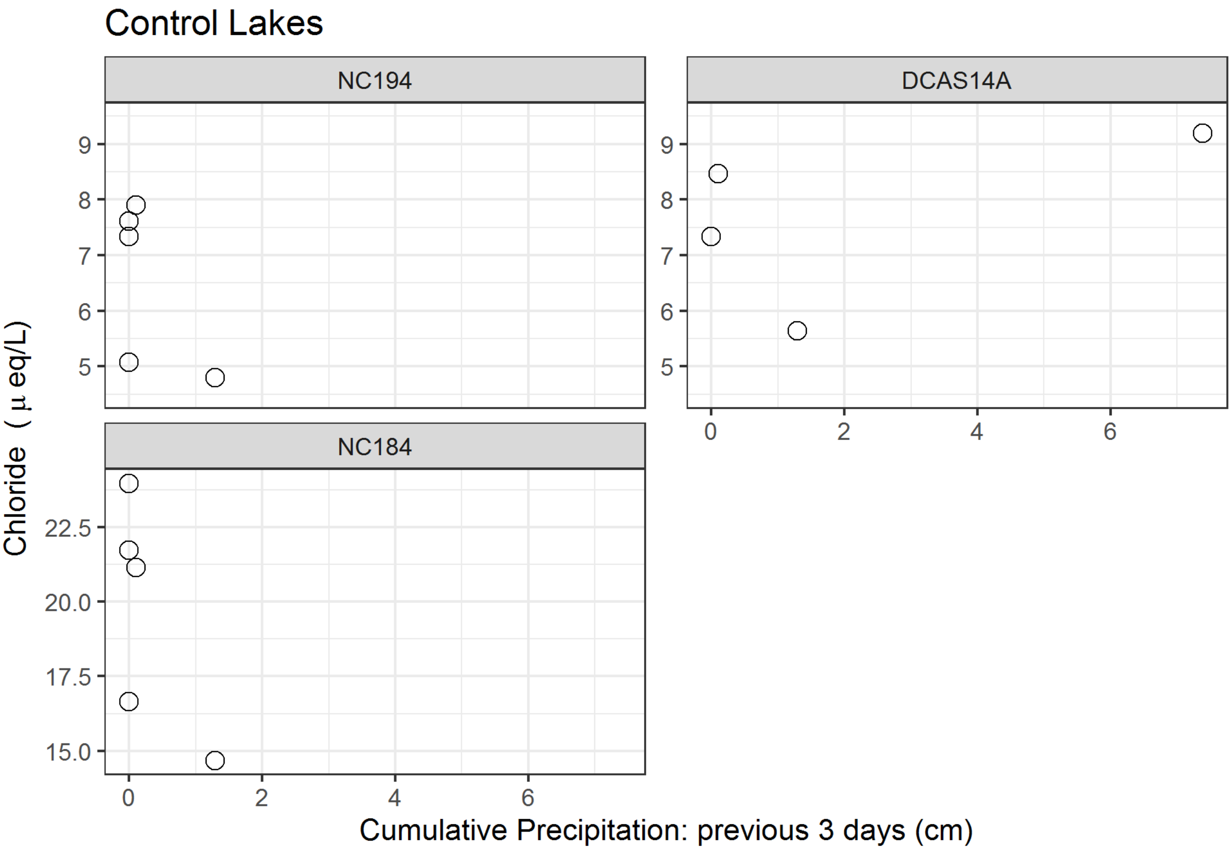


Figure 7.84: Chloride (µeq/l) vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

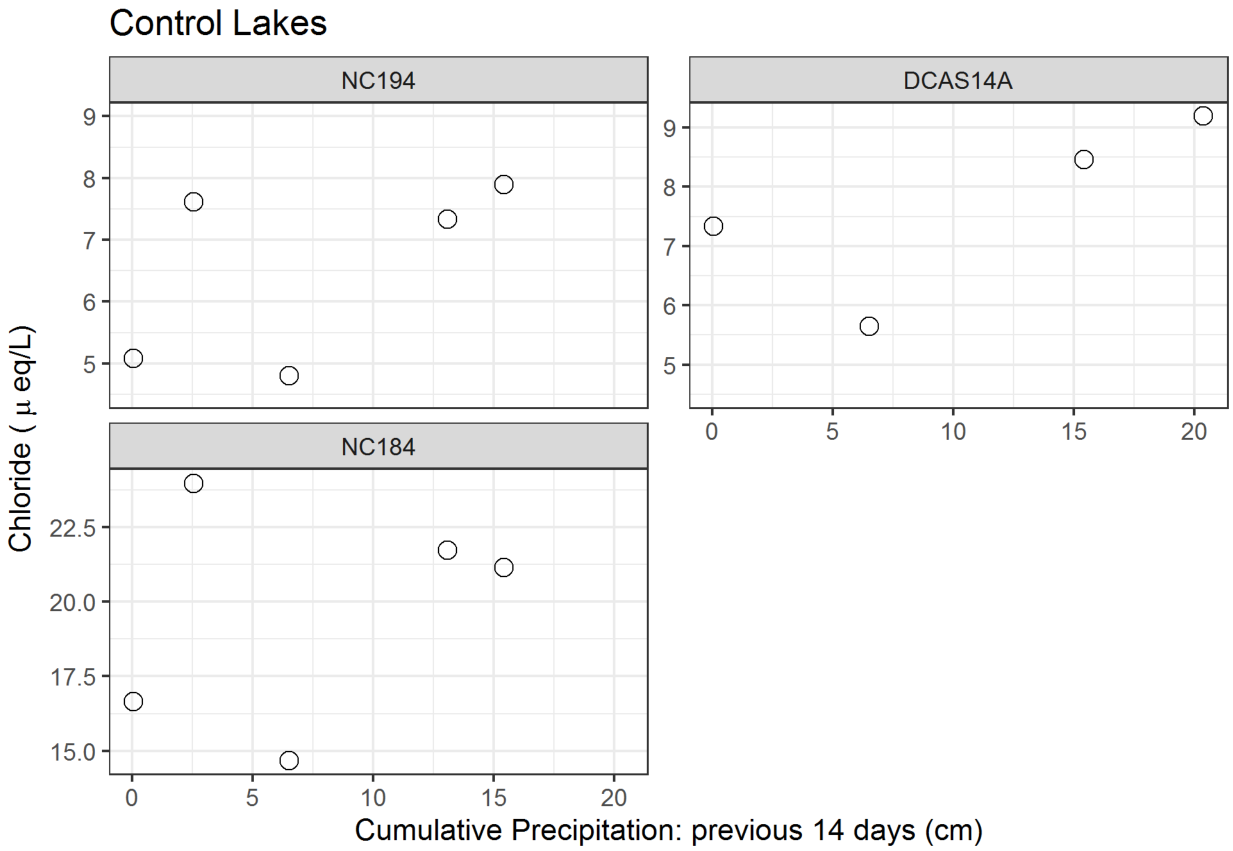


Figure 7.85: Chloride (µeq/l) vs. cumulative precipitation (cm) over the previous fourteen days for the control lakes (DCAS14A, NC184, NC194).

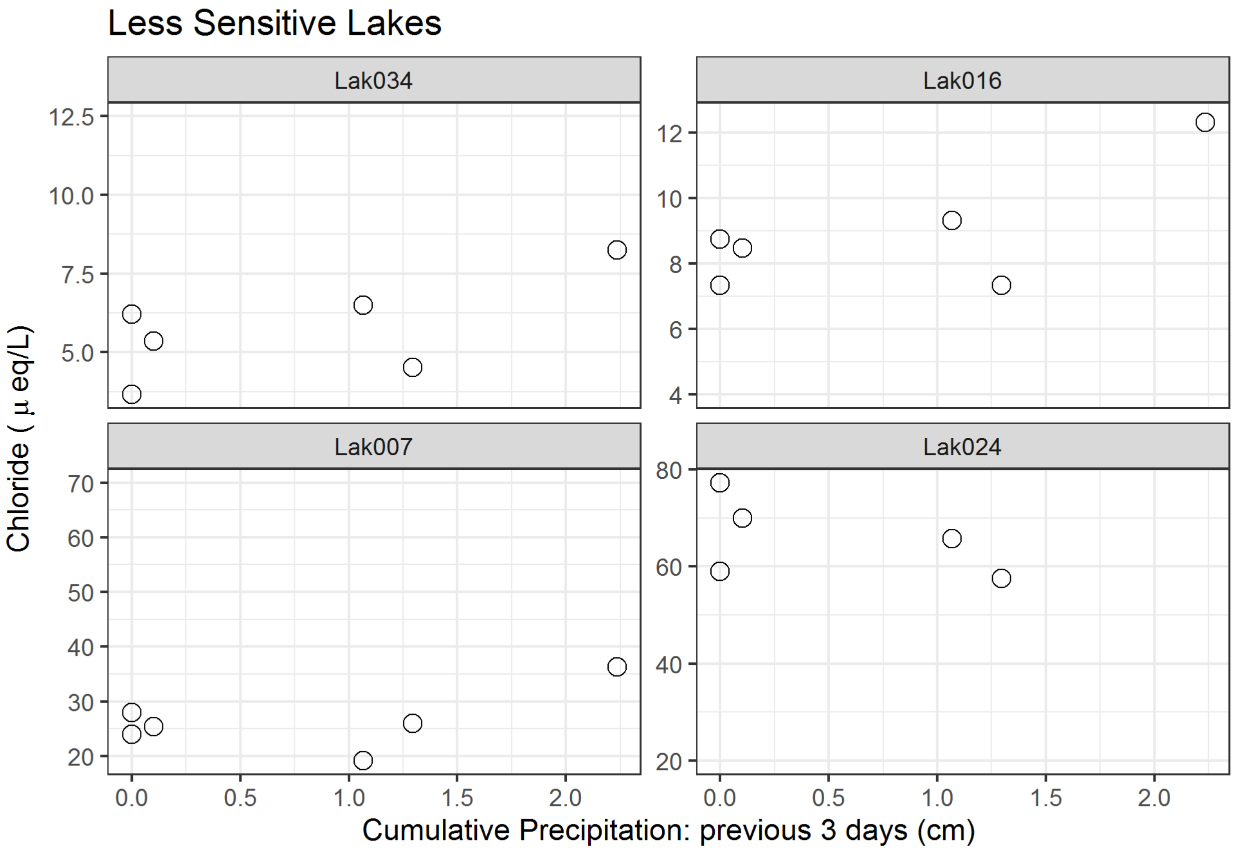


Figure 7.86: Chloride (µeq/l) vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

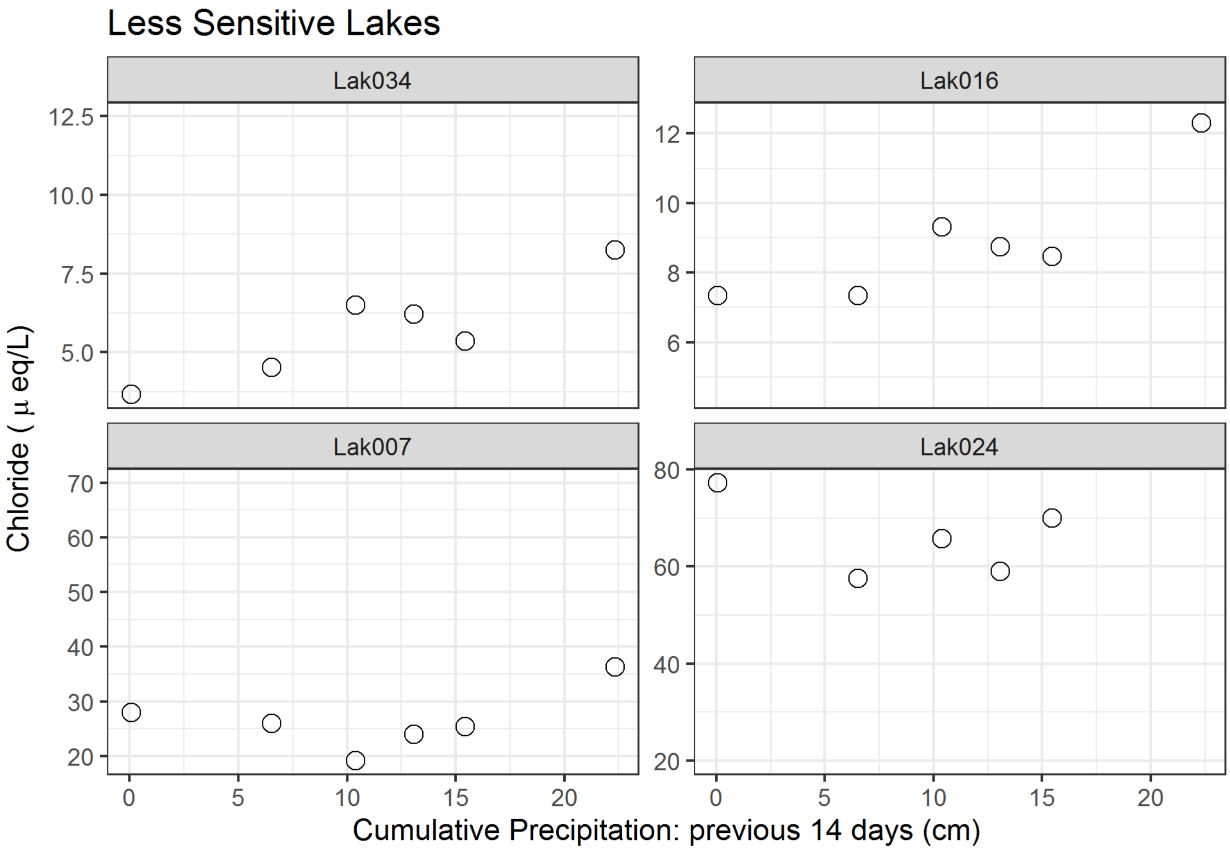


Figure 7.87: Chloride (µeq/l) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

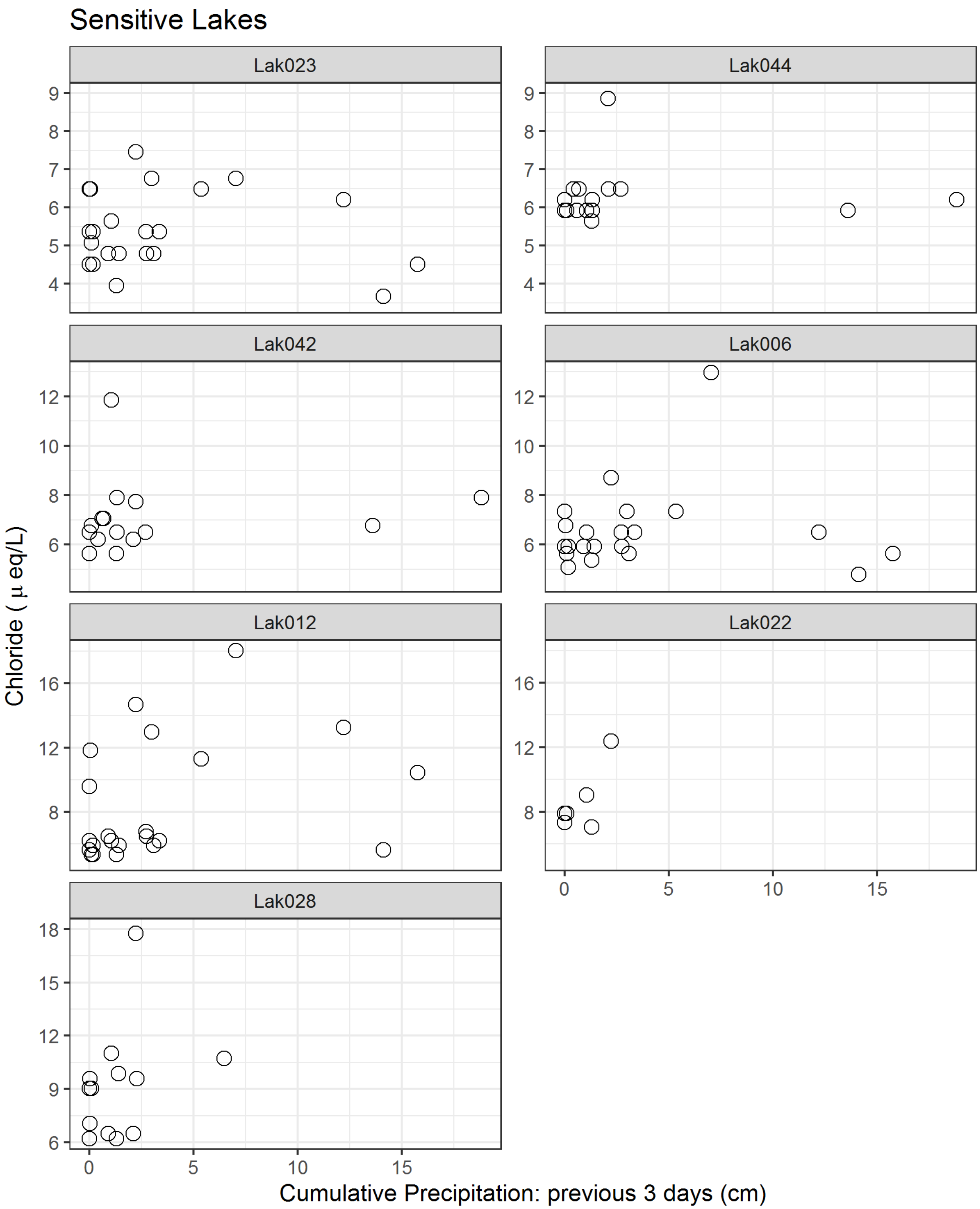


Figure 7.88: Chloride (μeq/l) vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

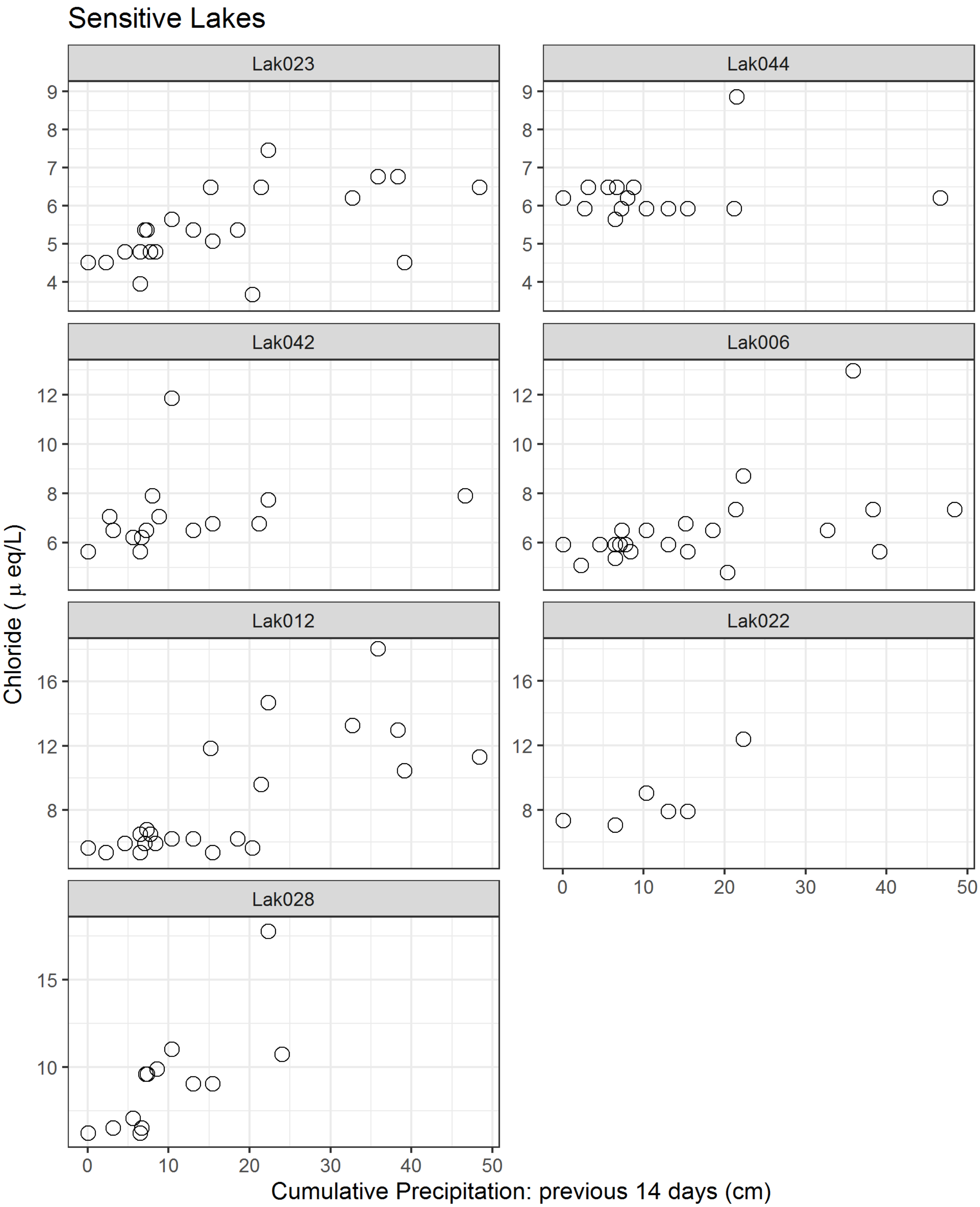


Figure 7.89: Chloride (µeq/l) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.2.8 DOC vs. Precipitation

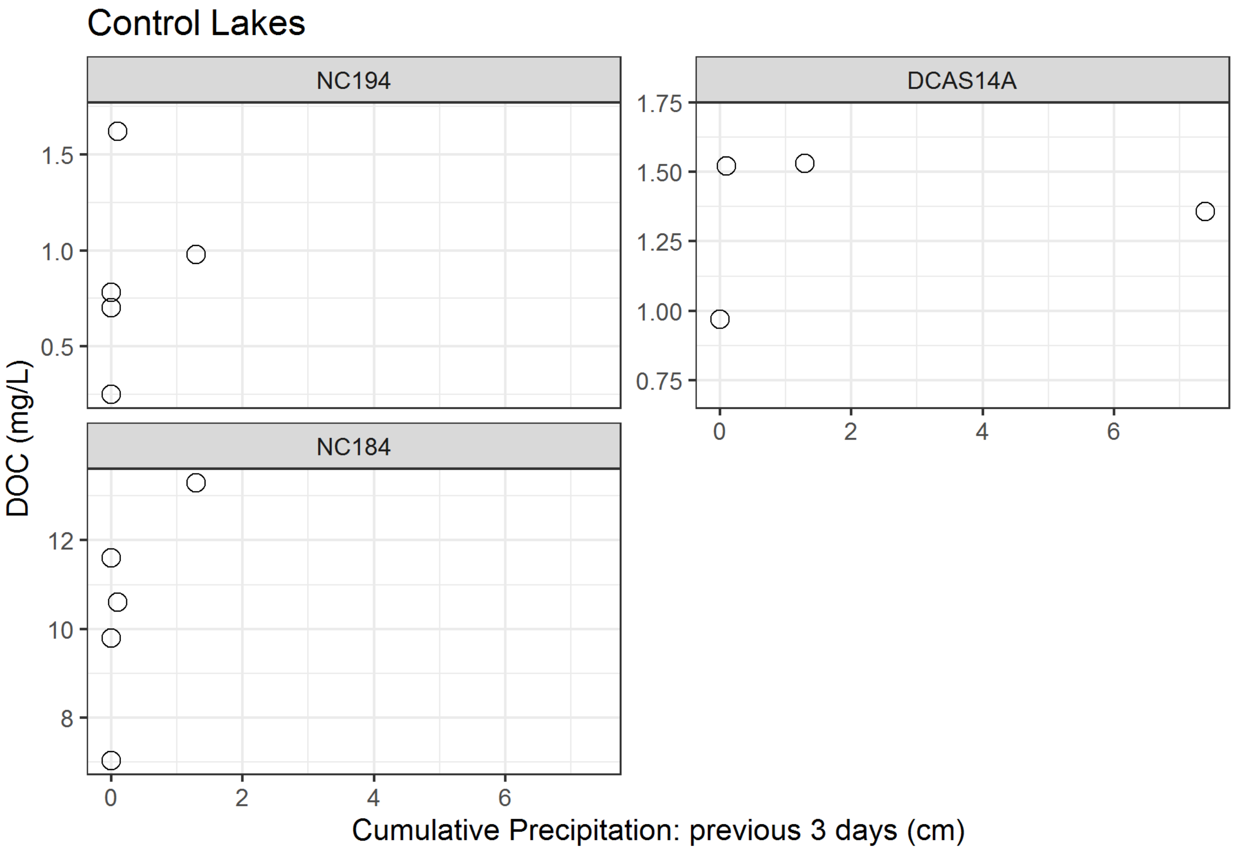


Figure 7.90: DOC (mg/L) vs. cumulative precipitation (cm) over the previous three days for the control lakes (DCAS14A, NC184, NC194).

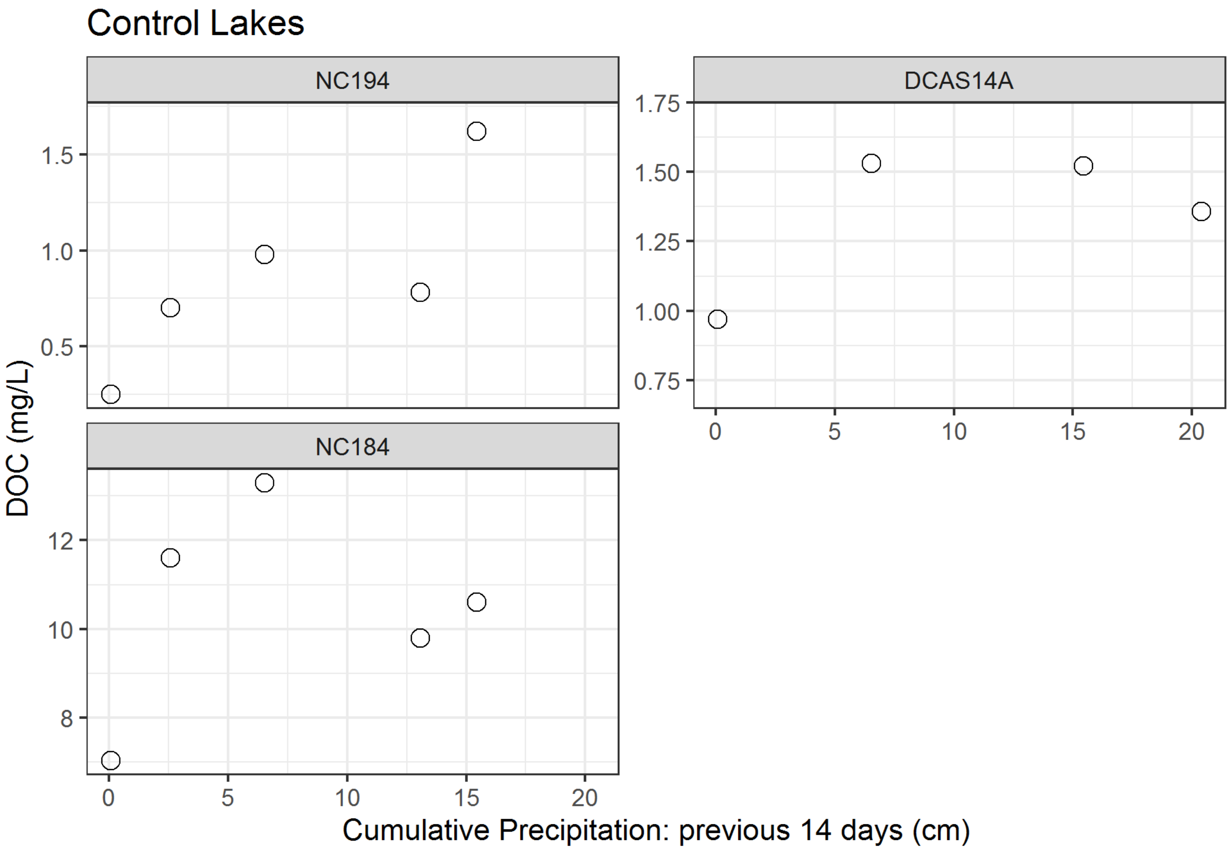


Figure 7.91: DOC (mg/L) vs. cumulative precipitation (cm) over the previous fourteen days for the control lakes (DCAS14A, NC184, NC194).

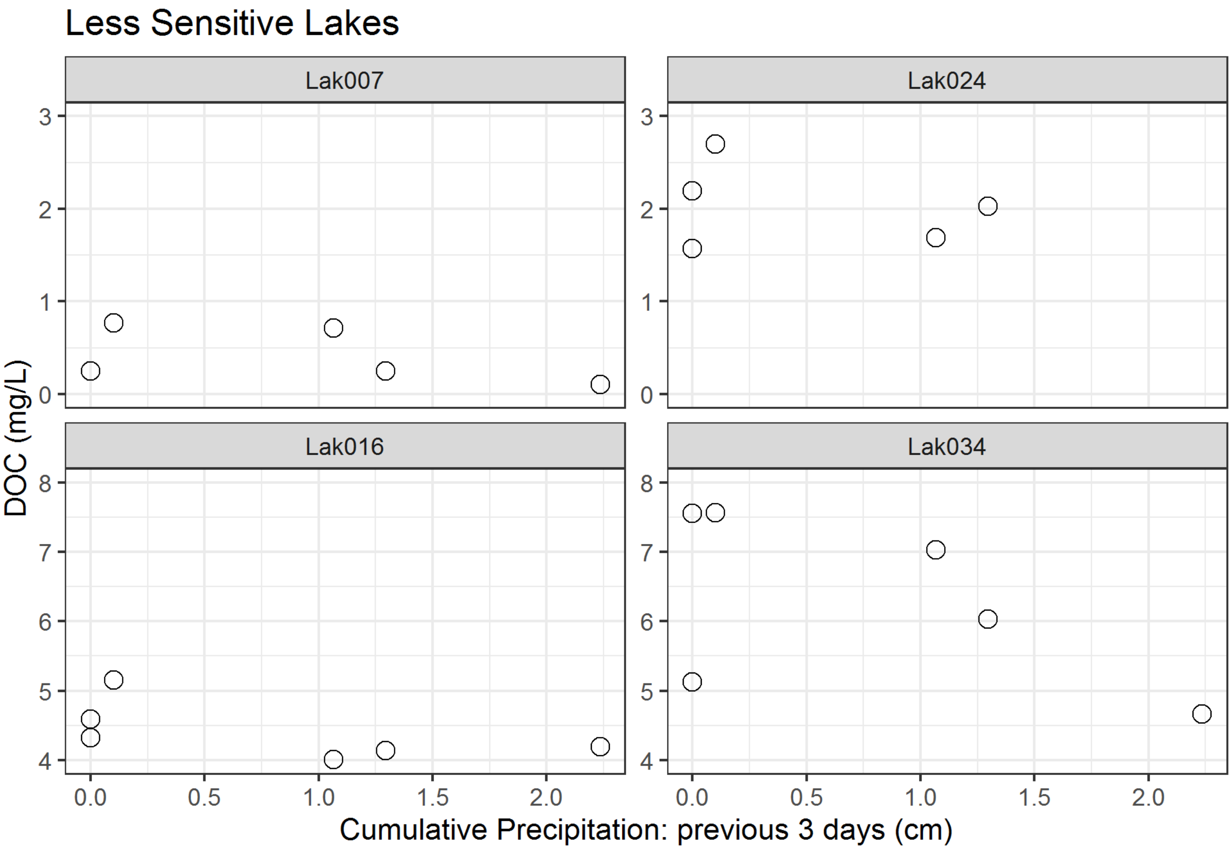


Figure 7.92: DOC (mg/L) vs. cumulative precipitation (cm) over the previous three days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

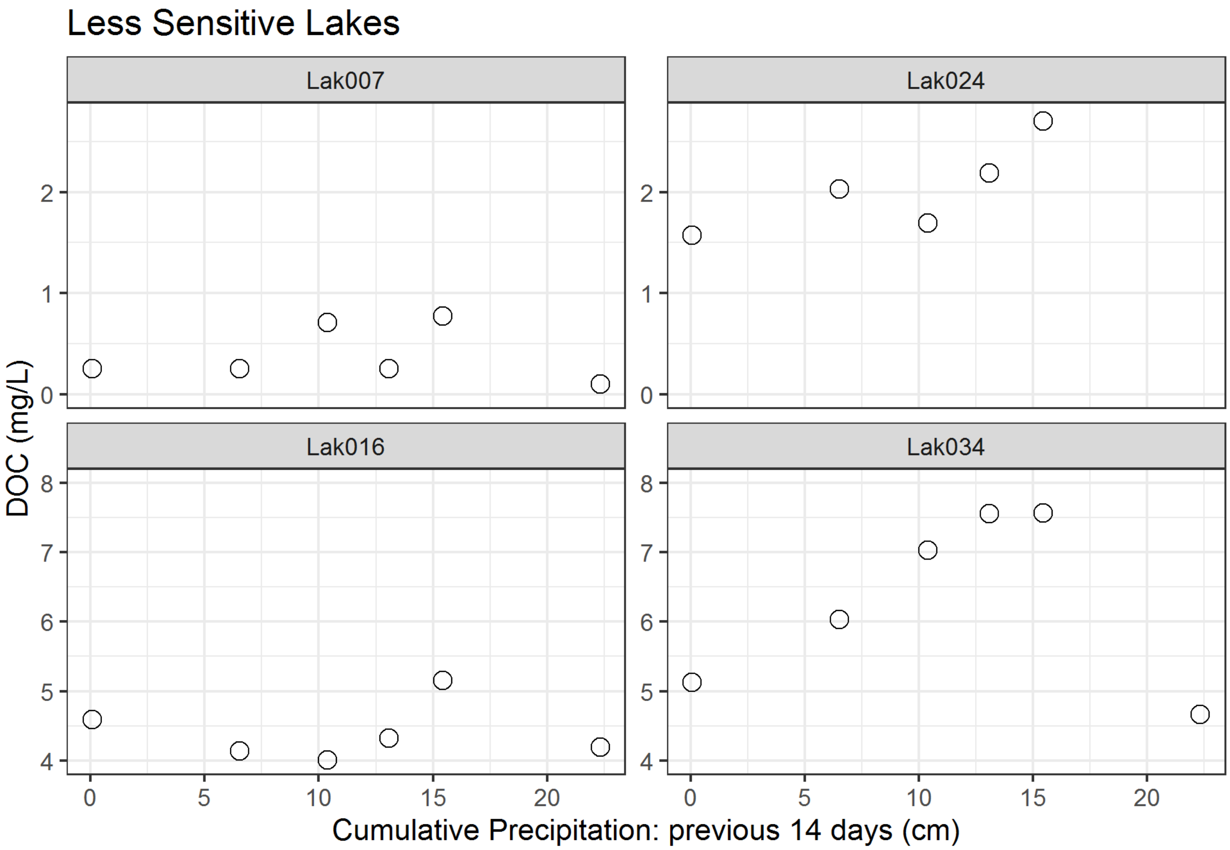


Figure 7.93: DOC (mg/L) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

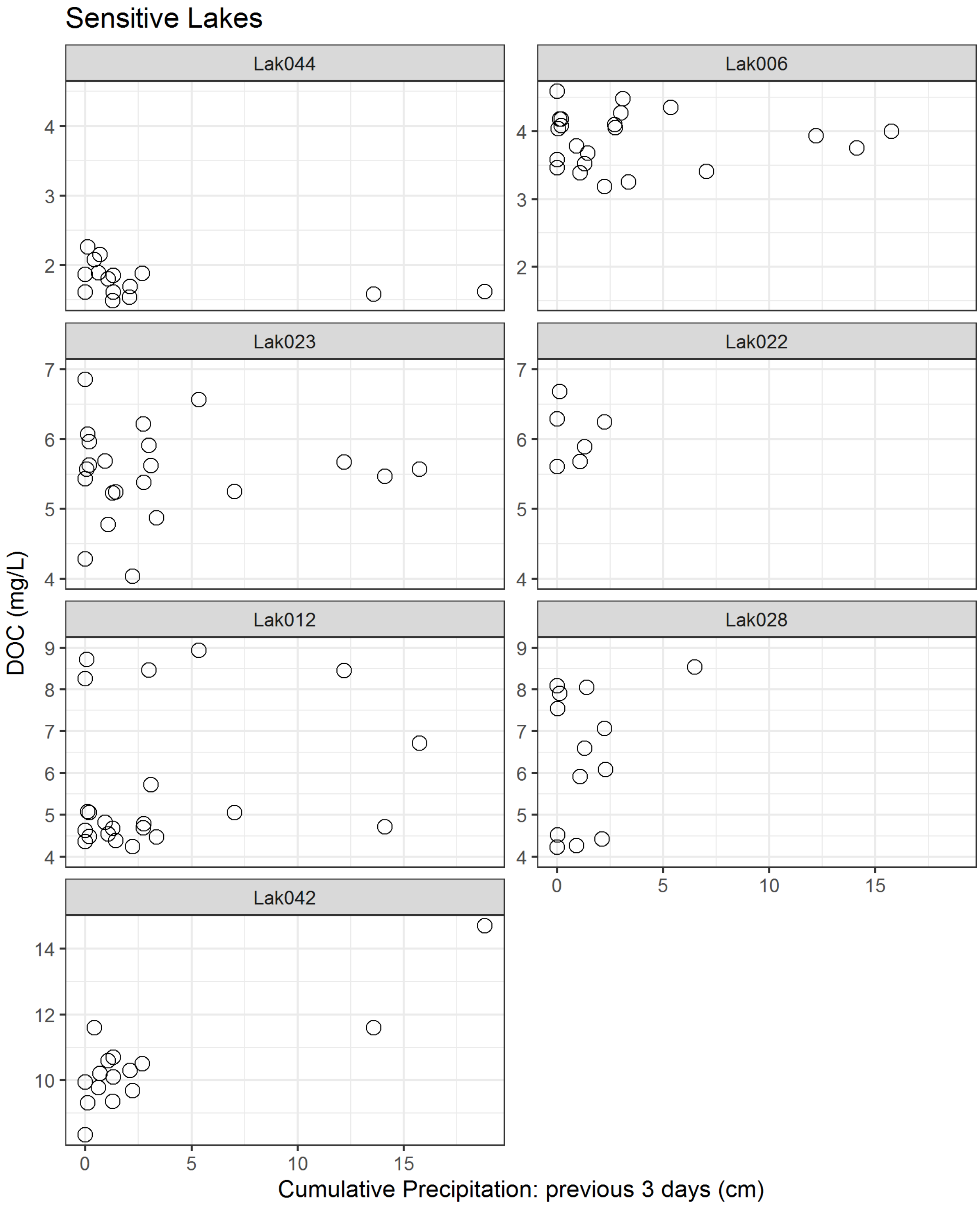


Figure 7.94: DOC (mg/L) vs. cumulative precipitation (cm) over the previous three days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

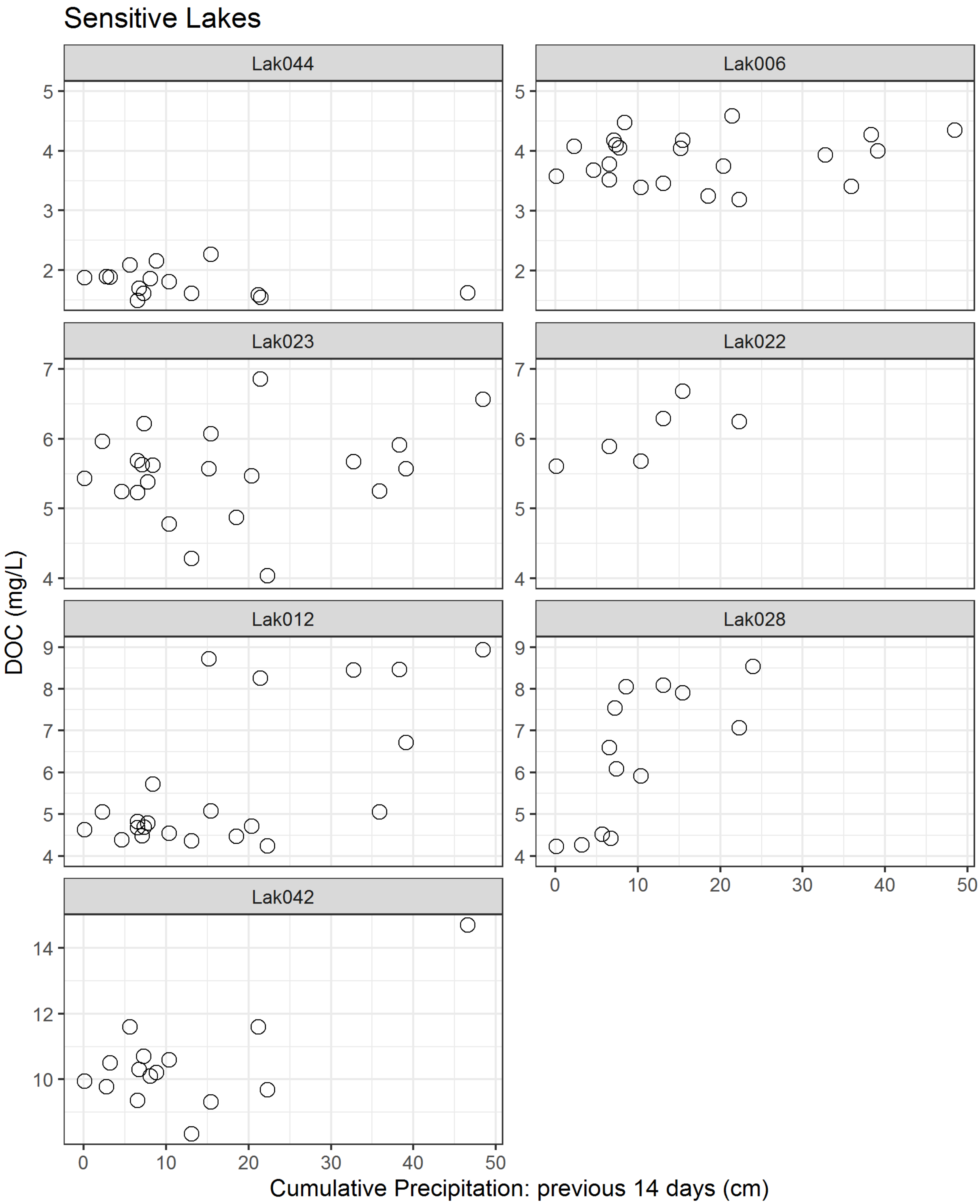


Figure 7.95: DOC (mg/L) vs. cumulative precipitation (cm) over the previous fourteen days for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.3 Water Chemistry Relative to Emissions

Purpose of analyses: As discussed in the evidentiary framework (Section 7 of the EEM Program Plan), the relationship between lake SO_4 concentrations and recent SO_2 emissions can help to inform the interpretation of the causes of changes in water chemistry. The absence of any positive correlation between lake SO_4 concentrations and recent SO_2 emissions (or any temporal trend of increasing SO_4) is evidence against the new smelter being a cause of changes in lake SO_4. However, the lack of a correlation could also reflect the fact that emissions are only a proxy indicator of the actual deposition at each lake. Estimates of lake-specific deposition are only available with the revised CALPUFF model for the period from 2016 to 2018, and therefore don't provide contrast between the pre-KMP and post-KMP period. While the presence of a positive correlation between lake SO_4 concentrations and SO_2 emissions is consistent with the hypothesis of the new smelter causing changes in lake SO_4, such a correlation is not by itself incontrovertible evidence that smelter emissions caused the increase in lake SO_4. For example, drought conditions can cause SO_4 that was historically stored in a reduced form in wetlands to be re-oxidized and then (once the drought is over) washed into the lake, causing an increase in SO_4 and decreased pH (Yan et al. 1996). It is important therefore to look at multiple factors before drawing conclusions on the most likely causes of year-to-year changes in lake chemistry. Since the control lakes were deliberately chosen to be well outside the main plume of the smelter, we would expect to see no correlation between lake SO_4 concentrations and recent SO_2 emissions in the control lakes. We expect to see stronger correlations in lakes directly within the plume.

An increase in lake SO_4 with recent SO_2 emissions is a necessary condition for there to be a causal connection between smelter emissions and lake chemistry, though increased lake SO_4 does not necessarily mean that a lake has acidified. Assessing whether acidification has occurred in a lake with increased lake SO_4 requires an examination of changes in Gran ANC and pH (see simplified evidentiary framework in Figure 7.35). Less sensitive lakes will show increases in lake SO_4 without any decrease in Gran ANC or pH, as they have sufficient buffering capacity in their watersheds and surface waters to neutralize the acidity that accompanies SO_4.

Explanation of the graphs and tables of results: The graphs in Sections 7.6.2.3.1, 7.6.2.3.2, and 7.6.2.3.3 show (respectively) mean lake SO_4, Gran ANC and pH, in an October sampling period versus the total emissions (in tonnes) during the previous 12 months (i.e., from October 1 of the previous year to September 30 of the year in which the sampling occurred).

7.6.2.3.1 SO_4 vs. Emissions

- See Section 7.6.4.2.6 for statistical analyses of the ability of total SO_2 emissions to explain observed patterns of changes in sulphate over time, beyond those patterns observed in control lakes.

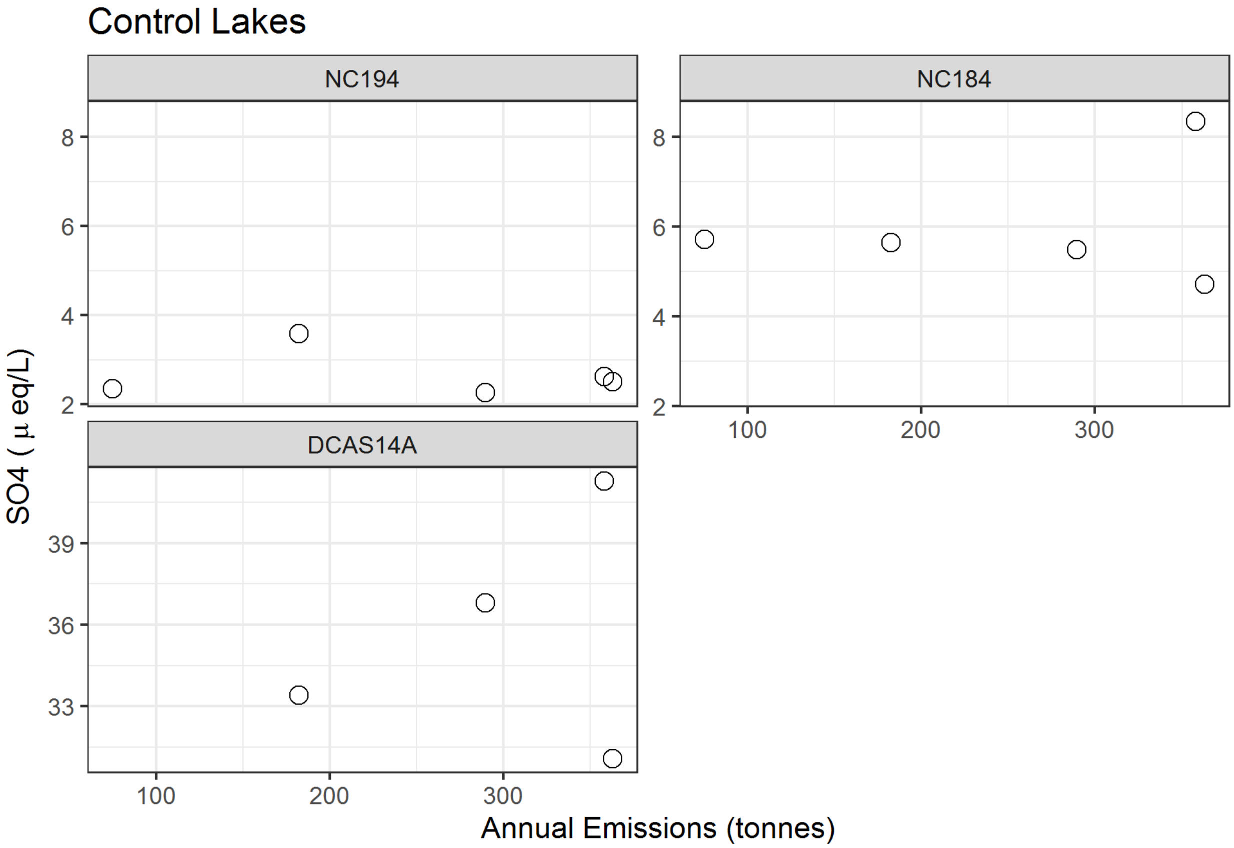


Figure 7.96: SO_4 concentrations vs. annual emissions (in tonnes) for the control lakes (DCAS14A, NC184, NC194).

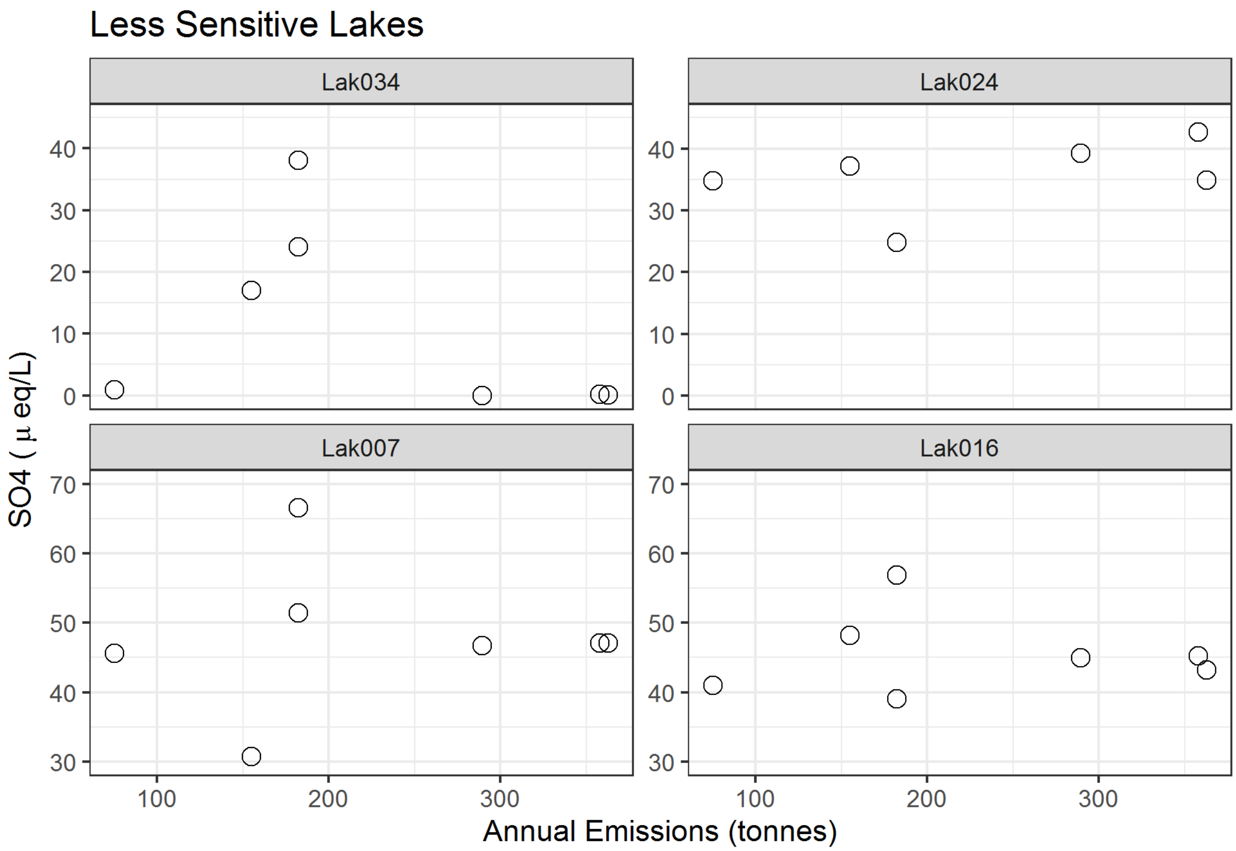


Figure 7.97: SO_4 concentrations vs. annual emissions (in tonnes) for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

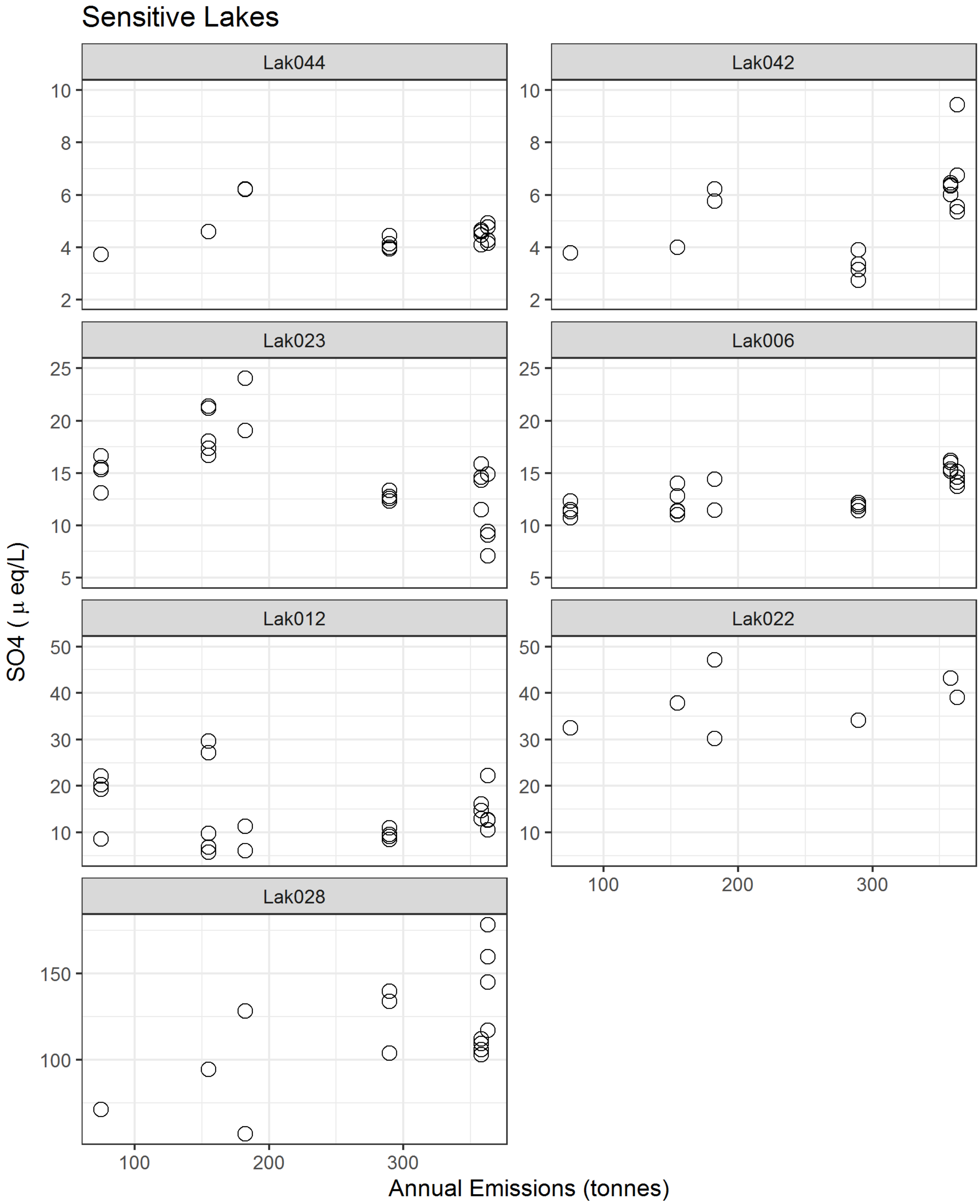


Figure 7.98: SO_4 concentrations vs. annual emissions (in tonnes) for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.3.2 Gran ANC vs. Emissions

- See Section 7.6.4.4.6 for statistical analyses of the ability of total SO_2 emissions to explain observed patterns of changes in Gran ANC over time, beyond those patterns observed in control lakes.

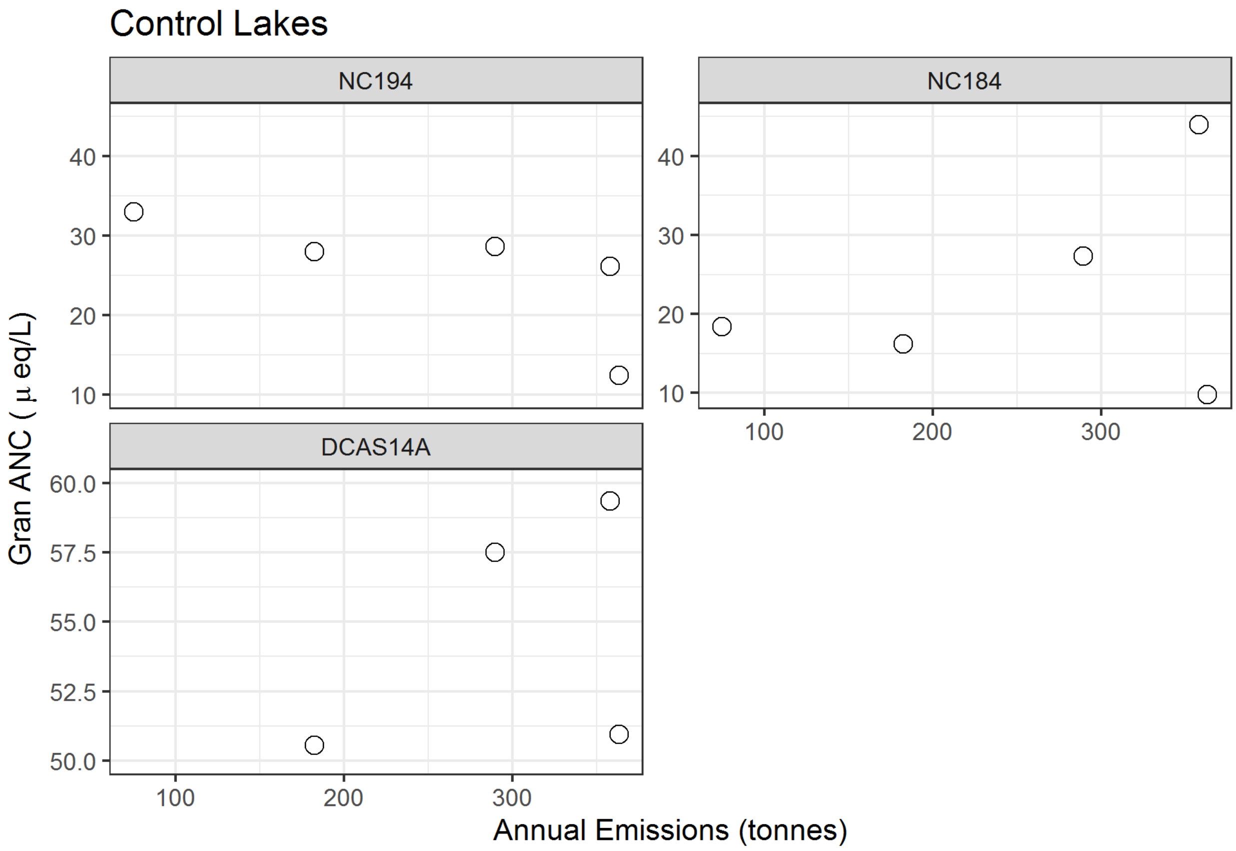


Figure 7.99: Gran ANC vs. annual emissions of SO_2 (in tonnes) for the control lakes (DCAS14A, NC184, NC194).

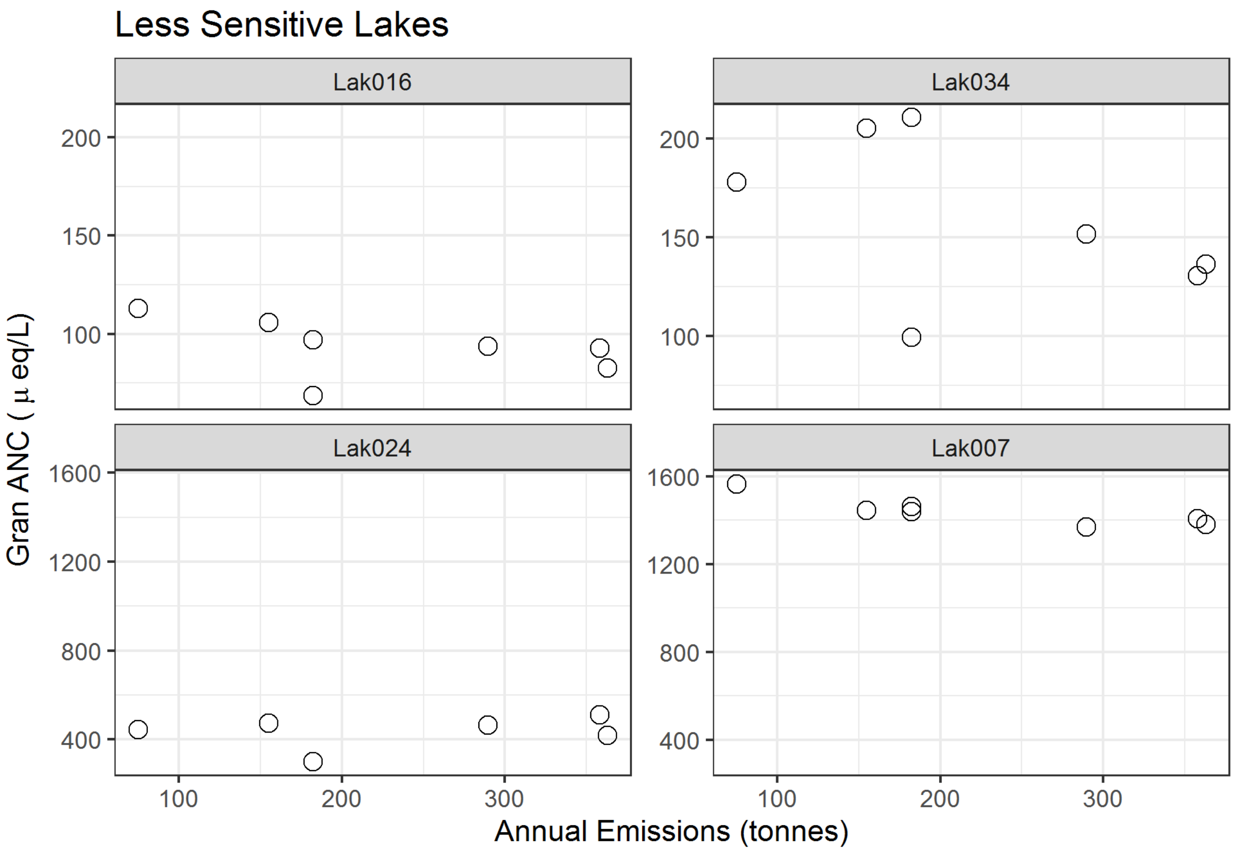


Figure 7.100: Gran ANC vs. annual emissions of SO_2 (in tonnes) for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

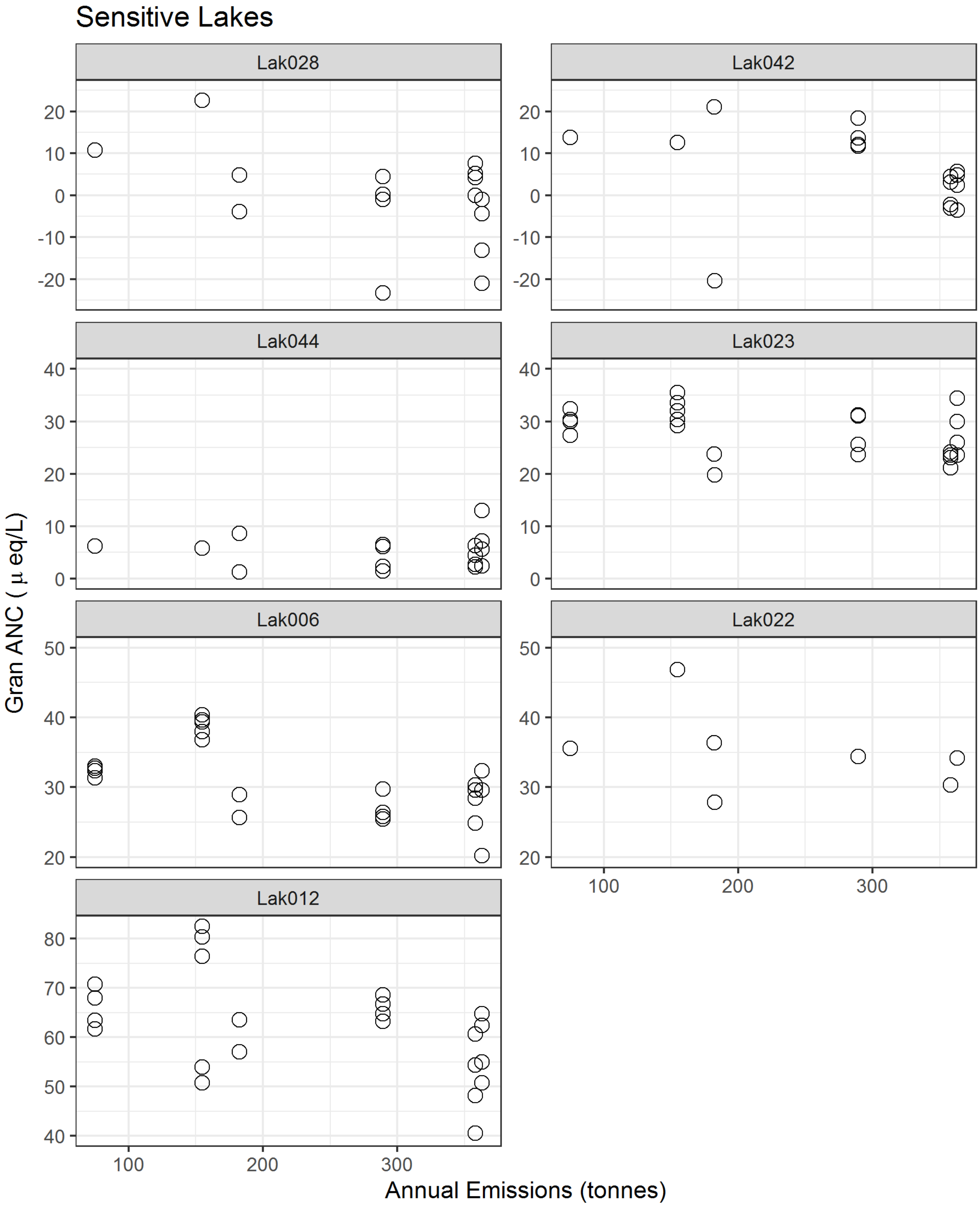


Figure 7.101: Gran ANC vs. annual emissions of SO_2 (in tonnes) for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.2.3.3 pH vs. Emissions

- See Section 7.6.4.3.6 for statistical analyses of the ability of total SO_2 emissions to explain observed patterns of changes in pH over time, beyond those patterns observed in control lakes.

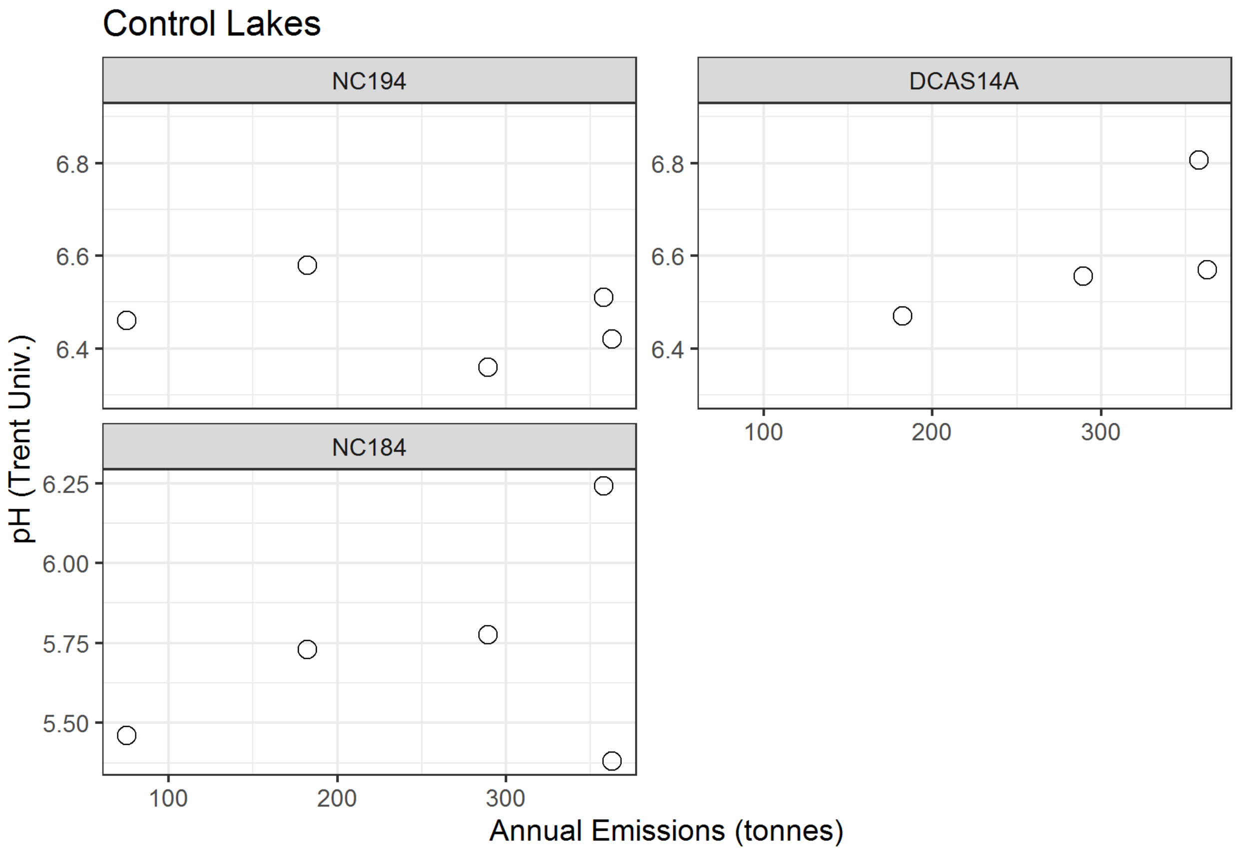


Figure 7.102: pH vs. annual emissions (in tonnes) for the control lakes (DCAS14A, NC184, NC194). The grey vertical lines correspond to measurement error of +/- 0.2.

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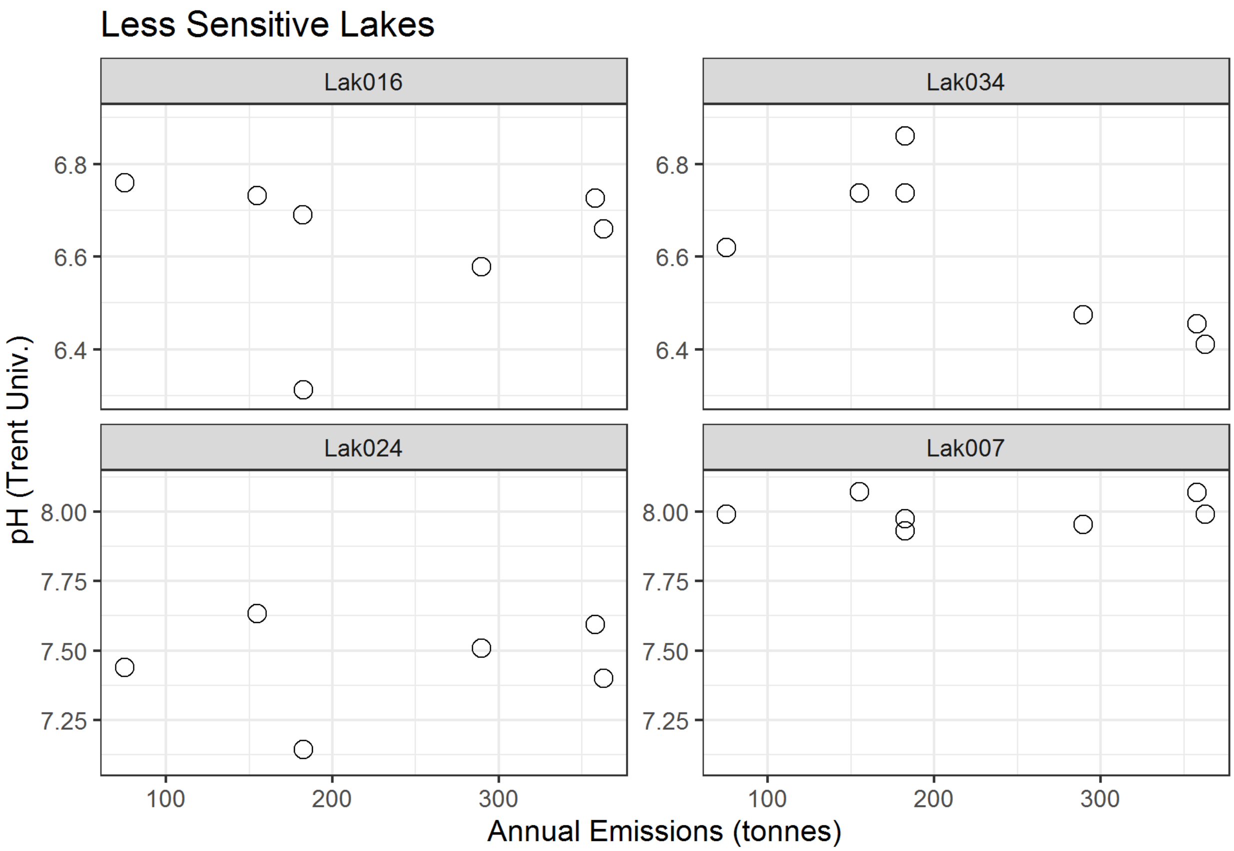


Figure 7.103: pH vs. annual emissions (in tonnes) for the EEM less sensitive lakes (LAK007, LAK016, LAK024, LAK034).

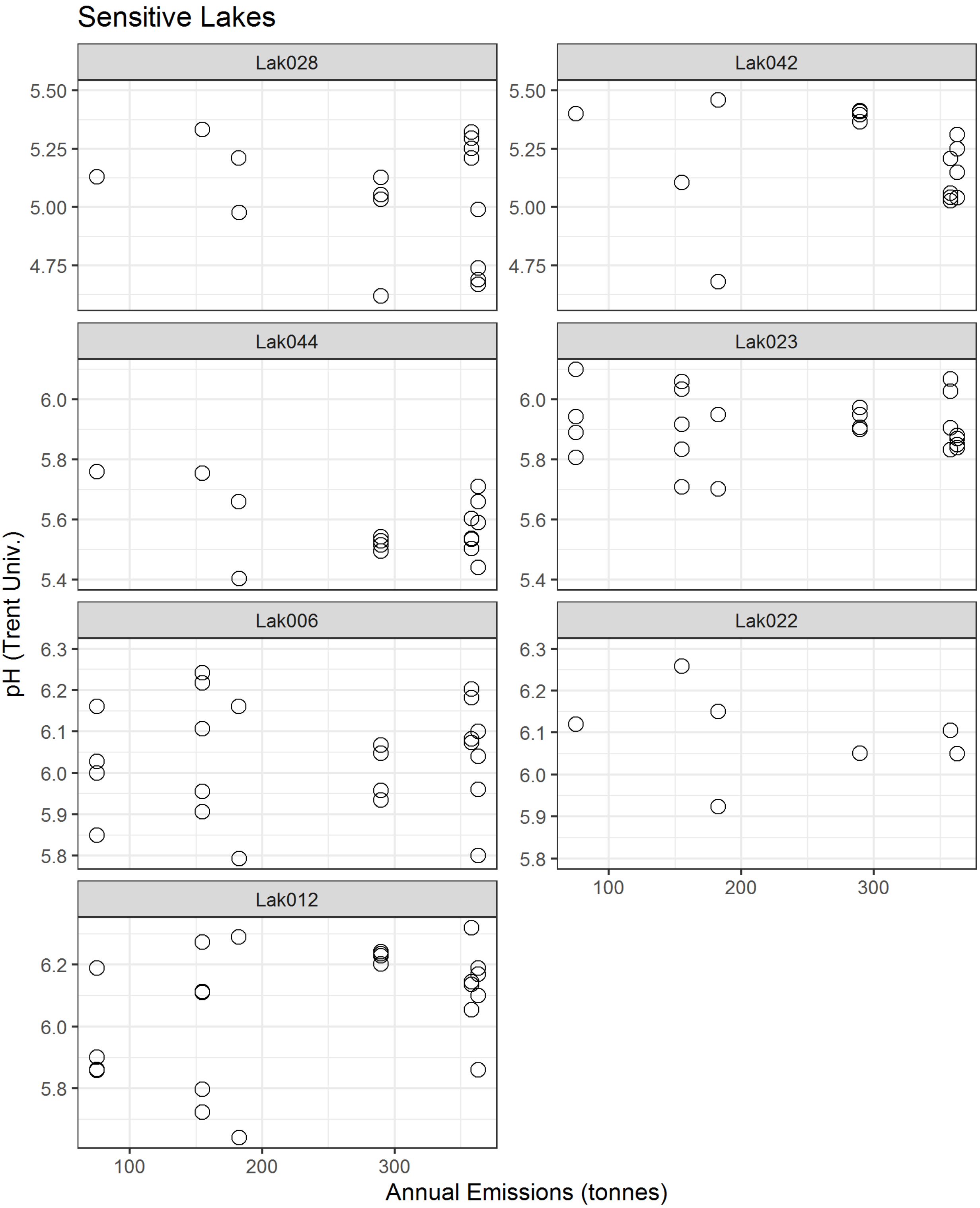


Figure 7.104: pH vs. annual emissions (in tonnes) for the EEM sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, LAK044).

7.6.3 Overview of Statistical Power Analyses

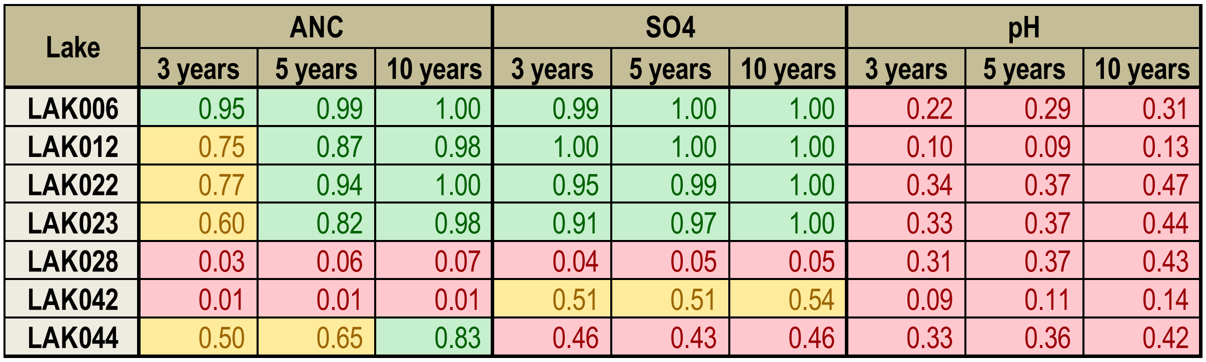
In 2015, ESSA conducted a power analysis to assess the ability to reliably detect changes in pH, Gran ANC and sulphate. This work was based on the data available from 2012 through 2014. Here are the key findings, adapted from ESSA 2016a (2015 EEM report) and ESSA 2016b (Technical Memo W05 on the power analysis):

- On average, the power to detect changes in pH that exceed the KPI threshold is low (< 0.5) and the lowest among the three primary metrics of pH, ANC and SO_4^{2-}.
- However, the power to detect changes in ANC and SO_4^{2-} is high (> 0.8 after a 5-year period) for 4 of the 7 sensitive EEM lakes (LAK006, 012, 022, 023), indicating the benefit of using multiple metrics.
- On average, power is lower for the combined set of metrics than each of them individually, indicating that although there is a definite benefit of considering all three metrics, it is best to analyse them individually.
- Power to detect changes varies by lake and parameter:
  - Across all of the metrics, LAK022 and LAK023 consistently have among the highest power, due to lower levels of variability in their water chemistry.
  - LAK028 and LAK042 have very low power (< 0.1) for ANC.
  - LAK028 has very low power (< 0.1) for SO_4^{2-}.
  - LAK012 and LAK042 have low power (< 0.2) for pH.
- If the long term variability in lake chemistry is actually lower than was observed during 2012-2014, then statistical power increases for most of the lakes for pH.
  - It is plausible that variability of the EEM lakes may have been overestimated given that the baseline period is short and non-static, the old smelter was being decommissioned, and the time of sampling varied (August in 2012, October in 2013 and 2014).
- If the simulated effect is a gradual change over 10 years rather than an abrupt change immediately following KMP, then the changes in all three metrics were much harder to successfully detect.
  - With gradual changes in lake chemistry, statistical power is very low across all lakes for ANC and pH and for half of the lakes for SO_4^{2-}.
- For all three lakes with intra-annual sampling during 2014 (LAK006, LAK012, LAK023), increasing the frequency of sampling increased the power
  - This was most pronounced for pH, which is important since pH has the lowest power
  - The increase in power for ANC and SO_4^{2-} is of minimal benefit since the three lakes already have high to very high power for those two metrics after 5 years.
  - Based on these findings, intra-annual sampling was added for LAK028, LAK042, and LAK044 through 2015 to 2018. It is not feasible to access LAK022 for multiple samples in the fall index period.
- Continuous monitoring further increased the power for pH, which again is particularly important given the otherwise low power to detect changes in pH.
- Across most of the lakes, metrics and scenarios, power was low or very low in the first few years after KMP. In general, at least five years of post-KMP data are required to reach adequate statistical power for Gran ANC. For this report, we have only 3 years of post-KMP data. Therefore, at least 2 more years of post-KMP data are required to attain adequate

statistical power for Gran ANC, preferably 3 more years of data (see Recommendations, Section 7.4 in the main report).

- Across most of the lakes and scenarios, false positive rates were generally very low for ANC and pH, but significantly higher for SO_4^{2-}, especially when fewer than 5 years of post-KMP observations were analyzed.
- Table 7.23 (from results summarized in Technical Memo W05) shows how the power to detect changes in ANC, SO_4 and pH varies across lakes and over different periods of time of post-KMP monitoring (3, 5 or 10 years). The power to detect changes in ANC and SO_4 was generally higher than the power to detect changes in pH in most of the lakes (except LAK028). Two of the lakes (LAK028 and LAK042) showed very low power to detect changes in ANC due to high variability in ANC over the 2012-14 period. Monitoring for 10 years did not significantly improve statistical power over monitoring for 5 years, when there was an immediate change in lake chemistry after the 3-year baseline period.

Table 7.23 Summary of results of power analysis, showing power to detect a change in lake chemistry by lake, using 2012-14 EEM data to estimate variability. The values shown are the statistical power to detect a decrease in pH or ANC, and an increase in SO_4 (i.e., threshold of change equal to zero) when a lake simulated an immediate pH decrease of 0.3 units (and the associated changes in ANC and SO_4 computed via the SSWC model) . Values greater than 0.8 are shown in green, values between 0.5 and 0.8 are shown in yellow, and values below 0.5 are shown in red.



Lake	ANC			SO4			pH		
	3 years	5 years	10 years	3 years	5 years	10 years	3 years	5 years	10 years
LAK006	0.95	0.99	1.00	0.99	1.00	1.00	0.22	0.29	0.31
LAK012	0.75	0.87	0.98	1.00	1.00	1.00	0.10	0.09	0.13
LAK022	0.77	0.94	1.00	0.95	0.99	1.00	0.34	0.37	0.47
LAK023	0.60	0.82	0.98	0.91	0.97	1.00	0.33	0.37	0.44
LAK028	0.03	0.06	0.07	0.04	0.05	0.05	0.31	0.37	0.43
LAK042	0.01	0.01	0.01	0.51	0.51	0.54	0.09	0.11	0.14
LAK044	0.50	0.65	0.83	0.46	0.43	0.46	0.33	0.36	0.42

Table 7.24 shows the number of years required to achieve power greater than 0.8 for each metric under two differing assumptions about the level of variability in the lakes. Two of the EEM lakes (LAK028 and LAK042) require more than 10 years of post-KMP monitoring to obtain 0.8 statistical power for Gran ANC, pH and SO_4. None of the EEM lakes achieve 0.8 statistical power in pH, even after 10 years.

The results in Table 7.24 show little effect of the two assumptions of variability, which requires some explanation. The results under the column "Observed variability (based on 2012-14 EEM data)" assume that long term variability in lake chemistry will reflect the variability observed in each EEM lake during 2012-14. This assumption may over-estimate variability and under-estimate the power to detect changes in lake chemistry, since 2012-2014 was the transition period during which the old smelter was being decommissioned, resulting in a reduction in emissions of SO_2 and potentially additional variability in the chemistry of some EEM lakes due to reduced sulphur deposition. The assumption "Lower Variability (based on EC lakes)" decreased the variability of each chemical parameter in each EEM lake by a fraction that reflected the ratio of variability in EC lakes to EEM lakes. These ratios were calculated from the 10 lakes monitored by Environment Canada from 2005 to 2014 in their Georgia Basin study in southwestern British Columbia (unpublished data provided by Dr. Patrick Shaw, Environment Canada). Like the EEM lakes, though to a lesser degree, the Environment Canada lakes showed greater variability in pH than in Gran ANC and sulphate.

Table 7.24 Summary of results from the 2015 power analyses, showing the number of years of post-KMP data required for power >0.8 to detect decreases in pH and ANC, or increases in SO_4, based on assuming variability is best represented by the observation from 2012-2014 or from the Environment Canada (EC) lakes in Georgia Basin.

Lake	ANC		SO_4		pH	
	Lower variability (based on EC lakes)	Observed variability (based on 2012-14 EEM data)	Lower variability (based on EC lakes)	Observed variability (based on 2012-14 EEM data)	Lower variability (based on EC lakes)	Observed variability (based on 2012-14 EEM data)
LAK006	3	3	3	3	>10	>10
LAK012	3	5	3	3	>10	>10
LAK022	3	5	3	3	>10	>10
LAK023	3	5	3	3	>10	>10
LAK028	>10	>10	>10	>10	>10	>10
LAK042	>10	>10	>10	>10	>10	>10
LAK044	5	10	>10	>10	>10	>10

7.6.4 Statistical Analyses of Trend and Temporal Patters, and comparison to EEM thresholds

The EEM Thresholds of interest are 0.3 units for ΔpH, and lake-specific thresholds for ΔANC that correspond to 0.3 units of ΔpH in each lake, as derived from multiple ANC titrations performed at Trent University. We know from the power analyses (summarized in Section 7.7.3) that pH is more variable than ANC, and that there is lower statistical power to detect changes in pH than to detect changes in ANC. Consistent with the simplified evidentiary framework in Figure 7.35, we begin by analyzing changes in sulphate concentrations between the pre-KMP period and the post-KMP period, and then move on to assess pH and Gran ANC.

We used the simplest methods first (in which all sources of variation are present in the data), and then use more complex methods to explicitly account for individual sources of variation. In the TOR for the Comprehensive Report, we proposed completing 8 analyses, which build incrementally, and are applied using both frequentist and Bayesian approaches. As we proceeded through the analysis we converged on seven frequentist methods:

1. Two-Sample Before-After T-Test Using Mean Values
2. Two-Sample Before-After T-Test Using Individual Samples
3. Before-After Control-Impact (BACI), Using Mean Values[18]

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[18] Measurements from the Control Lakes include 2013 samples as an estimate of pre-KMP conditions, and 2016-2018 samples as an estimate of post-KMP conditions.

4. Before-After Control-Impact (BACI), Using Individual Samples
5. Before-After Control-Impact (BACI), with Assumption of No Change in Control Lakes
6. Using Other Covariates to Explain Inter-Annual Variation
7. Temporal Trend Analyses

Given that we applied multiple statistical tests, we used an alpha level of 0.01 for examining the probability of an effect (or rejecting a null hypothesis), rather than a level of 0.05.

We also applied two Bayesian approaches:

1. Bayesian Analysis Supersedes the T-Test (using a range of informative priors)
2. Bayesian analysis with uninformative priors

In the TOR we indicated that if the frequentist approach showed a clear result for a lake (e.g., 99% confidence intervals for ΔANC do not overlap that lake's threshold for ΔANC) then there was no need to proceed with the Bayesian analysis for that parameter in that lake. However, to provide reviewers with the ability to compare results across all lakes and methods we have applied all frequentist and Bayesian analyses to each lake, for each of the three primary metrics.

7.6.4.1 Primer on Confidence Intervals

The confidence interval describes the amount of uncertainty surrounding our parameter estimate. It is possible to calculate confidence intervals for different levels of confidence (90%, 95%, 99%). Within a 99% confidence interval, we are 99% confident that the calculated interval contains the true value of the population parameter. In other words, if the experiment were repeated 100 times, in 99 cases we would expect the confidence interval to contain the true population parameter.

The figure below shows the 99% confidence interval for a parameter estimate across five experiments (A through E). The two dotted vertical lines are at zero and at -11, which corresponds to a "threshold", and anything lower than -11 is deemed to have exceeded the threshold.

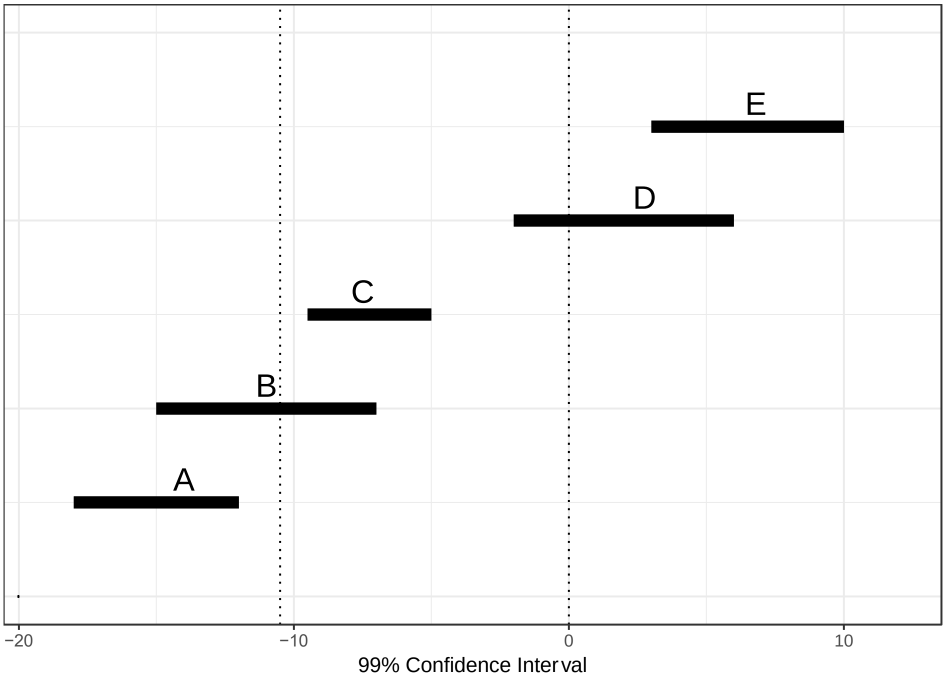


Figure 7.105: Example of confidence intervals with a threshold.

- Experiment A: The 99% CI spans values that are all lower than -11. In this case, there is 99% confidence that the parameter is lower than the -11 threshold.
- Experiment B: The 99% CI spans the -11 threshold and is entirely less than zero. In this case, we are 99% confident that the true parameter value is along this line, and shows a value below zero, but we cannot say whether it is above or below the -11 threshold.
- Experiment C: The 99% CI is entirely greater than the -11 threshold, and entirely less than zero. We can say with 99% confidence that the true value is negative, and that it is not lower than the threshold.
- Experiment D: The 99% CI spans zero. We cannot say with any confidence that the true parameter value is different from zero.
- Experiment E: The 99% CI is entirely greater than zero. We can say with 99% confidence that the true value is greater than zero and falls within the line.

7.6.4.2 Key Metric: SO_4

7.6.4.2.1 Method 1 (Frequentist): Two-Sample Before-After T-Test Using Mean Values

Description of Analyses:

We applied Two-sample Before-After t-tests of pre-KMP chemistry (either 2012 or 2012-2014, see discussion below) vs. post-KMP chemistry (2016-2018) for each individual lake, using mean values for each year, building on the methods of Kilgour et al. 1998. This is the simplest analysis, providing (for each lake) an estimate of the change in the mean value of each chemical component between the pre-KMP period and the post-KMP period (2016-2018). This analysis does not account for various sources of variation (e.g., natural variability unrelated to the smelter (as reflected in the control lakes), or variability within the October sampling period).

From the power analysis we know that it will be very difficult to show a statistically significant change given only 1 pre-KMP observation and 3 post-KMP observations. We calculated the Minimum Detectable Difference (MDD) to demonstrate what level of change would be detectable with high statistical power.

- *Form of Test:* $Y_t \sim BA$; where *Y* is the overall mean across both before and after categories of years, and BA is the effect of Pre-KMP (Before) vs Post-KMP (After).
- *Assumptions:*
    - The chemistry of component Y in a given lake is a function only of the time period (before vs after).
    - The mean value of component Y represents the state of component Y in a given year.
    - We can use process error from 2016-18 to provide an estimate of the year to year variability for the 2012 measurement.

Purpose of analyses:

Figures 11 and 12 in Volume 1 of the STAR (ESSA et al., 2013) demonstrate the expectation that the new smelter would result in both a higher level of sulphur deposition, and a different spatial pattern of deposition. We are therefore interested to learn which lakes experienced an increase in SO_4 concentrations, and which lakes experienced a decrease. There are four purposes to these analyses:

1. Assess if there has been a statistically significant change in SO_4 (i.e., Δ SO_4 is significantly different from 0) between two time periods: pre-KMP (2012) and post-KMP (2016-2018). This t-test simply assesses if there has been *any* statistically significant change in SO_4. Δ SO_4 is computed as the post-KMP mean minus the pre-KMP mean.

2. Assess whether the confidence intervals for Δ SO_4 span 0.0 (level of confidence that there has been an increase or decrease in SO_4) .

3. Assess what the Minimum Detectable Difference (MDD) in SO_4 is for each lake, under four different assumptions of the true standard deviation of SO_4.

4. Expanding the definition of the baseline / pre-KMP period to 2012-2014, assess if there has been a statistically significant change in SO_4 between the expanded pre-KMP period (2012-2014) and post-KMP (2016-2018). Emissions from the old smelter were declining between 2012 and 2014, so we would expect to see a greater likelihood of sulphate increases using the expanded baseline period.

We have **not** applied an expanded baseline period to pH and Gran ANC, because doing so would increase the risk of Type I error (a false positive) in testing for exceedances of pH and ANC thresholds. In most of the sensitive lakes, the pH and Gran ANC increased during the 2012-2014 period as SO_2 emissions from the old smelter declined (Figure 7.44, Figure 7.41). Including pH and ANC observations from 2013 and 2014 in the estimates of mean pre-KMP pH and mean pre-KMP Gran ANC would increase those metrics to a level that is not representative of the pre-KMP period prior to and including 2012, and increase the risk of a false exceedance of the thresholds for changes in pH and Gran ANC. However, as there are no thresholds applied to changes in SO_4 (lake biota are unaffected by increases in SO_4 as long as pH and Gran ANC do not decline), we are able to expand the pre-KMP baseline to 2012-2014 without increasing the risk of a Type 1 error.

Explanation of the graphs and tables of results:

See captions below.

Table 7.25: T-test of changes in mean SO_4 for each lake, between the pre-KMP period (2012) and post-KMP period (2016-2018). P-value is the probability of the ΔSO_4 being significantly different from zero ($p<0.01$ is the appropriate signficance level given the multiple statistical tests). Lwr and Upp are the lower and upper confidence levels for Δ SO_4. Sd_post is the standard deviation of mean SO_4 levels over the 3-year post-KMP period. MDD_sd is the minimum detectable difference in SO_4 that would be statistically significant at $p<0.01$ with 80% statistical power, given four different assumptions about the standard deviation of SO_4 during the pre-KMP period (1, 5, 10, 20 μeq/L). For example, in LAK006, a SO_4 change of 9.5 μeq/L is the minimum detectable difference with a pre-KMP SD of 1 μeq/L, but the MDD increases to 96 μeq/L if the SO_4 pre-KMP SD were 20 μeq/L.

SUBSET	SITE	p-value	lwr	upp	sd_post	MDD_sd_1	MDD_sd_5	MDD_sd_10	MDD_sd_20
Less Sensitive	LAK007	0.003	-7	-2	0.2	5	24	48	96
Less Sensitive	LAK016	0.053	-7	18	1.1	7	25	48	96
Less Sensitive	LAK024	0.088	-30	59	3.9	19	30	52	98
Less Sensitive	LAK034	0	-25	-23	0.09	5	24	48	96
Sensitive	LAK006	0.391	-17	22	1.7	9	25	49	96
Sensitive	LAK012	0.221	-21	30	2.2	12	26	49	97
Sensitive	LAK022	0.241	-43	60	4.5	22	32	53	98
Sensitive	LAK023	0.054	-28	11	1.7	9	25	49	96
Sensitive	LAK028	0.112	-191	335	23.0	110	113	120	146
Sensitive	LAK042	0.579	-23	20	1.9	10	26	49	96
Sensitive	LAK044	0.037	-6	2	0.3	5.	24	48	96

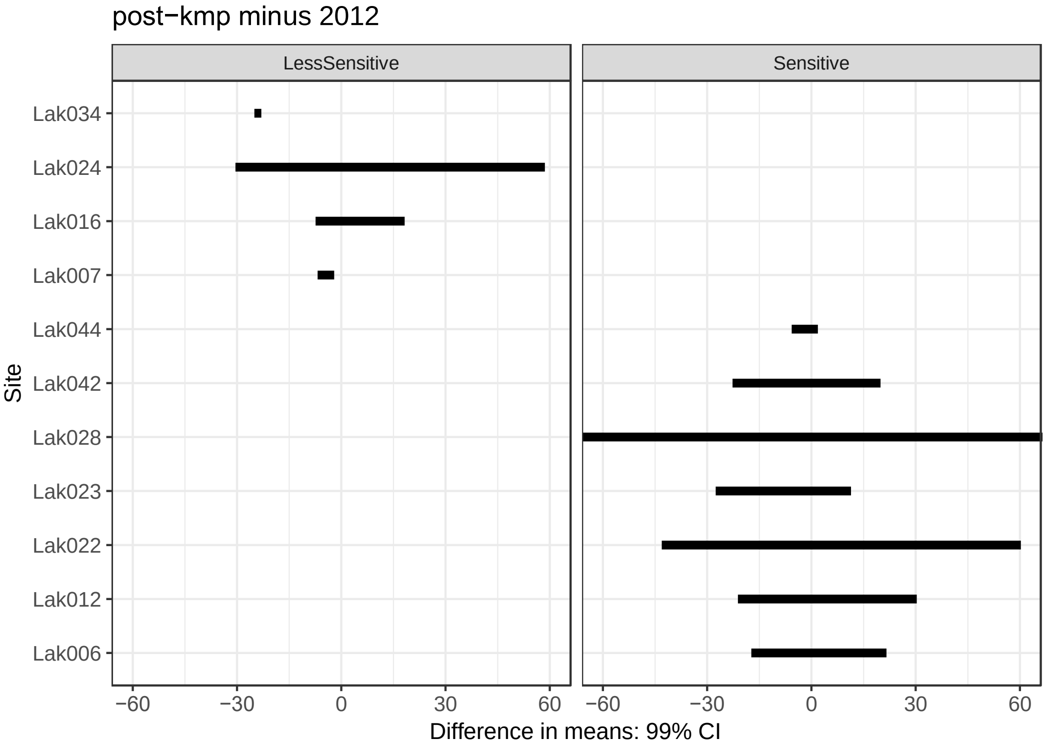


Figure 7.106: Using Method 1, 99% confidence intervals for the ΔSO_4 (mean SO_4 in post-KMP period (2016-2018) minus the mean SO_4 in the pre-KMP period (2012 only). The confidence intervals for ΔSO_4 overlap 0.0 for all sensitive lakes, and for LAK024 (Lakelse Lake) and LAK016. LAK028 has very wide confidence intervals for ΔSO_4. At the other extreme, LAK034 has very narrow 99% confidence intervals for ΔSO_4 and strong evidence of a significant decrease in SO_4 (about 24 μeq/L). LAK007 also has narrow 99% confidence intervals for ΔSO_4 and evidence of roughly a 3-8 μeq/L decrease in SO_4. There are no specific thresholds for ΔSO_4.

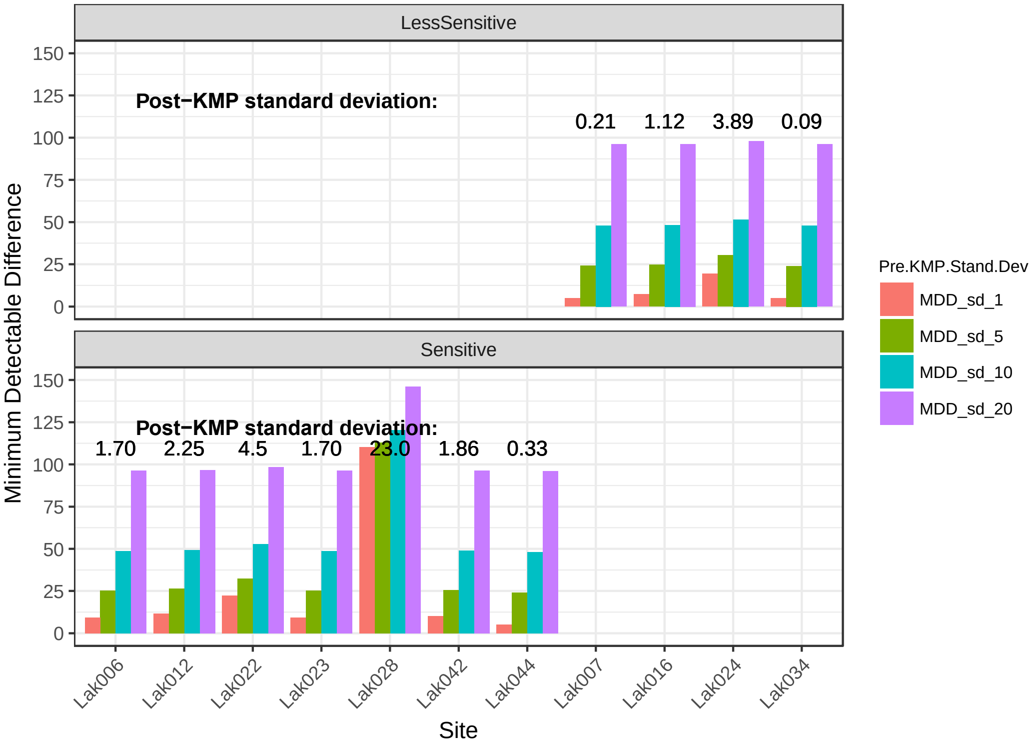


Figure 7.107: Minimum detectable differences (MDD) are shown for each lake, assuming four different values for the standard deviation (SD) of SO_4 in the pre-KMP period (2012). Since we have only one observation for the pre-KMP period (a single measurement in 2012), we can't compute the SD, but must assume it. LAK028 has very high values for MDD, due to its high variability in SO_4 (highest post-KMP SD). By contrast, LAK034 has a very low post-KMP SD. There are no specific thresholds for ΔSO_4.

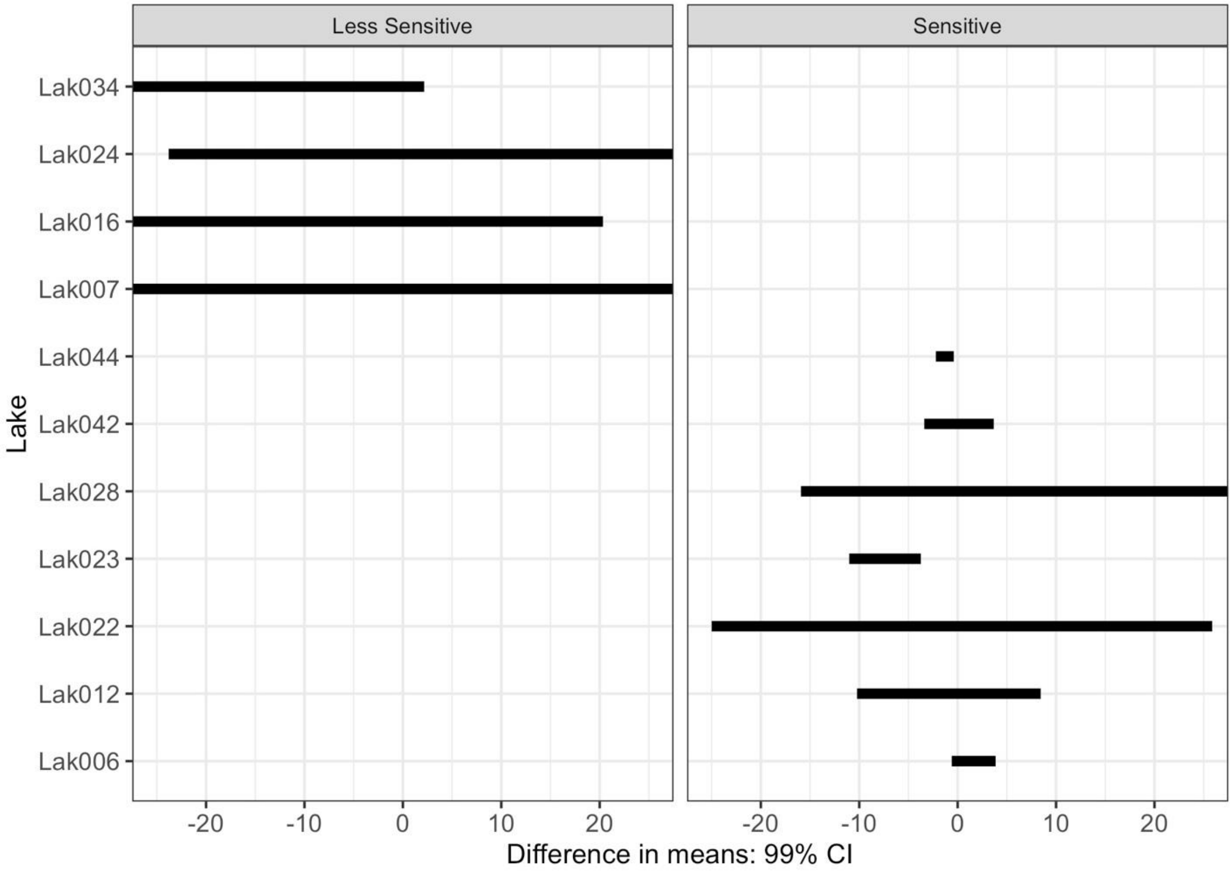


Figure 7.108: Using Method 1, 99% confidence intervals for the ΔSO_4 (mean SO_4 in post-KMP period (2016-2018) minus the mean SO_4 in the expanded pre-KMP period (2012-2014). The confidence intervals for ΔSO_4 are narrower with the expanded pre-KMP period, compared to using just 2012 (compare to Figure 7.106, noting the difference in the x-axis labels). The confidence intervals for ΔSO_4 overlap 0.0 for 5 of the 7 sensitive lakes, but now show declines in SO_4 for LAK023 and LAK044 (a pattern not apparent when just 2012 was used for the baseline - Figure 7.106). There are no specific thresholds for ΔSO_4.

Table 7.26. Minimum detectable difference (MDD) for a difference in SO_4 between the pre-KMP (2012-2014) and post-KMP (2016-2018) groups for each lake. The MDD is based on a significance level (alpha) of 0.05 with 80% power.

Lake	SUBSET	MDD
LAK006	Sensitive	6
LAK012	Sensitive	13
LAK022	Sensitive	21
LAK023	Sensitive	17
LAK028	Sensitive	111

LAK042	Sensitive	5
LAK044	Sensitive	3
LAK007	Less Sensitive	39
LAK016	Less Sensitive	20
LAK034	Less Sensitive	54

KEY FINDINGS:

- Only support for significant difference in SO_4 between baseline (2012) and Post-KMP period (2016-2018) is for two of the less sensitive lakes (LAK007 and LAK034), and support is for a *decline* in SO_4 over time. The confidence intervals for Δ SO_4 overlap zero in all of the sensitive lakes.
- With an expanded baseline period (2012-2014), two of the sensitive lakes (LAK023 and LAK044) show support for a decline in SO_4, but the confidence intervals for Δ SO_4 overlap zero in all of the less sensitive lakes.
- Due to high variability in SO_4, the minimum detectable differences are largest for LAK028.

7.6.4.2.2 Method 2 (Frequentist): Two-Sample Before-After T-Test Using Individual Samples

Description of Analyses:

This is a Two-sample Before-After test of 2012 chemistry vs. 2016-2018 for each individual lake, using 4 measurements from each year. This method provides greater insight than method 1, as it accounts for unequal sampling in various years and lakes (e.g., 1 sample in some lakes in some years, 4 samples in most lakes and years). The estimated before-after change between the pre-KMP and post-KMP periods removes the effect of natural variability within the sampling period.

- *Form of test:* $Y_t \sim BA + YRE$, where YRE = Year Random Effect due to multiple samples taken in the October sampling period;
- *Assumptions:*
  - Same as analysis 1, plus:
  - The chemistry of component Y in a given lake is a function of the time period (before vs after), as well as the variability within the October sampling window
  - All of the measured values of component Y during the October sampling window represent the state of component Y in a given year
  - Only include lakes with multiple within year measurements

Purpose of analyses:

The purpose of this analysis is similar to Method 1 (i.e., to determine if there is a significant difference between the post-KMP and pre-KMP values of SO_4), but the analysis removes the effect of natural variability during the sampling period. We are interested to see if this reduces the uncertainty in estimates of the ΔSO_4 between the post-KMP and pre-KMP periods, and narrows the confidence intervals on these estimates.

Explanation of the graphs and tables of results:

See captions below.

Table 7.27: Results for T-test for post-KMP SO_4 (2016-18) versus baseline SO_4 (2012), using individual samples, for the six sensitive lakes with multiple within-year samples. The "est.diff" is the SO_4 in the post-KMP period minus the SO_4 in the baseline period. A positive value for "est.diff" means that the SO_4 increased from the baseline period to the post-KMP period (e.g., LAK006, LAK012, LAK028), while a negative value indicates a decrease in SO_4 (e.g., LAK023, LAK042, LAK044) The "est.diff.se" is the standard error in SO_4, which is highest for LAK028 and LAK012, and lowest for LAK044. The "est.diff.lcl" and "est.diff.ucl" are the lower and upper confidence intervals (respectively) for "est.diff". The "p.value" is the probability of a significant difference in mean SO_4 between the two time periods (all p-values are >0.01, and therefore the differences between the two time periods are not statistically significant).

SITE	est. diff	SE	Lower	Upper	p.value
LAK006	2.5	2.3	-7	12	0.379
LAK012	6.8	4.3	-4	18	0.179
LAK023	-6.7	3.0	-14	1	0.075
LAK028	71.5	29.0	-11	154	0.073
LAK042	-0.8	2.4	-9	7	0.771
LAK044	-1.9	0.4	-3	-1	0.001

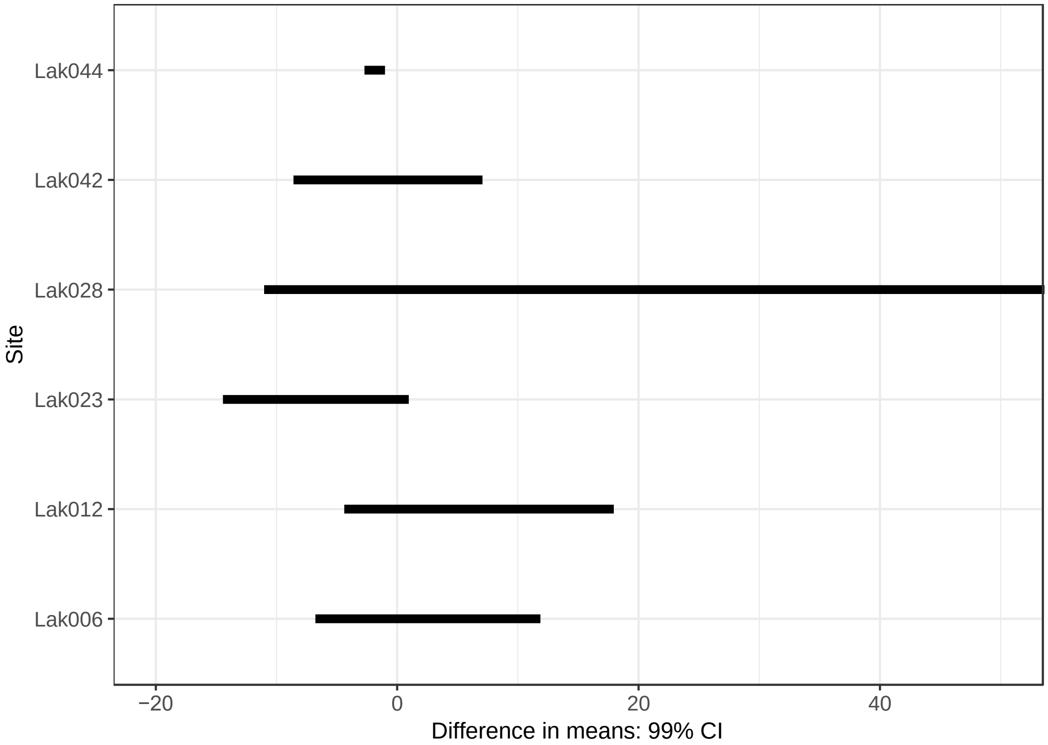


Figure 7.109: Using Method 2, 99% confidence intervals for the ΔSO_4 (mean SO_4 in post-KMP period (2016-2018) minus the mean SO_4 in the pre-KMP period (2012), accounting for within year variability. The confidence intervals for changes in mean SO_4 overlap 0.0 for all lakes except LAK044 (strong evidence of a small decrease in SO_4).

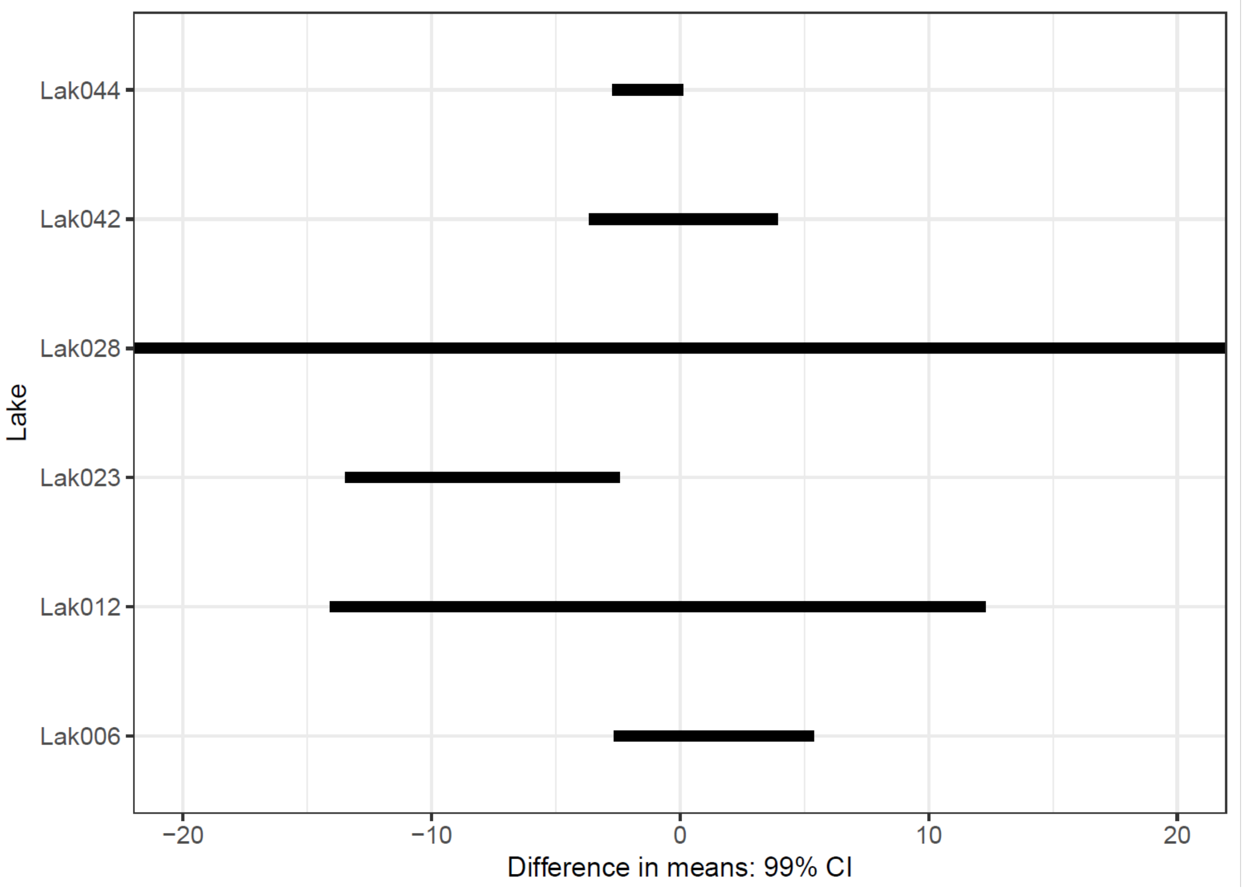


Figure 7.110: Using Method 2, 99% confidence intervals for the ΔSO_4 (mean SO_4 in post-KMP period (2016-2018) minus the mean SO_4 in the extended pre-KMP period (2012-2014), accounting for within year variability. The 99% confidence intervals for changes in mean SO_4 overlap 0.0 for all six lakes except LAK023 (strong evidence of a decrease in SO_4). The 99% confidence intervals for LAK044 do overlap zero, unlike in Figure 7.109.

KEY FINDINGS:

- The confidence intervals using Method 2 (Figure 7.109) are narrower than using Method 1 (Figure 7.108), showing the benefit of Method 2 over Method 1.
- Using 2012 as the baseline period, the only support for difference in mean SO_4 between baseline and Post-KMP period is for LAK044, and that support is for a decline over time. All other 99% confidence intervals overlap zero (the data are consistent with increases, decreases as well as no change in SO_4).
- Using 2012-2014 as the baseline period, the only support for difference in mean SO_4 between baseline and Post-KMP period is for LAK023, and that support is for a decline over time. All other 99% confidence intervals overlap zero.

7.6.4.2.3 Method 3 (Frequentist): Before-After Control-Impact (BACI), Using Mean Values

Description of Analyses:

The BACI (Before-After-Control-Impact) approach compares data from one sensitive lake to the data from a group of 3 control lakes. The focal questions for this analysis are slightly different: *how much change has occurred in chemical indicator Y between the pre-KMP period and the post-KMP period, relative to the changes observed in the control lakes? Is the direction and magnitude of change in the sensitive lake different from what was observed in the control lakes?*
This method explicitly accounts for natural variation in lake chemistry due to factors other than the smelter (e.g., year to year changes in precipitation and temperature) which affect both the EEM lakes and the control lakes. The effect of the smelter on a given lake is expressed in terms of how the chemical changes over time (between the pre-KMP and post-KMP periods) differ from the changes observed in the control lakes (taken as a group), taking into account before-after changes that have affected all lakes.

- *Form of test:* $Y_t \sim$ BA + ICE + BACI Interaction + LRE + YRE, where
    - ICE = Impact/Control Effect;
    - BACI Interaction = Treatment * Time Interaction (difference in how impact and control lakes changed over time; key variable in the analysis);
    - LRE = Lake Random Effect due to consistent differences between lakes (e.g., the sensitive lake always has a lower pH than two of the control lakes);
    - BA and YRE as in analysis 2
- *Assumptions:*
    - Same as analysis 2, plus:
    - Observed value from 2013 serves as a pre-KMP value for the control lakes (control lakes were not sampled in 2012); implicitly assume that 2012 and 2013 were similar
    - Variability in the control lakes over 2013, 2015-2018 used to help estimate variability in the sensitive lake in 2012

Purpose of analyses:

Use a BACI analysis to determine how the ΔSO_4 (post-KMP vs. pre-KMP) in each sensitive lake (Figure 7.38) compares to the Δ SO_4 in the control lakes (Figure 7.36), taken as a group. This analysis accounts for broad scale regional / climatic effects which could affect both the sensitive lakes and the control lakes.

Explanation of the graphs and tables of results:

See captions below.

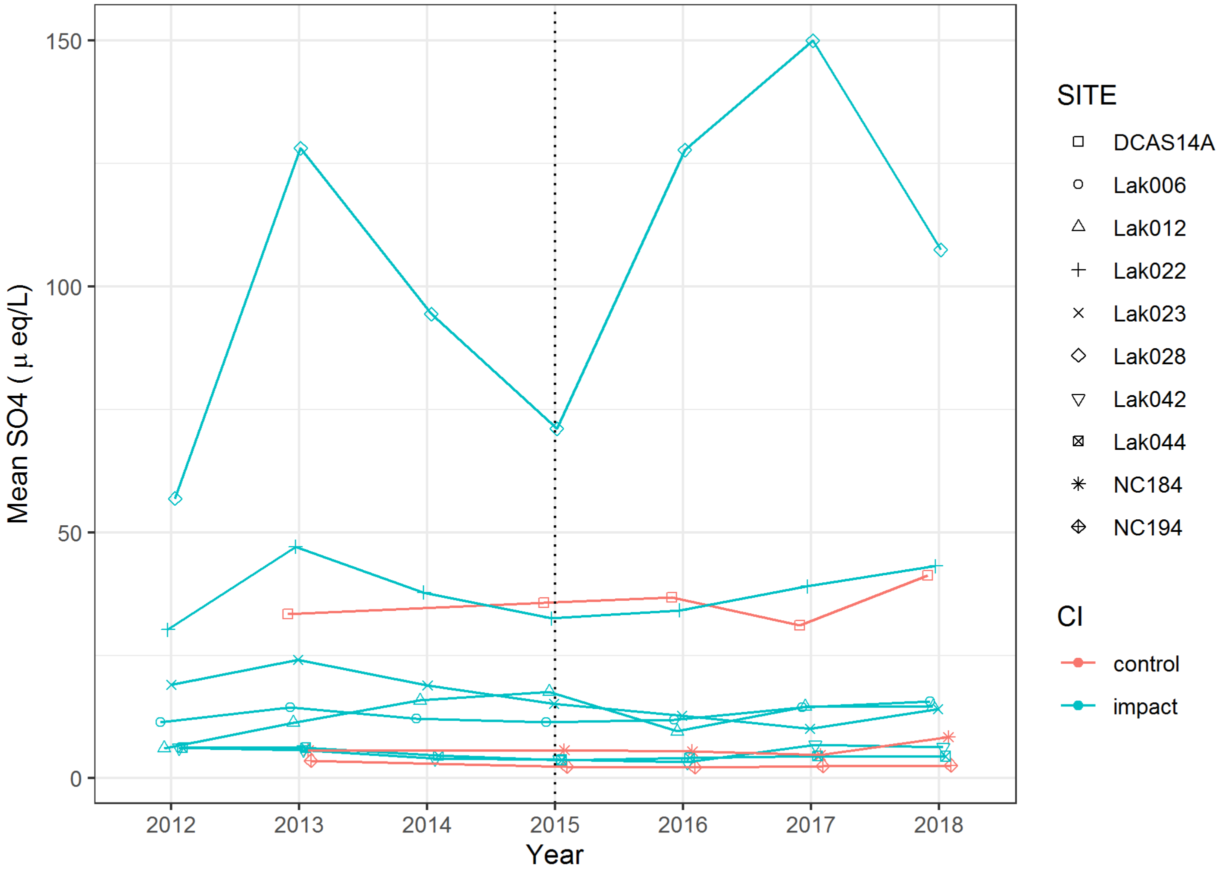


Figure 7.111: Change in mean SO_4 over time for sensitive lakes (blue lines) and control lakes (orange lines)

Table 7.28: BACI analyses of mean SO_4 for 7 sensitive and 3 control lakes, using Method 3. "BACI estimate" is a bit counter-intuitive: it is the Δ mean SO_4 in the controls (i.e., $SO_{4\ post\text{-}KMP}$ minus $SO_{4\ pre\text{-}KMP}$), averaged over the 3 control lakes, minus the Δ mean SO_4 in the sensitive lake. If BACI value is <0, then the Δ SO_4 was lower in the controls than in the sensitive lake (and, equivalently, the Δ SO_4 was greater (more positive) in the sensitive lake than in the controls). If BACI value is >0, then the SO_4 change in the controls was greater than that in the sensitive lake (and, equivalently, the Δ SO_4 was lower (less positive) in the sensitive lake than in the controls). The "t.ratio" is the t-statistic for the BACI estimate, and the p.value the significance of the test. LAK042 showed the strongest evidence of an increase in Δ mean SO_4but the estimate for this factor was not statistically significant.

Site	BACI estimate	SE	p.value	Interpretation of BACI estimate
LAK006	-1.7	2.2	0.437	change in SO_4 was more positive in LAK006 than in the control lakes (but NOT statistically significant)
LAK012	-6.0	2.7	0.038	change in SO_4 was more positive in LAK012 than in the control lakes (but NOT statistically significant)
LAK022	-7.8	3.5	0.059	change in SO_4 was more positive in LAK022 than in the control lakes (but NOT statistically significant)
LAK023	7.5	1.8	0.001	change in SO_4 was less positive in LAK023 than in the control lakes (and **statistically significant**)
LAK028	-70.7	13.2	0	change in SO_4 was more positive in LAK028 than in the control lakes (and **statistically significant**)
LAK042	1.6	1.6	0.532	change in SO_4 was less positive in LAK042 than in the control lakes (but NOT statistically significant)
LAK044	2.7	2.2	0.24	change in SO_4 was less positive in LAK044 than in the control lakes (but NOT statistically significant)

Table 7.29: BACI analysis of SO_4 with all lakes combined, using Method 3. BACI estimate is the average Δ mean SO_4 in the 3 control lakes (i.e., $SO_{4\ \text{post-KMP}}$ minus $SO_{4\ \text{pre-KMP}}$, averaged over the 3 control lakes), minus the average Δ mean SO_4 in the 7 sensitive lakes (i.e., $SO_{4\ \text{post-KMP}}$ minus $SO_{4\ \text{pre-KMP}}$, averaged over the 7 sensitive lakes). SE is the standard error of the BACI estimate. The t.ratio is the t-statistic for the BACI estimate, and the p.value the significance of the test.

contrast	estimate	SE	p.value
baci	-4.6	6.9	0.505

KEY FINDINGS:

- Support for an effect for LAK023 (decrease in SO_4 relative to controls) and LAK028 (increase in mean SO_4 relative to controls).
- No support for an effect when all lakes are combined.

7.6.4.2.4 *Method 4 (Frequentist): Before-After Control-Impact (BACI), Using Individual Samples*

Description of Analyses:

BACI approach with individual measurements rather than just using mean values. Same model as analysis #3 + lake*year interaction random effect. The differences between analyses 4 and 3 are analogous to the differences between analyses 2 and 1. The form of output is the same as in method #3, but now takes into account the variability observed during the sampling period.

Form of test: $SO_4 \sim BA*CI + (1|year2) + (1|SITE) + (1|year2:SITE)$

Purpose of analyses:

We wish to see if there is any change in the results of the BACI analysis (relative to Method 3) when we account for variability during the sampling period. This analysis is only possible for the 6 sensitive lakes with four samples / year; LAK022 has only one sample per year.

Explanation of the graphs and tables of results:

See captions below.

Table 7.30: BACI analysis of ΔSO_4 using Method 4. See Table 4-4 in main report for explanation of terms.

Site	BACI estimate	SE	p.value	Interpretation of BACI estimate
LAK006	-1.7	3.0	0.585	change in SO_4 was more positive in LAK006 than in the control lakes (but NOT statistically significant)
LAK012	-6.0	4.1	0.174	change in SO_4 was more positive in LAK012 than in the control lakes (but NOT statistically significant)
LAK023	7.5	2.7	0.016	change in SO_4 was less positive in LAK023 than in the control lakes (but NOT statistically significant)
LAK028	-70.7	22.7	0.011	change in SO_4 was more positive in LAK028 than in the control lakes (but NOT statistically significant)
LAK042	1.6	3.3	0.646	change in SO_4 was less positive in LAK042 than in the control lakes (but NOT statistically significant)
LAK044	2.7	3.1	0.41	change in SO_4 was less positive in LAK044 than in the control lakes (but NOT statistically significant)

Table 7.31. BACI analysis of ΔSO_4 with all lakes combined, using Method 4.

contrast	estimate	SE	p.value
baci	-3.2	8.7	0.714

KEY FINDINGS:

- Support for an effect diminishes when accounting for individual intra-annual SO_4 measurements; none are statistically significant.
- No support when all lakes are combined.

7.6.4.2.5 Method 5 (Frequentist): Before-After Control-Impact (BACI), with Assumption of No Change in Control Lakes

Description of Analyses:

Method 4 + assumption of no change in the mean of the control lakes between the before period and the after period. If we assume that there's no B/A change in control lakes (forcing ΔY in control lakes to be zero), the B/A change in the sensitive lake becomes the absolute change in component Y. This analysis removes some of the terms in the model 4. The form of output is the same as in method #4.

Purpose of analyses:

This is a sensitivity analysis on Method 4, to see how much difference the observations from the control lakes (and common patterns of year to year variability in the control lakes) make to the outcome of the BACI analysis. Removing the data from the control lakes reduces the number of degrees of freedom in the analysis. The analysis is done first using just mean values (as in Method 1), and then using all of the data (as in Method 2). We also use ANOVA to compare the fit of models which keep the control lakes' data constant, vs. allowing the control lakes' data to vary.

Explanation of the graphs and tables of results:

- See captions below

All lakes combined, mean SO_4, control lakes held constant

Table 7.32: BACI analysis using Method 5 applied to mean SO_4 values, holding control lakes' SO_4 constant. Structure of this table is similar to Method 3 (Table 7.29), but has only 7.44 degrees of freedom compared to 127.01

contrast	estimate	SE	p.value
baci	1.1	3.8	0.784

ANOVA (mean SO_4: control lakes either constant or allowed to vary)

Table 7.33: ANOVA analysis using Method 5 comparing the fit of two models to mean SO_4 values ("vary", which includes data from the control lakes; and "cons", which holds the control lakes constant). Analysis applied using two information criteria (AIC = Aikike Information Criteron; BIC = Bayesian Information Criteron). Lower (i.e., more negative) values for AIC and BIC indicate a better fit of the model to the data. Assuming constant values for the control lakes ("cons") provides a slightly better fit, but the differences between the two models are not statistically significant.

	Df	AIC	BIC	logLik	deviance	Chisq	ChiDF	Pr(>Chisq)
cons	6	1125.9	1143.6	-556.93	1113.9			
vary	7	1127.6	1148.3	-556.8	1113.6	0.257	1	0.612

All lakes combined: individual annual SO_4, control lakes held constant

Table 7.34: BACI analysis using Method 5 applied to all SO_4 values in the sensitive lakes (i.e., including within-year variability), holding control lakes' SO_4 constant. Structure of this table is similar to Method 4 (Table 7.31), but has only 6.5 degrees of freedom compared to 74.2

contrast	estimate	SE	p.value
baci	0.69	4.1	0.872

ANOVA (individual annual SO_4: control lakes held constant or allowed to vary)

Table 7.35: ANOVA analysis using Method 5 comparing the fit of two models to all SO_4 values ("vary", which includes data from the control lakes; and "cons", which holds the control lakes constant). Analysis applied using two information criteria (AIC = Aikike Information Criteron; BIC = Bayesian Information Criteron). Lower (i.e., more negative) values for AIC and BIC indicate a better fit of the model to the data. Assuming constant values for the control lakes ("cons") provides a slightly better fit, but the differences between the two models are not statistically significant.

	Df	AIC	BIC	logLik	deviance	Chisq	ChiDF	Pr(>Chisq)
cons	7	1134.2	1155	-560.11	1120.2			
vary	8	1136.2	1159.9	-560.09	1120.2	0.044	1	0.833

KEY FINDINGS:

- No support for an effect (for annual mean SO_4 or annual individual SO_4 measurements) when change in control lakes held constant over the time-frame.
- ANOVAs show no difference between models with control lakes varying or held constant over time.

7.6.4.2.6 Method 6 (Frequentist): Using Other Covariates to Explain Inter-Annual Variation

Description / Purpose of Analyses:

These analyses add other covariates (i.e., emissions, precipitation) to explain year to year variation. If these covariates help to explain variability in chemistry, then we could use 2013-2014 data, in addition to data from 2012, to characterize pre-KMP conditions, and contrast these conditions with post-KMP data from 2016-2018. The test ascribes some of the observed changes in chemical components to these covariates (e.g., changes in [SO_4] with emissions of SO_2 in the year prior to October sampling; changes in component concentrations with precipitation in either the 3 days or the 14 days prior to sampling). The overall form of the results is similar to method 4 (i.e., a BACI analysis), but potentially separates out variation due to changes in emissions, or due to fluctuations in precipitation (if these covariates are shown to be correlated with the measured chemistry).

Explanation of the graphs and tables of results:

We used total SO_2 emissions over the prior year (i.e., October 1 through Sept. 30, see Section 7.6.2.3) either the last 3-days or the last 14-days of precipitation at Haul Road (see Section 7.6.2.2) as covariates. The model also includes terms for three random effects: year, site, and year by site interactions.

Form of test: SO_4 ~ *BA*CI + EMISSIONS + PRECIPITATION + (1|YEAR) + (1|SITE) + (1:YEAR:SITE)*

Table 7.36: Before-After t-test for changes in SO_4, including covariates for emissions and the last 3 days of precipitation.

Fixed effects:	Estimate	Std Error	Pr(>|t|)
(Intercept)	-81.64	210.5	0.701
BAbefore	44.72	42.9	0.348
CIimpact	246.74	209.1	0.248
Emissions	0.29	0.2	0.270
Precipitation (3 day)	-1.05	0.9	0.245
BAbefore:CIimpact	-19.78	30.1	0.516

Table 7.37: Estimates of the random effects for year, site and year by site interactions, for the analyses in Table 7.36.

Random effects:			
Groups	Name	Variance	Std.Dev.
YEAR:SITE	(Intercept)	1174	34.2
SITE	(Intercept)	116869	341
YEAR	(Intercept)	16.0	4.0
Residual		426	20.6

Table 7.38: Before-After t-test for changes in SO_4, including covariates for emissions and the last 14 days of precipitation.

Fixed effects:	Estimate	Std Error	df	Pr(>|t|)
(Intercept)	-72.41	213.02	32	0.736
BAbefore	37.41	46.49	5	0.458
CIimpact	244.23	208.75	28.	0.252
Emissions	0.26	0.24	3	0.337
Precipitation (14 day)	-0.16	0.38	29	0.679
BAbefore:CIimpact	-16.55	31.34	38	0.601

Table 7.39: Estimates of the random effects for year, site and year by site interactions, for the analyses in Table 7.38.

Random effects:

Groups	Name	Variance	Std.Dev.
YEAR:SITE	(Intercept)	1297	36
SITE	(Intercept)	116426	341
YEAR	(Intercept)	39	6.3
Residual		398	20.0

KEY FINDINGS:

- Looking over all sensitive and less sensitive lakes, there is no evidence of a significant before-after change in mean SO_4 after accounting for year effects, site effects, emissions and the last 3 days of precipitation, or the last 14 days of precipitation.
- The signs of the covariates for precipitation were negative, consistent with a hypothesis of dilution of sulphate concentrations following precipitation events, but neither the 3-day or 14-day covariates were statistically significant.
- The sign of the emissions covariate was positive, consistent with expectations, but also not statistically significant when examined across all lakes. This isn't surprising given the range in responses of sulphate concentrations among the set of lakes in the EEM program.

7.6.4.2.7 Approach Supportive of Methods 8 and 9 (Frequentist): Temporal Trend Analyses

Description of Analyses:

We applied the Mann-Kendall (MK) non-parametric test for detecting monotonic trends. The MK test evaluates if values increase, decrease or stay the same over time. It analyses the sign of the difference between later-measured and earlier-measured data. The test assumes that values can be greater than, equal to, or less than another data. We tested for a change in SO_4 over time, and used alpha = 0.01 to correct for multiple tests

Purpose of analyses:

We are interested in testing the hypothesis that there is no monotonic trend in SO_4 over time (a significant increase or decrease in SO_4 would cause this hypothesis to be rejected). The Mann-Kendall non-parametric test for monotonic trend detection is similar to the non-parametric Seasonal Kendall tests used to assess water chemistry trends in other studies of acidification effects (e.g., Stoddard et al. 1993, 1996, 1998, 2003).

Explanation of the graphs and tables of results:

The Mann-Kendall non-parametric test calculates the sign of the differences between all possible pairs of differences between observations, and estimates S, the number of positive differences minus the number of negative differences. If S is a positive number, observations obtained later in time tend to be larger than observations made earlier. If S is a negative number, then observations made later in time tend to be smaller than observations made earlier. Transformations of S (described here) generate a statistic Z, which can be evaluated for its statistical significance. A positive value of Z indicates that the data tend to increase, while a negative value of Z indicates that the data tend to decrease. The value of the slope can be calculated using the Sen's slope approach, which is a nonparametric method to calculate the slope and is appropriate for time series data used in this trend analysis. However, if the Mann-Kendall test is not significant, there is no reason to proceed with the Sen's slope analysis.

Table 7.40: Results of the Mann-Kendall non-parametric test for monotonic trend in SO_4 values. No lakes exhibit a significant result for detecting a monotonic trend.

Lake	p.value
LAK006	0.955
LAK012	0.500
LAK022	0.955
LAK023	0.367
LAK028	0.633
LAK042	0.633
LAK044	0.846
LAK007	0.955
LAK016	0.846
LAK024	0.846
LAK034	0.500
NC184	0.500
NC194	0.500
DCAS14A	0.769

KEY FINDINGS:

- None of the lakes' data provide sufficient evidence to reject the null hypothesis that there was no monotonic trend in mean SO_4 (i.e., all p values are > 0.01)

7.6.4.2.8 Method 1a (Bayesian): Two-Sample Before-After Bayesian Analysis (Bayesian Estimation Supersedes the T-Test with informative priors) as applied to SO_4

Description of Analyses:

The intent of Bayesian analyses is to estimate the *posterior* distribution of a parameter of interest, which is the probability distribution of the parameter taking into account the data. The first step is for the analyst to specify a *prior* belief, or prior credibility distribution of possible parameter values. After the data have been collected, the prior beliefs are then updated using Bayes' rule to obtain the posterior distribution. We used the BEST approach (Kruschke 2013), applied to frequentist method 1. Results are expressed in terms of the posterior belief that a lake's SO_4 concentration increased between the pre-KMP and post-KMP periods.

Purpose of analyses:

The parameter of interest is the ΔSO_4 from the pre-KMP period (either 2012 or 2012-2014) to the 2016-2018 post-KMP period. This is the first question in the simplified evidentiary framework (Figure 7.35): *Has lake* SO_4 *increased since the pre-KMP period?*

Explanation of the graphs and tables of results:

See captions below. The statistical software used for analysis in Figure 7.112 computes Δ mean SO_4 as the mean SO_4 for the baseline pre-KMP period minus the mean SO_4 for the 2016-2018 post-KMP period. Positive values of this parameter are therefore indicative of a SO_4 decline. Figure 7.113 and Figure 7.114 (respectively) show the posterior distribution of Δ mean SO_4 for LAK028 and LAK034.

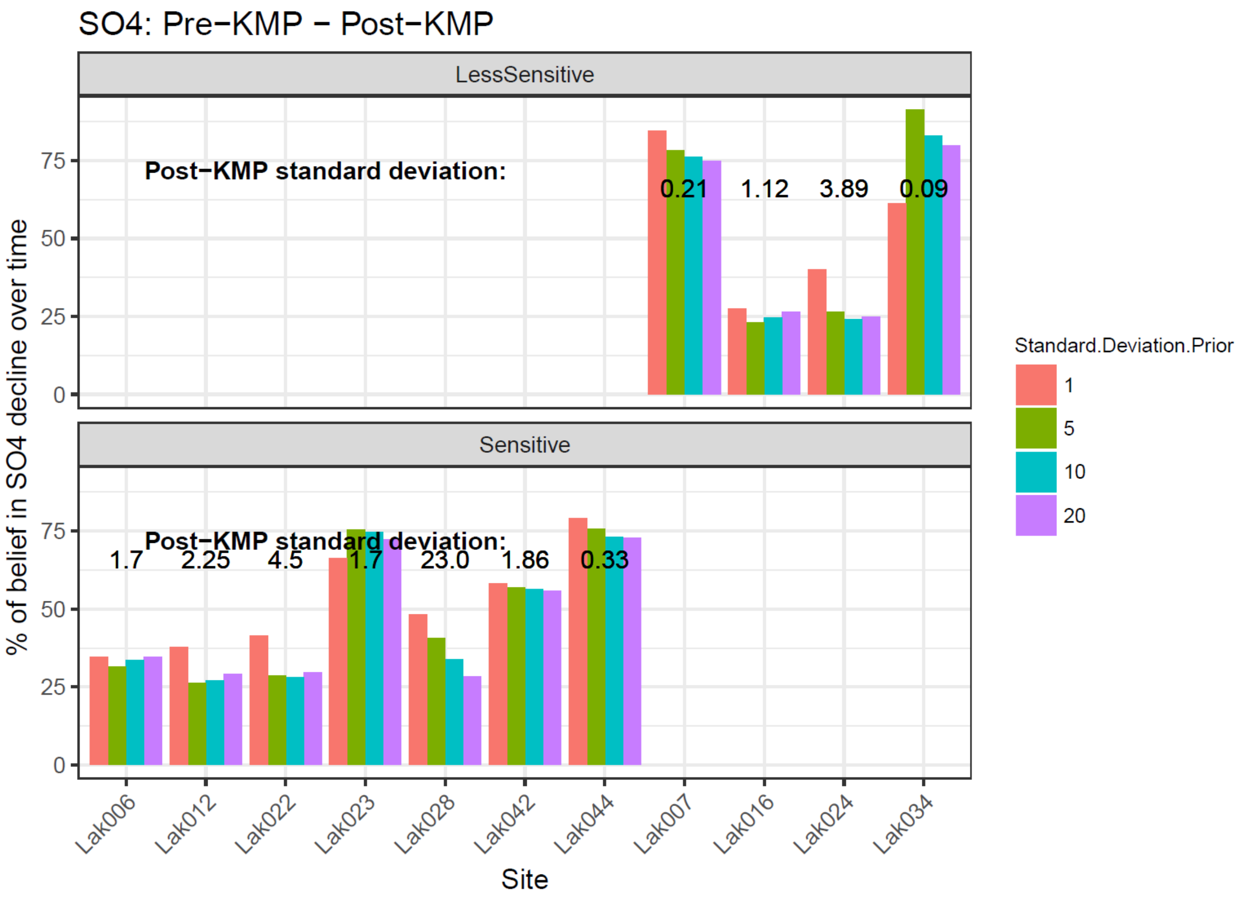


Figure 7.112: Percentage belief in a SO_4 decline over time, using Two-Sample Before-After Bayesian Analysis. The bars show the percentage belief for four different prior assumptions about the standard deviation of SO_4 across all lakes. The SD of SO_4 for the post-KMP period is included to provide some context for each lake, but is not directly comparable to the prior assumptions of SD. Strongest support for a decline in SO_4 is for lakes 007, 034, 023 and 044.

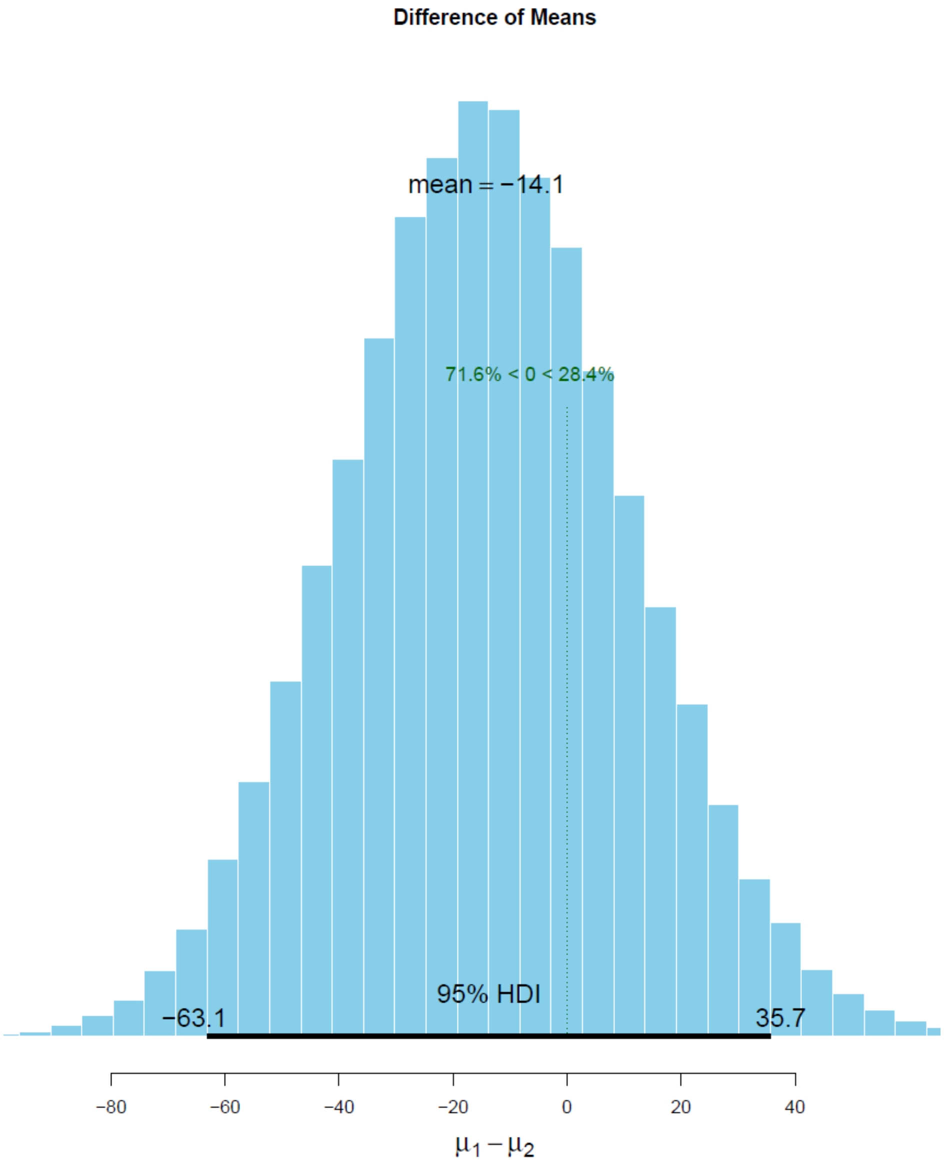


Figure 7.113: 95% High Density Interval for ΔSO_4 in LAK028 (Mean SO_4 during baseline - Mean SO_4 during post-KMP period), assuming a SD of SO_4 of 20. Negative values are consistent with an increase in SO_4 (71.6% belief). Positive values are consistent with an decrease in SO_4 (28.4% belief).

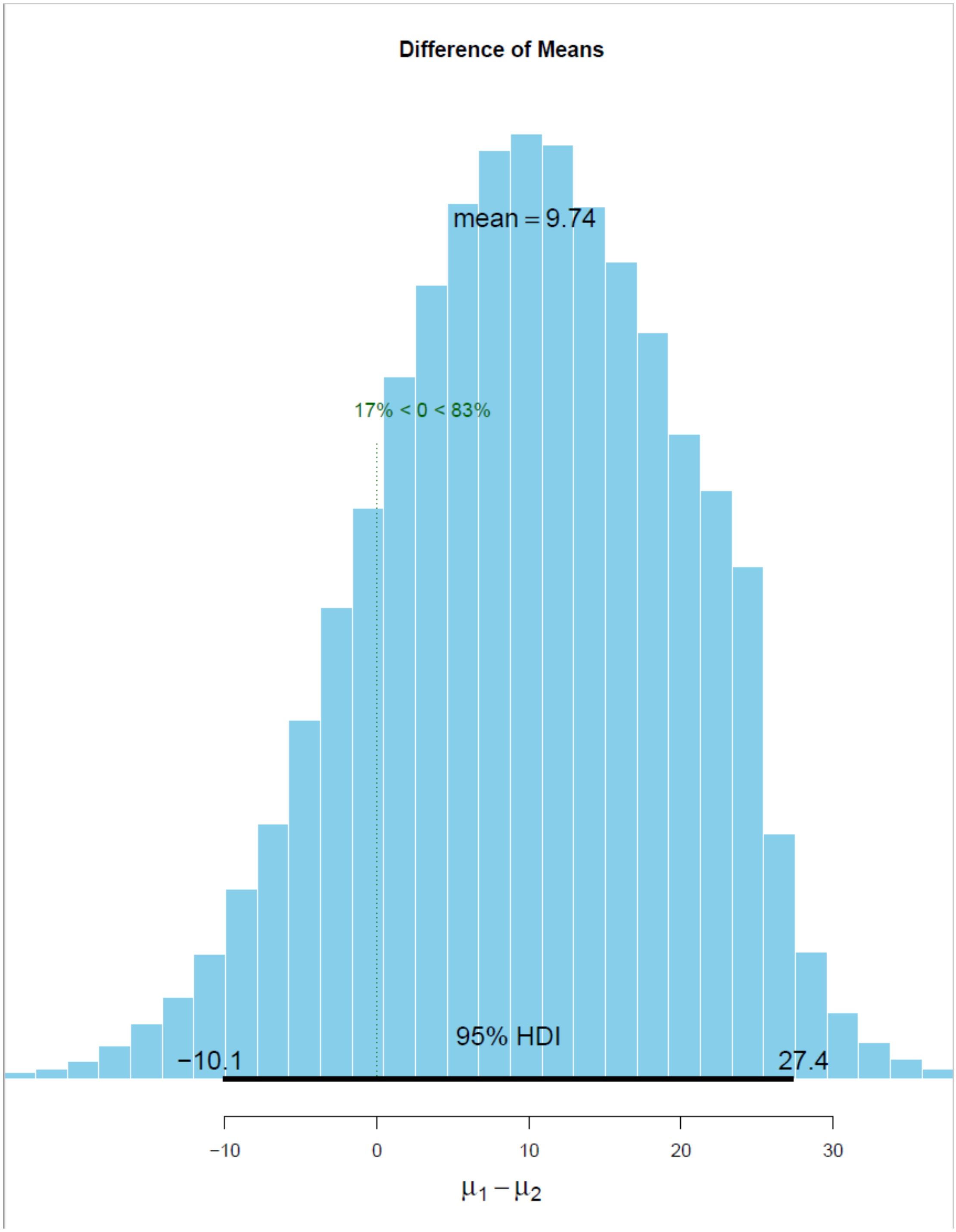


Figure 7.114: 95% High Density Interval for ΔSO_4 in LAK034 (Mean SO_4 during baseline - Mean SO_4 during post-KMP period), assuming a SD of SO_4 of 10. Negative values are consistent with an increase in SO_4 (17% belief). Positive values are consistent with an decrease in SO_4 (83% belief).

7.6.4.2.9 Method 1b (Bayesian): Two-Sample Before-After Bayesian Analysis (with uninformative priors)

Figure 7.115 and Figure 7.116 are violin plots showing the percent of the posterior distribution for ΔSO_4 that is greater than zero (i.e., an increase in SO_4). A violin plot is similar to the distributions of credible values of ΔSO_4 (e.g., Figure 7.113), except that the distribution is shown vertically rather than horizontally. Figure 7.115 uses a pre-KMP period of 2012, and Figure 7.116 uses a pre-KMP period of 2012-2014. The violin plots in Figure 7.115 and Figure 7.116 estimate the posterior distributions of Δ mean SO_4 without any prior assumption about its variability.

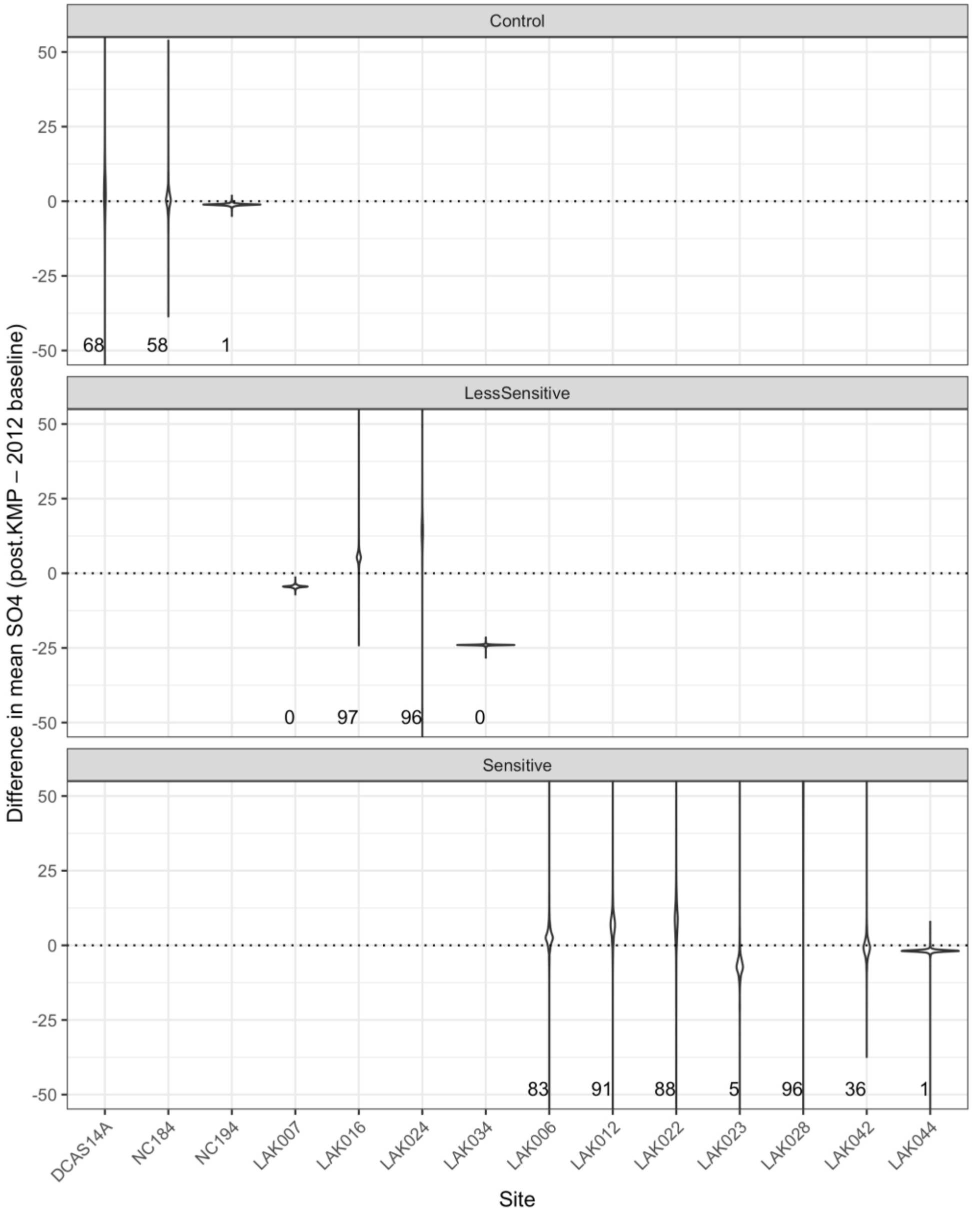


Figure 7.115: Violin plots showing the the posterior distributions of credible values for ΔSO_4, an increase in SO_4, and the percent of these distributions that is greater than 0 (indicating an increase over time between 2012 and 2016-2018).

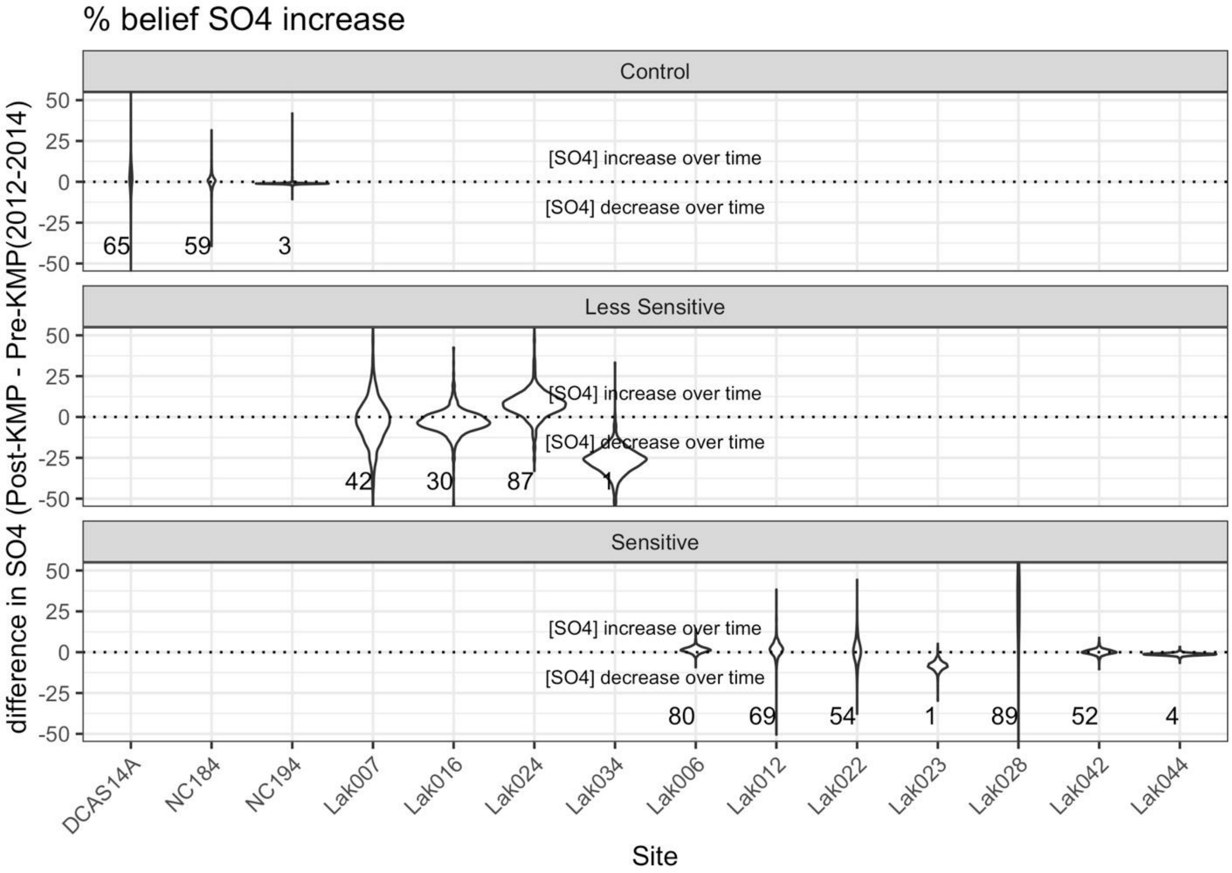


Figure 7.116: Violin plots showing the the posterior distributions of credible values for ΔSO_4, and the percent of these distributions that is greater than 0 (indicating an increase over time between 2012-2014 and 2016-2018).

KEY FINDINGS:

- Lakes with strong support (>80%) for an increase in mean SO_4 between pre-KMP (either 2012 or 2012-2014) and post-KMP (2016-2018) time periods: sensitive lakes LAK006, LAK012, LAK022 and LAK028, and less sensitive lakes LAK016 and LAK024 (Figure 7.115 and Figure 7.116).
- Lakes with very weak support (≤5%) for an increase in mean SO_4: sensitive lakes LAK023 and LAK044, less sensitive lakes LAK007 and LAK034, and control lake NC194 (Figure 7.115). Lakes 007, 023, 034 and 044 have intermediate to strong support for a sulphate decrease (Figure 7.112).

7.6.4.2.10 Method 2 (Bayesian): Two-Sample Before-After Bayesian Analysis, Using Individual Samples

Description of analyses:

This analysis is the Bayesian version of Method 2, taking into account all of the data, and accounting for variability within each year.

Purpose of analyses:

The purpose is similar to Method 1, but Method 2 uses all of the data rather than just the mean values.

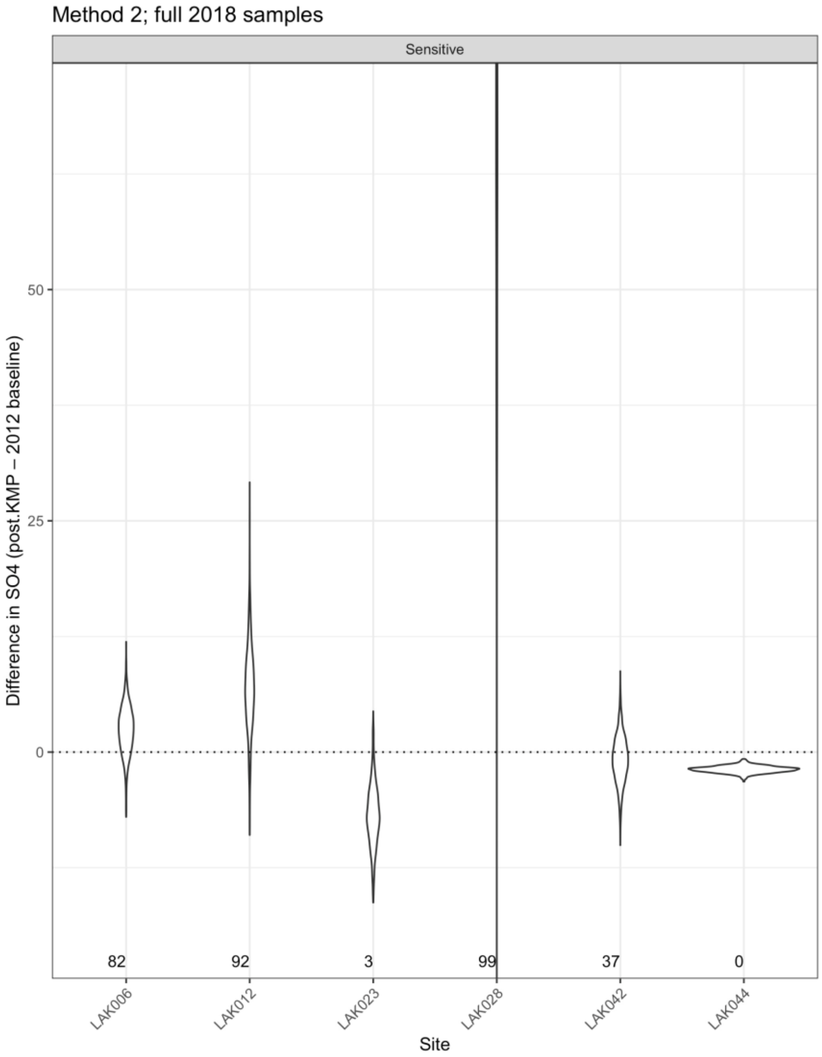


Figure 7.117: Violin plot showing the the posterior distributions of credible values for ΔSO_4 (2016-2018 vs. 2012) for the six sensitive lakes with multiple samples per year, with no prior assumptions about the variability in SO_4. The percent of these distributions that correspond to a change greater than zero is shown in numerals at the bottom of each plot.

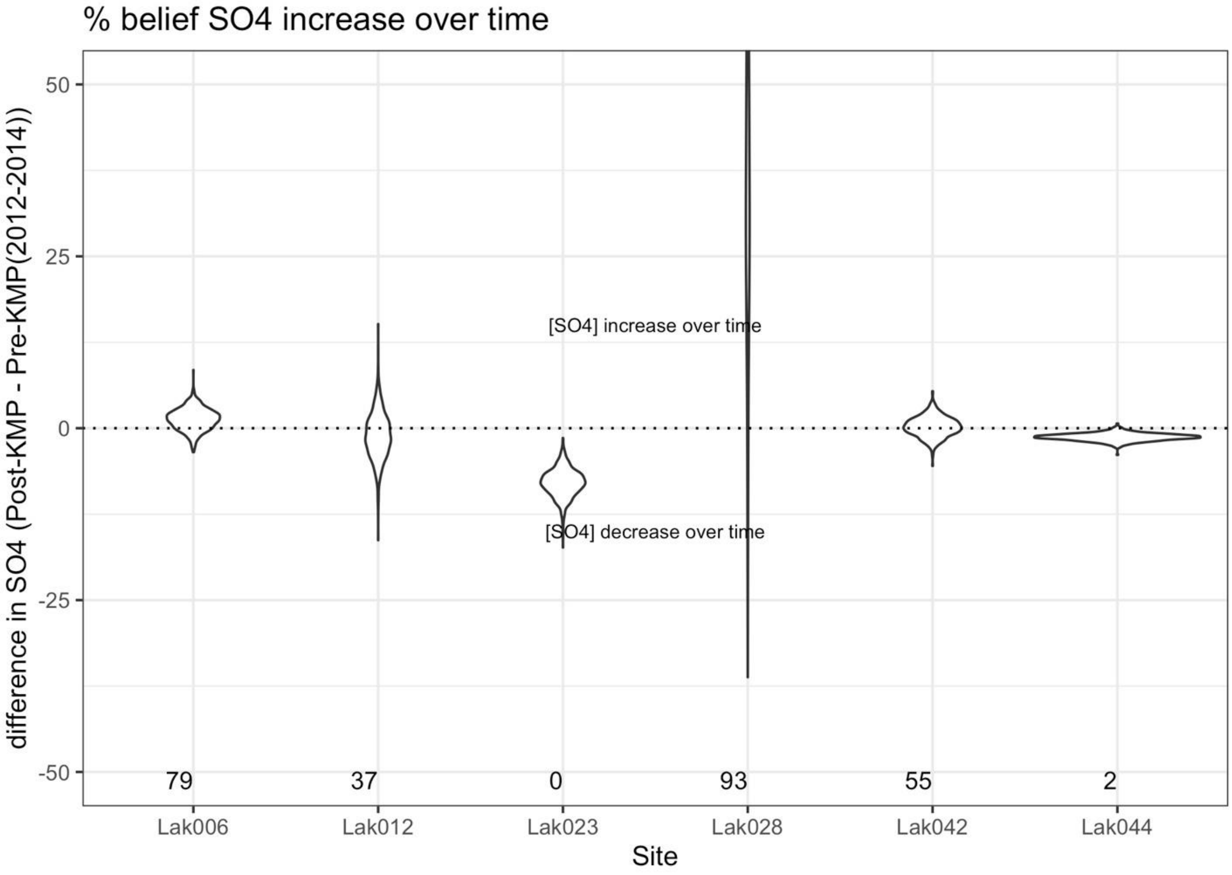


Figure 7.118: Violin plot showing the the posterior distributions of credible values for ΔSO_4 (2016-2018 vs. 2012-2014) for the six sensitive lakes with multiple samples per year, with no prior assumptions about the variability in SO_4. The percent of these distributions that correspond to a change greater than zero is shown in numerals at the bottom of each plot.

KEY FINDINGS:

- Sensitive lakes with strong support (> 80% belief) for an SO_4 increase in mean SO_4 since 2012: LAK006 (82%), LAK012 (92%), and LAK028 (99%)
- Sensitive lakes with intermediate support for an increase in SO_4: LAK042 (37%)
- Sensitive lakes with weak support for an increase in SO_4: LAK023 (3%) and LAK044 (0%)

7.6.4.3 Key Metric: pH

7.6.4.3.1 Method 1 (Frequentist): Two-Sample Before-After T-Test Using Mean Values

Description of Analyses:

See Section 7.6.4.2.1 for SO_4.

Purpose of Analyses:

Similar to Section 7.6.4.2.1 for SO_4. There are four purposes to these analyses:

1. Assess if there has been a statistically significant change in pH (i.e., Δ pH is significantly different from 0) between two time periods: pre-KMP (2012) and post-KMP (2016-2018). This t-test simply assesses if there has been *any* statistically significant change in pH. Δ pH is computed as the post-KMP mean minus the pre-KMP mean.

2. Assess whether the confidence intervals for Δ pH span 0.0 (level of confidence that there has been an increase or decrease in pH)

3. Assess whether the confidence intervals for Δ pH span the EEM threshold of -0.3 pH units (as described above).

4. Assess what the Minimum Detectable Difference (MDD) in pH is for each lake, under four different assumptions of the true standard deviation of pH during the pre-KMP period.

Explanation of the Graphs and Tables of Results:

Please see the captions below for each graph and table.

Table 7.41: T-test of changes in mean pH for each lake, between the pre-KMP period (2012) and post-KMP period (2016-2018). T.stat is the T-statistic. P-value is the probability of the ΔpH being significantly different from zero ($p<0.01$ is the appropriate signficance level given the multiple statistical tests). Lwr and Upp are the lower and upper confidence levels for ΔpH. Sd_post is the standard deviation of mean pH levels over the 3-year post-KMP period. MDD_sd is the minimum detectable difference in pH that would be statistically significant at $p<0.01$ with 0.8 statistical power, given four different assumptions about the standard deviation of pH during the pre-KMP period (0.05, 0.1, 0.2, 0.3). For example, in LAK007, a pH change of 0.37 is the minimum detectable difference with a pre-KMP SD of 0.05, but the MDD increases to 1.468 if the pre-KMP SD were 0.3.

SUBSET	LAKE	p-value	lwr	upp	sd_post	MDD_sd_0.05	MDD_sd_0.1	MDD_sd_0.2	MDD_sd_0.3
LessSensitive	LAK007	0.714	-0.64	0.70	0.06	0.37	0.56	1.00	1.47
LessSensitive	LAK016	0.057	-0.50	1.19	0.07	0.43	0.60	1.02	1.48
LessSensitive	LAK024	0.086	-0.76	1.47	0.10	0.53	0.67	1.07	1.51
LessSensitive	LAK034	0.017	-0.67	0.09	0.03	0.29	0.51	0.97	1.45
Sensitive	LAK006	0.132	-0.74	1.22	0.09	0.48	0.63	1.05	1.50
Sensitive	LAK012	0.026	-0.32	1.36	0.07	0.43	0.60	1.02	1.48
Sensitive	LAK022	0.058	-0.22	0.51	0.03	0.28	0.50	0.97	1.45
Sensitive	LAK023	0.068	-0.37	0.80	0.05	0.34	0.54	0.99	1.46
Sensitive	LAK028	0.943	-2.85	2.91	0.25	1.23	1.30	1.54	1.88
Sensitive	LAK042	0.097	-1.27	2.36	0.16	0.80	0.90	1.23	1.63
Sensitive	LAK044	0.084	-0.31	0.62	0.04	0.31	0.52	0.98	1.45

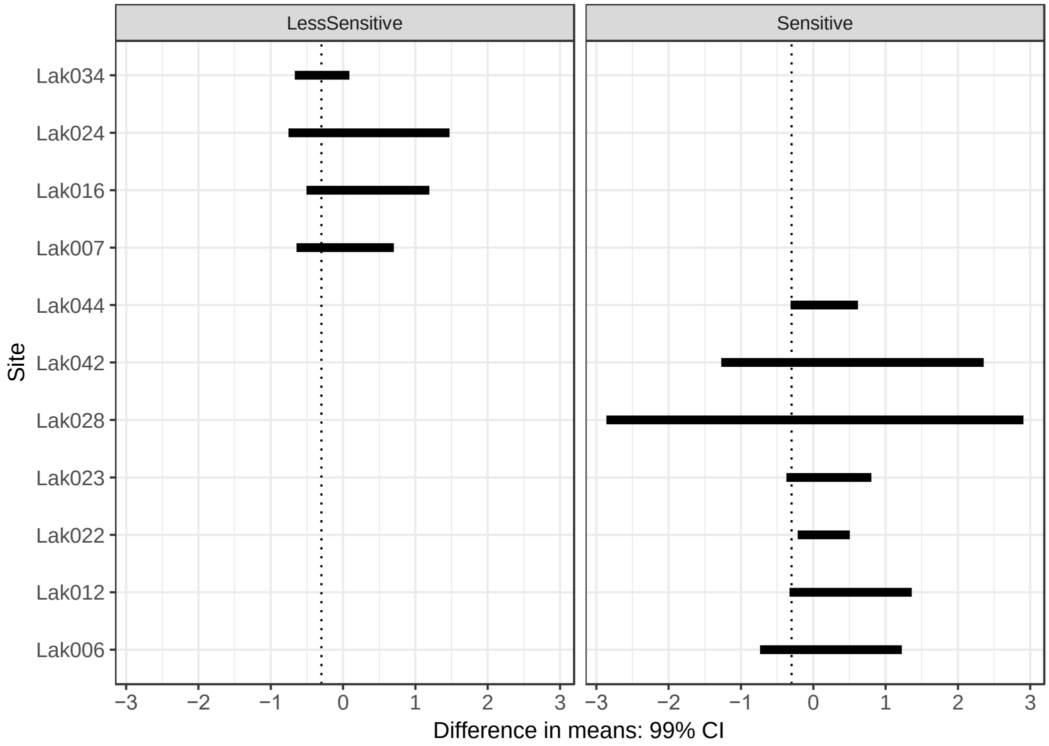


Figure 7.119: Using Method 1, 99% confidence intervals for the ΔpH (mean pH in post-KMP period minus the mean pH in the pre-KMP period). The confidence intervals for changes in mean pH overlap 0.0 and -0.3 for all lakes except for LAK022. The vertical dotted line is at -0.3 pH units.

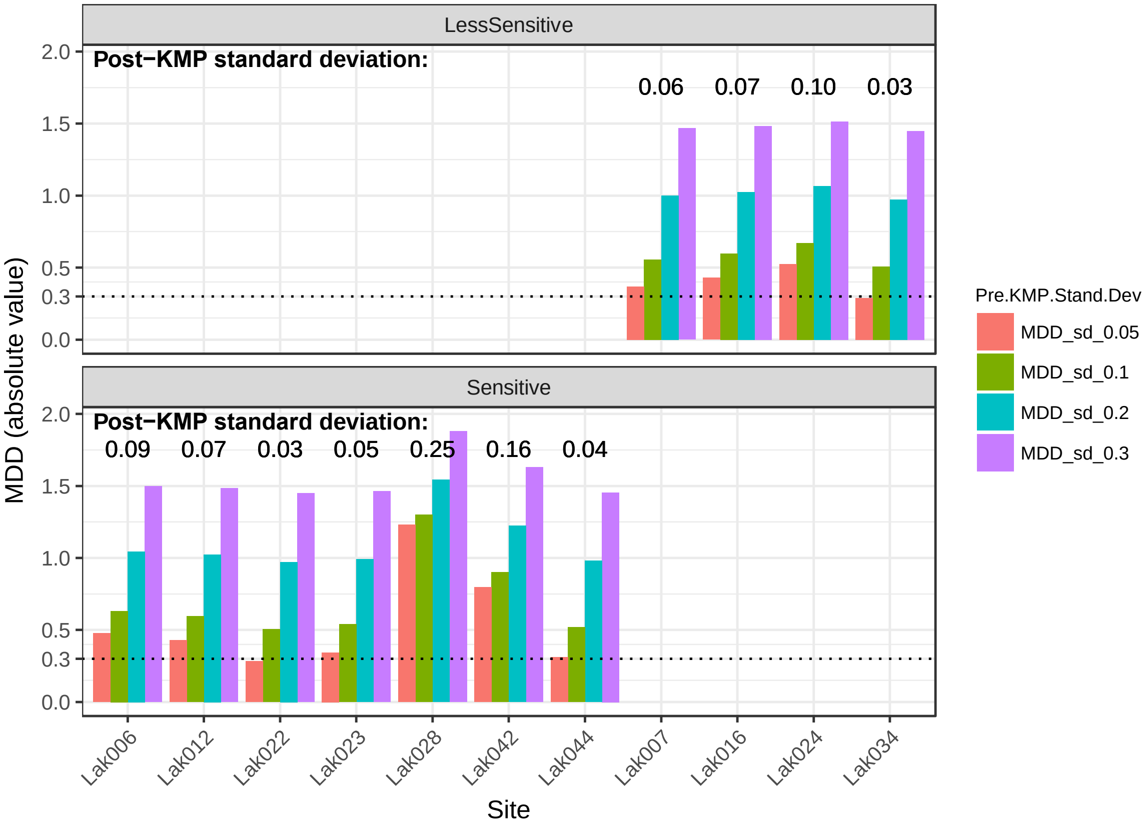


Figure 7.120: Minimum detectable differences (MDD) are shown for each lake, assuming four different values for the standard deviation (SD) of pH in the pre-KMP period (2012). Since we have only observation for the pre-KMP period (a single measurement in 2012), we can't compute the SD, but must assume it. The SD for the post-KMP period is written above the bars to provide some context for the pre-KMP assumptions, though variability could vary between the two periods. LAK028 has the highest SD in the post-KMP period, and also has the highest values for MDD. The dotted, horizontal line marks 0.3 pH units. Only LAK022 and LAK034 show an MDD < 0.3 (i.e., can detect a pH change of 0.3), and only for the lowest assumed value for SD (0.05).

KEY FINDINGS:

- As expected, it was very difficult to show a statistically significant change with such a small sample
- All 99% Confidence Intervals overlap -0.3 and zero (except LAK022)
- No t-statistics for any site have a p-value below 0.01
- Minimum Detectable Differences are generally greater than 0.3 at all assumed baseline KMP standard deviations (except for LAK022, LAK023, LAK034 and LAK044 at SD = 0.05)
- Cannot detect a difference in mean pH between baseline and Post-KMP groups

7.6.4.3.2 Method 2 (Frequentist): Two-Sample Before-After T-Test Using Individual Samples

Description of Analyses:

Same as for SO_4 in Section 7.6.4.2.2, but applied to pH.

Purpose of analyses:

The purpose of this analysis is similar to Method 1 (i.e., to determine if there is a significant difference between the post-KMP and pre-KMP values of pH), but the analysis removes the effect of natural variability during the sampling period. We are interested to see if this reduces the uncertainty in estimates of the ΔpH between the post-KMP and pre-KMP periods, and narrows the confidence intervals on these estimates.

Explanation of the graphs and tables of results:

See captions below.

Table 7.42: Results for T-test for post-KMP pH (2016-18) versus baseline pH (2012), using individual samples, for the six sensitive lakes with multiple within-year samples.. The "est.diff" is the pH in the post-KMP period minus the pH in the baseline period. A positive value for "est.diff" means that the pH increased from the baseline period to the post-KMP period, while a negative value indicates a decrease in pH. The "est.diff.se" is the standard error in pH, which is highest for LAK028, and lowest for LAK044. The "est.diff.lcl" and "est.diff.ucl" are the lower and upper confidence intervals (respectively) for "est.diff". The "p.value" is the probability of a significant difference in mean pH (<0.01 for LAK012, >0.01 for all other lakes).

SITE	est.diff	est.diff.se	est.diff.lcl	est.diff.ucl	p.value
LAK006	0.24	0.13	-0.08	0.57	0.11
LAK012	0.52	0.13	0.22	0.81	0.004
LAK023	0.22	0.08	0.02	0.42	0.04
LAK028	0.02	0.32	-1.00	1.05	0.95
LAK042	0.54	0.20	-0.13	1.21	0.08
LAK044	0.15	0.08	-0.03	0.33	0.09

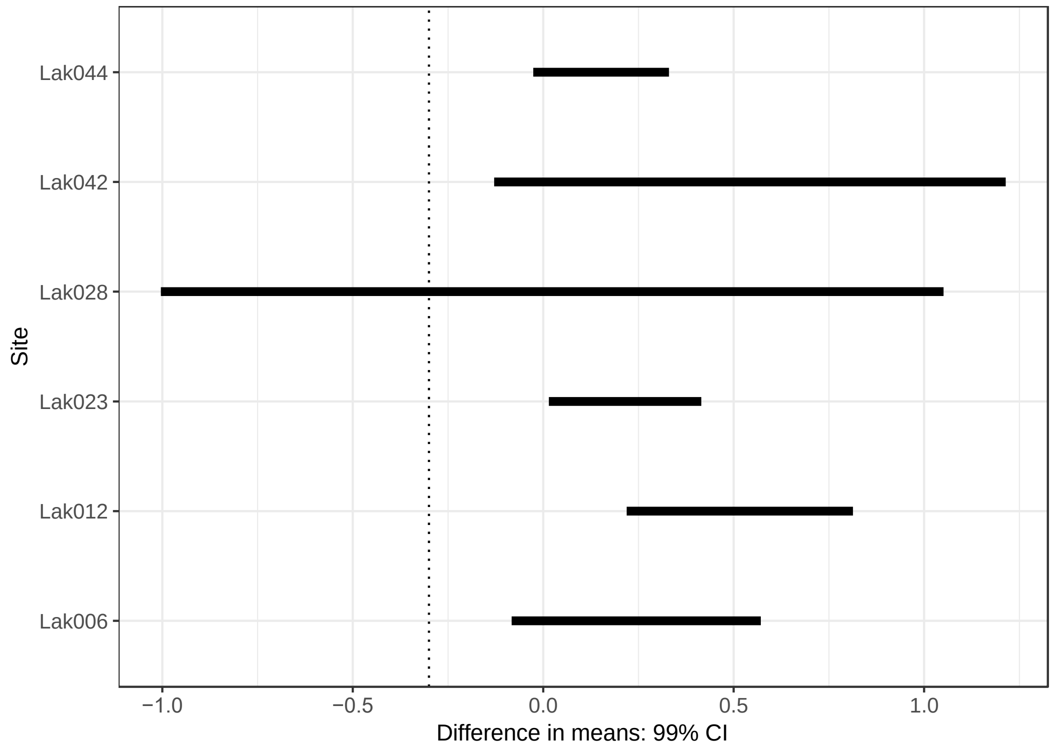


Figure 7.121: Using Method 2, 99% confidence intervals for the ΔpH (mean pH in post-KMP period minus the mean pH in the pre-KMP period, accounting for within year variability). The vertical dotted line is at -0.3 pH units. The confidence intervals for changes in mean pH do not overlap -0.3 in five of the six lakes, but do overlap -0.3 in LAK028. The confidence intervals are greater than zero for LAK012 and LAK023.

KEY FINDINGS:

- Including individual measurements during the fall index period (Method 2; Figure 7.121) narrows the confidence intervals on the before-after effect relative to Method 1 (Figure 7.119). This emphasizes the value of taking multiple samples (4) during the fall index period.
- For LAK006, LAK012, LAK023, LAK042, LAK044, the 99% Confidence Intervals using Method 2 are entirely greater than -0.3, providing strong evidence that the ΔpH did not exceed the threshold of -0.3 in these five lakes.
- In LAK028, which has the highest variability in pH, the 99% Confidence Interval overlaps -0.3 and zero (i.e., we cannot reject the hypothesis that the ΔpH exceeded the threshold of -0.3).
- LAK012 and LAK023 have CIs that are greater than zero, providing support for an increase in mean pH between 2012 and the post-KMP period.

7.6.4.3.3 Method 3 (Frequentist): Before-After Control-Impact (BACI), Using Mean Values

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.3, but applied to pH.

Purpose of analyses:

Use a BACI analysis to determine how the post-KMP vs. pre-KMP ΔpH in each sensitive lake compares to the ΔpH in the control lakes, taken as a group. This analysis accounts for broad scale regional/climatic effects which could affect both the sensitive lakes and the control lakes.

Explanation of the graphs and tables of results:

See figure and table captions below. We are using the significance value of 0.01 throughout as correction for multiple tests (it is not precisely the Bonferroni correction, but an analogous approximation).

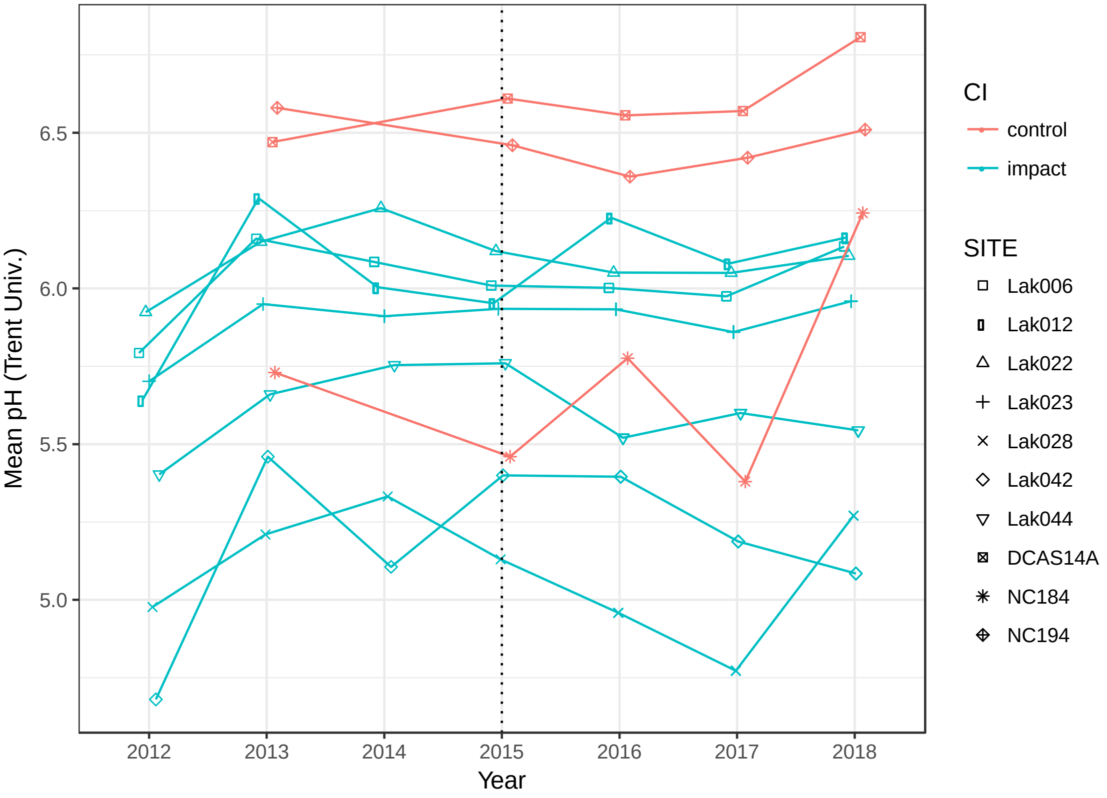


Figure 7.122: Change in mean pH over time for sensitive lakes (blue lines) and control lakes (orange lines).

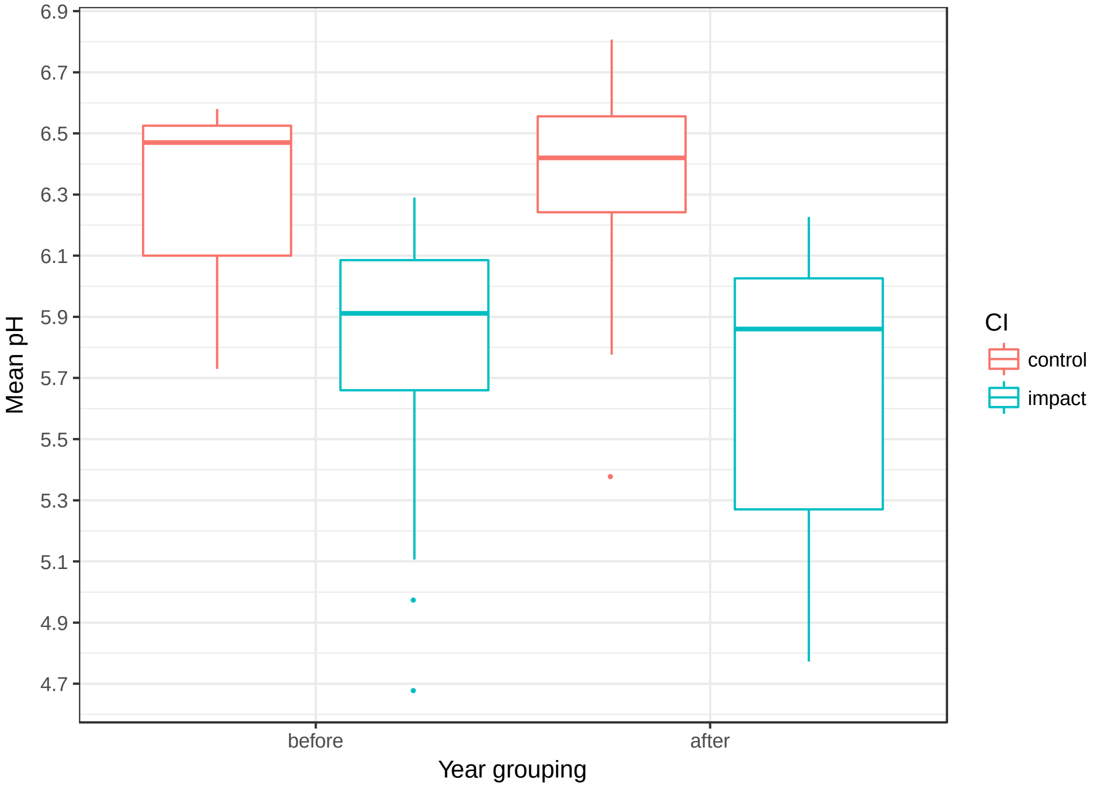


Figure 7.123: Box plots of the pH across the 3 control lakes (orange) and across the 7 sensitive lakes (blue). Top of box, mid-line and bottom of box are (respectively) the 75th, 50th and 25th percentiles of the distributions of the values of mean pH during the pre-KMP (before) and post-KMP periods (after). The medians for the before and after impact groups are similar, but the 25th percentile is lower in the after period than the before period. None of the lakes show significant changes between the after (post-KMP) period and the before (pre-KMP period).

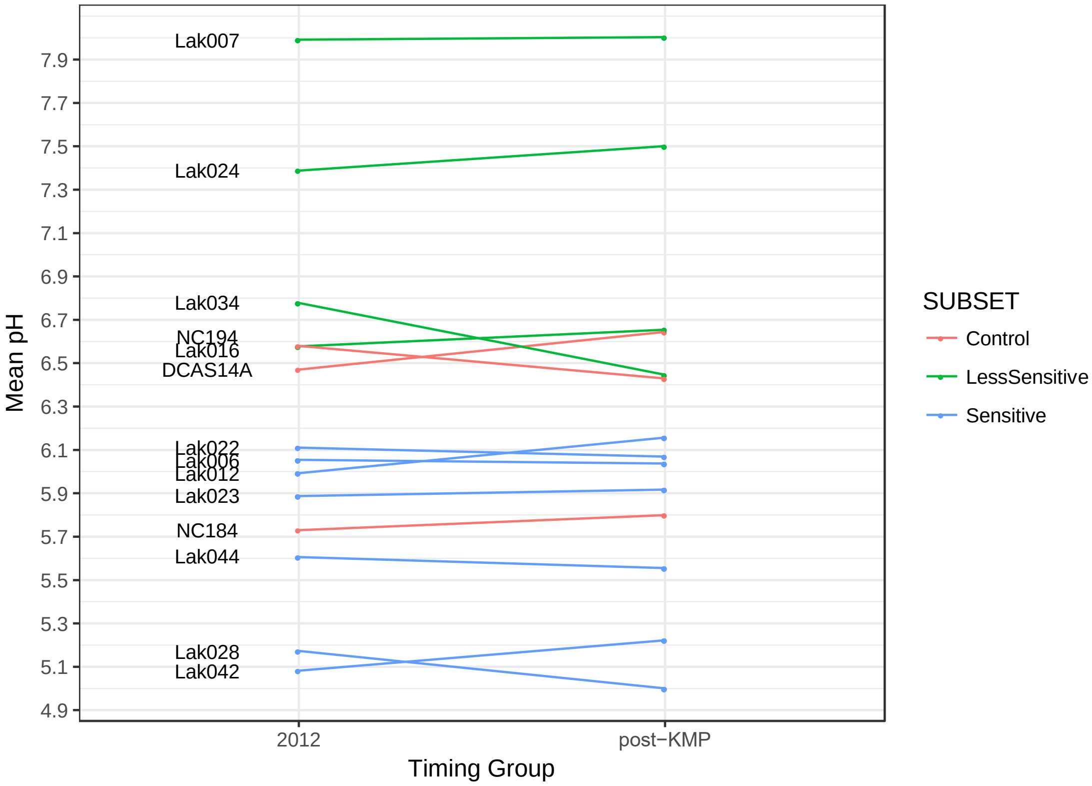


Figure 7.124: Changes in mean pH for control lakes (red), less sensitive lakes (green) and sensitive lakes (blue) between the pre-KMP period (2012) and the post-KMP period (average of mean annual pH for 2016, 2017, 2018).

Table 7.43: BACI analyses of mean pH for 7 sensitive and 3 control lakes, using Method 3. “BACI estimate” is a bit counter-intuitive: it is the Δ mean pH in the controls (i.e., $pH_{post\text{-}KMP}$ minus $pH_{pre\text{-}KMP}$), averaged over the 3 control lakes, minus the Δ mean pH in the sensitive lake (i.e., the mean difference of the control-impact differences). If BACI value is <0, then the ΔpH was lower in the controls than in the sensitive lake (and, equivalently, the ΔpH was greater in the sensitive lake than in the controls). If BACI value is >0, then the pH change in the controls was greater than that in the sensitive lake (and, equivalently, the ΔpH was less in the sensitive ake than in the controls). The “t.ratio” is the t-statistic for the BACI estimate, and the p.value the significance of the test.

Site	BACI estimate	SE	p.value	Interpretation of BACI estimate
LAK006	-0.21	0.15	0.183	change in pH was more positive in LAK006 than in the control lakes (but NOT statistically significant)
LAK012	-0.49	0.18	0.013	change in pH was more positive in LAK012 than in the control lakes (but NOT statistically significant)
LAK022	-0.11	0.24	0.648	change in pH was more positive in LAK022 than in the control lakes (but NOT statistically significant)
LAK023	-0.18	0.16	0.28	change in pH was more positive in LAK023 than in the control lakes (but NOT statistically significant)
LAK028	0.008	0.14	0.957	change in pH was similar in LAK028 to changes in the control lakes
LAK042	-0.51	0.23	0.037	change in pH was more positive in LAK042 than in the control lakes (but NOT statistically significant)
LAK044	-0.12	0.19	0.527	change in pH was more positive in LAK044 than in the control lakes (but NOT statistically significant)

Table 7.44: BACI analysis of ΔpH with all lakes combined, using Method 3. BACI estimate is the Δ mean pH in the 3 control lakes (i.e., $pH_{post\text{-}KMP}$ minus $pH_{pre\text{-}KMP}$, averaged over the 3 control lakes), minus the Δ mean pH in the 7 sensitive lakes (i.e., $pH_{post\text{-}KMP}$ minus $pH_{pre\text{-}KMP}$, averaged over the 7 sensitive lakes). SE is the standard error of the BACI estimate. The t.ratio is the t-statistic for the BACI estimate, and the p.value the significance of the test.

contrast	BACI estimate	SE	p.value
baci	-0.18	0.10	0.059

KEY FINDINGS:

- For the analysis of each sensitive lake compared to the 3 control lakes as a group:
    - None of the lakes showed a statistically significant effect – i.e., before-after differences that were significantly different than the before-after changes in the control lake group
    - Six of the seven sensitive lakes showed a ΔpH that was more positive than the ΔpH observed in the group of control lakes (negative effect in the BACI analysis), but none of these differences were statistically significant at $p<0.01$
    - Before-after changes in mean pH in LAK028 were similar to those observed in the control lakes.
    - All lakes have p-value above 0.01.
    - No support for an effect across any of the lakes individually or an effect for all lakes combined.
- For the analysis of the group of 7 sensitive lakes compared to the group of 3 control lakes:
    - The sensitive lake group showed a more positive ΔpH compared to the control lake group, but this difference was not statistically significant at $p<0.01$.

7.6.4.3.4 Method 4 (Frequentist): Before-After Control-Impact (BACI), Using Individual Samples

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.4, but applied to pH.

Purpose of analyses:

We wish to see if there is any change in the results of the BACI analysis when we account for variability during the sampling period. This analysis is only possible for the 6 sensitive lakes with four samples / year; LAK022 has only one sample per year.

Explanation of the graphs and tables of results:

See captions below

Table 7.45: BACI analysis of ΔpH using Method 4. See caption for Table 4-19 for explanation of terms. Power is the statistical power to detect ΔpH of 0.3, given the number of subsamples, number of years, and different standard deviation components.

Site	BACI estimate	SE	p.value	Power (%)	Interpretation of BACI estimate
LAK006	-0.21	0.22	0.36	23	change in pH was more positive in LAK006 than in the control lakes (but NOT statistically significant)
LAK012	-0.49	0.24	0.076	20	change in pH was more positive in LAK012 than the change in pH in the control lakes (but NOT statistically significant)

Site	BACI estimate	SE	p.value	Power (%)	Interpretation of BACI estimate
LAK023	-0.18	0.23	0.453	21	change in pH was more positive in LAK023 than in the control lakes (but NOT statistically significant)
LAK028	0.008	0.20	0.97	26	change in pH was in LAK028 was similar to changes in the control lakes
LAK042	-0.51	0.29	0.113	16	change in pH was more positive in LAK042 than in the control lakes (but NOT statistically significant)
LAK044	-0.12	0.25	0.645	19	change in pH was more positive in LAK044 than in the control lakes (but NOT statistically significant)

Table 7.46: BACI analysis of ΔpH with all lakes combined, using Method 4. Structure of this table is similar to Table 7.44.

contrast	BACI estimate	SE	p.value
baci	-0.18	0.12	0.154

KEY FINDINGS:

- All lakes have p-value above 0.01. In all six lakes, the p-values were higher using Method 4 than Method 3, indicating that inclusion of within-year variability for 6 sensitive lakes (Method 4) made an effect for ΔpH even less likely than under Method 3.
- No support for BACI effect in ΔpH across any of the lakes individually (Table 7.45) or an effect for all lakes combined (Table 7.46).
- The analysis for six sensitive lakes combined as a group under Method 4 (Table 7.46) has fewer degrees of freedom and a higher p-value than when all seven lakes were combined under Method 3 (Table 7.44), confirming that Method 4 did not reduce the uncertainty in the estimated effect relative to Method 3.

7.6.4.3.5 Method 5 (Frequentist): Before-After Control-Impact (BACI), with Assumption of No Change in Control Lakes

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.5, but applied to pH. Note that the range of fluctuation in pH in the control lakes over 2013 and 2015-2018 is generally close to the range of pH measurement error of ± 0.2 pH units.

Purpose of analyses:

This is a sensitivity analysis on Method 4, to see how much difference the observations from the control lakes (and common patterns of year to year variability in the control lakes) make to the outcome of the BACI analysis. Removing the data from the control lakes reduces the number of degrees of freedom in the analysis. The analysis is done first using just mean values (as in Method 1), and then using all of the data (as in Method 2). We also use ANOVA to compare the fit of models which keep the control lakes' data constant, vs. allowing the control lakes' data to vary.

Explanation of the graphs and tables of results:

See captions below

Table 7.47: BACI analysis using Method 5 applied to mean pH values, holding control lakes' pH constant. Structure of this table is similar to Method 3 (Table 7.44).

contrast	BACI estimate	SE	p.value
baci	0.20	0.08	0.026

Table 7.48: ANOVA analysis using Method 5 comparing the fit of two models to mean pH values ("vary", which includes data from the control lakes; and "cons", which holds the control lakes constant). Analysis applied using two information criteria (AIC = Aikike Information Criteron; BIC = Bayesian Information Criteron). Lower (i.e., more negative) values for AIC and BIC indicate a better fit of the model to the data. Including data from the control lakes ("vary") provides a slightly better fit, but the differences between the two models are not statistically significant.

	Df	AIC	BIC	logLik	deviance	Chisq	ChiDF	Pr(>Chisq)
vary	6	-46.16	-29.96	29.08	-58.158			
cons	7	-44.25	-25.34	29.12	-58.246	0.0884	1	0.766

Table 7.49: BACI analysis using Method 5 applied to all pH values in the sensitive lakes (i.e., including within-year variability), holding control lakes' pH constant. Structure of this table is similar to Method 3 (Table 7.44).

contrast	BACI estimate	SE	p.value
baci	0.07	0.09	0.453

Table 7.50: ANOVA analysis using Method 5 comparing the fit of two models to all pH values ("vary", which includes data from the control lakes; and "cons", which holds the control lakes constant). Analysis applied using two information criteria (AIC = Aikike Information Criteron; BIC = Bayesian Information Criteron). Lower (i.e., more negative) values for AIC and BIC indicate a better fit of the model to the data. Including data from the control lakes ("vary") provides a slightly better fit, but the differences between the two models are not statistically significant.

	Df	AIC	BIC	logLik	deviance	Chisq	ChiDF	Pr(>Chisq)
Vary	7	-36.03	-17.13	25.02	-50.031			
Cons	8	-34.09	-12.49	25.05	-50.095	0.0639	1	0.801

KEY FINDINGS:

- Removing the variability contributed by the data from the control lakes (Method 5) yields a positive effect in the BACI analysis (Table 7.47), as compared to a negative effect when control lake data were included (Method 3 (Table 7.44) and Method 4 (Table 7.46)). However, none of these methods showed statistically significant effects at p<0.01.
- The ANOVA analyses (Table 7.48 and Table 7.50) indicate that inclusion of data from the control lakes provides a slightly better fit to the data than assuming no changes in the control lakes, but the differences in model fit between these two approaches are not statistically significant.
- Since comparisons of Method 5 with Methods 3 and 4 indicate that data from the control lakes can affect the sign of the BACI analysis, and since accounting for regional climate effects is important, we conclude that sampling should continue in the control lakes, and these data should continue to be used in BACI analyses.

7.6.4.3.6 Method 6 (Frequentist): Using Other Covariates to Explain Inter-Annual Variation

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.6, but applied to pH.

Purpose of analyses:

The previously described analyses intentionally excluded 2013 and 2014 from the baseline period. We did this because the winding down of the old smelter during this period resulted in reduced emissions and apparent increases in pH in some of the sensitive lakes (Figure 7.44), which would lead to an inaccurate estimate of baseline pH if we had used 2012-2014 data to compute baseline pH. If covariates such as emissions and precipitation help to explain variability in water chemistry, then we could potentially include data from 2012-2014 in the baseline period, and have three years of baseline data rather than just one, which, together with three years of post-KMP data (2016-2018) would improve statistical power.

Explanation of the graphs and tables of results:

We used total SO_2 emissions over the prior year (i.e., October 1 through Sept. 30, see Section 7.6.2.3) and the last 3-days and 14-days of precipitation at Haul Road (see Section 7.6.2.2) as covariates. The model also includes terms for three random effects: year, site, and year by site interactions.

*pH_trent ~ BA*CI + EMISSIONS + PRECIPITATION + (1|YEAR) + (1|SITE) + (1:YEAR:SITE)*

Table 7.51: Before-After t-test for changes in pH, including covariates for emissions and previous 3-day sum of precipitation. No effect of timing (BA, before KMP vs. post-KMP), treatment (CI, control lake or impact lake) or the BACI interaction (BA:CI), 3-day precipitation or Emissions was observed for pH.. df is degrees of freedom. t-value is the test statistics. Pr(>|t|) is the pvalue.

Fixed effects:	Estimate	Std Error	df	Pr(>|t|)
(Intercept)	6.16	0.56	12	0.00
BAbefore	0.04	0.19	3	0.84
CIimpact	0.30	0.48	27	0.54
Emissions	0.00	0.00	2	0.73
Precipitation (3 day)	-0.01	0.00	39	0.06
BAbefore:CIimpact	0.14	0.11	39	0.22

Table 7.52: Variance and standard deviation of the random effects for year, site and year by site interactions. The SITE random effect accounts for a substantial portion of the variation in pH.

Random effects:		
Groups	Variance	Std.Dev.
YEAR:SITE	0.01	0.11
SITE	0.60	0.78
YEAR	0.002	0.04
Residual	0.01	0.10

Table 7.53: Before-After t-test for changes in pH, including covariates for emissions and previous 14-day sum of precipitation. No effect of timing (BA, before KMP vs. post-KMP) or treatment (CI, control lake or impact lake) or the BACI interaction (BA:CI), 14-day precipitation or Emissions was observed for pH. df is degrees of freedom. t-value is the test statistics. Pr(>|t|) is the pvalue.

Fixed effects:	Estimate	Std Error	df	Pr(>|t|)
(Intercept)	6.29E+00	5.82E-01	1.06E+01	4.85E-07
BAbefore	-3.48E-02	2.06E-01	2.45E+00	0.879
CIimpact	2.78E-01	4.79E-01	2.66E+01	0.566
Emissions	4.96E-05	1.08E-03	1.87E+00	0.968
Precipitation (14 day)	-2.73E-03	1.94E-03	3.92E+01	0.168
BAbefore:CIimpact	1.74E-01	1.16E-01	3.97E+01	0.141

Table 7.54: Variance and standard deviation of the random effects for year, site and year by site interactions. The SITE random effect accounts for a substantial portion of the variation in pH.

Random effects:			
Groups	Name	Variance	Std.Dev.
YEAR:SITE	(Intercept)	0.01	0.10
SITE	(Intercept)	0.61	0.78
YEAR	(Intercept)	0.002	0.05
Residual		0.001	0.11

KEY FINDINGS:

- Adding covariates for emissions and precipitation did not help to explain variability in the ΔpH between the post-KMP and pre-KMP periods.
- The signs of the covariates for 3-day and 14-day precipitation are negative, which is consistent with our expectations (i.e., pH is negatively correlated with the amount of precipitation during the previous time-period), but these terms are not statistically significant at alpha = 0.05.

7.6.4.3.7 Approach Supportive of Methods 8 and 9 (Frequentist): Temporal Trend Analyses

Description and Purpose of Analyses:

As explained in Section 7.6.4.2.7 for SO_4.

Table 7.55: Results of the Mann-Kendall non-parametric test for monotonic trend in pH values. No lakes exhibit a significant result for detecting a monotonic trend.

Lake	p.value
LAK006	0.500
LAK012	0.633
LAK022	0.367
LAK023	0.500
LAK028	0.500
LAK042	0.045
LAK044	0.367
LAK007	0.765
LAK016	0.500
LAK024	0.633
LAK034	0.154
NC184	0.597
NC194	0.403
DCAS14A	0.890

KEY FINDINGS:

- None of the lakes' data provide sufficient evidence to reject the null hypothesis that there was no monotonic trend in mean pH (i.e., all p values are > 0.01)

7.6.4.3.8 Method 1a (Bayesian): Two-Sample Before-After Bayesian Analysis (Bayesian Estimation Supersedes the T-Test with informative priors)

Description of Analyses:

The intent of Bayesian analyses is to estimate the *posterior* distribution of a parameter of interest, which is the probability distribution of the parameter taking into account the data. The first step is for the analyst to specify a *prior* belief, or prior credibility distribution of possible parameter values. After the data have been collected, the prior beliefs are then updated using Bayes' rule to obtain the posterior distribution. In this case, the parameter of interest is the ΔpH from the baseline 2012 measurement to the 2016-2018 post-KMP period. The statistical software used for this analysis computes Δ mean pH as the mean pH for the baseline period minus the mean pH for the 2016-2018 post-KMP period. Positive values of this parameter are therefore indicative of a pH decline.

In the introduction to these analyses in the TOR we stated that if the frequentist approach shows a clear result for a lake (e.g., 99% confidence intervals for ΔpH do not overlap that lake's threshold for ΔpH) then there's no need to proceed with the Bayesian analysis for that parameter in that lake. Using frequentist method 1 for ΔpH, all of the 99% confidence intervals for the seven sensitive lakes overlapped the 0.3 threshold, so it would be logical to use the Bayesian approach for all seven sensitive lakes. However, with frequentist method 2 for ΔpH, the 99% confidence intervals for ΔpH did not overlap -0.3 in five of the six sensitive lakes with multiple samples in October: LAK006, LAK012, LAK023, LAK042 and LAK044. Using Method 2, the 99% confidence intervals for LAK028 did however overlap -0.3 in LAK028. Based on Method 2, we only need to include the Bayesian approach for LAK028. However, we decided to complete the Bayesian approach for all lakes, so that we could see how consistent our inferences would be using different statistical methods.

We also examine the percent belief that there was any decline in mean pH between the pre-KMP (2012) and post-KMP (2016-18) periods (Figure 7.128). The percent belief in any decline covers a larger fraction of the posterior distribution of ΔpH, and therefore generates higher values of percent belief than for a decline with exceeds the 0.3 unit threshold.

Explanation of the graphs and tables of results:

See captions below.

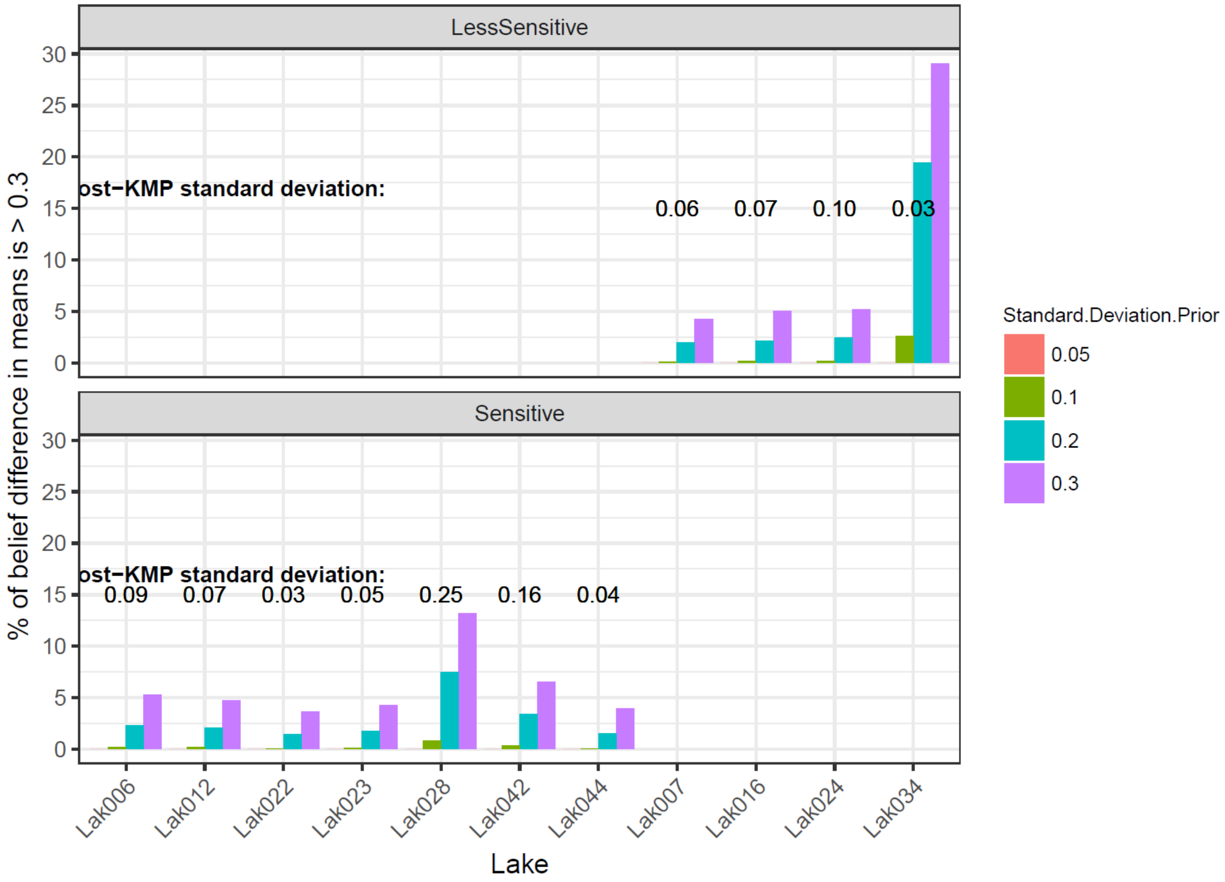


Figure 7.125: Percentage belief that ΔpH is greater than 0.3, using Two-Sample Before-After Bayesian Analysis. The bars show the percentage belief for four different prior assumptions about the standard deviation of pH of a lake across the entire time period (note that the orange bars for a SD of 0.05 are too small to be visible on the graphs). The SD of pH for the post-KMP period is included to provide some context for each lake, but is not directly comparable to the prior assumptions of SD. For example, using an SD prior of 0.2 (blue bars), only LAK028 and LAK034 have more than a 5% belief that ΔpH is greater than 0.3. Figure 7.126 provides a further illustration of the posterior distribution for ΔpH.

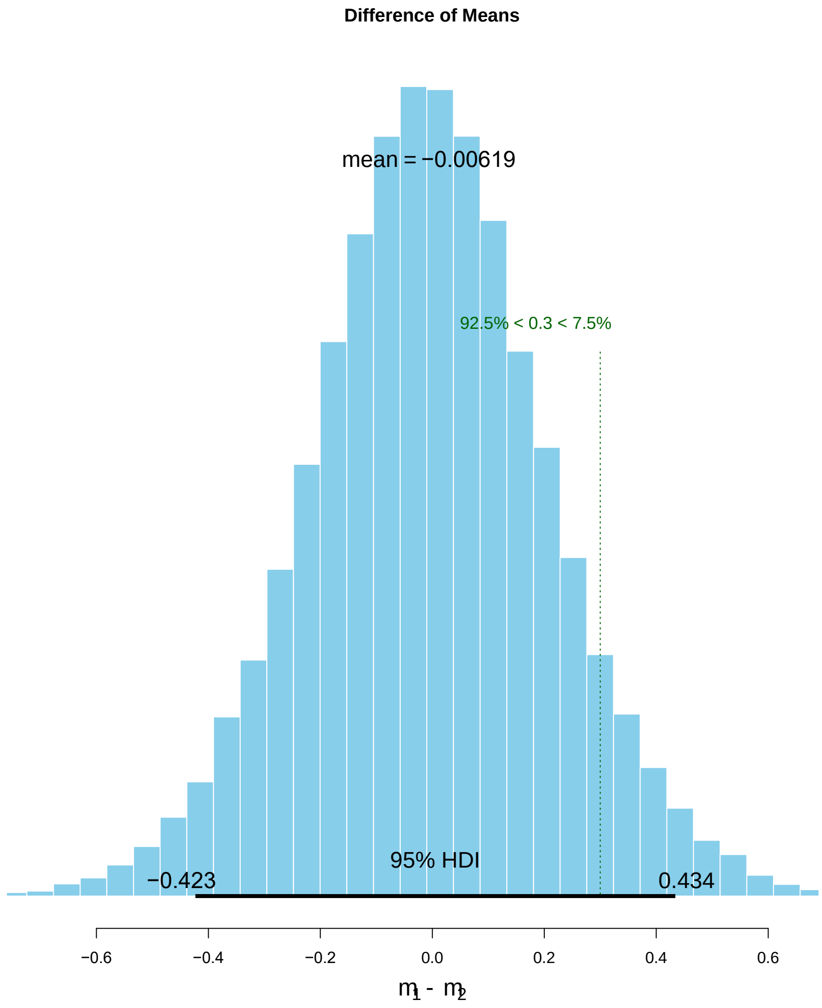


Figure 7.126: Example of BEST output, for LAK028 using an SD prior of 0.2, of a histogram of the percent belief in different values for ΔpH (i.e., the posterior distribution of ΔpH). (NOTE: the configuration of this analyses is [baseline] – [post-KMP] so therefore positive values represent a pH decrease from the baseline). The bold horizontal bar shows the values that lay within the 95% high density interval (HDI). The dashed vertical line represents a change of 0.3 pH units, showing that there is a 7.5% belief (percent of the total area under the distribution to the right of the 0.3 line) that there has been a decrease in pH in LAK028 of greater than 0.3 pH units. Conversely, there is a 92.5% belief that the ΔpH is less than 0.3.

7.6.4.3.9 Method 1b (Bayesian): Two-Sample Before-After Bayesian Analysis (with uninformative priors)

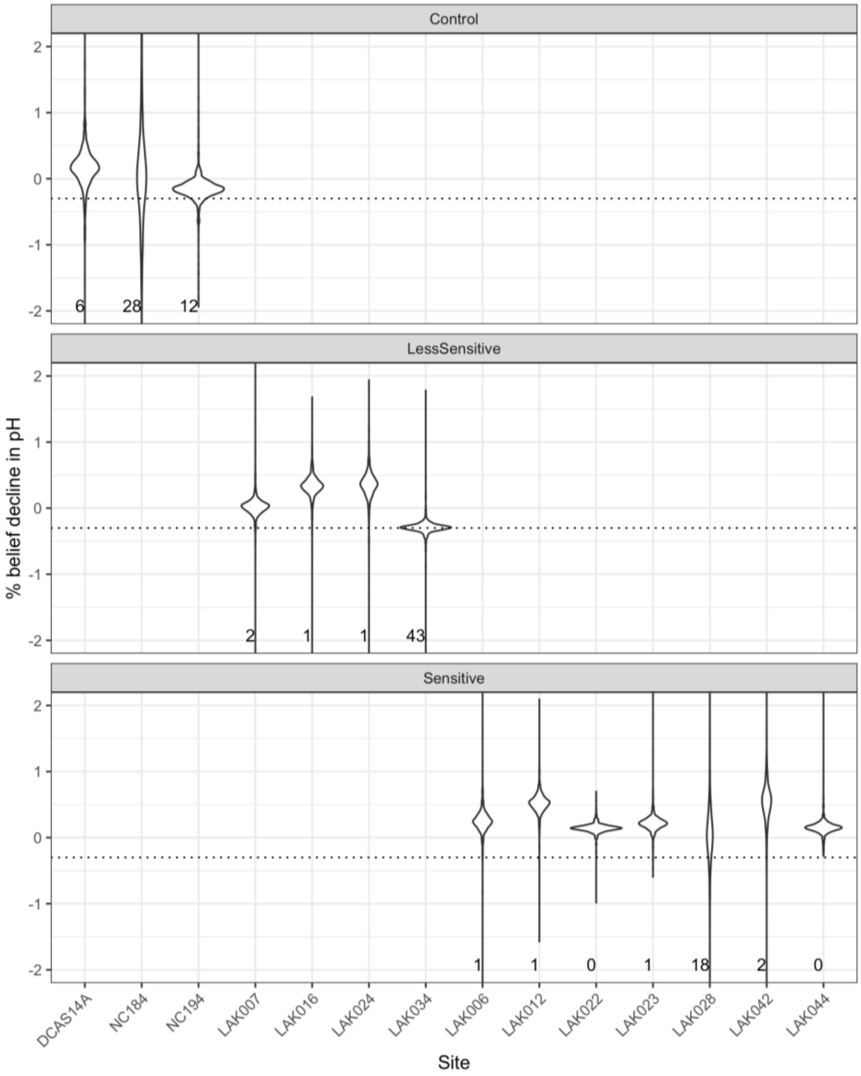


Figure 7.127: Violin plots showing the the posterior distributions of credible values for ΔpH, with no prior assumptions about the variability in pH. The percent of these distributions that correspond to a change greater than 0.3 (dotted line) are shown in numerals at the bottom of each plot.

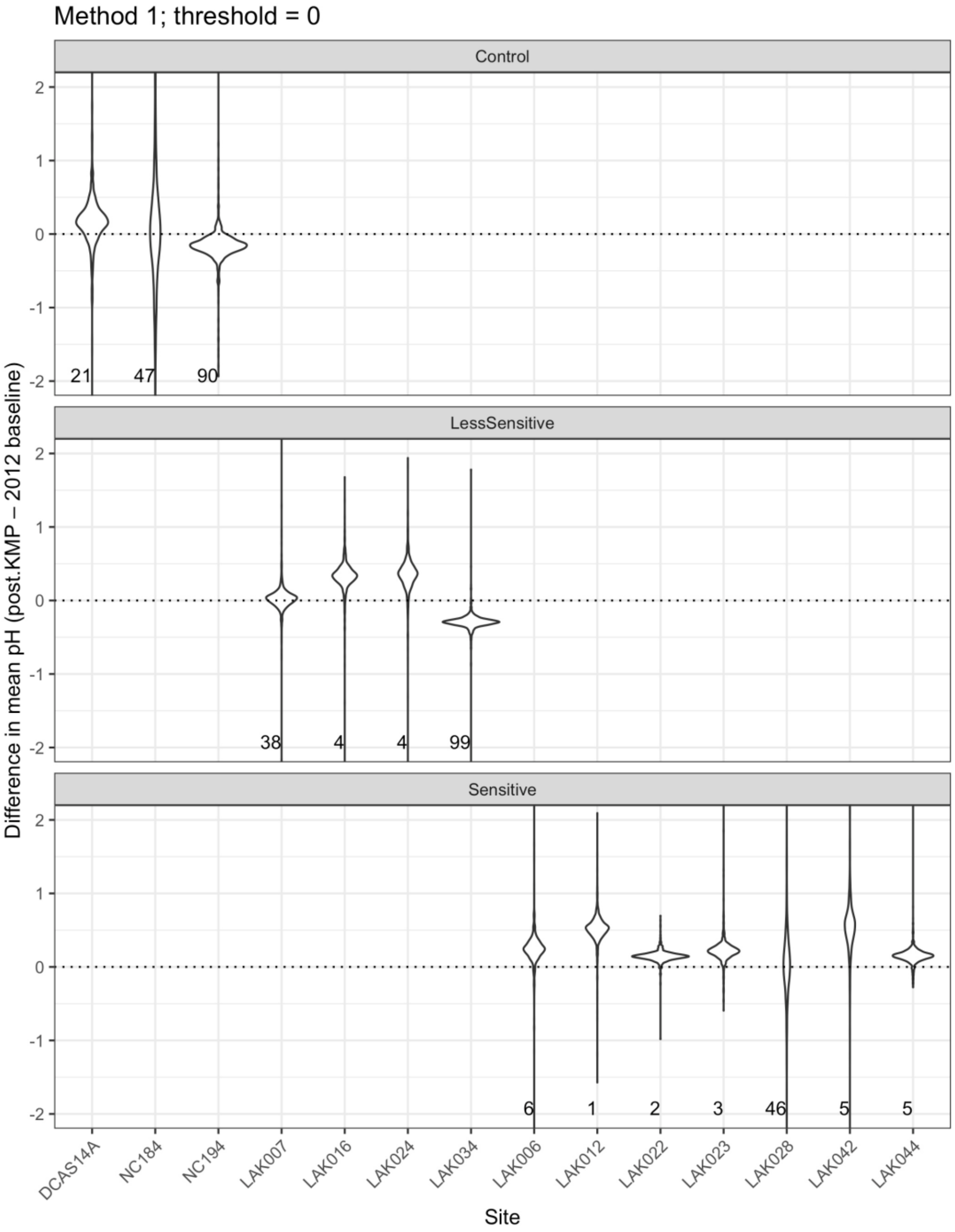


Figure 7.128: Violin plots showing the the posterior distributions of credible values for ΔpH, with no prior assumptions about the variability in pH. The percent of these distributions that correspond to a change greater than 0.0 (i.e. any decrease in mean pH between the two time periods) are shown in numerals at the bottom of each plot.

KEY FINDINGS:

- Six of the seven sensitive lakes, and three of the four less sensitive lakes show very little support for the hypothesis that ΔpH (baseline mean pH minus post-KMP mean pH) was greater than 0.3. This is demonstrated by the fact that the percent belief in a ΔpH > 0.3 is less than 6% for all of these lakes, across a wide range of prior assumptions about the standard deviation of pH (Figure 7.125), and less than 3% when no prior assumptions are made about the variability in pH (violin plot in Figure 7.127). LAK028 shows a 18% belief that the ΔpH exceeded the 0.3 threshold (Figure 7.127), or conversely, a 82% belief that the ΔpH did not exceed the 0.3 threshold. In Figure 7.128, LAK028 shows a 46% belief in some pH decline (i.e., roughly equal chances of a pH increase or a pH decrease)
- For the less sensitive lakes, only LAK034 exhibited more than a 3% belief that ΔpH is greater than 0.3 (violin plot in Figure 7.127). LAK034 showed close to a 0.3 unit decline in pH over the period from 2012 to 2016-2018 (Figure 7.43), consistent with a 43% belief that it exceeded the 0.3 threshold of change in pH Figure 7.127). As noted above, SO_4 declined concurrently with pH in LAK034, so the pH decline in LAK034 was not associated with SO_2 emissions.
- Two of the control lakes (NC184 and NC194) show intermediate levels of belief that their ΔpH was greater than 0.3 (28% and 12% respectively).

7.6.4.3.10 Method 2 (Bayesian): Two-Sample Before-After Bayesian Analysis, Using Individual Samples

Description of Analyses:

This analysis is the Bayesian version of Method 2, taking into account all of the data, and accounting for variability within each year.

Purpose of analyses:

The purpose is similar to Bayesian Method 1, but uses all of the data rather than just the mean values.

Explanation of the graphs and tables of results:

See figure captions.

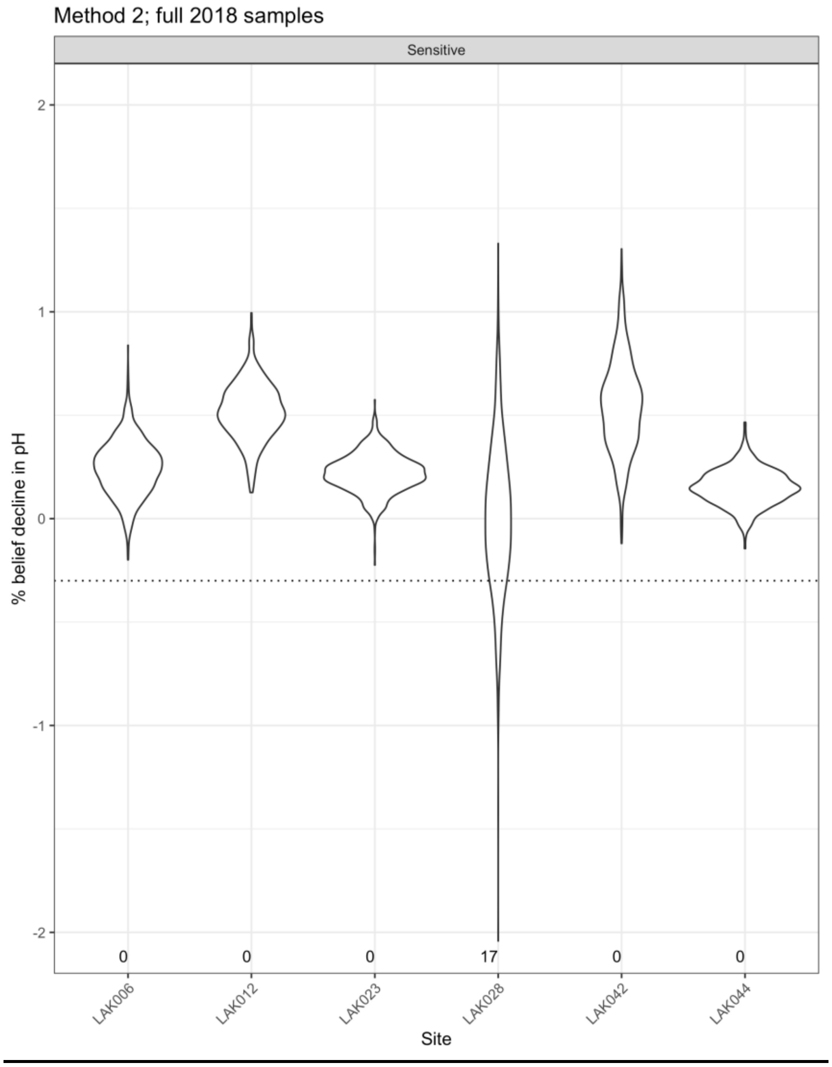


Figure 7.129: Violin plot showing the the posterior distributions of credible values for ΔpH for the six sensitive lakes with multiple samples per year, with no prior assumptions about the variability in pH. The percent of these distributions that correspond to a change greater than 0.3 (dotted line) are shown in numerals at the bottom of each plot.

KEY FINDINGS:

- Using all of the data under Method 2 provides a narrower distribution for 6 of the 7 sensitive lakes, which all have 0% belief that the ΔpH exceeded the 0.3 threshold.
- For LAK028, using all of the data under Method 2 provides a similar level of belief (17%, versus 18% under Method 1) that the ΔpH exceeded the 0.3 threshold.

7.6.4.4 Key Metric: ANC

7.6.4.4.1 Method 1 (Frequentist): Two-Sample Before-After T-Test Using Mean Values

Description of Analyses:

See Section 7.6.4.2.1 for SO_4.

Purpose of analyses:

This is exactly the same analysis as Method 1 for pH, except applied to ANC, for which there are lake-specific ANC thresholds reflecting the ΔANC that within each lake would correspond to a ΔpH of 0.3 units below the 2012 pH values. These thresholds were derived from laboratory titrations completed at the Trent University lab, and reflect the particular mix of buffering (i.e., bicarbonate and organic anions) found within each lake.

Explanation of the graphs and tables of results:

Please see captions below.

Table 7.56: T-test of changes in mean ANC for each lake, between the pre-KMP period (2012) and post-KMP period (2016-2018). T.stat is the T-statistic. P-value is the probability of the ΔANC being significantly different from zero (p<0.01 is the appropriate signficance level given the multiple statistical tests). Lwr and Upp are the lower and upper confidence levels for ΔANC. Sd_post is the standard deviation of mean ANC levels over the 3-year post-KMP period (much lower for the sensitive lakes than the less sensitive lakes since their GranANC is lower). MDD_sd is the minimum detectable difference in ANC that would be statistically significant at p<0.01 with 80% statistical power, given four different assumptions about the standard deviation of ANC during the pre-KMP period (1, 5, 10, 15 µeq/L). For example, in LAK006, a Gran ANC change of 6 µeq/L is the minimum detectable difference with a pre-KMP SD of 1 µeq/L, but the MDD increases to 72 µeq/L if the pre-KMP SD were 15 µeq/L.

SUBSET	SITE	p-value	lwr	upp	sd_post	MDD_sd_1	MDD_sd_5	MDD_sd_10	MDD_sd_15
LessSensitive	LAK007	0.153	-279	176	30	96	98	107	120
LessSensitive	LAK016	0.096	-49	91	12	30	38	56	78
LessSensitive	LAK024	0.093	-371	698	90	224	225	229	235
LessSensitive	LAK034	0.085	-84	165	22	52	57	71	89
Sensitive	LAK006	0.147	-6	11	1	6	24	48	72
Sensitive	LAK012	0.895	-84	87	6	36	43	60	80
Sensitive	LAK022	0.194	-21	32	3	12	26	49	73
Sensitive	LAK023	0.197	-28	41	4	15	28	50	73
Sensitive	LAK028	0.961	-82	82	6	35	42	59	80
Sensitive	LAK042	0.09	-57	109	14	35	42	59	80
Sensitive	LAK044	0.206	-16	24	2	10	25	49	72

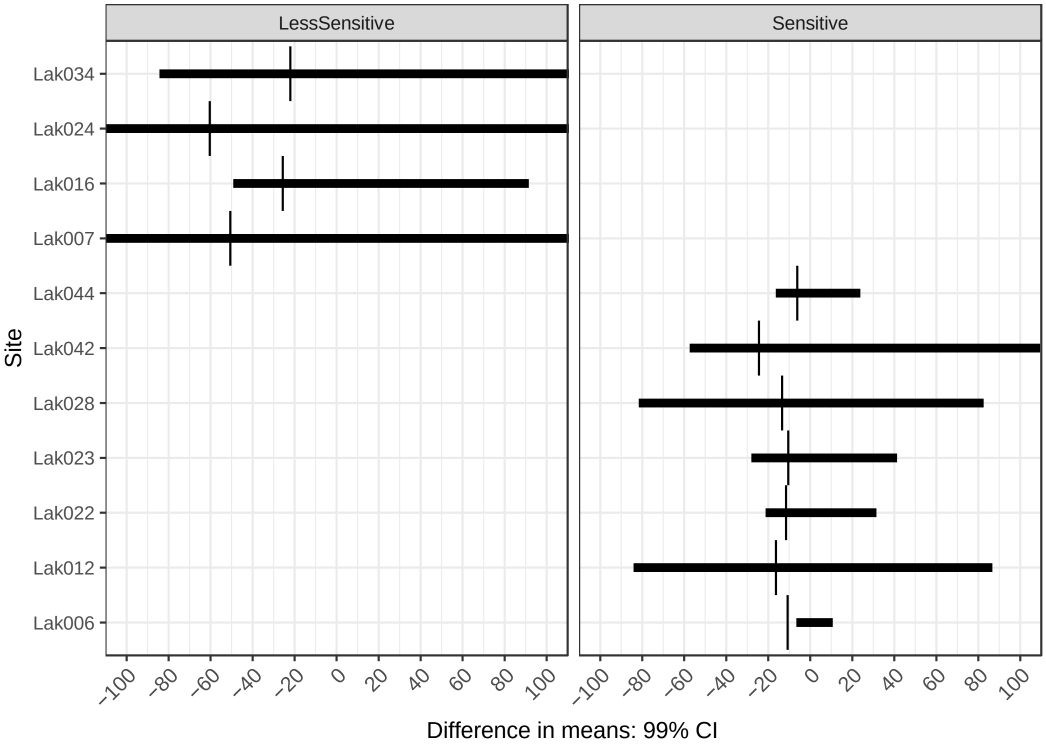


Figure 7.130: Using Method 1, 99% confidence intervals for the ΔANC (mean ANC in post-KMP period minus the mean ANC in the pre-KMP period). The confidence intervals for changes in mean pH overlap 0.0 and the lake-specific ANC thresholds (vertical lines) for all lakes except for LAK006 (where the confidence interval overlaps 0.0 but not the lake's ANC threshold).

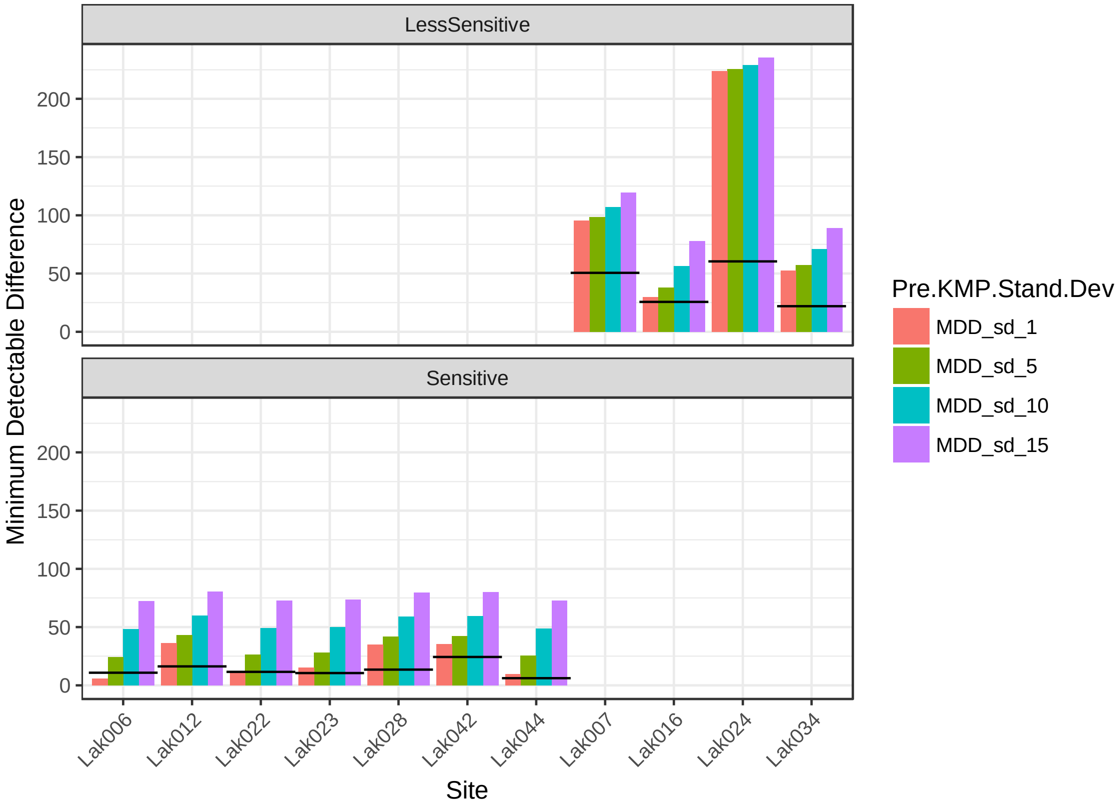


Figure 7.131: Minimum detectable differences (MDD) are shown for each lake, assuming four different values for the standard deviation (SD) of Gran ANC in the pre-KMP period (2012). Since we have only one observation for the pre-KMP period (a single measurement in 2012), we can't compute the SD, but must assume it. The horizontal lines mark the lake-specific thresholds for Gran ANC. Only LAK006 has an MDD less than its threshold, and only for the lowest assumed SD (1 µeq/L). For this lowest assumed SD, the t-test is able to detect (with high statistical power) changes less than the ANC threshold within LAK006. In all other lakes, this t-test is only able to detect changes greater than the lake-specific ANC thresholds.

KEY FINDINGS:

- All 99% Confidence Intervals for ΔANC overlap zero and all but one (LAK006) overlap their lake specific thresholds.
- No t-statistics for any site have a p-value below 0.01.
- All Minimum Detectable Differences are greater than the lake-specific median threshold, except for LAK006.

7.6.4.4.2 Method 2 (Frequentist): Two-Sample Before-After T-Test Using Individual Samples

Description of Analyses:

Same as for SO_4 in Section 7.6.4.2.2, but applied to Gran ANC.

Purpose of analyses:

The purpose of this analysis is similar to Method 1 (i.e., to determine if there is a significant difference between the post-KMP and pre-KMP values of ANC), but the analysis removes the effect of natural variability during the sampling period. We are interested to see if this reduces the uncertainty in estimates of the ΔANC between the post-KMP and pre-KMP periods, and narrows the confidence intervals on these estimates.

Explanation of the graphs and tables of results:

See captions below.

Table 7.57: Results for T-test for post-KMP Gran ANC (2016-18) versus baseline Gran ANC(2012), using individual samples, for the six sensitive lakes with multiple within-year samples. The "est.diff" is the ANC in the post-KMP period minus the ANC in the baseline period. A positive value for "est.diff" means that the ANC increased from the baseline period to the post-KMP period, while a negative value indicates a decrease in ANC. The "est.diff.se" is the standard error in ANC, which is highest for LAK028 and LAK012, and lowest for LAK044. The "est.diff.lcl" and "est.diff.ucl" are the lower and upper confidence intervals (respectively) for "est.diff". The "p.value" is the probability of a significant difference in mean ANC between the two time periods (all p-values are >0.01, and therefore the differences between the two time periods are not statistically significant).

SITE	est.diff	est.diff.se	est.diff.lcl	est.diff.ucl	p.value
LAK006	2.0	3.4	-5.6	9.7	0.569
LAK012	1.3	10.1	-27.6	30.2	0.906
LAK023	6.6	4.7	-5.0	18.3	0.207
LAK028	0.5	11.4	-27.3	28.2	0.97
LAK042	26.1	9.0	-5.1	57.3	0.074
LAK044	3.7	3.4	-3.9	11.4	0.298

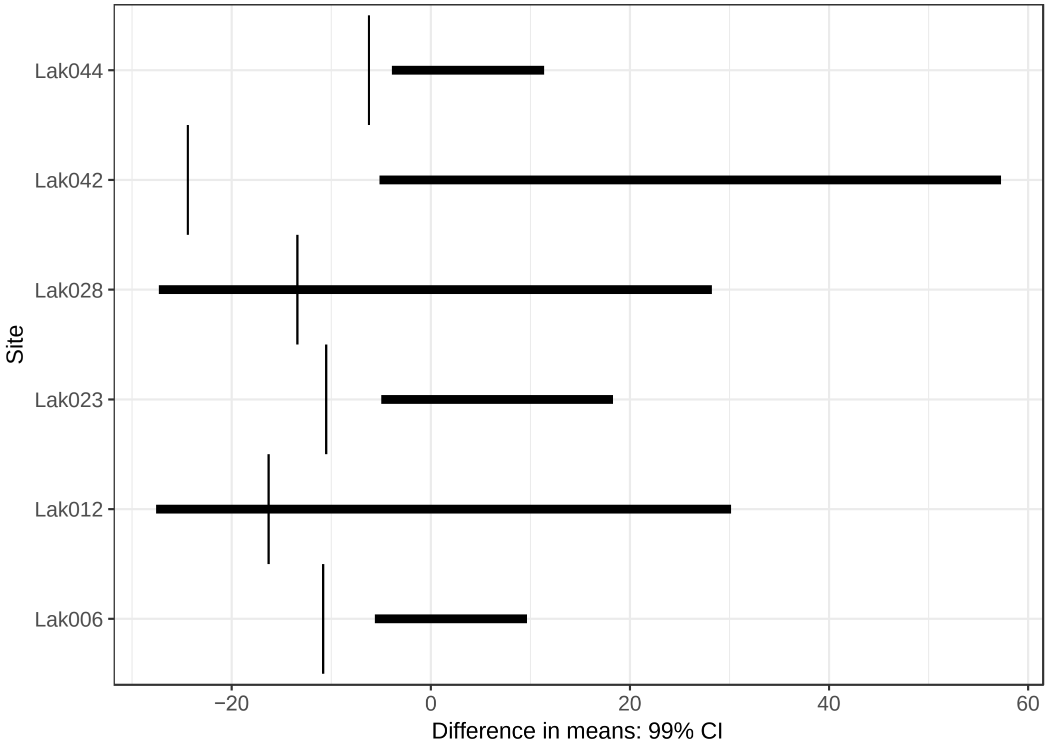


Figure 7.132: Using Method 2, 99% confidence intervals for the ΔANC (mean ANC in post-KMP period minus the mean ANC in the pre-KMP period, accounting for within year variability). The vertical lines provide the lake-specific ANC thresholds, as described above. The confidence intervals for changes in mean ANC do not overlap the ANC thresholds in four of the six lakes (LAK006, LAK023, LAK042, LAK044), but do overlap the thresholds in LAK012 and LAK028.

KEY FINDINGS:

- No support for any difference between pre-KMP (2012) and post-KMP (2016-2018) - all of the confidence intervals overlap zero, and none of the differences were significant at $p<0.01$.
- No support for any decline in mean Gran ANC greater than the threshold for LAK006, LAK023, LAK042, and LAK044 – i.e., the confidence intervals are completely above the threshold.
- The confidence intervals for LAK012 and LAK028 are relatively wide (Figure 7.132) and overlap their respective thresholds. This is partly because these two lakes had the lowest values of ΔANC (see “est.diff” column in Table 7.57) and partly because they had the highest variability in ΔANC (see “est.diff.se” column in Table 7.57). The data for these two lakes are therefore insufficient to reject the hypothesis (at a 99% level of confidence, using this T-test) that their ANC thresholds were exceeded.

7.6.4.4.3 Method 3 (Frequentist): Before-After Control-Impact (BACI), Using Mean Values

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.3, but applied to Gran ANC.

Purpose of analyses:

Use a BACI analysis to determine how the ΔANC (post-KMP vs. pre-KMP) in each sensitive lake compares to the ΔANC in the control lakes, taken as a group. This analysis accounts for broad scale regional / climatic effects which could affect both the sensitive lakes and the control lakes.

Explanation of the graphs and tables of results:

See figure and table captions below. We are using the significance value of 0.01 throughout as correction for multiple tests (it is not precisely the Bonferroni correction, but an analogous approximation).

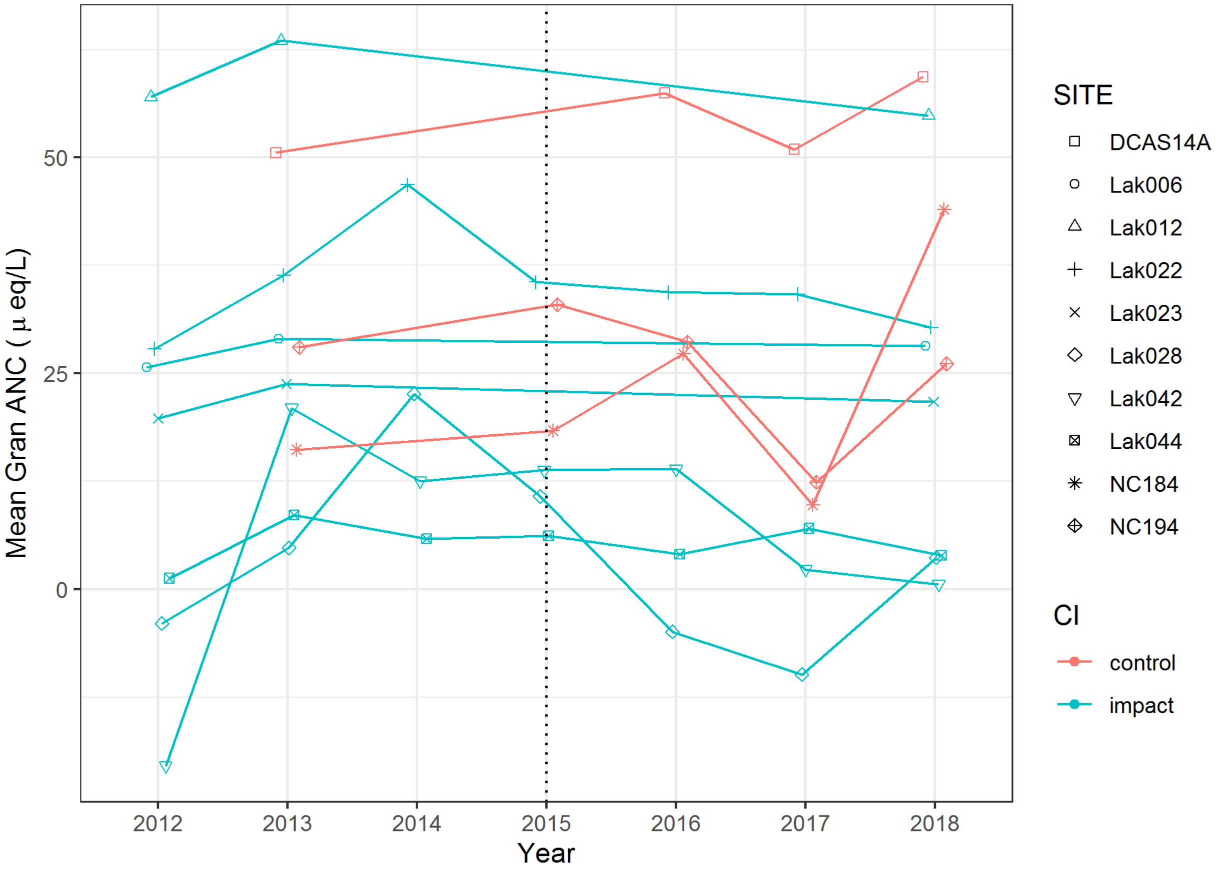


Figure 7.133: Change in mean Gran ANC over time for sensitive lakes (blue lines) and control lakes (orange lines).

Table 7.58: BACI analyses of mean Gran ANC for 7 sensitive and 3 control lakes, using Method 3. "BACI estimate" is a bit counter-intuitive: it is the Δ mean Gran ANC in the controls (i.e., $ANC_{post\text{-}KMP}$ minus $ANC_{pre\text{-}KMP}$), averaged over the 3 control lakes, minus the Δ mean ANC in the sensitive lake. If BACI value is <0, then the ΔANC was lower in the controls than in the sensitive lake (and, equivalently, the ΔANC was greater (more positive) in the sensitive lake than in the controls). If BACI value is >0, then the ANC change in the controls was greater than that in the sensitive lake (and, equivalently, the ΔANC was lower (less positive) in the sensitive lake than in the controls). The "t.ratio" is the t-statistic for the BACI estimate, and the p.value the significance of the test. LAK042 showed the strongest evidence for an increase in Gran ANC, but it is not statistically significant.

Site	BACI estimate	SE	p.value	Interpretation of BACI estimate
LAK006	1.5	8.4	0.846	change in Gran ANC was less positive in LAK006 than in the control lakes (but NOT statistically significant)
LAK012	2.2	8.4	0.813	change in Gran ANC was less positive in LAK012 than in the control lakes (but NOT statistically significant)
LAK022	-1.6	10.7	0.885	change in Gran ANC was more positive in LAK022 than in the control lakes (but NOT statistically significant)
LAK023	-3.1	8.4	0.721	change in Gran ANC was more positive in LAK023 than in the control lakes (but NOT statistically significant)
LAK028	3.0	5.9	0.607	change in Gran ANC was less positive in LAK028 than in the control lakes (but NOT statistically significant)
LAK042	-22.5	8.3	0.015	change in Gran ANC was more positive in LAK042 than in the control lakes (but NOT statistically significant)
LAK044	-0.2	8.3	0.979	change in Gran ANC was more positive in LAK044 than in the control lakes (but NOT statistically significant)

Table 7.59: BACI analysis of Gran ANC with all lakes combined, using Method 3. BACI estimate is the average Δ mean ANC in the 3 control lakes (i.e., $ANC_{post\text{-}KMP}$ minus $ANC_{pre\text{-}KMP}$, averaged over the 3 control lakes), minus the average Δ mean ANC in the 7 sensitive lakes (i.e., $ANC_{post\text{-}KMP}$ minus $ANC_{pre\text{-}KMP}$, averaged over the 7 sensitive lakes). SE is the standard error of the BACI estimate. The t.ratio is the t-statistic for the BACI estimate, and the p.value the significance of the test.

contrast	estimate	SE	p.value
baci	-14.1	12.9	0.2785

KEY FINDINGS:

- All lakes have p-value above 0.01. No support for a significant effect in Δmean Gran ANC across any of the lakes individually or a significant effect for all lakes combined.

7.6.4.4.4 *Method 4 (Frequentist): Before-After Control-Impact (BACI), Using Individual Samples*

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.4, but applied to Gran ANC.

Purpose of analyses:

We wish to see if there is any change in the results of the BACI analysis (relative to Method 3) when we account for variability during the sampling period. This analysis is only possible for the 6 sensitive lakes with four samples / year; LAK022 has only one sample per year.

Explanation of the graphs and tables of results:

See captions below.

Table 7.60: BACI analysis of ΔGran ANC using Method 4. See Table 4-4 in the main report for explanation of terms.

Site	BACI estimate	SE	p.value	Interpretation of BACI estimate
LAK006	1.5	10.1	0.885	change in Gran ANC was less positive in LAK006 than in the control lakes (but NOT statistically significant)
LAK012	2.2	12.2	0.858	change in Gran ANC was less positive in LAK012 than in the control lakes (but NOT statistically significant)
LAK023	-3.1	11.1	0.784	change in Gran ANC was more positive in LAK023 than in the control lakes (but NOT statistically significant)
LAK028	3.1	10.1	0.765	change in Gran ANC was less positive in LAK028 than in the control lakes (but NOT statistically significant)
LAK042	-22.5	10.8	0.07	change in Gran ANC was more positive in LAK042 than in the control lakes (but NOT statistically significant)
LAK044	-0.2	10.7	0.984	change in Gran ANC was more positive in LAK044 than in the control lakes (but NOT statistically significant)

Table 7.61: BACI analysis of ΔANC with all lakes combined, using Method 4.

contrast	estimate	SE	p.value

baci	-11.0	18.5	0.5567

KEY FINDINGS:

- All lakes have p-value above 0.01. No support for a significant effect in Δ mean Gran ANC across any of the lakes individually or a significant effect for all lakes combined.
- The p-value for an effect for Gran ANC is higher under Method 4 (Table 7.60 and Table 7.61) than under Method 3 (Table 7.58 and Table 7.59), indicating that inclusion of within year variability under Method 4 makes an effect even less likely to be statistically significant.

7.6.4.4.5 Method 5 (Frequentist): Before-After Control-Impact (BACI), with Assumption of No Change in Control Lakes

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.5, but applied to Gran ANC.

Purpose of analyses:

This is a sensitivity analysis on Method 4, to see how much difference the observations from the control lakes (and common patterns of year to year variability in the control lakes) make to the outcome of the BACI analysis. Removing the data from the control lakes reduces the number of degrees of freedom in the analysis. The analysis is done first using just mean values (as in Method 1), and then using all of the data (as in Method 2). We also use ANOVA to compare the fit of models which keep the control lakes' data constant, vs. allowing the control lakes' data to vary.

Explanation of the graphs and tables of results:

See captions below.

Table 7.62: BACI analysis using Method 5 applied to mean ANC values, holding control lakes' ANC constant. Structure of this table is similar to Method 3 (Table 7.59), but has only 13.94 degrees of freedom compared to 125.86.

contrast	estimate	SE	p.value
baci	3.84	9.74	0.70

Table 7.63: ANOVA analysis using Method 5 comparing the fit of two models to mean ANC values ("vary", which includes data from the control lakes; and "cons", which holds the control lakes constant). Analysis applied using two information criteria (AIC = Aikike Information Criteron; BIC = Bayesian Information Criteron). Lower (i.e., more negative) values for AIC and BIC indicate a better fit of the model to the data. Assuming constant values for the control lakes ("cons") provides a slightly better fit, but the differences between the two models are not statistically significant.

	Df	AIC	BIC	logLik	deviance	Chisq	ChiDF	Pr(>Chisq)
cons	6	1361.5	1379.2	-674.73	1349.5			
vary	7	1362.3	1383.1	-674.17	1348.3	1.1253	1	0.29

Table 7.64: BACI analysis using Method 5 applied to all ANC values in the sensitive lakes (i.e., including within-year variability), holding control lakes' ANC constant. Structure of this table is similar to Method 4 (Table 7.61).

contrast	estimate	SE	p.value
baci	-1.12	12.03	0.93

Table 7.65: ANOVA analysis using Method 5 comparing the fit of two models to all ANC values ("vary", which includes data from the control lakes; and "cons", which holds the control lakes constant). Analysis applied using two information criteria (AIC = Aikike Information Criteron; BIC = Bayesian Information Criteron). Lower (i.e., more negative) values for AIC and BIC indicate a better fit of the model to the data. Assuming constant values for the control lakes ("cons") provides a slightly better fit, but the differences between the two models are not statistically significant.

	Df	AIC	BIC	logLik	deviance	Chisq	ChiDF	Pr(>Chisq)
cons	7	1288.2	1308.9	-637.1	1274.2			
vary	8	1289.6	1313.3	-636.82	1273.6	0.5494	1	0.46

KEY FINDINGS:

- No support for a significant effect in ΔANC (for annual mean Gran ANC or annual individual Gran ANC measurements) when change in control lakes held constant over the time-frame.
- ANOVAs show no difference between models with control lakes varying or held constant over time.
- It is important to continue to monitor the control lakes and use all their actual data in BACI analyses, as this will provide greater power to detect an effect than assuming constant values in the control lakes.

7.6.4.4.6 Method 6 (Frequentist): Using Other Covariates to Explain Inter-Annual Variation

Description of Analyses:

Same as described for SO_4 in Section 7.6.4.2.6, but applied to Gran ANC.

Purpose of analyses:

As described for Method 6 under pH, the previously described analyses intentionally excluded 2013 and 2014 from the baseline period. We did this because the winding down of the old smelter during this period resulted in reduced emissions and apparent increases in Gran ANC in some of the sensitive lakes (Figure 7.41), which would lead to an inaccurate estimate of baseline Gran ANC if we had used 2012-2014 data to compute baseline Gran ANC. If covariates such as emissions and precipitation help to explain variability in water chemistry, then we could potentially include data from 2012-2014 in the baseline period, and have three years of baseline data rather than just one, which, together with three years of post-KMP data (2016-2018) would improve statistical power.

Explanation of the graphs and tables of results:

We used total SO_2 emissions over the prior year (i.e., October 1 through Sept. 30, see Section 7.6.2.3) and the last 3-days or 14-days of precipitation at Haul Road (see Section 7.6.2.2) as covariates. The model also includes terms for three random effects: year, site, and year by site interactions

Table 7.66: Before-After t-test for changes in ANC, including covariates for emissions and 3-day precipitation.

Fixed effects:	Estimate	Std Error	df	Pr(>|t|)
(Intercept)	-47.4	203.7	56	0.817
BAbefore	41.5	80.7	60	0.609
CIimpact	261.4	173.2	27	0.143
Emissions	0.2	0.4	60	0.495
Precipitation (3-day)	-3.3	2.8	62	0.25
BAbefore:CIimpact	-8.8	62.6	60	0.889

Table 7.67: Estimates of the random effects for year, site and year by site interactions.

Random effects:

Groups	Name	Variance	Std.Dev.
YEAR:SITE	(Intercept)	0	0
SITE	(Intercept)	77479	278
YEAR	(Intercept)	0	0
Residual		7155	84.6

Table 7.68: Before-After t-test for changes in ANC, including covariates for emissions and 14-day precipitation.

Fixed effects:	Estimate	Std Error	df	Pr(>|t|)
(Intercept)	-13.8	208.8	8	0.95
BAbefore	18.2	82.2	3	0.84
CIimpact	254.1	174.1	27	0.16
Emissions	0.15	0.4	1	0.75
Precipitation (14-day)	-0.08	1.2	15	0.95
BAbefore:CIimpact	-5.2	63.8	47	0.94

Table 7.69: Estimates of the random effects for year, site and year by site interactions.

Random effects:			
Groups	Name	Variance	Std.Dev.
YEAR:SITE	(Intercept)	0	0
SITE	(Intercept)	78325	279
YEAR	(Intercept)	59.5	7.72
Residual		7262	85.2

KEY FINDINGS:

- Adding covariates for emissions and precipitation do not help explain variability in Gran ANC.
- The sign of the covariates for precipitation are negative, consistent with our expectations from the literature, but the terms are not statistically significant.

7.6.4.4.7 Approach Supportive of Methods 8 and 9 (Frequentist): Temporal Trend Analyses

Description of Analyses:

As explained in Section 7.6.4.2.7 for SO_4.

Table 7.70: Results of the Mann-Kendall non-parametric test for monotonic trend in SO_4 values. No lakes exhibit a significant result for detecting a monotonic trend.

Lake	p.value
LAK006	0.500
LAK012	0.045
LAK022	0.045
LAK023	0.154
LAK028	0.367
LAK042	0.154
LAK044	0.367
LAK007	0.500
LAK016	0.154
LAK024	0.633
LAK034	0.045
NC184	0.769
NC194	0.231
DCAS14A	0.846

KEY FINDINGS:

- None of the lakes' data provide sufficient evidence to reject the null hypothesis that there was no monotonic trend in Gran ANC (i.e., all p values are > 0.01)

7.6.4.4.8 Method 1a (Bayesian): Two-Sample Before-After Bayesian Analysis (Bayesian Estimation Supersedes the T-Test with informative priors) as applied to Gran ANC

Description of Analyses:

As described for pH in Section 7.6.4.3.8.

Purpose of analyses:

The rationale for this analysis is described in Section 7.6.4.3.8 for pH. In this case, the parameter of interest is the ΔGran ANC from the baseline 2012 measurement to the 2016-2018 post-KMP period. The statistical software used for this analysis computes Δ mean ANC as the mean ANC for the baseline period minus the mean ANC for the 2016-2018 post-KMP period. Positive values of this parameter are therefore indicative of an ANC decline.

In the introduction to these analyses in the TOR we stated that if the frequentist approach shows a clear result for a lake (e.g., 99% confidence intervals for ΔANC do not overlap that lake's threshold for ΔANC) then there's no need to proceed with the Bayesian analysis for that parameter in that lake. Using frequentist method 1 for ΔANC, all of the 99% confidence intervals for the seven sensitive lakes overlapped their lake-specific ANC thresholds, so it would be logical to use the Bayesian approach for all seven sensitive lakes. However, with frequentist method 2 for ΔANC, the 99% confidence intervals for ΔANC did not have that overlap their ANC thresholds in four of the six sensitive lakes with multiple samples in October: LAK006, LAK023, LAK042 and LAK044. Using method 2, the 99% confidence intervals for LAK012 and LAK028 did however overlap their lake-specific thresholds. Based on Method 2, we only need to include the Bayesian approach for LAK012 and LAK028. However, we decided to complete the Bayesian approach for all lakes, so that we could see how consistent our inferences would be using different statistical methods.

Explanation of the graphs and tables of results:

See captions below.

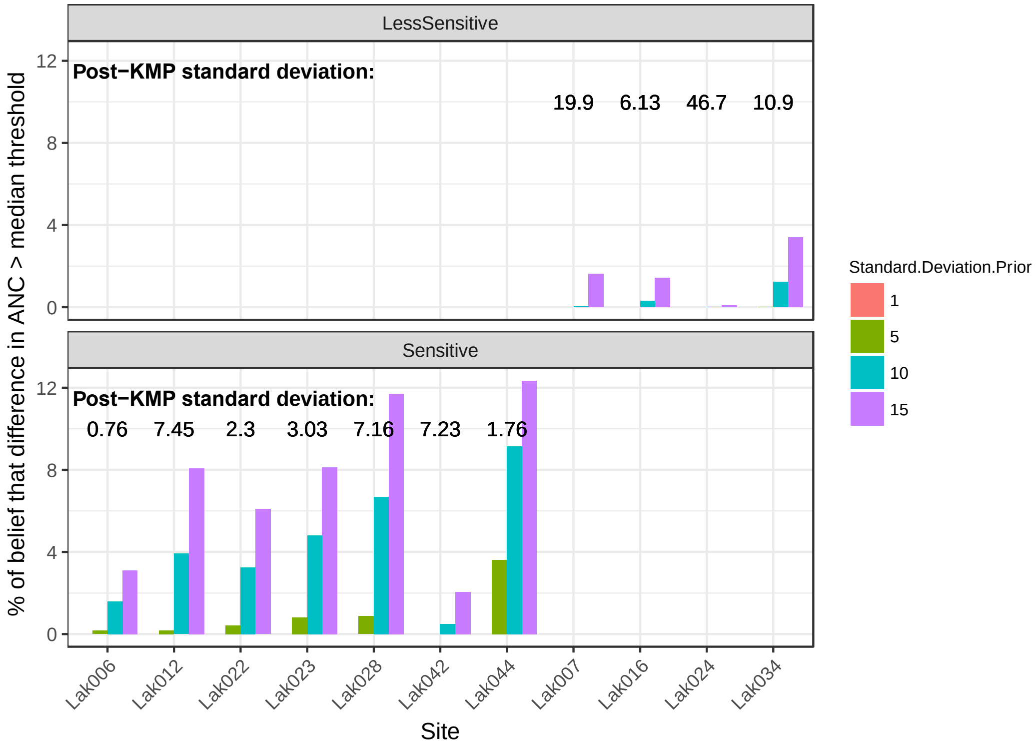


Figure 7.134: Percentage belief that ΔANC is greater than the lake-specific median threshold for ΔANC, using Two-Sample Before-After Bayesian Analysis. The bars show the percentage belief for four different prior assumptions about the standard deviation of Gran ANC across all lakes (note that the orange bars for a SD of 1 μeq/L are too small to be visible on the graphs). The SD of Gran ANC for the post-KMP period is included to provide some context for each lake, but is not directly comparable to the prior assumptions of SD. For example, using an SD prior of 5 μeq/L (green bars), all lakes have less than a 5% belief that ΔANC is greater than their lake-specific thresholds. Using an SD prior of 10 μeq/L (blue bars), all but two lakes have less than a 5% belief that they've exceeded their thresholds for ΔGran ANC. The two exceptions are LAK028 (6% belief that it has exceeded its threshold) and LAK044 (8.5% belief).

7.6.4.4.9 Method 1b (Bayesian): Two-Sample Before-After Bayesian Analysis (with uninformative priors)

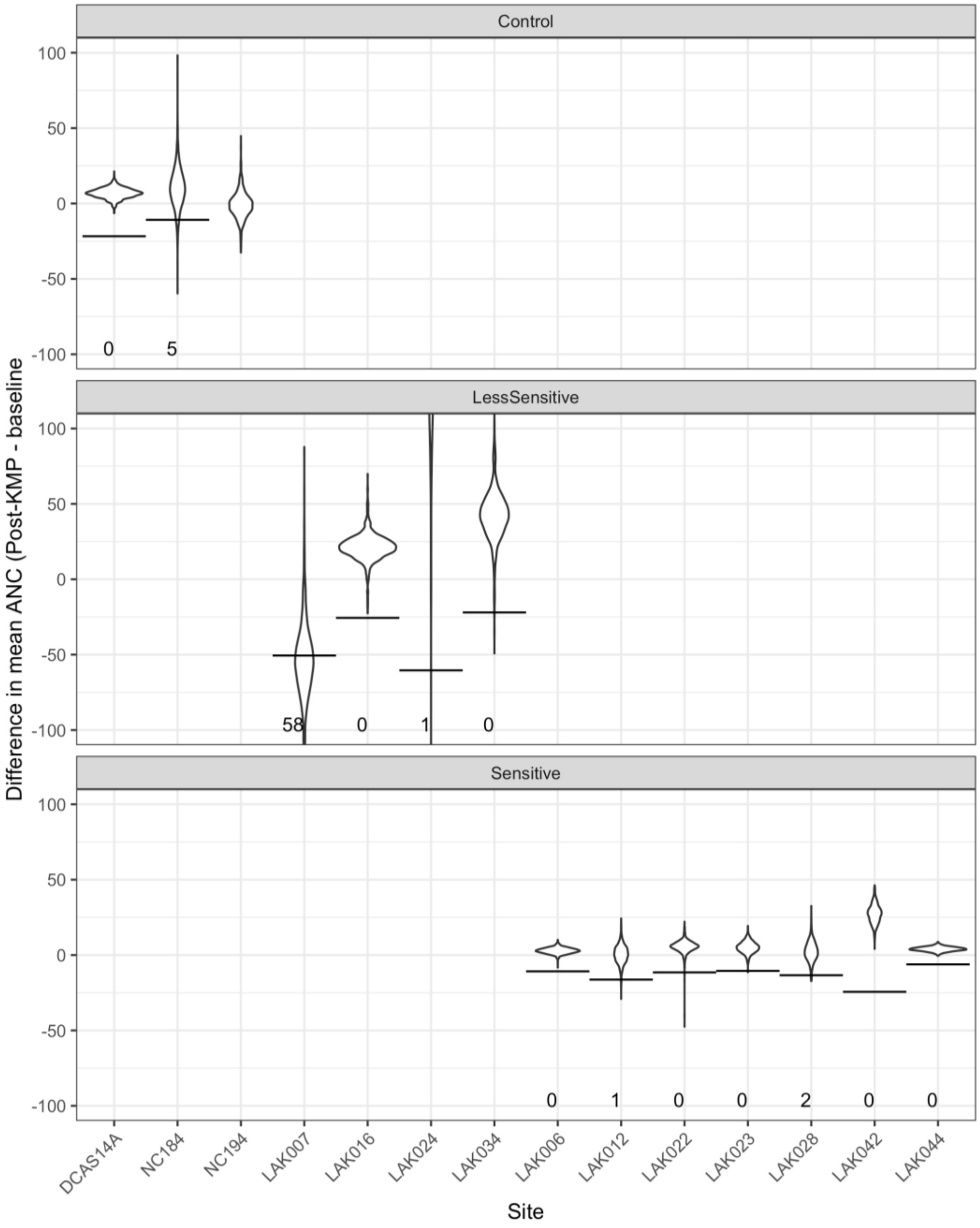


Figure 7.135: Violin plots showing the the posterior distributions of credible values for ΔGran ANC, with no prior assumptions about the variability in GranANC. The percent of these distributions that correspond to a change greater than lake-specific thresholds (dotted line) are shown in numerals at the bottom of each plot.

KEY FINDINGS:

- Minimal % of belief that Δ mean Gran ANC (between baseline and post-KMP periods) is greater than the lake-specific threshold for ΔGran ANC.
- With a low SD prior of 5 μeq/L (Figure 7.134, green bars), all seven sensitive lakes have less than a 5% belief that ΔGran ANC is greater than their lake-specific thresholds.
- With an intermediate SD prior of 10 μeq/L (Figure 7.134, blue bars), only LAK028 and LAK044 exhibit more than a 5% belief that the observed Δ mean Gran ANC is greater than their lake-specific thresholds (6% and 8.5% belief respectively).
- With no prior assumptions about variability in ANC (violin plots in Figure 7.135), 3 of the 4 less sensitive lakes have ≤1% belief that Δ mean Gran ANC is greater than their lake-specific thresholds, while LAK007 has a 58% belief that Δ mean Gran ANC is greater than its lake-specific threshold (note however that LAK007 has very high Gran ANC and shows no significant increase in SO_4 or decrease in pH) so these changes are not related to the smelter.
- All 7 sensitive lakes show ≤ 2% belief that Δ mean Gran ANC is greater than their lake-specific thresholds.

7.6.4.4.10 Method 2 (Bayesian): Two-Sample Before-After Bayesian Analysis, Using Individual Samples

Description of analyses:

This analysis is the Bayesian version of Method 2, taking into account all of the data, and accounting for variability within each year.

Purpose of analyses:

The purpose is similar to Method 1, but Method 2 uses all of the data rather than just the mean values.

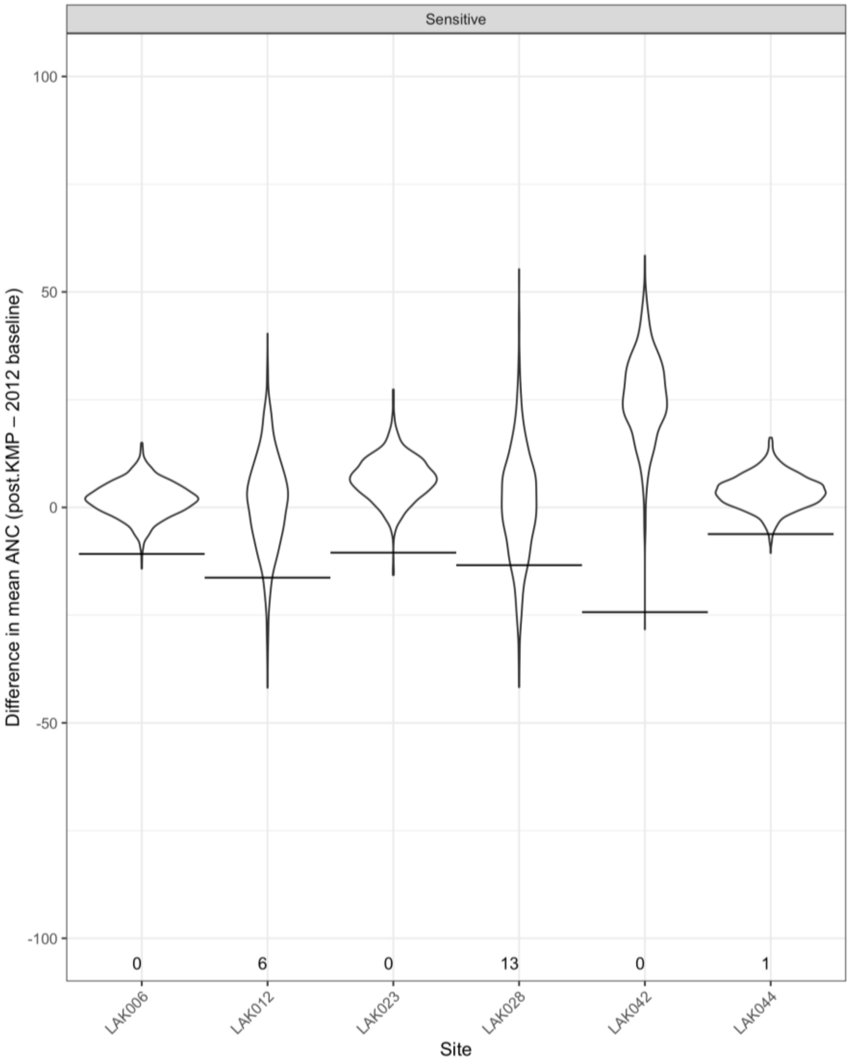


Figure 7.136: Violin plot showing the posterior distributions of credible values for ΔGranANC for the six sensitive lakes with multiple samples per year, with no prior assumptions about the variability in GranANC. The percent of these distributions that correspond to a change greater than the lake-specific threshold (dotted line) are shown in numerals at the bottom of each plot.

KEY FINDINGS:

- Using all of the data under Method 2, two sensitive lakes (LAK012 and LAK028) show a higher % belief that the ΔGran ANC exceeded their lake specific thresholds than was found for either lake in Method 1.
- LAK012 and LAK028, which have shown an increase in SO_4, show 6% and 13% belief that the ΔGran ANC exceeded their lake specific thresholds. These are still low levels of percent belief (< 20%).

7.6.4.5 Analyses of Data from Intensively Monitored Lakes

Starting in 2014, intensive monitoring was implemented in three of the EEM lakes – End Lake (LAK006), Little End Lake (LAK012) and West Lake (LAK023). These three lakes were selected based on being accessible by road, thus making repeated visits much more feasible than for remote lakes requiring access by helicopter or hiking. During the fall of 2014, the intensive monitoring included continuous pH monitors and multiple site visits to collect intra-season water samples for additional lab analyses and pH measurements. In 2015, the continuous pH monitors were deployed from mid-April until mid-November. During October 2015, three additional within-season water chemistry samples were taken at these three lakes, subsequent to annual sampling across all of the lakes (i.e., four samples in total for each of the intensively monitored lakes in 2015). Lake level monitoring was added in 2016-2018 in End Lake, Little End Lake, and West Lake to provide an accurate, local measure of the timing of storm events, so as to better explain observed variation in pH (monitored continuously) and other water quality parameters of interest monitored during October (particularly sulphate, nitrate, DOC, ANC, and base cations).

Continuous pH monitoring has occurred since 2015 in three lakes: LAK006 (End Lake), LAK012 (Little End Lake) and LAK023 (West Lake). From 2015 to 2018, a Manta2 model 2.5 multiprobe was used to take pH measurements every half hour in each of the three intensively monitored lakes. Each meter was recalibrated every two weeks against known buffer solutions (Limnotek 2019). Statistical analyses have shown that the Manta pH measurements were consistently significantly higher that field pH measurements using a WTW ProfilLine 3210 meter and higher than lab analyses of air-equilibrated pH completed at Trent University using an auto-titrator (Limnotek 2019). The cause of these differences was determined to be that the Manta meters' settings did not allow enough time for the pH to stabilize, which can take up to 30 minutes in low ionic strength waters. In addition, by 2019 the Manta meters had reached the end of their expected lifetime. They have since been replaced by Onset pH loggers which compare well with field pH measurements.

Due to the above-described problems, we are not able to make use of the data from the Manta meters. However, we have been able to make use of the calibration data from the fall of 2014 through the summer of 2019, which provide estimates of field pH every two weeks in each of these three lakes. We applied a Seasonal Mann-Kendall test, using average values for each season per year to reduce auto-correlation. The data show trends in field pH in all three lakes (Figure 7.137, Figure 7.138, Figure 7.139), but only the trends in West Lake were statistically significant (Table 7.71). The measurements of field pH were generally lower in the fall than in spring and summer (in 9 out the 12 lake-years of data with spring, summer and fall measurements), and highest in the spring or summer.

There are three important caveats about this analysis: 1) SO_2 emissions declined from 2012 to 2014, and lab pH values increased in each of these three lakes (Figure 7.44*),* so the field pH values in late 2014 and early 2015 are not representative of pre-KMP conditions; 2) field pH values are more variable than lab pH values, due to super saturation of CO_2 in the samples; and 3) lake sulphate declined in West Lake (LAK023) between the pre-KMP and post-KMP periods (see Section 7.6.4.2.1).

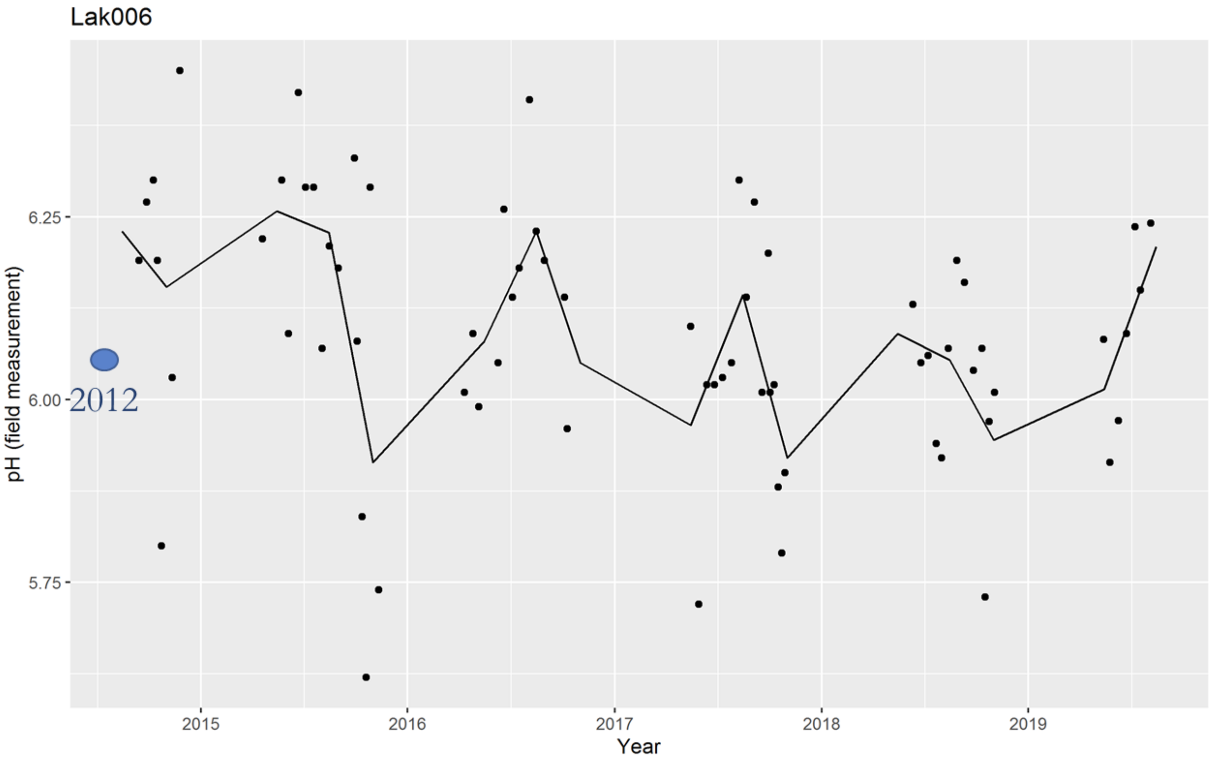


Figure 7.137: Trend in field pH in LAK006 (End Lake). Points shown are the seasonal mean values. The spring mean pH is the average of measurements in April, May, and June. The summer mean pH is the average of measurements in July and August. The fall mean pH was the average of measurements in September, October, and November. Blue dot is the field pH measurement in August of 2012.

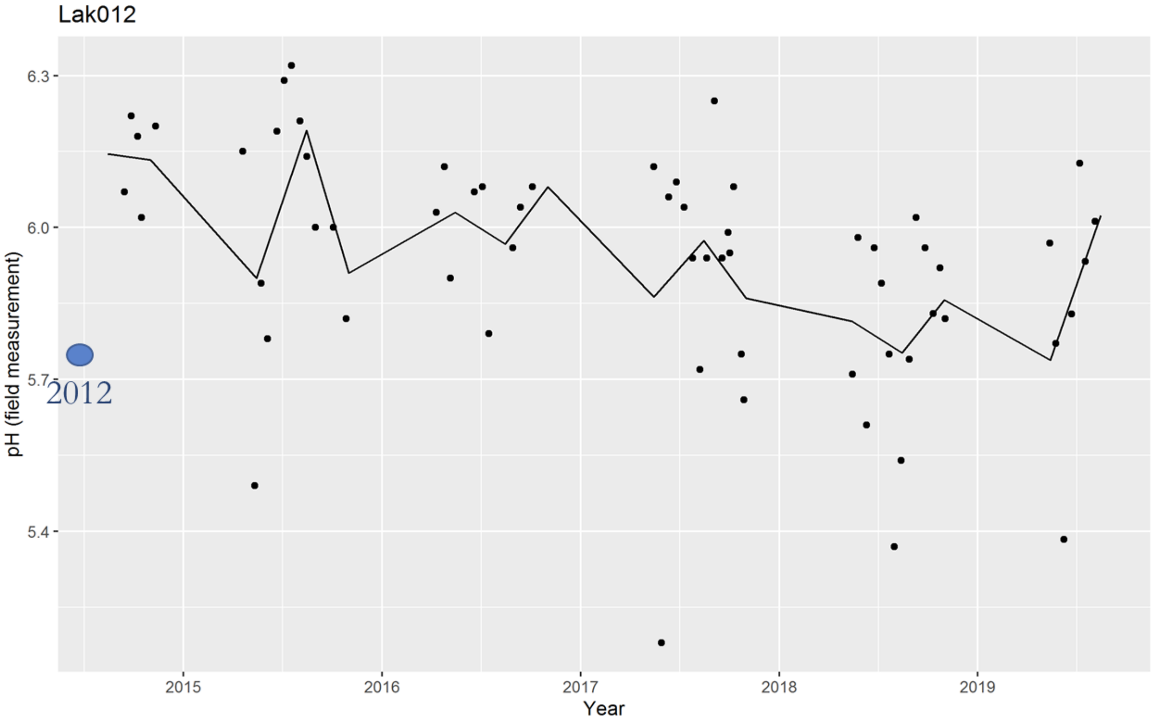


Figure 7.138: Trend in field pH in LAK012 (Little End Lake). Points shown are the seasonal mean values. The spring mean pH is the average of measurements in April, May, and June. The summer mean pH is the average of measurements in July and August. The fall mean pH was the average of measurements in September, October, and November. Blue dot is the field pH measurement in August of 2012.

Figure 7.139: Trend in field pH in LAK023 (West Lake). Points shown are the seasonal mean values. The spring mean pH is the average of measurements in April, May, and June. The summer mean pH is the average of measurements in July and August. The fall mean pH was the average of measurements in September, October, and November. Blue dot is the field pH measurement in August of 2012.

Table 7.71: Results of Seasonal Mann-Kendall tests on the three intensively monitored lakes.

Lake	n	p.value	Sen's Slope (pH/year)	Slope over 5 years
LAK006	17	0.039	-0.052	-0.26
LAK012	17	0.464	-0.048	-0.24
LAK023	17	0.008	-0.023	-0.12

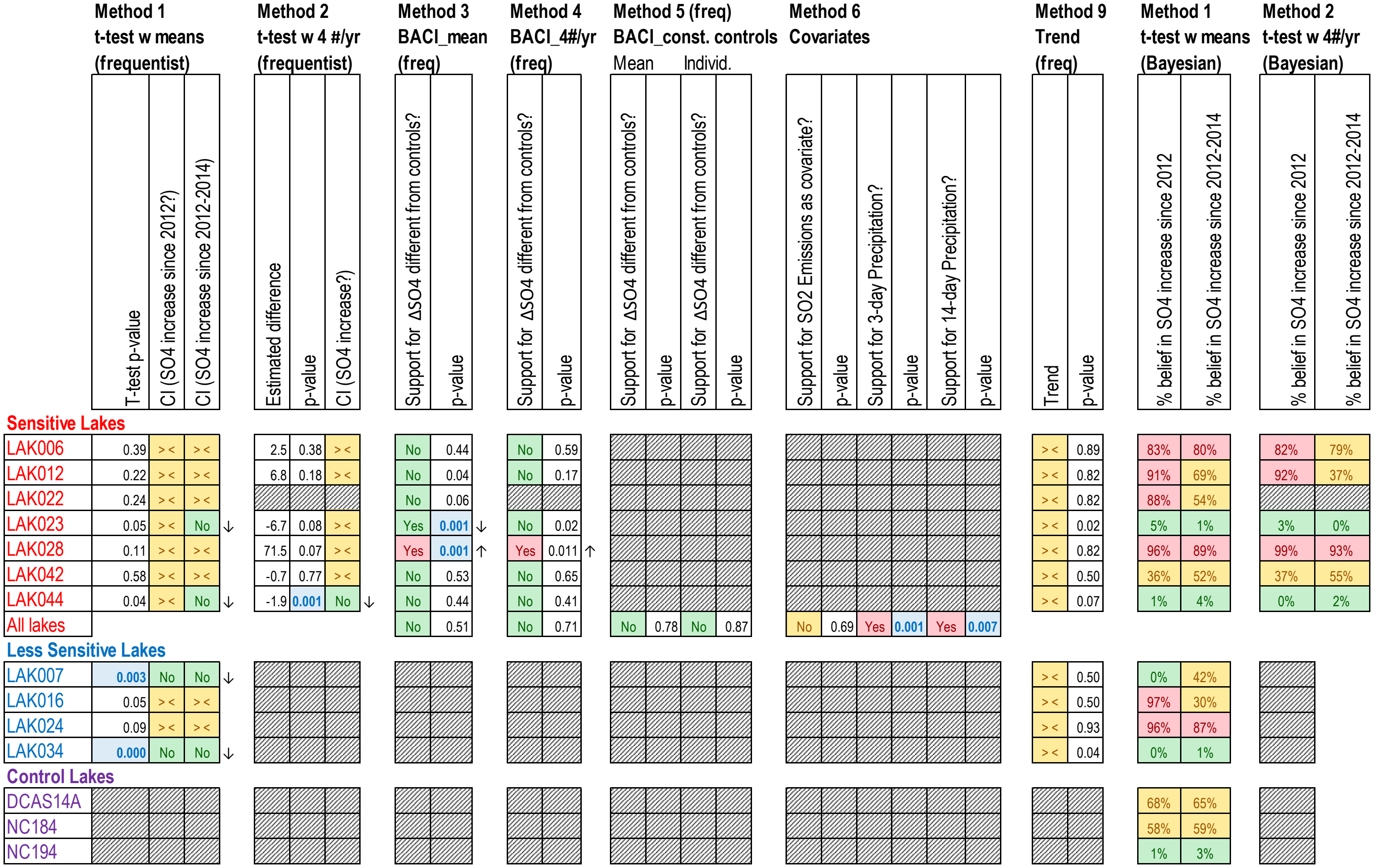
7.6.4.6 Summary of Statistical Analyses

7.6.4.6.1 Summary of Results of the Statistical Analysis Methods Applied

Below we summarize the complete set of statistical analyses of changes in SO_4 (Table 7.72), pH (Table 7.73), and Gran ANC (Table 7.74), based on the annual fall sampling. The order of these tables is important, as illustrated in the simplified evidentiary framework (Figure 7.35). A lake which has limited support for an increase in sulphate (e.g., LAK023, LAK044, LAK007, LAK034, all with % belief < 2%) does not require any further consideration of its changes in pH and ANC, since those chemical changes are not related to SO_2 emissions from the smelter. Of the six lakes which **do** show strong evidence of increases in sulphate (i.e., LAK006, 012, 022, 028, 016, 024), all had limited support for pH declines below the 0.3 threshold (Table 7.73) and limited support for ANC declines below the lake-specific thresholds (Table 7.74).

Table 7.72: Summary of statistical analyses of changes in lake [SO_4] in the EEM lakes.

Statistical Analysis of Changes in SO_4



	Method 1 t-test w means (frequentist)			Method 2 t-test w 4 #/yr (frequentist)			Method 3 BACI_mean (freq)		Method 4 BACI_4#/yr (freq)		Method 5 (freq) BACI_const. controls Mean		Individ.		Method 6 Covariates						Method 9 Trend (freq)		Method 1 t-test w means (Bayesian)		Method 2 t-test w 4#/yr (Bayesian)	
	T-test p-value	CI (SO4 increase since 2012?)	CI (SO4 increase since 2012-2014)	Estimated difference	p-value	CI (SO4 increase?)	Support for ΔSO4 different from controls?	p-value	Support for ΔSO4 different from controls?	p-value	Support for ΔSO4 different from controls?	p-value	Support for ΔSO4 different from controls?	p-value	Support for SO2 Emissions as covariate?	p-value	Support for 3-day Precipitation?	p-value	Support for 14-day Precipitation?	p-value	Trend	p-value	% belief in SO4 increase since 2012	% belief in SO4 increase since 2012-2014	% belief in SO4 increase since 2012	% belief in SO4 increase since 2012-2014
Sensitive Lakes																										
LAK006	0.39	> <	> <	2.5	0.38	> <	No	0.44	No	0.59	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.89	83%	80%	82%	79%
LAK012	0.22	> <	> <	6.8	0.18	> <	No	0.04	No	0.17	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.82	91%	69%	92%	37%
LAK022	0.24	> <	> <	▨	▨	▨	No	0.06	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.82	88%	54%	▨	▨
LAK023	0.05	> <	No ↓	-6.7	0.08	> <	Yes	0.001 ↓	No	0.02	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.02	5%	1%	3%	0%
LAK028	0.11	> <	> <	71.5	0.07	> <	Yes	0.001 ↑	Yes	0.011 ↑	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.82	96%	89%	99%	93%
LAK042	0.58	> <	> <	-0.7	0.77	> <	No	0.53	No	0.65	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	36%	52%	37%	55%
LAK044	0.04	> <	No ↓	-1.9	0.001	No ↓	No	0.44	No	0.41	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.07	1%	4%	0%	2%
All lakes							No	0.51	No	0.71	No	0.78	No	0.87	No	0.69	Yes	0.001	Yes	0.007						
Less Sensitive Lakes																										
LAK007	0.003	No	No ↓	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	0%	42%	▨	
LAK016	0.05	> <	> <	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	97%	30%	▨	
LAK024	0.09	> <	> <	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.93	96%	87%	▨	
LAK034	0.000	No	No ↓	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.04	0%	1%	▨	
Control Lakes																										
DCAS14A	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	68%	65%	▨	
NC184	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	58%	59%	▨	
NC194	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	1%	3%	▨	

🟥 confident increase in SO4 (>80% belief) or statistically significant increase

🟩 confident that SO4 did not increase (<20% belief) or statistically sig't decrease

> < uncertainty with respect to the threshold (20-80% belief) or no trend

▨ n/a

x.xx statistically significant p-value

(↑ = statisticaly significant increase; ↓ = statistically significant decrease)

Table 7.73: Summary of statistical analyses of changes in lake pH in the EEM lakes.

Statistical Analysis of Changes in pH

	Method 1 t-test w means (frequentist)				Method 2 t-test w 4 #/yr (frequentist)				Method 3 BACI_mean (freq)		Method 4 BACI_4#/yr (freq)		Method 5 (freq) BACI_const. controls				Method 6 Covariates						Method 9 Trend (freq)		Method 1 t-test w means (Bayesian)		Method 2 t-test w 4#/yr (Bayesian)	
													Mean		Individ.													
	T-test p-value	CI (pH decline beyond 0.3 theshold?)	CI (pH decline?)	MDD (assuming post-KMP SD)	Estimated difference	p-value	CI (pH decline beyond 0.3 theshold?)	CI (pH decline?)	Support for ΔpH different from controls?	p-value	Support for ΔpH different from controls?	p-value	Support for ΔpH different from controls?	p-value	Support for ΔpH different from controls?	p-value	Support for SO2 Emissions as covariate?	p-value	Support for 3-day Precipitation?	p-value	Support for 14-day Precipitation?	p-value	Trend	p-value	% belief in pH decline beyond 0.3	% belief in pH decline	% belief in pH decline beyond 0.3?	% belief in pH decline
Sensitive Lakes																												
LAK006	0.13	> <	> <	0.6	0.24	0.11	No	> <	No	0.18	No	0.36	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	1%	6%	0%	3%
LAK012	0.03	> <	> <	0.4	0.52	**0.00**	No	No	No	0.013	No	0.076	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.73	1%	1%	0%	0%
LAK022	0.06	No	> <	0.3	▨	▨	▨	▨	No	0.65	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.38	0%	2%	▨	▨
LAK023	0.07	> <	> <	0.3	0.22	0.04	No	No	No	0.28	No	0.453	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.73	1%	3%	0%	1%
LAK028	0.94	> <	> <	1.9	0.02	0.95	> <	> <	No	0.96	No	0.97	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.38	18%	46%	17%	50%
LAK042	0.10	> <	> <	1.2	0.54	0.08	No	> <	No	0.04	No	0.113	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.38	2%	5%	0%	1%
LAK044	0.08	> <	> <	0.3	0.15	0.09	No	No	No	0.53	No	0.645	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	0%	5%	0%	4%
All lakes									No	0.06	No	0.154	No	0.03	No	0.45	No	0.6	No	0.01 [2]	Yes	**0.001** [3]						
Less Sensitive Lakes																												
LAK007	0.71	> <	> <	0.4	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.78	2%	38%	▨	
LAK016	0.06	> <	> <	0.4	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.73	1%	4%	▨	
LAK024	0.09	> <	> <	0.7	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.65	1%	4%	▨	
LAK034	0.02	> <	> <	0.3	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	↓ [1]	0.01	43%	99%	▨	
Control Lakes																												
DCAS14A	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	6%	21%	▨	
NC184	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	28%	47%	▨	
NC194	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	12%	89%	▨	

🟥 confident exceedance of threshold (>80% belief) or statistically significant decline in pH

🟩 confident non-exceedance of threshold (<20% belief) or statistically significant increase in pH

> < uncertainty with respect to the threshold (20-80% belief) or no trend

▨ n/a

x.xx statistically significant p-value

Notes:

[1] Mann-Kendall non-parametric test for LAK034 showed Pr (null hypothesis of no trend in pH) = 0.011; negative trend in pH

[2] P=0.012; estimate = -0.033 (e.g., 3 cm of cumulative precipitation in last 3 days could lower pH by 0.1 units)

[3] P=0.001; estimate = -0.008 (e.g., 12.5 cm of cumulative precipitation in last 14 days could lower pH by 0.1 units)

Table 7.74: Summary of statistical analyses of changes in Gran ANC in the EEM lakes.

Statistical Analysis of Changes in Gran ANC

	Method 1			Method 2				Method 3		Method 4		Method 5 (freq)				Method 6						Method 9		Method 1		Method 2	
	t-test w means			t-test w 4 #/yr				BACI_mean		BACI_4#/yr		BACI_const. controls				Covariates						Trend		t-test w means		t-test w 4#/y	
	(frequentist)			(frequentist)				(freq)		(freq)		Mean		Individ.								(freq)		(Bayesian)		(Bayesian)	
	T-test p-value	CI (ANC decline beyond threshold?)	CI (ANC decline?)	Estimated difference	p-value	CI (ANC decline beyond threshold?)	CI (ANC decline?)	Support for ΔANC different from controls?	p-value	Support for ΔANC different from controls?	p-value	Support for ΔANC different from controls?	p-value	Support for ΔANC different from controls?	p-value	Support for SO2 Emissions as covariate?	p-value	Support for 3-day Precipitation?	p-value	Support for 14-day Precipitation?	p-value	Trend	p-value	% belief in ANC decline beyond threshold	% belief in ANC decline	% belief in ANC decline beyond threshold	% belief in ANC decline
Sensitive Lakes																											
LAK006	0.15	No	> <	2.0	0.56	No	> <	No	0.85	No	0.89	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	0%	6%	0%	30%
LAK012	0.90	> <	> <	1.3	0.90	> <	> <	No	0.81	No	0.86	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.27	1%	46%	6%	44%
LAK022	0.20	> <	> <	▨	▨	▨	▨	No	0.89	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.18	0%	6%	▨	▨
LAK023	0.20	> <	> <	6.7	0.21	No	> <	No	0.72	No	0.78	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	0%	8%	0%	9%
LAK028	0.96	> <	> <	0.4	0.97	> <	> <	No	0.61	No	0.76	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.27	2%	34%	13%	47%
LAK042	0.09	> <	> <	26.0	0.07	No	> <	No	0.02	No	0.07	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.38	0%	0%	0%	1%
LAK044	0.21	> <	> <	3.7	0.30	No	> <	No	0.98	No	0.98	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	0%	0%	1%	16%
All lakes								No	0.28	No	0.55	No	0.7	No	0.93	No	0.32	No	0.73	No	0.52						
Less Sensitive Lakes																											
LAK007	0.15	> <	> <	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.27	58%	97%	▨	
LAK016	0.10	> <	> <	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.50	0%	1%	▨	
LAK024	0.09	> <	> <	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.77	1%	2%	▨	
LAK034	0.09	> <	> <	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	> <	0.12	0%	2%	▨	
Control Lakes																											
DCAS14A	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	0%	3%	▨	
NC184	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	5%	19%	▨	
NC194	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	55%	▨	

🟥 confident exceedance of threshold (>80% belief) or statistically significant decline in ANC
🟩 confident non-exceedance of threshold (<20% belief) or statistically significant increase in ANC
> < uncertainty with respect to the threshold (20-80% belief) or no trend

▨ n/a
x.xx statistically significant p-value

7.6.4.6.2 Summary of Findings of Statistical Analyses

Table 7.75: Summary of findings across all lakes monitored in the EEM program. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F. Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red.

LAKE	Changes in SO_4 (% belief in SO_4 increase / decrease from Bayesian analysis - Method 1 violin plot)	Changes in Gran ANC (% belief that ANC threshold exceeded, from Bayesian analysis - Method 1 violin plot)	Changes in pH (% belief that pH threshold exceeded, from Bayesian analysis - Method 1 violin plot)	OVERALL INTERPRETATION[1]
Sensitive Lakes				
LAK006	83% belief in increase	0%	1%	SO_4 increase; no evidence of S-induced acidification
LAK012	91% belief in increase	1%	1%	SO_4^{2-} increase; some-evidence of S-induced acidification but no evidence of exceeding the ANC or pH thresholds established in the EEM Plan to protect aquatic biota
LAK022	88% belief in increase	0%	0%	SO_4 increase; no evidence of S-induced acidification
LAK023	5% belief in increase	0%	1%	SO_4 decrease; no evidence of S-induced acidification
LAK028	96% belief in increase	2%	18%	SO_4^{2-} increase; some evidence of S-induced acidification; low belief in exceeding the pH threshold and no evidence of exceeding its ANC threshold; conditions were potentially damaging to biota pre-KMP and remained so (see Section 7.3.4.2 in main report).
LAK042	36% belief in increase	0%	2%	No clear change in SO_4; no evidence of S-induced acidification
LAK044	1% belief in increase	0%	0%	SO_4 decrease; no evidence of S-induced acidification
Less Sensitive Lakes				
LAK007	0% belief in increase	58%	2%	SO_4 decrease; no evidence of S-induced acidification
LAK016	97% belief in increase	0%	1%	SO_4 increase; no evidence of S-induced acidification
LAK024	96% belief in increase	1%	1%	SO_4 increase; no evidence of S-induced acidification
LAK034	0% belief in increase	0%	43% [2]	SO_4 decrease; no evidence of S-induced acidification
Control Lakes				
DCAS14A	68% belief in increase[3]	0%	6%	No clear change in SO_4; no evidence of S-induced acidification
NC184	58% belief in negligible increase [3]	5%	28% [4]	No clear change in SO_4; no evidence of S-induced acidification
NC194	1% belief in increase	TBD[5]	12% [4]	SO_4 decrease; no evidence of S-induced acidification

[1] The overall interpretation is also based in part on the level of support for any level of decline in ANC or pH, as are shown in Section 7.6.4.6 of Aquatic Appendix F (see Tables 7.72 and 7.73). Only two lakes show evidence of any level of decline in ANC or pH. LAK028 shows moderate support for declines in ANC and pH (34% belief and 46% belief, respectively) and LAK012 shows moderate support for a decline in ANC only (46% belief), but both of these lakes show no to low support for exceedance of the ANC and pH thresholds (as shown in the table). The coding of these two lakes in this table thus aligns with the results of the Evidentiary Framework.

[2] Not related to S deposition as lake SO_4 has declined in LAK034.

[3] Magnitude of increase in [SO_4] between 2013 and 2016-2018 is very small in NC184 (0.5 μeq/L), and only 4 samples were available for statistical analysis.

[4] Mean pH in NC184 changed from ~5.7 (2013) to ~5.8 (2016-18); Mean pH in NC194 changed from ~6.6 (2013) to ~6.4 (2016-18).

[5] Lake NC194 did not have a lab titration from which we could determine an ANC threshold. It had a 55% belief in an ANC decline (about 6 μeq/L between 2013 and 2016-2018), though very low belief (1%) in a SO_4 increase, so the ANC decline was not related to SO_4.

Applying the simplified evidentiary framework from Figure 7.35 to the entire set of 14 lakes, we obtain Figure 7.140. The results of applying this decision tree are as follows:

- At the first blue decision box (Has lake $[SO_4]$ increased since pre-KMP period?), six lakes are eliminated from further consideration of smelter effects, as there is strong evidence of decreases in their sulphate concentrations: Sensitive lakes 023 and 044; Less Sensitive lakes 007 and 034; Control lakes NC194 and NC184. Control lake DCAS14A is also eliminated from further consideration, as all of the control lakes are well outside of the smelter's plume (see Figure 7.35), and therefore any changes in lake sulphate were not associated with the smelter. In addition, observed increases over time in sulphate were negligible in both NC184 (0.5 µeq/L), and DCAS14A (i.e., 3 µeq/L); Table 7.30. Control lake NC194 showed an observed decrease in sulphate concentrations of 1.1 µeq/L (Table 7.30).
- At the second blue decision box (Has lake pH or Gran ANC decreased since pre-KMP period?), five more lakes are eliminated from further consideration of smelter effects, as there is strong evidence that their pH and Gran ANC concentrations have not declined: Sensitive lakes 006, 022, 042; and Less Sensitive lakes 016, 024. The evidence is insufficient to reject the hypothesis of declines in Gran ANC for sensitive lakes 012 and 028 (46% and 34% belief in an ANC decline, Table 7.74), so they move on to the next part of the decision tree.
- At the third blue decision box, we find that lakes 012 and 028 have not exceeded the thresholds for either pH or Gran ANC (low % belief, see Table 7.75). These lakes should be closely monitored over time. In the ranking of lakes within the EEM Plan (Appendix D in ESSA et al., 2014), both of these lakes were considered to be of low importance.

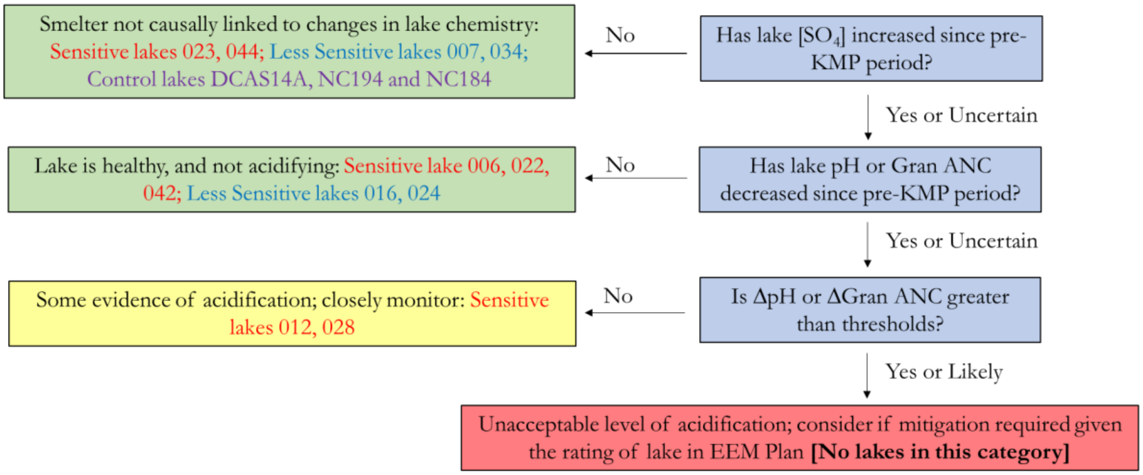
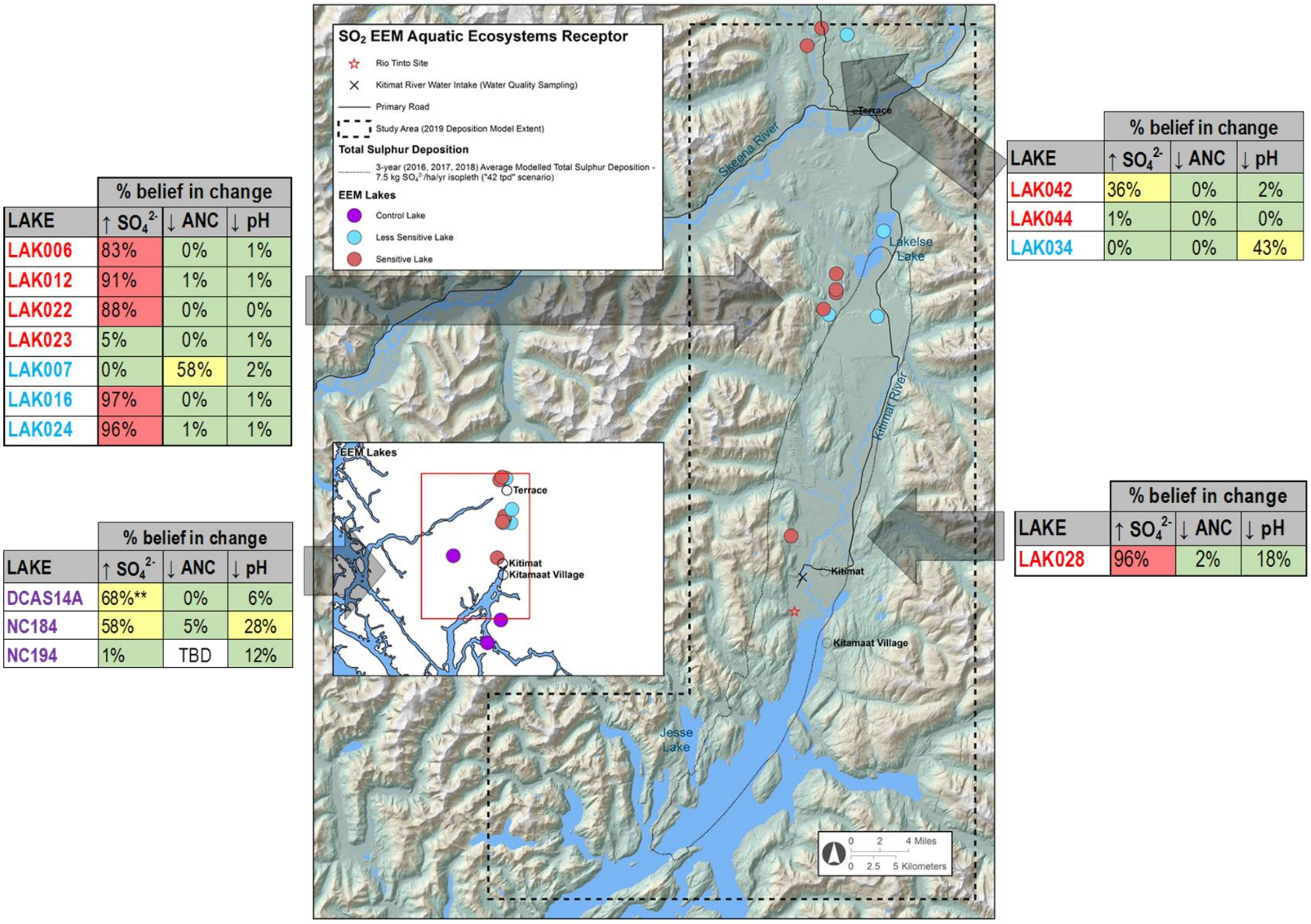


Figure 7.140: Application of the simplified evidentiary framework to the entire set of 14 lakes.

Figure 7.141 summarizes the patterns of change in water chemistry on a map of the study area, so as to elucidate any effects of lake location, specifically distance from the smelter. Six of the eight lakes to the south of Lakelse Lake showed strong evidence of increases in sulphate. It isn't clear why LAK023 and LAK007 were exceptions to this pattern – perhaps they are topographically more isolated from the path of the plume. None of the lakes with strong evidence for increases in sulphate showed any support for changes in pH or Gran ANC beyond the thresholds. Lakes to the north of Terrace (LAK034, LAK044, LAK042) are well outside of the deposition isopleth for 7.5

kg SO_4 / ha / year, consistent with low to intermediate support for sulphate change (0%, 32% and 0% belief, respectively). The control lakes were selected to be well outside of the plume. Two of the control lakes showed intermediate levels of support for increases in sulphate between 2013 and 2016-2018, but the amount of change in sulphate concentrations was very small (Figure 7.36).



LAKE	% belief in change		
	↑ SO_4^{2-}	↓ ANC	↓ pH
LAK006	83%	0%	1%
LAK012	91%	1%	1%
LAK022	88%	0%	0%
LAK023	5%	0%	1%
LAK007	0%	58%	2%
LAK016	97%	0%	1%
LAK024	96%	1%	1%

LAKE	% belief in change		
	↑ SO_4^{2-}	↓ ANC	↓ pH
DCAS14A	68%**	0%	6%
NC184	58%	5%	28%
NC194	1%	TBD	12%

LAKE	% belief in change		
	↑ SO_4^{2-}	↓ ANC	↓ pH
LAK042	36%	0%	2%
LAK044	1%	0%	0%
LAK034	0%	0%	43%

LAKE	% belief in change		
	↑ SO_4^{2-}	↓ ANC	↓ pH
LAK028	96%	2%	18%

Figure 7.141: Spatial distribution of percent belief in chemical change. Numbers show % belief in: a) SO_4^{2-} increase (no threshold), b) pH decrease below 0.3 threshold, and c) ANC decrease below lake-specific ANC threshold. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F. NC194 does not have an estimated ANC threshold because it did not have appropriate titration data available. **The increase in SO_4^{2-} in control lake DCAS014A was only ~3 μeq/L, and only 0.5 μeq/L in NC184. Background deposition of 3.6 kg SO_4^{2-}/ha/yr is not included in the isopleth.

7.6.4.7 Other methods described in the Terms of Reference

7.6.4.7.1 Principal Component Analyses (PCA)

In the TOR we considered using Principle Components Analysis (PCA) on each lake's measurements, and then using the Principle Components in the BACI analysis, and comparing the results to methods 3 and 4. The PCA approach would describe (for each lake) the combination of chemical constituents which explains the greatest amount of variability in the 2012-2018 dataset. The overall form of the results would be similar to methods 3 and 4, but would show the changes in the first principle component, over time and relative to the control lakes. We did not pursue this approach, because we didn't think it would yield any information of incremental benefit. Principle Components are difficult to interpret, and PCA is more helpful for exploratory analysis of multiple metrics to generate hypotheses. In this situation, we have specific questions and hypotheses of interest, as summarized in the simplified evidentiary framework (Figure 7.35), and a strong foundation of acidification literature describing the expected relationships among water chemistry variables in lakes subjected to acidic deposition.

7.6.4.7.2 *Control-Impact Analysis with Three Time Periods*

In the TOR we also considered building on method #6, conducting an analysis with 3 time periods: Before (2012); Transition (2013-2015); and After (2016-2018), using covariates established in method #6. The advantage of this approach would be that having more years gives a better estimate of process error. The overall form of the results would be similar to method 4, but with three time periods (before, transition, after) rather than just two (before, after). Unfortunately, we were not able to pursue this approach, because we found in method #6 that neither emissions nor precipitation covariates were statistically significant in explaining the observed changes in sulphate, pH or Gran ANC. We considered using lake-specific estimates of deposition as covariates (from the revised CALPUFF model), but these are only available for the post-KMP period of 2016-2018 and therefore do not provide sufficient contrast with the pre-KMP period of 2012-2014. CALPUFF modelling of deposition in the STAR did include estimates for the pre-KMP period, but used a different set of meteorological years (2006, 2008, 2009) and had other differences in methodology.

7.6.4.7.3 *Examination of Temporal Trends within Groups of Lakes*

In the TOR we considered examining temporal trends in lake chemistry within groups of lakes (e.g., those closest to the smelter, those at an intermediate distance, and those furthest away). Grouping lakes would provide higher levels of statistical power, and is the approach used by Stoddard et al. (1993, 1996, 1998, 2003) for assessing trends in the northeastern U.S. Due to the paucity of baseline data, analyses of covariance may be helpful in elucidating trends (e.g., Wiens and Parker 1995). We concluded that we did not have enough sensitive lakes (n=7) to apply this approach. The spatial analysis of changes in water chemistry (Figure 7.141) does provide insights on the patterns of changes in lakes at different distances from the smelter.

7.6.5 References Cited

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants, and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Volume 1: Executive Summary for Final Report. Prepared for Rio Tinto Alcan, Kitimat, B.C. pp.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto Alcan, Kitimat, B.C. 99 pp.

ESSA Technologies Ltd. 2016a. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project –2015 Annual Report. Prepared for Rio Tinto Alcan, Kitimat, B.C. pp.

ESSA Technologies Ltd. 2016b. KMP SO_2 EEM Program – Technical Memo W05. Power Analyses Technical Appendix. March 2016. 32 pp.

Kilgour, B.W., K.M. Sommers, D.E. Matthews. 1998. Using the normal range as a criterion for ecological significance in environmental monitoring and assessment. Ecoscience 5(4): 542-550.

Kruschke 2013. BEST - Bayesian Estimation Supersedes T-Test, J Exp. Psychol Gen. 142(2): 573-603

Stoddard, J.L. and J.H. Kellogg. 1993. Trends and patterns in lake acidification in the State of Vermont: evidence from the long-term monitoring project. Water, Air and Soil Pollution 67: 301-317.

Stoddard, J. L., A. D. Newell, N. S. Urquhart, and D. Kugler. 1996. The TIME project design: II. Detection of regional acidification trends. Water Resources Research 32:2529-2538.

Stoddard, J.L., C.T. Driscoll, J.S. Kahl, and J.H. Kellogg. 1998. A regional analysis of lake acidification trends for the northeastern U.S. 1982-1994.

Stoddard, J.L., J.S. Kahl, F.A. Deviney, D.R. DeWalle, C.T. Driscoll, A.T. Herlihy, J.H. Kellogg, P.S. Murdoch, J.R. Webb, and K.E. Webster. 2003. Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990. EPA 620/R-03/001. US Environmental Protection Agency, Office of Research and Development. National Health and Environmental Effects Research Laboratory, Research Triangle Park, NC 27711. 92 pp.

Wigington, Jr. P.J., D. R. DeWalle, P. S. Murdoch, W. A. Kretser, H. A. Simonin,J. Van Sickle, J. P. Baker. 1996. Episodic Acidification of Small Streams in the Northeastern United States: Ionic Controls of Episodes. Ecological Applications, Vol. 6, No. 2 (May, 1996), pp. 389-407 URL: http://www.jstor.org/stable/2269378.

Yan, N.D., W. Keller, N.M. Scully, D.R.S. Lean, and P.J. Dillon. 1996. Increased UV-B penetration in a lake owing to drought-induced acidification. Nature 381:141-143

7.7 Aquatic Appendix G: Critical Loads and Steady-state pH Modeling

This report has been inserted in its original format as a PDF file on the subsequent pages, and as such has different headers and footers from this main appendix file.

Aquatic Appendix G:
Critical Loads and Steady-state pH Modeling

1 Appendix Introduction

The purpose of this appendix is to document and communicate the details of the critical loads modeling and prediction of future steady-state pH of the EEM and STAR lakes under a variety of scenarios. This appendix contains descriptions and results of extensive sensitivity analyses conducted but only the results of the core analyses (i.e., base case and/or "best case") are reported in the aquatic chapter of the main report.

2 Critical Loads and Exceedances

2.1 Introduction / Background

The first major component of the analyses presented in this appendix is the modeling of critical loads and estimation of potential exceedances.

We used the Steady-State Water Chemistry (SSWC) model (Henriksen and Posch 2001, Henriksen et al. 2002 and UNECE 2004) to estimate both the critical loads of acidity for each of the lakes and streams in the study area and the amount (if any) by which these critical loads might be exceeded under scenarios of increased deposition from emissions. We followed closely the implementation of the model as described in Henriksen et al. 2002. Section 8.6.3.4 of the STAR report (ESSA et al. 2013) offers a detailed description of the model application and how its components were adapted for our analyses (i.e., STAR, EEM and Comprehensive Review).

The critical load for each lake or water body measures the amount of acid that could be neutralized by cation exchange and is calculated using hydrological (i.e., average annual runoff), water chemistry (i.e., base cations, F-factor or proportion of incoming acidity neutralized by cation exchange, and the limit of acid neutralizing capacity, ANC, protective for aquatic biota) and pre-KMP sulphate deposition data. These critical load values were then compared with modelled current and potential future sulphur deposition values in order to predict whether the critical loads would be exceeded – i.e., if deposition is higher than the critical load it indicates that the natural buffering or neutralizing capacity of the watershed has been exceeded, which could potentially lead to the acidification of the water body.

We calculated the level of exceedance (if any) of the critical loads estimated in the STAR (or KAA) for every lake within the study area under multiple deposition scenarios. We then generated new, improved estimates of the critical loads for the EEM lakes using the data collected from 2012 to 2018, again calculating the level of exceedance under multiple deposition scenarios. We also conducted a broad set of sensitivity analyses that apply varying assumptions about the model inputs.

2.2 Objectives for Critical Loads Modeling

Critical Loads Objectives:

1. Do the updated modeled emissions show changes in the number and magnitude of exceedances of the CLs estimated in the STAR?
2. How do improved data inputs change the CLs and exceedances originally estimated?
3. For lakes with post-STAR sampling data, what are our best, improved estimates of the CLs?
4. What is the number and magnitude of exceedances of the new CLs under the update deposition scenarios?
5. How sensitive are the new CLs and exceedances for the EEM lakes to the input assumptions?
6. How sensitive are the estimated exceedances to uncertainty in the deposition estimates?

2.3 SSWC Model Inputs

The model inputs for the SSWC model are described below in terms of what improvements are available relative to the data used in the STAR. These data are only described at a very high level so as to communicate the key elements of each input. These inputs are described extensively elsewhere (e.g., STAR, KAA, and/or other receptor/pathway chapters within the Comprehensive Review).

The lakes included in these analyses are: 41 lakes from the STAR (including the 7 sensitive EEM lakes and 4 less sensitive EEM lakes), 8 lakes from the KAA that fall within the CALPUFF model area, and 2 additional lakes sampled as one-off requests during the early years of the EEM.

2.3.1 Lake Chemistry Data

In the STAR, the available lake chemistry data was from a single sampling event in 2012. Similarly, the additional lakes only have lake chemistry data for a single year (i.e., 2013 for the KAA lakes, 2013 for MOE3, and 2014 for MOE6). For the lakes included in the EEM program, we now have six additional years of data, including multiple samples per year for particular lakes and years. In general, the critical load of a lake is a property of the lake that is not expected to change with time – additional years of data can help improve our estimate of the critical load but should not be interpreted as representing a change in the critical load over time. [1] To develop the best estimate of critical load for each of the lakes with additional data (i.e., those within the EEM program), we used all of the annual and/or with-season samples for each lake. As an alternative approach, we used only the post-KMP chemistry data (2016-2018) as a sensitivity analysis.

2.3.2 Runoff Estimates

The runoff estimates used in the STAR were generated from a runoff model that used precipitation data from the historic climate normal period of 1961-1990. In recent years, precipitation has been notably lower than historic levels. Steady-state modeling requires an understanding of long-term average conditions. However, we

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[1] The only exception to this statement would be for a lake that has undergone considerable acidification over the time period of monitoring, such that its watershed base cation supply has been depleted, and its current lake chemistry no longer reflects the future ability of the lake and its watershed to neutralize deposition. In such a situation of rapid change, calculations based on current lake chemistry could lead to an over-estimate of a lake's critical load. This is not the case for any of the EEM lakes. LAK028 (the only lake with evidence of acidification) also showed evidence of acidification in the pre-KMP period. It has not shown subsequent declines in pH or ANC in excess of the established thresholds despite an increase in sulphate and shows no evidence of a declining supply of base cations.

do not yet know if the observed decrease in precipitation will prove to have been only a temporary deviation from the long-term average or a shift in the long-term average. To understand the implications of a longer-term decline in runoff, we revised the STAR estimate of runoff based on the ratio of recent precipitation (2016-2018) to historic precipitation (1961-1990). The table below shows that on average, across the four stations available, the average precipitation in 2016-2018 was 91% of the average precipitation during the reference period upon which the STAR estimate of runoff was based. The sensitivity analyses we conducted used a 10% reduction in precipitation. The table below also shows that the average precipitation in 2010-2012 was not strongly different than the reference period, which suggests that the runoff estimates used in the STAR appear were reasonable to use.

Station Name	**Precipitation**			**No. Months with Recorded Precipitation**		**Change in Precipitation**	
	1961-1990 (Reference) (mm / year)	**2010-2012 (mm / year)**	**2016-2018 (mm / year)**	**2010-2012**	**2016-2018**	**Reference period to 2010-2012**	**Reference period to 2016-2018**
Terrace PCC	1173	1163	1016	36	36	0.99	0.87
Terrace A	1290	NA	1195	0	36	NA	0.93
Kitimat Townnsite	2241	2299	2095	36	36	1.03	0.93
Kitimat 2	2262	2548	1913[a]	32	12[a]	1.13	0.85[a]
AVERAGE	**1741**	**1793[b]**	**1435**	**NA**	**NA**	**1.03[b]**	**0.91**

[a] While 18 months of data were available; the months were not randomly distributed. Only the data for 2018 was retained.
[b] Average for 2010-2012 was calculated as "=(Average(Terrace PCC, Average(Kitimat Townsite, Kitimat 2)))"

2.3.3 F-factor

We used the model-based F-factors estimated during the STAR. For the EEM lakes only, we conducted a sensitivity analysis in which we developed and applied new model-based F-factors using only post-KMP lake chemistry data and estimated runoff – i.e., this represents the F-factor that *would have* been estimated if we only had the recent, post-KMP data. However, we believe that these revised estimates are not as strong as the original estimates because they rely on data from a period in which lake chemistry is dynamically responding to increased deposition. For example, if the F-factor of a particular lake is greater than zero and SO_4 has increased, then we would expect to see an observable increase in base cations, but if we re-estimate the F-factor based on this new chemistry (as per the rules of the SSWC model, see Table 8.6-3, pg. 240 in Volume 2 of the STAR) the higher concentration of base cations would result in a higher F-factor.

Empirical Estimates of F-factor

It may be possible to estimate the F-factor based on observed changes in lake chemistry (i.e., F-factor = $\Delta BC / SO_4$). We expected that even with seven years of monitoring data, the changes in base cations and sulphate were too small relative to the inherent variability in the data to estimate valid F-factors, with the potential exception of LAK028. However, we tested the calculation of an empirical-based F-factor over four different time intervals to a) determine if this generated any valid values (i.e., between 0 and 1), and b) compare such values to the estimates from the STAR and the sensitivity estimates from the 2013 EEM program (see table below).

As shown in the table, most of the empirical estimates do not result in valid values (red in table). As expected, LAK028 is the only lake that consistently resulted in seemingly valid estimates across different intervals. In cases where a lake resulted in a valid value in only one or two of the four time intervals tested, we believe that this result was only due to random chance and does not represent a reasonable estimate of the F-factor. We therefore only applied sensitivity analyses with an empirical-based F-factor for LAK028.

The F-factor is meant to represent soil cation exchange (i.e., deposited hydrogen ions being exchanged for base cations in the watershed. However, there are two other possible explanations for the post-KMP increase in the concentration base cations in LAK028: 1) post-KMP increases in the deposition of base cations that originate from the smelter; and 2) a concentration effect (reduced dilution), due to an almost 20% decrease in precipitation in the post-KMP period at Haul Road site (but not at Lakelse Lake, see section 3.2 of the main report). The first possible explanation (increased emissions of base cations) is not supported by the deposition monitoring results at Haul Road, which showed increased deposition of H^+ and SO_4, but not base cations, between pre-KMP (2013-2015) and post-KMP (2016-2018) periods. The second possible explanation (a concentration effect) might be responsible for ~20% increases in the concentrations of *both* base cations and sulphate at LAK028. But since the F-factor is the ratio of changes in base cations to changes in sulphate, this concentration effect would be present in both the numerator and denominator, and therefore would not affect the estimate of the F-factor.

	Model-based Estimates		**Empirical-based Estimates**			
LAKE	**STAR (2012)**	**EEM (2013)**	**2012 to 2018**	**2012 to avg 2016-18**	**avg 2012-14 to 2018**	**avg 2012-14 to avg 2016-18**
Lak006	0.21	0.20	*3.40*	*4.54*	*4.55*	*8.28*
LAK007	1.00	1.00	*3.03*	*2.16*	*-0.13*	*-1.49*
LAK012	0.40	0.36	*-1.81*	*-1.35*	*-2.82*	*-2.04*
LAK016	0.56	0.56	*2.77*	*2.44*	*-4.36*	*-2.27*
LAK022	0.32	0.35	*1.68*	*1.93*	*2.66*	*17.46*
LAK023	0.23	0.22	*-1.93*	*-1.02*	*-0.89*	*-0.38*
LAK024	1.00	▨	*14.37*	*15.52*	*14.66*	*16.85*
LAK028	0.44	0.69	0.85	0.89	0.65	0.85
LAK034	0.55	0.68	0.75	0.44	*2.22*	*1.92*
LAK042	0.13	0.14	*45.77*	*-14.81*	0.15	*61.04*
LAK044	0.04	0.04	*-1.99*	*-2.10*	*-1.75*	*-1.93*

2.3.4 Pre-industrial Sulphate - $SO_{4\,o}$

In the STAR, we estimated pre-industrial sulphate as the difference between observed and expected lake sulphate ($SO_{4\,o} = SO_{4\,t} - SO_{4\,exp}$), where expected sulphate was based on current sulphur deposition (as sulphate) and runoff ($SO_{4\,exp}$ = S_dep / Q). This method is based on the assumption that sulphur deposition and lake chemistry are currently in equilibrium. However, we do not believe this has been the case in the first few post-KMP years and therefore have continued to use the estimates from the STAR. We believe this is the most defensible approach as lake chemistry was likely to have been in greater equilibrium with deposition during the STAR since it did not follow an abrupt change.

2.3.5 Critical ANC Limit

As in the STAR, we determined the critical ANC limit by fitting the Small and Sutton (1986) model to the regional laboratory pH and Gran ANC to define the relationship between pH and ANC and then identify the ANC level equivalent to pH = 6.0. However, as compared to the STAR, we have much more data – we used all the data from the STAR lakes plus all the lake samples collected during 2013-2018. Whereas the STAR had 61 data points (41 lakes and 20 streams) with which to characterize the regional pH-ANC relationship, we now have 270 data points with valid data. Similar to the STAR we also tested the “modified Small and Sutton curve” as developed by Marmorek et al. (1996) to account for the influence of DOC on pH; however, we again found that the modified version did not fit the data any better than the unmodified and therefore used the unmodified version. The results are shown in Figure 2-1. An $\mathrm{ANC_{limit}}$ of 31 µeq/L corresponds to a pH of 6.0.

The fitted equation is:

$$pH = 5.259 + \frac{1}{ln\,10} arcsinh\left[\frac{(Gran\ ANC) - 2.071}{10.731}\right]$$

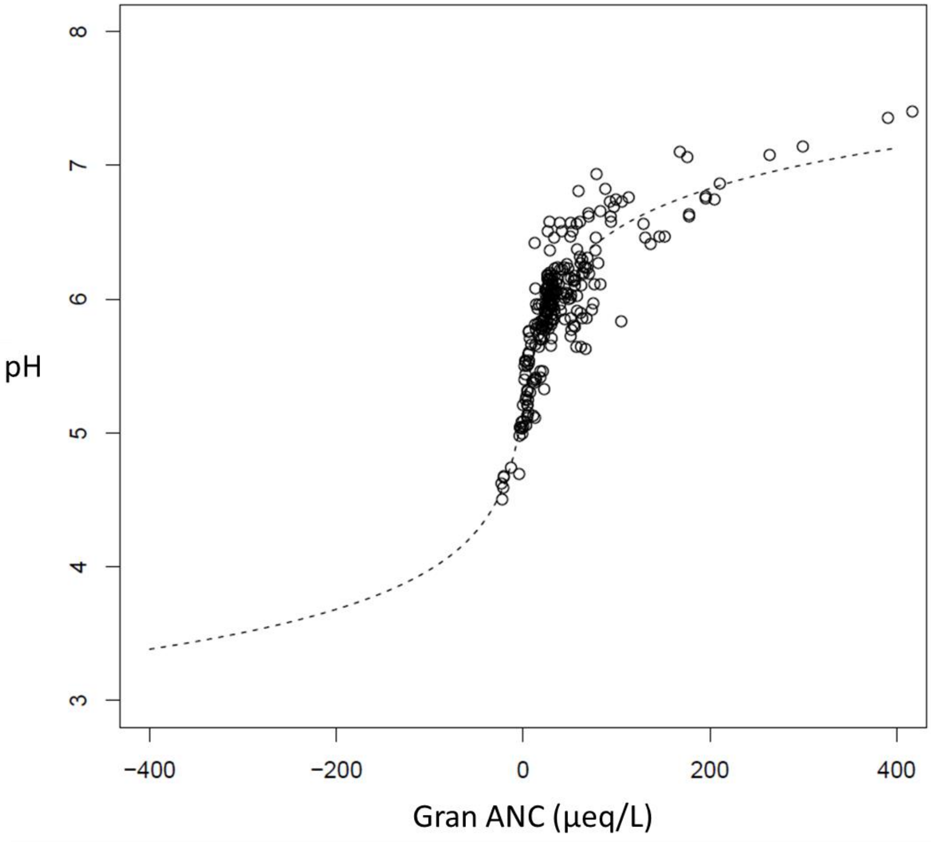

Figure 2-1. Application of the Small and Sutton (1986) equation to Gran ANC and lab pH data from 270 lake samples from STAR and EEM lakes and KAA lakes within the study boundary. An $\mathrm{ANC_{limit}}$ of 31 µeq/L corresponds to a pH of 6.0.

Using $\mathrm{ANC_{OAA}}$

We explored the possibility of using an alternative critical ANC limit based on $\mathrm{ANC_{OAA}}$. Based on the ANC literature review in Aquatic Appendix B, a threshold of $\mathrm{ANC_{OAA}}$ = 25 µeq/L would be appropriate to use as an ANC critical limit. However, because this limit is lower than the ANC critical limit identified above, it would result in the estimation of higher critical loads and therefore lower exceedances (see description of SSWC model in Table 8.6-3, pg. 240 in Volume 2 of the STAR). But because the values are not highly different (25 μeq/L vs. 31 μeq/L), the absolute differences in the estimated critical loads and exceedances would not be expected to be substantially different. Therefore rather than recalculate the critical loads and exceedances with both critical limits we decided to simply apply the 31 μeq/L critical limit only as the more conservative of the two (i.e., evaluating the potential impacts on aquatic ecosystems using the higher critical limit that results in lower estimates of critical loads and higher exceedances is a more cautious approach).

2.3.6 Sulphur Deposition Estimates

We applied the new sulphur deposition estimates as derived from the updated CALPUFF modelling for three emissions scenarios (as described in Section 3). The three emissions scenarios are intended to represent: 1) actual current emissions (29.3 tpd SO_2), 2) likely future emissions (35 tpd SO_2), and 3) the maximum emissions under the permit (42 tpd). For each scenario, we used the gridded output from the CALPUFF model to estimate the area-weighted deposition within the watershed of each study lake, as per the methodology applied in the STAR and KAA.

As described in Section 3, we compared CALPUFF model estimates to the empirical observations from installed monitors to assess the level of agreement. The results showed that there can be substantial differences between the modelled estimates and the empirical observations at particular locations. To explicitly consider the potential impact of uncertainty in the CALPUFF model, we conducted sensitivity analyses with deposition values that were half or double the estimated levels.

The "pre-KMP" and "post-KMP" deposition estimates from the STAR are also referenced and/or used in limited places, as appropriate.

2.3.6.1 Background Sulphur Deposition

We added background sulphur deposition to the CALPUFF estimates of deposition. We used a value of 7.5 meq/m^2/yr, consistent with other chapters in the Comprehensive Review. The context and support for this value is provided in Terrestrial Ecosystems Appendix section titled "Background Sulphur Deposition".

2.3.7 Summary of Model Inputs

The model inputs described above are summarized in Table 2-1, differentiating among STAR inputs, improved inputs, and potential alternatives.

Table 2-1. Model inputs for SSWC model, as used in the STAR plus updated data now available for improved estimates and/or sensitivity analyses.

	What was used in STAR	Updated / Improved Data	Sensitivity Analyses
Lake Chemistry	• 2012 lake data (2013 for KAA lakes)	• 2012-2018 lake data *[EEM lakes only]*	• 2016-2018 lake data *[EEM lakes only]*
Run-off	• STAR runoff		• STAR runoff scaled based on 2016-18 precipitation
F-factor	• Model-based (STAR estimates)		• Model-based (revised runoff, 2016-18 chemistry) *[EEM lakes only]*
$SO_{4\,o}$	• Model-based (STAR estimates)		
ANC limit	• STAR regional pH-ANC curve (@ pH=6)	• Updated regional pH-ANC curve (@ pH=6)	
Deposition estimates	2012 CALPUFF modeling based on 2006, 2008, 2009: • Pre-KMP • Post-KMP	2019 CALPUFF modeling based on 2016-2018 • 29.3 tpd (actual current) • 35 tpd (likely future) • 42 tpd (permit limit)	• 0.5x modeled deposition • 2.0x modeled deposition

2.4 SSWC Model Scenarios and Sensitivity Analyses

This section outlines the SSWC model scenarios and sensitivity analyses run to address each of the critical loads objectives. The table below gives a high-level overview of the types of model scenarios run for the extensive and intensive sets of lakes and the deposition scenarios used in each case.

Set of Lakes	Critical Loads	Exceedances (deposition scenarios)
All STAR lakes (and add'l KAA lakes in study area)	Base case - original STAR CLs	29.3 tpd, 35 tpd, 42 tpd
	Sensitivity analyses	29.3 tpd
EEM lakes	Base case – new CLs with best updated data	29.3 tpd, 35 tpd, 42 tpd
	Sensitivity analyses	42 tpd

2.4.1 Exceedance of STAR (and revised) Critical Loads for ALL lakes

Critical Loads Objective 1: Do the updated modeled emissions show changes in the number and magnitude of exceedances of the CLs estimated in the STAR?

SSWC CL Run #1 → original STAR (and KAA) CLs ("BASE CASE")

Exceedances → evaluated under all 3 deposition scenarios

Critical Loads Objective 2: How do improved data inputs change the CLs and exceedances originally estimated?

SSWC CL Run #2 (sensitivity) → BASE CASE + revised (lower) runoff

SSWC CL Run #3 (sensitivity) → BASE CASE + revised ANC limit based on updated pH-ANC rel'n

Exceedances → evaluated under actual current emissions scenario (29.3 tpd)

2.4.2 New Estimates of Critical Loads and Exceedances for EEM lakes only

Critical Loads Objective 3: For lakes with post-STAR sampling data, what are our best, improved estimates of the CLs?

SSWC CL Run #4 → new CLs with most defensible inputs ("BEST CASE")

The following table indicates the data inputs used to develop the "BEST CASE" new estimates for the CLs of the EEM lakes. The rationale for each selection is discussed in Section 2.3 above.

Data to use for "BEST CASE"	
Lakes	• EEM lakes (sensitive, less sensitive)
Lake Chemistry	• 2012-18 lake data
Run-off	• STAR runoff
F-factor	• STAR model estimate
$SO_{4\,o}$	• Model-based (STAR estimates)
ANC limit	• Updated pH-ANC curve (@ pH=6)

Critical Loads Objective 4: What is the number and magnitude of exceedances of the new CLs under the update deposition scenarios?

Exceedances → BEST CASE CLs evaluated under all 3 deposition scenarios

Critical Loads Objective 5: How sensitive are the new CLs and exceedances for the EEM lakes to the input assumptions?

SSWC CL Run #5 (sensitivity) → BEST CASE + 2016-2018 lake chemistry data

SSWC CL Run #6 (sensitivity) → BEST CASE + revised (lower) runoff

SSWC CL Run #7 (sensitivity) → BEST CASE + revised F-factor

SSWC CL Run #9 (sensitivity) → BEST CASE + original ANC limit

Exceedances → SSWC CL Runs #5-#9 evaluated under "permit" scenario (42 tpd)

2.4.3 Summary of Critical Loads Model Scenarios and Sensitivity Analyses

The table below provides a visual summary of all the SSWC model scenarios and sensitivity runs described in the previous sections. There are two "base cases" (denoted by the green columns) – one that is applicable to the entire set of STAR and additional lakes, and one that is applicable only to the EEM lakes. The data inputs used in each base case are marked with **black 'X's** whereas the **red 'X's** indicate the changes from the base case, as applied in various sensitivity analyses.

		STAR CLs with new deposition (All lakes)			New CLs calculated from present (EEM lakes only)				
Model Input	**Data Set / Method**	**STAR CLs – original, unmodified**	**STAR CLs – revised run-off**	**STAR CLs – revised ANC limit**	**NEW CLs – with best inputs**	**NEW CLs – post-KMP lake chemistry**	**NEW CLs – revised run-off**	**NEW CLs – alternate F-factor**	**NEW CLs – original ANC limit**
Estimation of CRITICAL LOADS (different versions with varying inputs)									
Lakes	All lakes	X	X	X					
	EEM lakes				X	X	X	X	X
Lake Chemistry	2012 lake data	X	X	X					
	2012-2018 lake data				X		X	X	X
	2016-2018 lake data					X			
Run-off	STAR (higher) runoff	X		X	X	X		X	X
	Revised (lower) runoff		X				X		
F-factor	Model-based (STAR estimate)	X	X	X	X	X	X		X
	Model-based (revised runoff, new chem.)							X	
ANC limit	STAR pH-ANC curve (@ pH=6)	X	X						X
	Updated pH-ANC curve (@ pH=6)			X	X	X	X	X	
Estimation of EXCEEDANCES of critical loads under each emissions scenario									
Deposition estimates	29.3 tpd (actual current)	✓	✓	✓	✓				
	35 tpd (likely future)	✓			✓				
	42 tpd (permit limit)	✓			✓	✓	✓	✓	✓

2.4.4 Sensitivity Analyses on CALPUFF Modeled Deposition Estimates

Critical Loads Objective 6: How sensitive are the estimated exceedances to uncertainty in the deposition estimates?

As discussed under the model inputs, we applied sensitivity analyses on the CALPUFF deposition estimates of 50% and 200% to assess the impact of uncertainty in the deposition modeling on the calculated exceedances. We conducted these sensitivity analyses on: a) exceedances of the base case critical loads for all lakes under current deposition levels, and b) exceedances of the best case critical loads for the EEM lakes under maximum future deposition levels, i.e.:

Ex(A) for SSWC CL Run #1 under 29.3 tpd & 42 tpd, uncertainty factors of 0.5, 1.0, 2.0

Ex(A) for SSWC CL Run #4 under 29.3 tpd & 42 tpd, uncertainty factors of 0.5, 1.0, 2.0

2.5 SSWC Model Results

2.5.1 Exceedance of STAR (and revised) Critical Loads for ALL lakes

2.5.1.1 Base Case

Exceedances of the base case (i.e., original critical loads as calculated in the STAR and/or KAA based on initial sampling in 2012 or 2013 only) under current deposition are shown in Table 2-2 and mapped in Figure 2-3.

Seven lakes show exceedances of those original critical loads. Of these seven lakes, five lakes have critical loads of zero (LAK044, LAK047, LAK054, DCAS09A, DCAS09B) and one lake has a critical load very near to zero (1.2 meq/m^2/yr; LAK056).

The number of exceedances does not change with the deposition scenario used and the magnitude of exceedance changes by a relatively small amount, especially relative to the difference with the STAR results. Under the STAR's "post-KMP" deposition estimates (based on the 42 tpd SO_2 emissions permit limit), there were three additional lakes with predicted exceedances that are no longer predicted to have exceedances. Even with the inclusion of background deposition (which was not accounted for in the STAR), these three lakes are not predicted to have exceedances under any of the new emissions scenarios.

Note that the KAA study did not have a specific equivalent post-KMP emissions scenario that isolated the operation of the smelter from increases in other regional emissions sources, therefore are only "post-KMP" results for the lakes that were part of the STAR.

Table 2-2. Original critical loads for the STAR and KAA lakes within the study area and exceedances under different emissions scenarios. Red cells indicate lakes with critical loads of zero and/or positive exceedances under a particular deposition scenario. Exceedances reported in the STAR under the "post-KMP" scenario are included for comparison. Note that the STAR "post-KMP" scenario did not include background deposition, whereas the exceedances estimated under the three new deposition scenarios do include background deposition of 7.5 meq/m^2/yr. Exceedances are calculated based on sulphur deposition values (dominant factor) and nitrate leaching (minor factor), which is not shown in the table.

Lake	Years used for CL	Critical Load (meq/m^2/yr)	Sulphur Deposition (under 29.3 tpd scenario)		Exceedance under different emissions scenarios (meq/m^2/yr)			
			(meq/m^2/yr)	(kg/ha/yr)	29.3 tpd	35 tpd	42 tpd	STAR "post-KMP"
EEM Sensitive Lakes								
LAK006	2012	28.4	8.9	4.3	-11.9	-10.5	-8.5	14.3
LAK012	2012	79.4	8.5	4.1	-63.1	-61.8	-59.9	-37.5
LAK022	2012	53.9	8.1	3.9	-38.0	-36.8	-34.9	-12.3
LAK023	2012	31.9	8.0	3.9	-16.1	-14.9	-13.1	9.1
LAK028	2012	47.5	47.0	22.6	7.6	13.6	24.2	49.8
LAK042	2012	15.9	2.4	1.2	-5.6	-5.2	-4.6	0.2
LAK044	2012	0.0	2.2	1.0	9.8	10.7	11.3	16.7
EEM Less Sensitive Lakes								
LAK007	2012	1393.5	15.7	7.5	-1369.8	-1367.1	-1363.4	-1358.4
LAK016	2012	115.6	9.6	4.6	-98.2	-96.8	-94.6	-71.0
LAK024	2012	370.0	8.4	4.0	-353.9	-352.4	-350.4	-347.6
LAK034	2012	124.7	3.2	1.5	-113.7	-113.0	-112.2	-105.5
Other STAR Lakes								
LAK001	2012	602.7	6.4	3.1	-588.5	-587.5	-586.0	-568.7
LAK002	2012	113.2	7.3	3.5	-98.1	-96.9	-95.2	-78.6
LAK003	2012	504.3	26.0	12.5	-470.5	-466.4	-460.3	-433.4
LAK004	2012	205.2	5.4	2.6	-192.0	-191.1	-189.8	-173.5
LAK005	2012	113.7	10.7	5.2	-95.3	-93.7	-91.2	-66.6
LAK008	2012	1696.9	15.0	7.2	-1673.9	-1671.5	-1668.0	-1650.2
LAK011	2012	99.3	4.9	2.3	-86.8	-86.0	-84.9	-70.2
LAK013	2012	720.6	9.3	4.5	-703.6	-702.1	-699.9	-687.0
LAK014	2012	110.9	9.2	4.4	-94.0	-92.7	-90.5	-68.1
LAK015	2012	225.6	26.5	12.7	-190.1	-185.4	-179.1	-162.3
LAK017	2012	231.7	21.7	10.4	-201.8	-198.0	-192.8	-198.5
LAK018	2012	1473.9	16.1	7.7	-1449.2	-1446.4	-1442.6	-1439.5
LAK027	2012	253.9	32.3	15.5	-214.0	-210.1	-202.8	-167.7
LAK030	2012	793.7	48.8	23.4	-730.0	-724.9	-714.1	-669.1
LAK032	2012	948.8	2.5	1.2	-938.5	-938.0	-937.4	-932.3
LAK035	2012	91.1	4.6	2.2	-78.7	-77.8	-76.7	-74.2
LAK037	2012	134.5	4.6	2.2	-122.1	-121.3	-120.3	-115.1
LAK038	2012	178.3	4.9	2.4	-165.7	-164.8	-163.7	-158.7
LAK039	2012	98.3	4.7	2.3	-85.9	-85.1	-84.1	-79.4
LAK041	2012	54.2	1.2	0.6	-44.3	-44.1	-43.8	-47.8
LAK045	2012	227.0	1.4	0.7	-215.9	-215.6	-215.3	-220.1
LAK047	2012	0.0	1.8	0.9	11.4	11.7	12.1	10.3
LAK049	2012	234.8	2.0	1.0	-223.1	-222.7	-222.2	-222.3
LAK050	2012	117.3	1.5	0.7	-103.7	-103.4	-103.0	-105.5
LAK051	2012	236.4	2.3	1.1	-226.3	-225.8	-225.3	-225.0
LAK053	2012	102.8	6.5	3.1	-87.8	-86.1	-84.5	-91.3
LAK054	2012	0.0	14.5	7.0	23.0	25.2	28.5	14.9
LAK055	2012	120.3	13.0	6.2	-99.4	-97.4	-94.5	-107.2
LAK056	2012	1.2	12.8	6.1	19.8	21.6	24.6	12.4
LAK057	2012	420.7	13.0	6.3	-399.1	-397.2	-394.2	-407.0
KAA Lakes Located within 2019 Deposition Modeling Area								
MOE3	2013	617.0	6.7	3.2	-601.8	-600.8	-599.3	
DCAS10A	2013	44.4	1.7	0.8	-34.3	-34.0	-33.6	
DCAS10B	2013	35.2	1.7	0.8	-25.1	-24.8	-24.4	
DCAS17A	2013	431.9	3.6	1.7	-420.1	-419.4	-418.5	
DCAS02C	2013	75.1	3.6	1.7	-63.6	-62.2	-61.2	

DCAS07A	2013	0.0	2.2	1.1	11.1	12.0	12.6	
DCAS07B	2013	0.0	2.4	1.1	11.3	12.2	12.9	
DCAS09A	2013	71.9	2.4	1.2	-55.4	-54.4	-53.7	
DCAS09B	2013	29.1	2.3	1.1	-18.2	-17.2	-16.6	
Additional Lakes Sampled During EEM								
MOE6[2]	2014	414.1	24.6	11.8	-388.1	-384.6	-379.1	

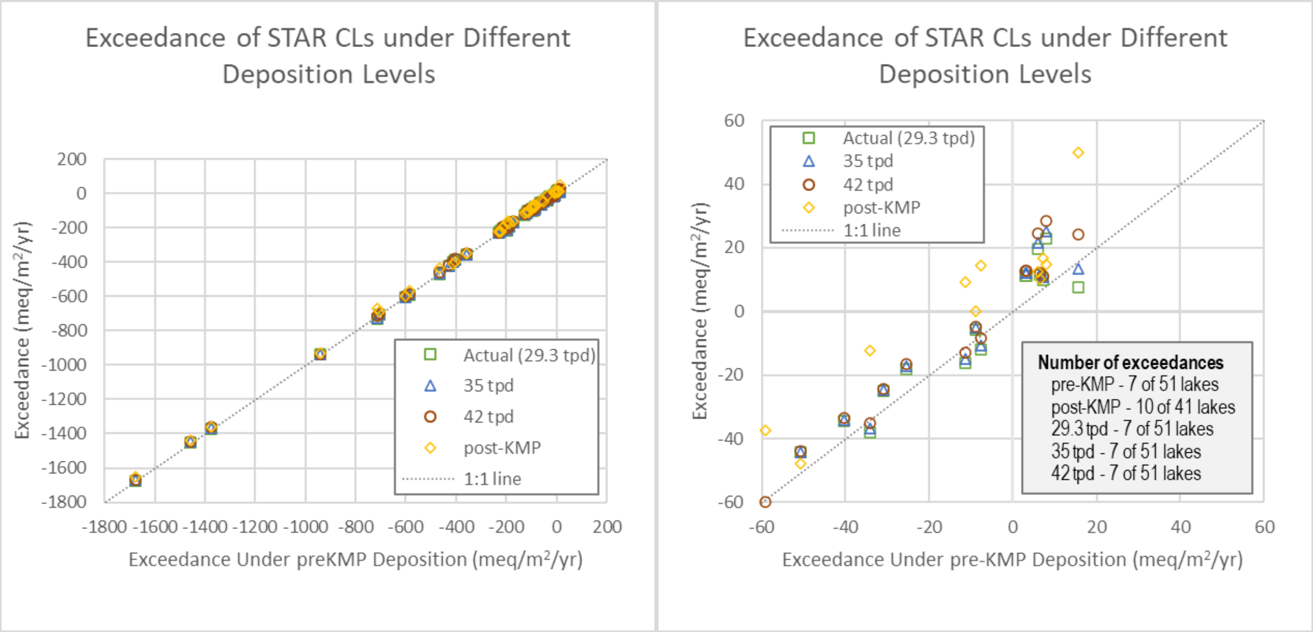

Figure 2-2. Exceedances of original STAR (or KAA) critical loads under different emissions scenarios (. The two panels show the same data, but the right-hand panel is focused on the distribution of lakes near Ex=0. As described in the text, there are nine lakes that do not have "post-KMP" results from earlier work.

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[2] A critical load was not previously calculated for MOE6 (see 2013/14 Annual Report). However, this critical load was calculated using the same approach and data as applied to the STAR or KAA lakes, which assumes the pre-KMP deposition data used to estimate original sulphate is still appropriate to use even though this lake was sampled in 2014.

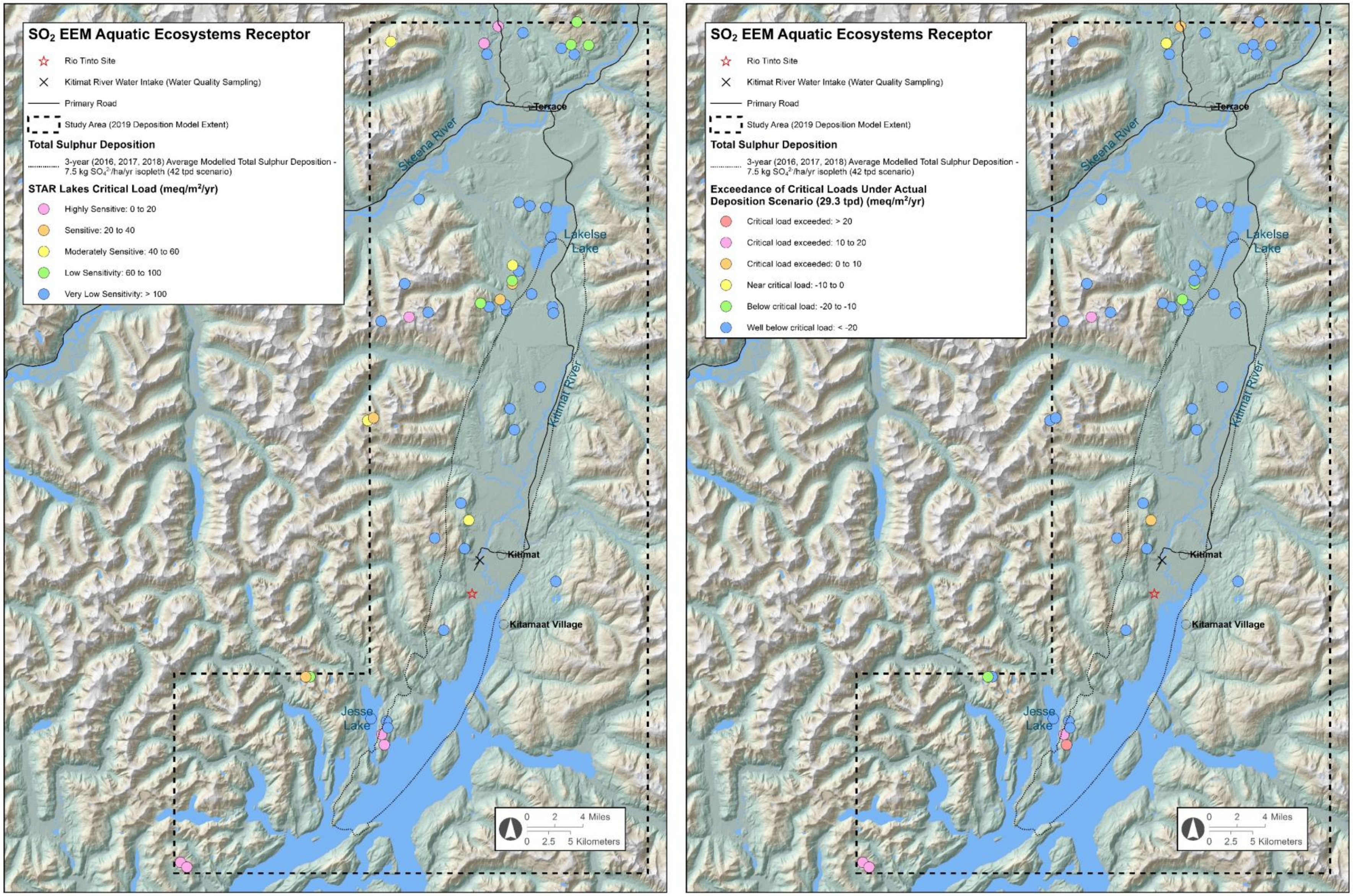

Figure 2-3. Original estimated critical loads (left) and predicted exceedances under actual current emissions (29.3 tpd; right) for all lakes within the study area.

2.5.1.2 Sensitivity Analyses

Results of the sensitivity analyses conducted on the original STAR (and/or KAA) critical loads and exceedances across all lakes in the study area are shown below.

Recall that the three sensitivity analyses are:

- Revised runoff: lower runoff (i.e., 90% of STAR levels, based on lower recent precipitation levels).
- Revised ANC$_{limit}$: higher ANC$_{limit}$ based on the updated pH-ANC relationship developed from all the available data.

As shown in Figure 2-4, both lower run-off and a higher ANC$_{limit}$ result in lower estimated critical loads. The revised ANC$_{limit}$ (both versions) makes a negligible difference for larger critical loads (i.e., >100 meq/m^2/yr).

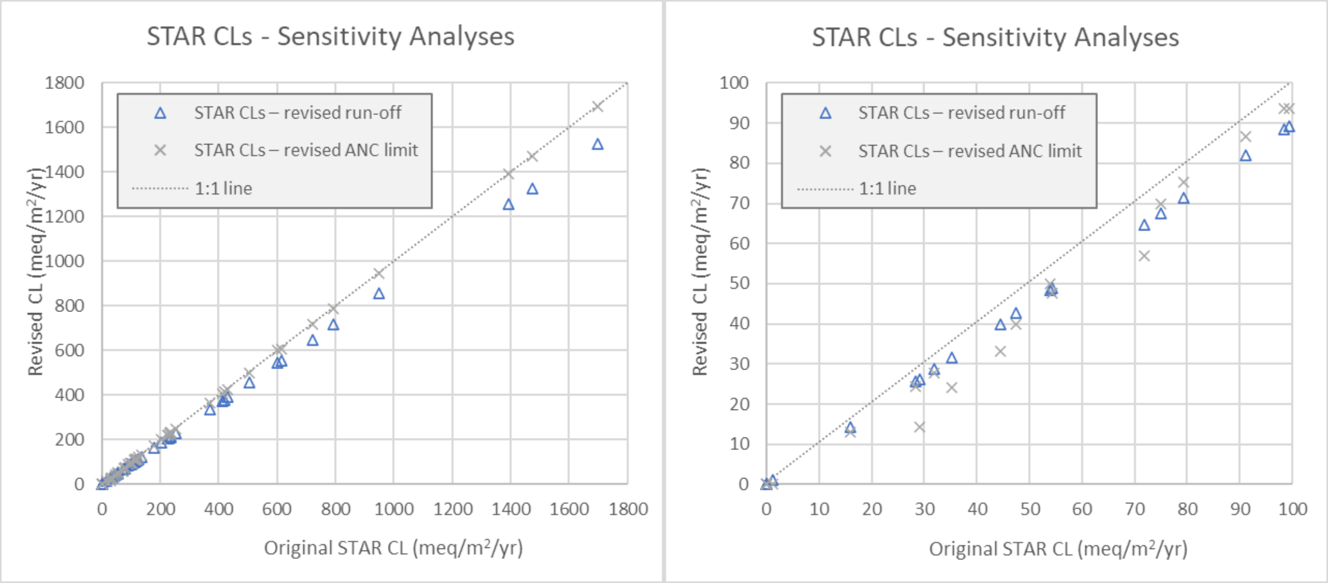

Figure 2-4. Sensitivity analyses on original critical loads for all lakes within the study area.

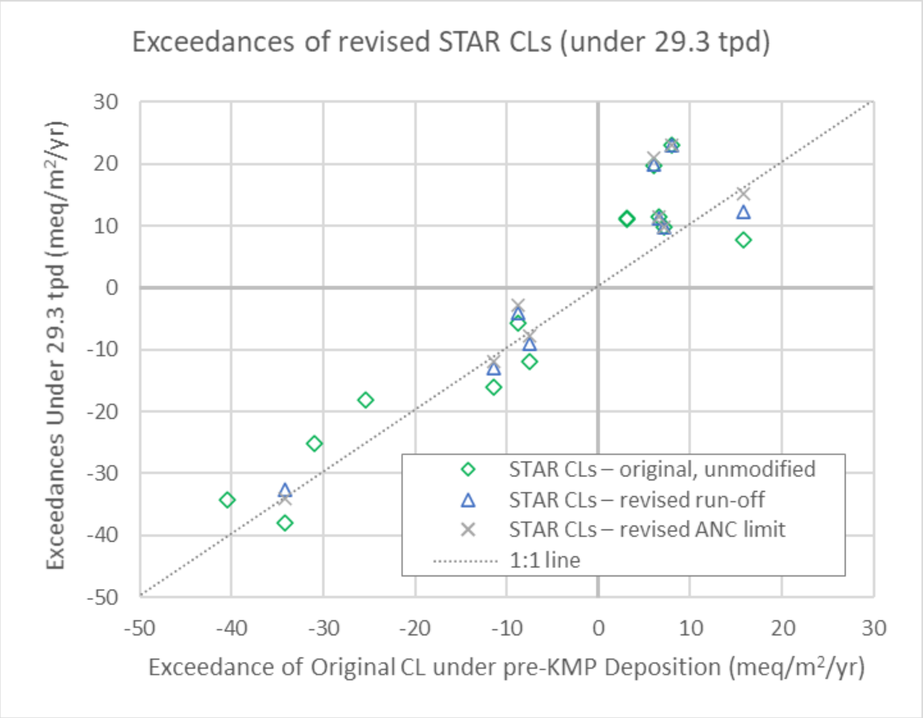

Figure 2-5. Exceedances of alternate sensitivity analyses on the original STAR critical loads under current deposition levels (i.e., 29.3 tpd modeled emissions). Results of sensitivity analyses are plotted relative to the exceedances calculated in the STAR under the "pre-KMP" emissions scenario.

Figure 2-5 shows how the number of lakes with calculated exceedances under current deposition (i.e., modeled deposition from the 29.3 tpd emissions scenario) varies with the sensitivity analyses applied to the estimation of critical loads. Using the original critical loads, there are 7 lakes (out of the 51 lakes in the study area) that show an exceedance under 29.3 tpd.

The results show that there are no additional exceedances under the 29.3 tpd scenario than were estimated under pre-KMP conditions.

The number of lakes with exceedances does not change when using lower runoff or the higher $\mathrm{ANC}_{\mathrm{limit}}$ based on the complete data set of pH and Gran ANC.

2.5.2 New Estimates of Critical Loads and Exceedances for EEM lakes only

2.5.2.1 Best Case

The new “best case” estimates for critical loads for the EEM lakes and exceedances under different emissions scenarios are summarized in Table 2-3 and mapped in Figure 2-8.

Only one lake (LAK044) shows an exceedance an exceedance under the 42 tpd emissions scenario, and because it has a critical load of zero, it has an exceedance under all emissions scenarios. In the STAR, five of these lakes were predicted to have exceedances under the “post-KMP” emissions scenario (i.e., also based on 42 tons SO_2 per day).

Table 2-3. New estimates of critical loads and exceedances for the EEM lakes based on the best available model inputs. Red cells indicate lakes with critical loads of zero and/or positive exceedances under a particular deposition scenario. Exceedances are calculated based on sulphur deposition values (dominant factor) and nitrate leaching (minor factor), which is not shown in the table.

Lake	**Years used for CL**	**Critical Load** (meq/m^2/yr)		**Sulphur Deposition** (under 42 tpd scenario)		**Exceedance under different emissions scenarios (meq/m^2/yr)**		
		New	**STAR**	(meq/m^2/yr)	(kg/ha/yr)	**29.3 tpd**	**35 tpd**	**42 tpd**
EEM Sensitive Lakes								
LAK006	2012-18	29.4	28.4	12.2	5.9	-12.3	-10.9	-8.9
LAK012	2012-18	68.1	79.4	11.8	5.7	-51.5	-50.2	-48.3
LAK022	2012-18	58.3	53.9	11.2	5.4	-42.4	-41.2	-39.3
LAK023	2012-18	33.3	31.9	11.1	5.3	-17.0	-15.8	-13.9
LAK028	2012-18	81.1	47.5	63.6	30.5	-25.0	-19.1	-8.5
LAK042	2012-18	17.4	15.9	3.4	1.6	-7.3	-6.9	-6.3
LAK044	2012-18	0.0	0.0	3.6	1.7	9.9	10.8	11.4
EEM Less Sensitive Lakes								
LAK007	2012-18	1383.4	1393.5	22.1	10.6	-1359.9	-1357.1	-1353.5
LAK016	2012-18	118.1	115.6	13.2	6.4	-100.3	-98.9	-96.7
LAK024	2012-18	551.6	370.0	11.8	5.7	-534.9	-533.3	-531.4
LAK034	2012-18	138.4	124.7	4.7	2.2	-127.4	-126.7	-126.0

For eight of the 11 EEM lakes, the revised estimates of critical loads are quite similar to the original estimates in the STAR (Table 2-4, Figure 2-6). The revised critical load estimates are higher than the STAR for LAK024 and LAK028 and lower for LAK012.

The exceedances of the revised critical loads under the 42 tpd emissions scenario are consistently smaller in magnitude than those predicted in the STAR (Figure 2-7). Among the three new modeled emissions scenarios, the magnitude of exceedance increases as deposition increases but there are no additional exceedances – that is, the number of exceedances is not sensitive to the emissions scenario.

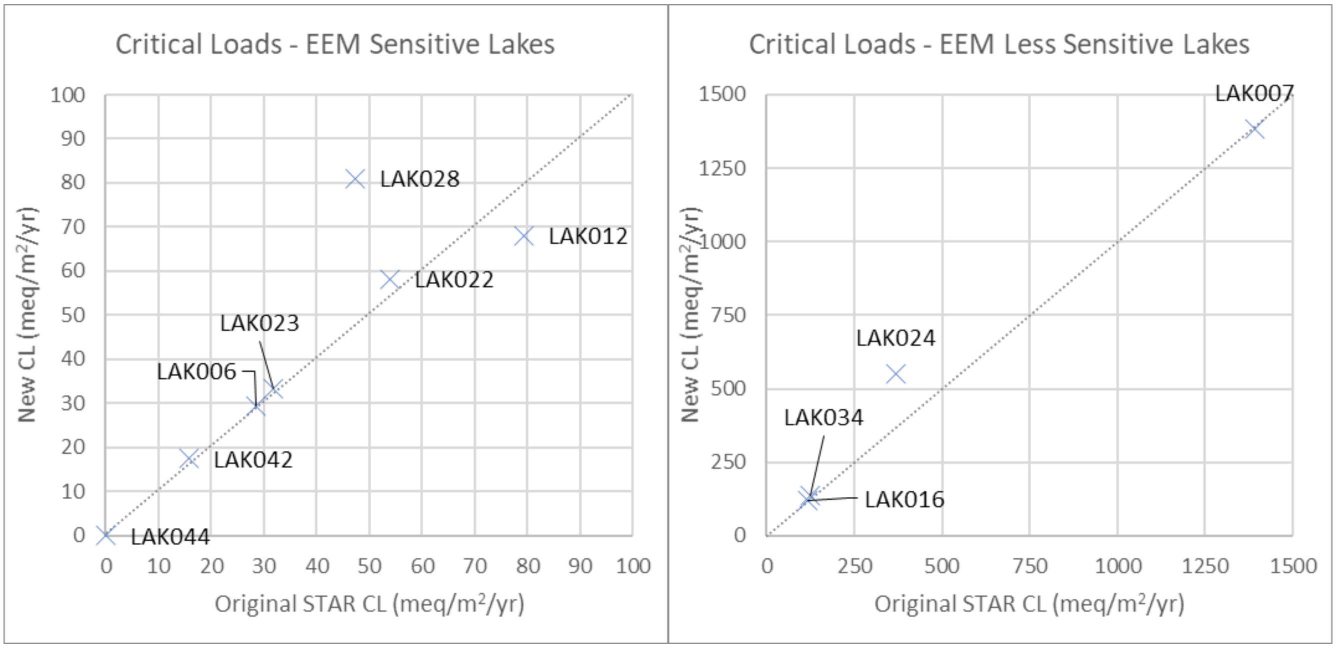

Figure 2-6. Critical loads for EEM lakes – "best case" revised estimates relative to estimates from the STAR. The sensitive lakes are shown in the left panel and the less sensitive lakes are shown in the right panel.

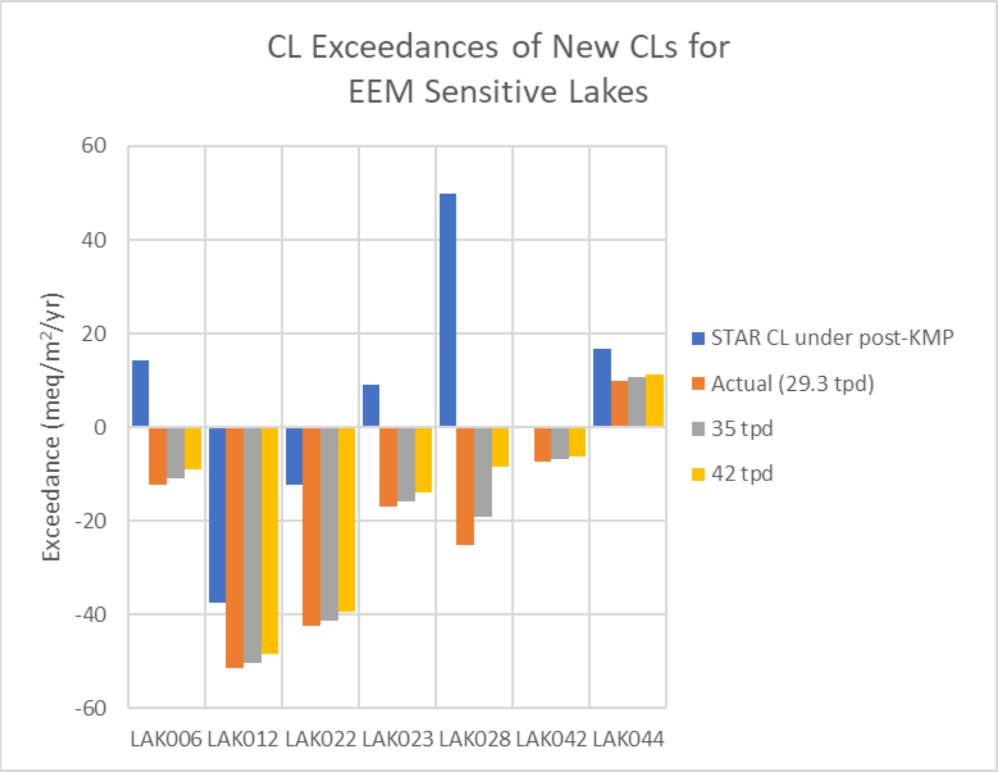

Figure 2-7. Critical load exceedances for the EEM lakes under different levels of deposition. Results from the STAR under the "post-KMP" emissions scenario are included for comparison. Note that the STAR "post-KMP" scenario did not include background deposition, whereas the exceedances estimated under the three new deposition scenarios do include background deposition of 7.5 meq/m2/yr. The exceedance for LAK042 from the STAR was smaller than perceptible on this graph (+0.2 meq/m²/yr).

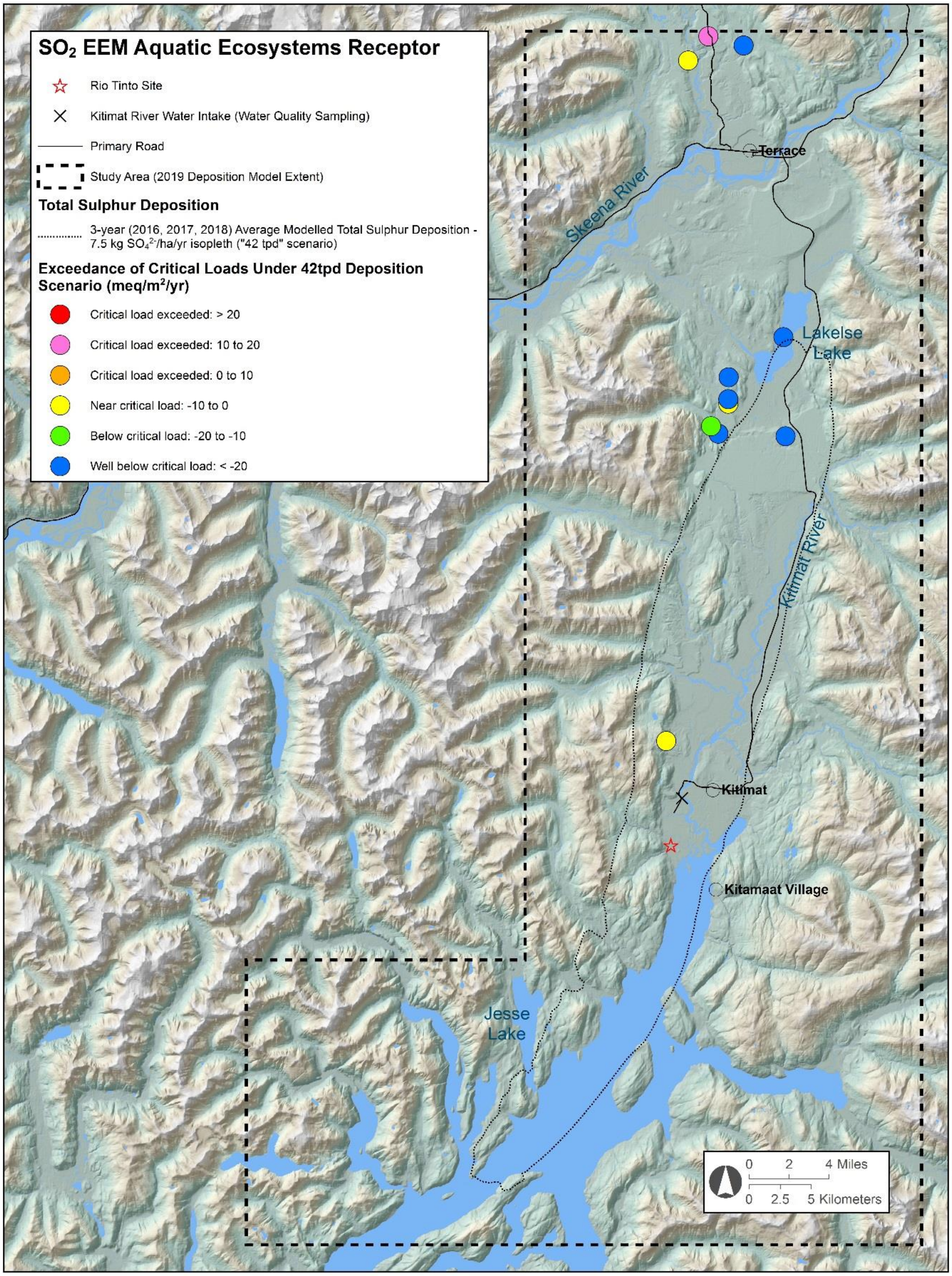

Figure 2-8. Exceedances of new critical loads for EEM lakes with modeled deposition under the 42 tpd emissions scenario.

2.5.2.2 Sensitivity Analyses

The critical loads estimated under the sensitivity analyses are shown in Table 2-4 and Figure 2-9

Table 2-4. New Critical Loads for EEM Lakes with best inputs and additional sensitivity analyses. Red cells indicate critical loads <5 meq/m²/yr.

	NEW CLs – with best inputs	NEW CLs – post-KMP lake chem.	NEW CLs – revised run-off	NEW CLs – alternate F-factor	NEW CLs – original ANC limit
EEM Sensitive Lakes					
LAK006	29.4	34.0	26.4	28.9	33.5
LAK012	68.1	65.2	61.3	68.4	72.2
LAK022	58.3	61.5	52.5	57.0	62.2
LAK023	33.3	35.3	30.0	33.0	37.5
LAK028	81.1	91.3	73.0	37.0	88.6
LAK042	17.4	20.0	15.7	17.4	20.3
LAK044	0.0	0.0	0.0	0.0	0.0
EEM Less Sensitive Lakes					
LAK007	1383.4	1384.1	1245.1	1383.4	1387.9
LAK016	118.1	120.6	106.3	117.0	122.4
LAK024	551.6	611.6	496.5	551.6	557.3
LAK034	138.4	118.0	124.6	138.4	141.9

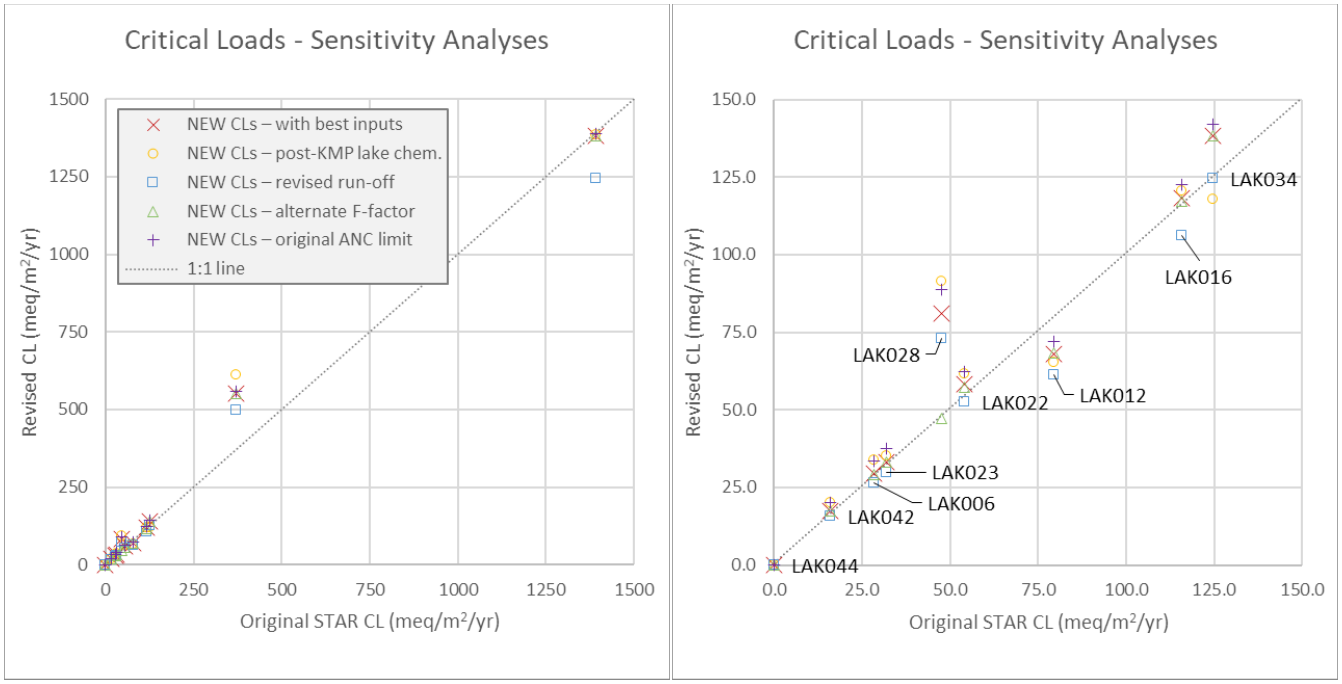

Figure 2-9. New critical loads for EEM Lakes with best inputs and additional sensitivity analyses, compared against the critical loads estimated in the STAR. Both panels contain the same data, with greater detail on results for the sensitive EEM lakes in the right panel.

The sensitivity analyses show:

- **Lower runoff:** If future run-off is lower than historic (i.e., decreased precipitation in the past three years is more representative of future conditions than the historic climate normal period), then critical loads will be lower. However, for lakes with the lowest runoff or lowest critical loads, this effect is smaller.
- **Post-KMP chemistry:** LAK024, LAK028 and LAK034 are the only lakes with strong sensitivity to using this reduced data set. These lakes have notable differences between the two potential data sets and therefore a notable difference in the estimated critical loads. For LAK024, Gran ANC, SO_4^{2-} and base cations are all higher when only using the data for 2016-2018. For LAK028, Gran ANC is lower but SO_4^{2-} and base cations are higher. For LAK034, SO_4^{2-} and base cations are lower.
- **Alternate F-factor:** LAK028 is the only lake that is sensitive to use of a revised F-factor. As SO_4^{2-} has increased, so have base cations (result of a non-zero F-factor indicating some watershed neutralization of acid deposition), but this means the base cation concentration used to calculate the model-based F-factor is higher, resulting in a higher estimated F-factor. In the SSWC model, a higher F-factor leads to a lower estimate of original base cations and therefore a higher critical load. The substantial difference in critical load may be somewhat distorted from the "true" critical load because current lake chemistry may not be in equilibrium with current emissions (which is a necessary assumption for some of the calculations in the SSWC).
- **Original ANC_{limit}:** The relatively small difference in ANC_{limit} between the STAR and updated value has minimal effect on the estimated critical loads.

LAK044 is not sensitive to changes in assumptions because the estimated critical load is always zero under all sensitivity analyses. The lakes with the next three lowest critical loads (LAK042, LAK006, and LAK023) are not very sensitive to any of the changes in assumptions.

Table 2-5. Exceedances of revised critical loads for EEM Lakes and sensitivity analyses, for deposition under the 42 tpd emissions scenario. Red cells indicate positive exceedances (>0 $meq/m^2/yr$).

	Exceedances of critical loads sensitivity analyses under 42 tpd emissions scenario				
Lakes	NEW CLs – with best inputs	NEW CLs – post-KMP lake chem.	NEW CLs – revised run-off	NEW CLs – alternate F-factor	NEW CLs – original ANC limit
EEM Sensitive Lakes					
LAK006	-8.9	-13.9	-6.0	-8.7	-13.0
LAK012	-48.3	-45.3	-41.5	-48.5	-52.3
LAK022	-39.3	-42.5	-33.5	-38.3	-43.2
LAK023	-13.9	-16.2	-10.7	-13.6	-18.1
LAK028	-8.5	-18.0	-0.5	25.4	-16.0
LAK042	-6.3	-8.8	-4.6	-6.2	-9.1
LAK044	11.4	11.4	11.3	11.4	11.4
EEM Less Sensitive Lakes					
LAK007	-1353.5	-1354.1	-1215.2	-1353.5	-1357.9
LAK016	-96.7	-99.4	-84.9	-95.8	-101.0
LAK024	-531.4	-591.1	-476.3	-531.4	-537.1
LAK034	-126.0	-105.5	-112.1	-126.0	-129.4

The sensitivity analyses of the estimated exceedances of critical loads under the 42 tpd emissions scenario show (Table 2-5, Figure 2-10):

- LAK044 always shows exceedance because the critical load is zero
- LAK028 shows an exceedance when using the alternate F-factor. However, as discussed above, the calculation of the model-based F-factor estimation is greatly affected by changes in SO_4^{2-} and base cations and model-based estimation may not result in an appropriate F-factor when lake chemistry is not in equilibrium with deposition.

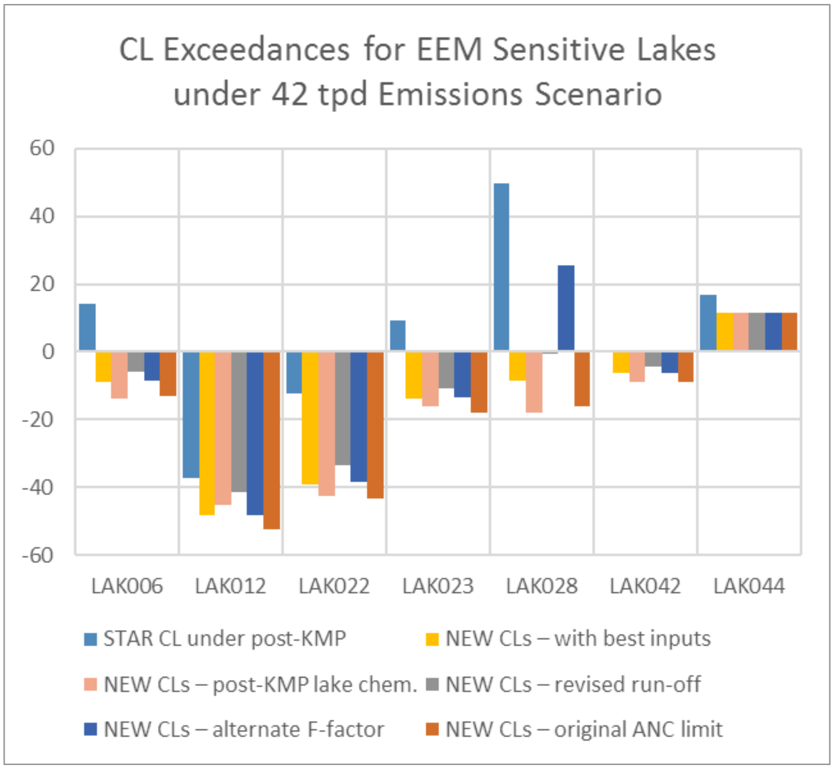

Figure 2-10. Estimated exceedances of critical loads under the 42 tpd emissions for each of the EEM sensitive lakes, by sensitivity analysis.

With seven years of sampling data, it is possible that an empirically based F-factor could be estimated based on the observational data. We had predicted that LAK028 would be the only lake with changes in base cations and sulphate of a sufficient magnitude to generate an empirically based estimate of the F-factor. However, we looked at the ratio of changes in base cations to changes in sulphate for all of the lakes across different time periods within the seven-year period of record. As predicted, LAK028 is the only lake for which a valid F-factor (i.e., between 0 and 1) could be calculated. Given the sensitivity of LAK028 to the alternate F-factor (as above), we explored multiple ways of estimating the F-factor, and the resulting impacts on the estimated critical load and exceedance, for LAK028 (Table 2-6).

All of the alternate methods of estimating a potential F-factor for LAK028 generate a higher F-factor and therefore a lower critical load (because the higher F-factor leads to a lower estimate of original pre-industrial base cations) and thus higher estimated exceedances. Interestingly, updating the estimate of the F-factor for LAK028 using the full observation record leads to an estimated CL of 47.2 (second row in Table 2-6), very similar to the STAR estimate of 47.5 (Table 2-3). The various sensitivity analyses in Table 2-6 suggest that it is quite possible that the deposition associated with emissions of 42 tpd would be in excess of the CL for LAK028. Even so, LAK028 has shown no pH decrease from 2012 to 2016-2018, and is expected to have only a small decrease in pH (0.2 pH units) between 2016-2018 and steady state conditions under 42 tpd (see section 3 on steady state predictions of future pH).

Table 2-6. Sensitivity of LAK028 critical loads and exceedances to changes in the F-factor UNDER 42 tpd

Critical Loads Sensitivity Scenario		**F-factor applied**				**Critical Load (meq/m^2/yr)**	**Exceedance under 42 tpd (meq/m^2/yr)**
	Description / rationale	**Type of estimate**	**Inputs**		**Value**		
NEW CLs – with best inputs	STAR estimate	Model	STAR runoff, baseline chemistry		0.44	88.1	-8.5
NEW CLs – alternate F-factors	Update STAR estimate with full observation record	Model	STAR runoff, 2012-2018 chemistry		0.69	47.2	25.4
Post-KMP F-factor	If estimated only using post-KMP data	Model	Current runoff (lower), 2016-2018		0.70	45.2	27.4
Empirical F-factor	F-factor implied by observed changes	Measured	Observed changes in BC and SO_4 from 2012-2014 to 2016-2018		0.85	24.2	48.5
F-factor estimated from regression of observations	F-factor implied by observed relationship	Estimated	Slope of the regression for the relationship between BC and SO_4 for 2012 to 2018 based on:	Mean annual values	0.68	47.9	24.7
				Individual samples	0.81	29.8	42.9

2.5.3 Sensitivity Analyses on CALPUFF Modeled Deposition Estimates

As discussed elsewhere in the Comprehensive Review, the CALPUFF model may be under/overestimating deposition in different regions of the study area. We performed sensitivity analyses of exceedances under deposition levels of 50% (0.5x) and 200% (2.0x) of the modeled deposition estimates for the original critical loads across all lakes under 29.3 tpd (Table 2-7) and for the new critical loads for the EEM lakes under 42 tpd.

For the full set of lakes (using original critical loads under current emissions), the number of lakes with estimated exceedances decreases by one (LAK028) under the 50% reduction in deposition, but there is no change in the number of lakes with estimated exceedances under the doubling of deposition values.

For the EEM lakes (using new critical loads under maximum future emissions), there is one lake with an estimated exceedance under the existing modeled deposition (LAK044), which does not change under the 50%

reduction in deposition. When the deposition values are doubled, two additional lakes show exceedances (LAK006 and LAK028).

Table 2-7. Sensitivity of exceedances (under 29.3 tpd) of original STAR/KAA critical loads for all lakes within the study area to uncertainty in the CALPUFF deposition estimates.

	Exceedance of Original CLs under Actual Current Emissions (29.3 tpd)		
	0.5x deposition	1.0x deposition	2.0x deposition
EEM Sensitive Lakes			
LAK006	-16.3	-11.9	-3.0
LAK012	-67.4	-63.1	-54.6
LAK022	-42.1	-38.0	-29.9
LAK023	-20.2	-16.1	-8.1
LAK028	-15.9	7.6	54.7
LAK042	-6.8	-5.6	-3.2
LAK044	8.7	9.8	12.0
EEM Less Sensitive Lakes			
LAK007	-1377.7	-1369.8	-1354.2
LAK016	-103.0	-98.2	-88.6
LAK024	-358.1	-353.9	-345.5
LAK034	-115.3	-113.7	-110.4
Other STAR Lakes			
LAK001	-591.7	-588.5	-582.0
LAK002	-101.7	-98.1	-90.7
LAK003	-483.5	-470.5	-444.5
LAK004	-194.6	-192.0	-186.6
LAK005	-100.6	-95.3	-84.5
LAK008	-1681.4	-1673.9	-1658.9
LAK011	-89.3	-86.8	-82.0
LAK013	-708.3	-703.6	-694.2
LAK014	-98.6	-94.0	-84.9
LAK015	-203.3	-190.1	-163.6
LAK017	-212.6	-201.8	-180.1
LAK018	-1457.3	-1449.2	-1433.1
LAK027	-230.2	-214.0	-181.8
LAK030	-754.4	-730.0	-681.2
LAK032	-939.7	-938.5	-935.9
LAK035	-81.0	-78.7	-74.0
LAK037	-124.4	-122.1	-117.5
LAK038	-168.1	-165.7	-160.7
LAK039	-88.3	-85.9	-81.2
LAK041	-44.9	-44.3	-43.1
LAK045	-216.6	-215.9	-214.5
LAK047	10.5	11.4	13.2
LAK049	-224.1	-223.1	-221.1
LAK050	-104.4	-103.7	-102.1
LAK051	-227.5	-226.3	-224.0
LAK053	-91.1	-87.8	-81.3
LAK054	15.8	23.0	37.6

LAK055	-105.9	-99.4	-86.5
LAK056	13.4	19.8	32.6
LAK057	-405.7	-399.1	-386.1
KAA Lakes Located within 2019 Deposition Modeling Area			
MOE3	-605.2	-601.8	-595.1
DCAS10A	-35.2	-34.3	-32.6
DCAS10B	-26.0	-25.1	-23.4
DCAS17A	-421.9	-420.1	-416.5
DCAS02C	-65.4	-63.6	-60.0
DCAS07A	10.0	11.1	13.3
DCAS07B	10.1	11.3	13.6
DCAS09A	-56.6	-55.4	-53.0
DCAS09B	-19.3	-18.2	-15.9
Additional Lakes Sampled during the EEM			
MOE6	-400.4	-388.1	-363.5

Table 2-8. Sensitivity of exceedances (under 42 tpd) of new critical loads for EEM lakes to uncertainty in the CALPUFF deposition estimates.

	Exceedance of New CL for EEM Lakes under "Permit" Emissions (42 tpd)		
	0.5x deposition	1.0x deposition	2.0x deposition
EEM Sensitive Lakes			
LAK006	-15.0	-8.9	3.3
LAK012	-54.1	-48.3	-36.5
LAK022	-44.9	-39.3	-28.1
LAK023	-19.5	-13.9	-2.8
LAK028	-40.3	-8.5	55.1
LAK042	-8.0	-6.3	-2.9
LAK044	9.5	11.4	15.0
EEM Less Sensitive Lakes			
LAK007	-1364.5	-1353.5	-1331.4
LAK016	-103.3	-96.7	-83.4
LAK024	-537.3	-531.4	-519.6
LAK034	-128.3	-126.0	-121.3

3 Future Steady-state pH

3.1 Introduction / Background

The second major component of the analyses presented in this appendix is the prediction of future steady-state pH under conditions of increased acidic deposition.

To assess the eventual steady-state pH that will result from acidic deposition under a particular emissions scenario we have applied the same methodology as we used in the STAR. In the STAR we developed an approach based on the ESSA/DFO model described in Marmorek et al. (1990). This model predicts the change in ANC (ΔANC) based on the lake's water chemistry (i.e., it considers the F factor), the change in sulphur deposition and the runoff of the watershed. The implementation of this model is described in detail in Section 8.6.3.4 of the STAR report (ESSA et al. 2013).

We then used the resulting steady-state ANC value (ANC_{∞}) as an input to the titration curve based on Small and Sutton (1986) to calculate the steady-state pH (pH_{∞}). This semi-independent method for estimating potential change in pH, as it is based on the ESSA/DFO model rather than the SSWC model, relies on current ANC rather than current base cations as a starting point. It should be stressed that both methods use the same F-factor, which in turn is derived from current base cation concentrations and is a key uncertainty in both models.

We generated new, improved predictions of pH_{∞} for the EEM lakes using the data collected from 2012 to 2018. Then we conducted a broad set of sensitivity analyses that apply varying assumptions about the model inputs. We also applied limited sensitivity analyses to the original predictions of pH_{∞} (i.e., from the STAR or KAA) across all of the lakes within the study area, in places where updated model inputs are available across the entire set of lakes.

3.2 Objectives for Steady-state pH Modeling

Steady-state pH Objectives:

1. How do the STAR predictions of pH_{∞} change with updated data that can be applied to all lakes?
2. For lakes with post-KMP sampling data, what is our best, improved prediction of pH_{∞}?
3. How sensitive are "best estimates" for pH_{∞} to variation in the input assumptions?
4. How sensitive are the estimates of steady-state pH to uncertainty in the deposition estimates?

3.3 ESSA-DFO Model Inputs

The model inputs for the ESSA-DFO model are described below in terms of what improvements are available relative to the data used in the STAR. These data are only described at a very high level so as to communicate the key elements of each input. These inputs are described extensively elsewhere (e.g., STAR, KAA, and/or other receptor/pathway chapters within the Comprehensive Review).

3.3.1 Lake Chemistry Data

We have calculated "current" pH and Gran ANC as the average of 2016-2018 conditions.

3.3.2 Sulphur Deposition Estimates

The sulphur deposition estimates (including background deposition) are explained earlier in Section 2.3.6 and in full detail in the Atmospheric Pathways chapter and appendices.

The updated CALPUFF modelling allows prospective modelling of changes in pH using the ESSA-DFO model because it provides deposition estimates under current emissions levels (i.e., 29.3 tpd scenario) and two future scenarios – one representing the likely future emissions (i.e., 35 tpd) and one representing the maximum future emissions (i.e., 42 tpd). These data are essential because the ESSA-DFO model is based the magnitude of *changes in deposition.* However, this means that the updated CALPUFF estimates do no allow retrospective modelling of the change in pH from pre-KMP conditions to current conditions because we do not have deposition modeling estimates from those two time periods produced within the same modelling framework – i.e., the modelling framework (including meteorological years, input data and other assumptions) that was used to generate the pre-KMP scenario in the STAR is different than the framework used to produce the updated 29.3 tpd scenario, and therefore they cannot be directly compared to generate estimates of changes in deposition within a particular watershed.

3.3.3 Runoff Estimates

See Section 2.3.2.

3.3.4 F-factor

See Section 2.3.3.

3.3.5 pH-ANC Relationship

See Section 2.3.5.

3.3.6 Summary of Model Inputs

The model inputs described above are summarized in Table 3-1, differentiating among STAR inputs, improved inputs, and potential alternatives.

Table 3-1. Model inputs for ESSA-DFO model, as used in the STAR plus updated data now available for improved estimates and/or sensitivity analyses.

	What was used in STAR	Best updated data	Potential alternatives (sensitivity)
Lake Chemistry	• 2012 lake data (2013 for KAA)	• 2016-2018 lake data	
Δ S Dep	• Pre-KMP vs. Post-KMP	• 29.3 tpd (actual current) vs. 42 tpd (permit limit)	• 29.3 tpd (actual current) vs. 35 tpd (likely future) • 0.5x modeled deposition • 2.0x modeled deposition
Run-off	• STAR runoff		• STAR runoff scaled based on 2016-18 precipitation
F-factor	• Model-based (STAR estimate)		• Model-based (revised runoff, 2016-18 chemistry) *[EEM lakes only]*
pH-ANC relationship	• STAR pH-ANC curve	• Updated pH-ANC curve	

3.4 ESSA-DFO Model Scenarios

This section outlines the ESSA-DFO model scenarios and sensitivity analyses run to address each of the steady-state pH modeling objectives.

3.4.1 ESSA-DFO – Revisions to STAR predictions of pH_∞ for ALL lakes

Steady-state pH Objective 1: How do the STAR predictions of pH∞ change with updated data that can be applied to all lakes?

ESSA-DFO Run #1 → original predictions (“BASE CASE”)

ESSA-DFO Run #2 (sensitivity) → BASE CASE + revised (lower) runoff

ESSA-DFO Run #3 (sensitivity) → BASE CASE + revised pH-ANC relationship

3.4.2 ESSA-DFO – New, Improved Predictions of pH_∞ for EEM lakes only

Steady-state pH Objective 2: For lakes with post-KMP sampling data, what is our best, improved prediction of pH_∞ ?

ESSA-DFO Run #4 → new prediction of pH_∞ of with best inputs (“BEST CASE”)

The following table indicates the data inputs used to develop the “BEST CASE” new estimates for the CLs of the EEM lakes. The rationale for each selection is discussed in Section 3.3 above.

	Data to use
Lakes	• EEM lakes (sensitive, less sensitive, control)
Lake Chemistry	• 2016-18 lake data
Δ S Dep	• 29.3 tpd to 42 tpd
Runoff	• STAR runoff
F-factor	• STAR model estimate
pH-ANC relationship	• Updated pH-ANC curve (@ pH=6)

Steady-state pH Objective 3: How sensitive are “best estimates” for pH_∞ to variation in the input assumptions?

ESSA-DFO Run #6 (sensitivity) → BEST CASE + revised (lower) runoff

ESSA-DFO Run #7 (sensitivity) → BEST CASE + revised F-factor

ESSA-DFO Run #8 (sensitivity) → BEST CASE + original pH-ANC relationship

3.4.3 Summary of ESSA-DFO Model Runs

The table below provides a visual summary of all the ESSA-DFO model scenarios and sensitivity runs described in the previous sections. There are two “base cases” (denoted by the green columns) – one that is applicable to the entire set of STAR and additional lakes, and one that is applicable only to the EEM lakes. The data inputs used in each base case are marked with **black ‘X’s** whereas the **red ‘X’s** indicate the changes from the base case, as applied in various sensitivity analyses.

		STAR predictions (All lakes)			New predictions (EEM lakes)			
Model Input	**Data Set / Method**	STAR pred. – original results	STAR pred. – revised runoff	STAR pred. – improved pH-ANC	NEW pred. – with best inputs	NEW pred. – revised runoff	NEW pred. – revised F-factors	NEW pred. – original pH-ANC
Estimation of pH∞								
Lake Chemistry	2012 lake data	X	X	X				
	2016-2018 lake data				X	X		X
Runoff (future)	Original (higher) runoff	X		X	X		X	X
	Revised (lower) runoff		X			X		
F-factor	Model-based (STAR estimate)	X	X	X	X	X		X
	Model-based (revised runoff, post-KMP chem.)						X	
pH-ANC relation	STAR regional pH-ANC curve	X	X					X
	Updated pH-ANC curve			X	X	X	X	
Emissions Scenario								
∆ S Dep	preKMP to postKMP	✓	✓	✓				
	29.3 tpd to 42 tpd				✓	✓	✓	✓
	29.3 tpd to 35 tpd				✓			

3.4.1 Sensitivity Analyses on CALPUFF Modeled Deposition Estimates

Steady-state pH Objective 4: How sensitive are the “best case” estimates of steady-state pH to uncertainty in the deposition estimates?

ESSA-DFO Run #4 under 29.3 tpd & 42 tpd, with uncertainty factors of 0.5, 1.0, 1.5, 2.0

3.5 ESSA-DFO Model Results

3.5.1 Original predictions of pH∞ for ALL lakes and sensitivity analyses

The following results and sensitivity analyses only apply to the STAR lakes. The KAA lakes could not be analyzed in the same way because we do not have deposition estimates for these lakes that align with the “post-KMP” emissions scenario in the STAR. The KAA study did not include a scenario that included maximum smelter emissions (i.e., 42 tpd SO_2 under the permit) in isolation from increases in emissions from other regional sources.

There are two sensitivity analyses that are possible to apply to the STAR predictions the entire set of available lakes – a) reduced run-off and b) the revised pH-ANC relationship. In order to compare the effect of changes in these inputs with the results from the STAR, the same deposition data must be used (i.e., changes in deposition between the “pre-KMP” and “post-KMP” modelled deposition used in the STAR). Furthermore, it is not possible to do a valid sensitivity analysis with the revised deposition modeling (i.e., to see the effect of using the new 42 tpd results) because we do not have an estimate of pre-KMP deposition that was generated within the same modeling framework in order to calculate a change in deposition.

The results of these sensitivity analyses and the original STAR results are shown in Table 3-2 and Figure 2-2.

The sensitivity analyses show that an assumption of lower run-off (i.e., if recent precipitation levels are more representative of future precipitation levels than the historic data used in the STAR) leads to a lower prediction for steady-state pH and therefore a greater ∆pH from 2012. The effect is largest for the lakes for which the STAR already predicted the largest changes in pH (i.e., the lakes selected for the EEM). Using the updated, revised pH-ANC relationship led to some increases and some decrease in the predicted ∆pH as compared to the STAR results, but generally had an effect of smaller magnitude. However, in both cases there was no change in the number of EEM lakes with decreases of more than 0.1 or 0.3 pH units

For the STAR lakes, there is one lake (LAK005) that shows a predicted decrease of more than 0.1 pH units under both sensitivity analyses (but did not in the original STAR results). However, this actually reflects a very minor change and there is no difference among the scenarios when rounded to a single decimal place (i.e., in the STAR the predicted was a decrease of 0.098 pH units.

The conclusions of the STAR are not sensitive to the changes tested.

Table 3-2. Predictions of pH_{∞} and ΔpH (from 2012) from the STAR and two sensitivity analyses across all STAR lakes. Note that these analyses are based on the same deposition modelling as applied in the STAR (i.e., “pre-KMP” and “post-KMP” modeled deposition), as discussed further in the text.

Lake	**2012 pH**	**STAR predictions**		**STAR prediction with revised (lower) runoff**		**STAR prediction with revised pH-ANC relationship**	
		pH_{∞}	**Δ pH**	**pH_{∞}**	**Δ pH**	**pH_{∞}**	**Δ pH**
EEM Sensitive Lakes							
LAK006	5.8	5.3	-0.5	5.2	-0.6	5.3	-0.5
LAK012	5.6	5.5	-0.1	5.5	-0.1	5.5	-0.1
LAK022	5.9	5.5	-0.4	5.5	-0.5	5.5	-0.4
LAK023	5.7	5.2	-0.5	5.1	-0.6	5.2	-0.5
LAK028	5.0	4.6	-0.4	4.6	-0.4	4.7	-0.3
LAK042	4.7	4.5	-0.2	4.5	-0.2	4.5	-0.2
LAK044	5.4	4.9	-0.5	4.8	-0.6	4.9	-0.5
EEM Less Sensitive Lakes							
LAK007	8.0	8.0	0.0	8.0	0.0	8.0	0.0
LAK016	6.3	6.2	-0.1	6.2	-0.1	6.2	-0.1
LAK024	7.1	7.1	0.0	7.1	0.0	7.1	0.0
LAK034	6.7	6.7	0.0	6.7	0.0	6.7	0.0
Other STAR Lakes							
LAK001	7.6	7.6	0.0	7.6	0.0	7.6	0.0
LAK002	6.6	6.6	-0.1	6.6	-0.1	6.6	-0.1
LAK003	7.1	7.1	0.0	7.1	0.0	7.1	0.0
LAK004	6.5	6.5	0.0	6.5	0.0	6.5	0.0
LAK005	6.1	6.0	-0.1	6.0	-0.1	6.0	-0.1
LAK008	7.9	7.9	0.0	7.9	0.0	7.9	0.0
LAK011	6.6	6.6	0.0	6.6	0.0	6.6	0.0
LAK013	7.4	7.4	0.0	7.4	0.0	7.4	0.0
LAK014	6.5	6.4	-0.1	6.4	-0.1	6.4	-0.1
LAK015	6.0	6.0	0.0	6.0	0.0	6.0	0.0
LAK017	6.8	6.8	0.0	6.8	0.0	6.8	0.0
LAK018	8.1	8.1	0.0	8.1	0.0	8.1	0.0
LAK027	6.6	6.6	0.0	6.6	0.0	6.6	0.0
LAK030	7.4	7.4	0.0	7.4	0.0	7.4	0.0
LAK032	7.0	7.0	0.0	7.0	0.0	7.0	0.0
LAK035	6.2	6.2	-0.1	6.2	-0.1	6.2	-0.1
LAK037	6.6	6.5	0.0	6.5	0.0	6.5	0.0
LAK038	6.6	6.5	0.0	6.5	0.0	6.5	0.0
LAK039	6.4	6.3	0.0	6.3	0.0	6.3	0.0
LAK041	6.5	6.5	0.0	6.5	0.0	6.5	0.0
LAK045	6.9	6.9	0.0	6.9	0.0	6.9	0.0
LAK047	6.0	5.9	0.0	5.9	0.0	5.9	0.0
LAK049	6.8	6.8	0.0	6.8	0.0	6.8	0.0
LAK050	6.5	6.5	0.0	6.5	0.0	6.5	0.0
LAK051	6.8	6.7	0.0	6.7	0.0	6.7	0.0
LAK053	6.6	6.6	0.0	6.6	0.0	6.6	0.0
LAK054	4.6	4.5	-0.1	4.5	-0.1	4.5	-0.1
LAK055	6.2	6.1	0.0	6.1	0.0	6.1	0.0
LAK056	4.5	4.4	-0.1	4.4	-0.1	4.4	-0.1
LAK057	6.6	6.6	0.0	6.6	0.0	6.6	0.0

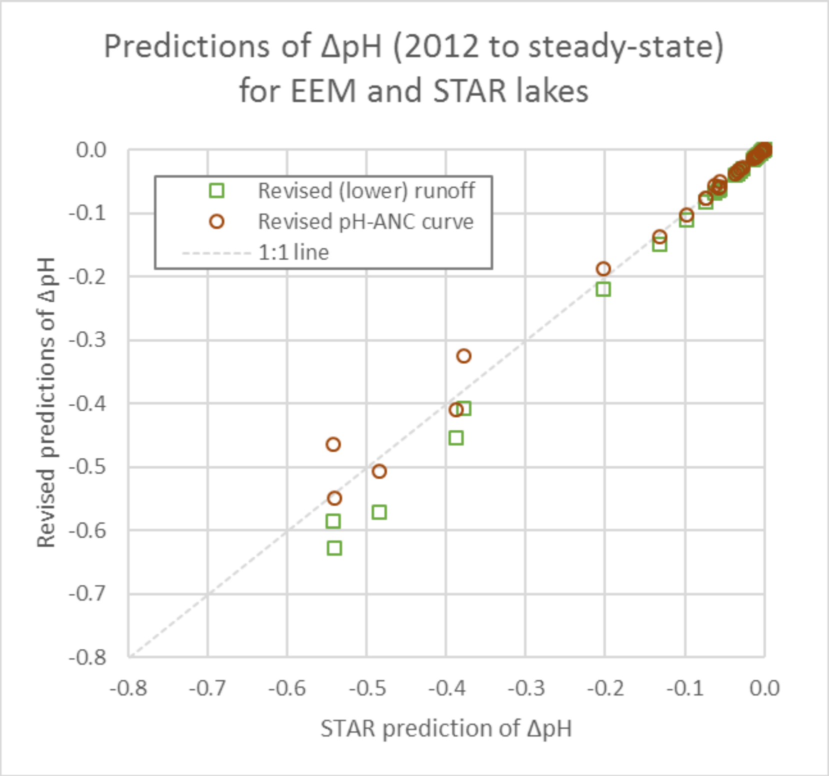

Figure 3-1. Sensitivity analyses of STAR predictions of the change from 2012 pH to steady-state pH.

3.5.2 New, Improved Predictions of $\underline{pH_{\infty}}$ for EEM lakes only

The interpretation of the results in this section is confounded by the fact that while none of the EEM lakes are predicted to increase in pH under increased sulphur deposition (i.e., relative to post-KMP conditions, 2016-2018), the increases in pH already observed since 2012 mean that the new predictions for future steady-state pH are in fact still above 2012 pH levels. The new predictions for steady-state pH (i.e., based on post-KMP data, 2016-2018) show a decrease or no change for all EEM lakes relative to current condition; however, for 10 of the 11 EEM lakes, these changes are substantially smaller than the observed *increases* in pH from 2012 to the post-KMP period (Figure 3-2). The only exception is LAK034, which is not predicted to change at all from its current pH but has already shown a decrease in pH of 0.3 pH units (as described in the evidentiary framework, this change is not causally linked to the smelter because sulphate has decreased to zero over this same period and therefore the observed decrease in pH cannot possibly be associated with increasing sulphate) . These predicted changes in pH (from current levels) and smaller than those predicted in the STAR (Figure 3-3). Given that the predicted decreases are predominantly much smaller than the observed increase thus far, this means that when expressed as a change relative to 2012 (relevant for comparing results to the STAR and the baseline period defined in the EEM), *the calculated changes from 2012 show increases in pH for many of the lakes*. However, this is an indirect effect of the observed changes and should not be interpreted as a prediction that increased deposition will drive increases in pH in these particular lakes.

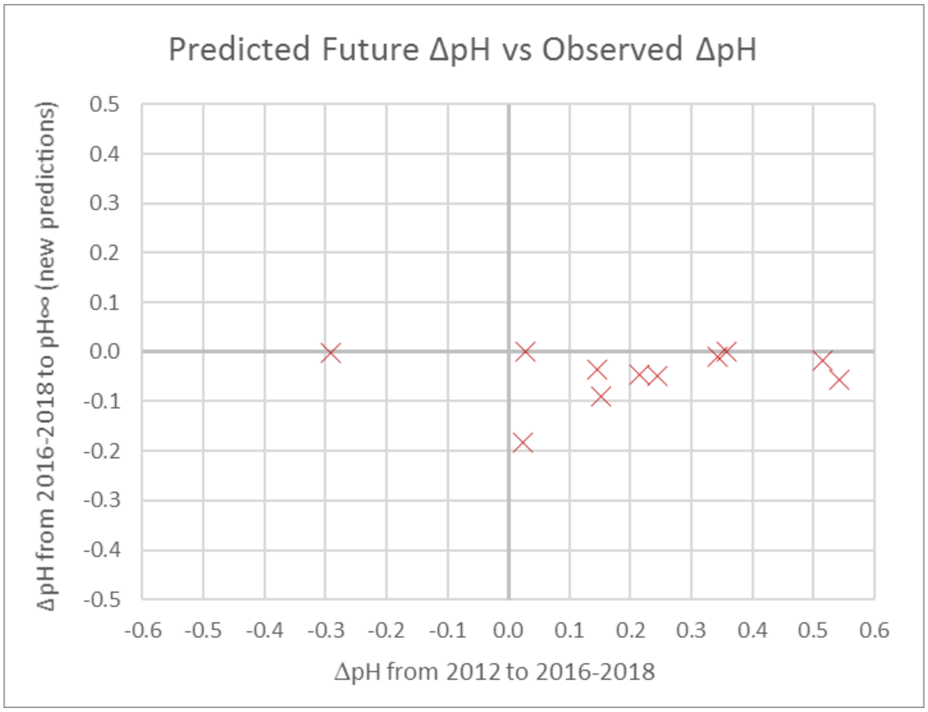

Figure 3-2. Predicted changes in pH from post-KMP (2016-2018) to future steady-state relative to the observed changes in pH during the EEM program thus far (i.e., 2012 to post-KMP). Predicted changes in pH are based on the increase in modeled deposition from current emissions (29.3 tpd) to the maximum future emissions level (42 tpd).

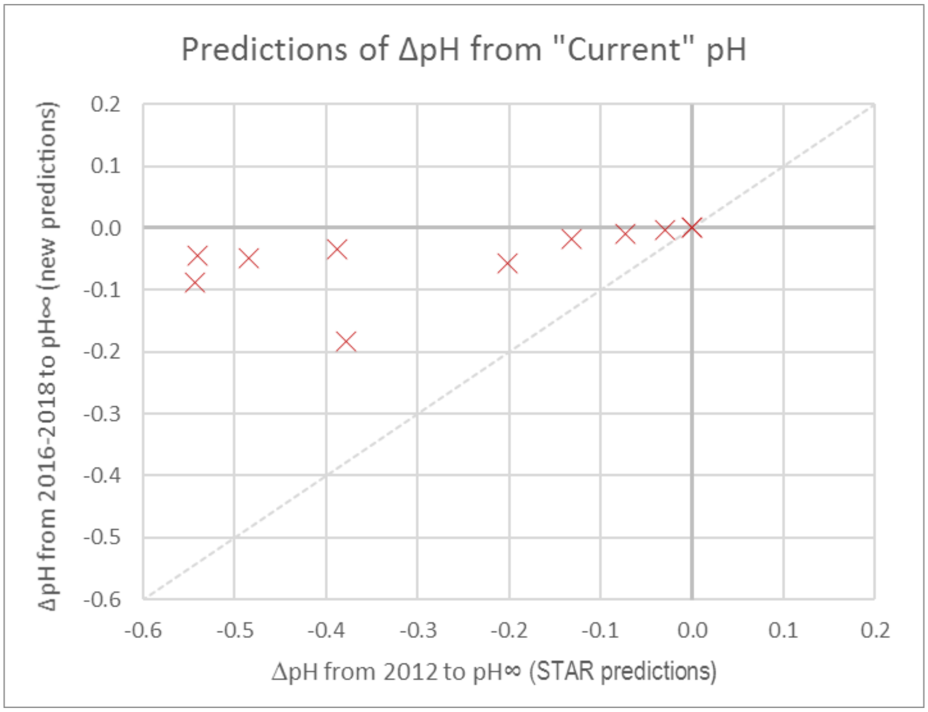

Figure 3-3. Predicted changes in pH from "current" time period (i.e, 2012 for the STAR predictions; 2016-2018 for new predictions). The STAR predictions were based on the change in deposition from the "pre-KMP" to the "post-KMP" modeled deposition. The new predictions are based on the increase in modeled deposition from current emissions (29.3 tpd) to the maximum future emissions level (42 tpd).

3.5.2.1 Core Scenario

The results for changes in pH from 2012 to steady-state conditions under 42 tpd based on the new, updated predictions of steady-state pH are shown in Figure 3-4. All lakes except LAK034 and LAK028 predict steady-state pH above 2012 levels (but still below post-KMP pH). The predicted decrease for LAK028 is smaller than predicted in the STAR. LAK034 shows larger predicted decrease than STAR prediction but this is misleading – LAK034 is not predicted to change at all from current pH, but pH is currently already below its 2012 levels (due to non-sulphate driven decrease in pH).

Figure 3-5 shows the STAR and current predictions for steady-state pH relative to observed pH values for 2012 and the post-KMP period (2016-2018) for all of the EEM lakes. This provides an alternative way of visualizing the common patterns – i.e., that pH is predicted to decrease or remain unchanged for all of the EEM lakes relative to current pH, but because current pH is predominantly above 2012 pH levels, these steady-state predictions appear to show an increase in pH when compared to 2012.

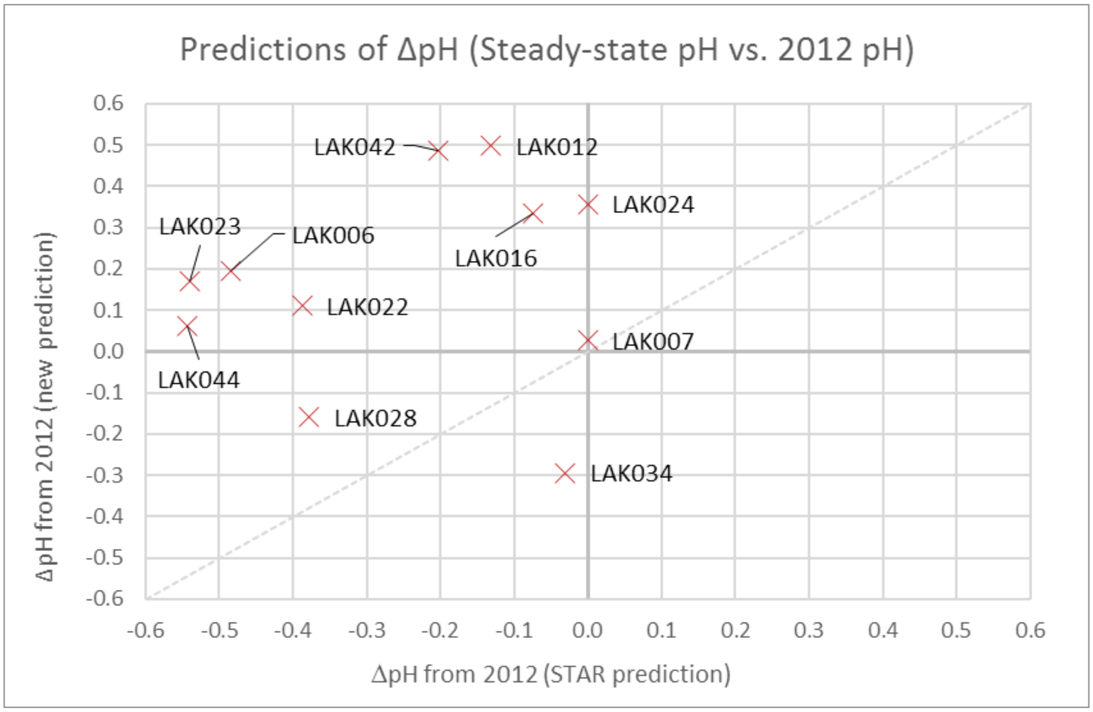

Figure 3-4. Predicted ΔpH (steady-state pH vs. 2012) based on new predictions of steady-state pH vs. STAR predictions. The STAR predictions were based on the change in deposition from the "pre-KMP" to the "post-KMP" modeled deposition. The new predictions are based on the increase in modeled deposition from current emissions (29.3 tpd) to the maximum future emissions level (42 tpd).

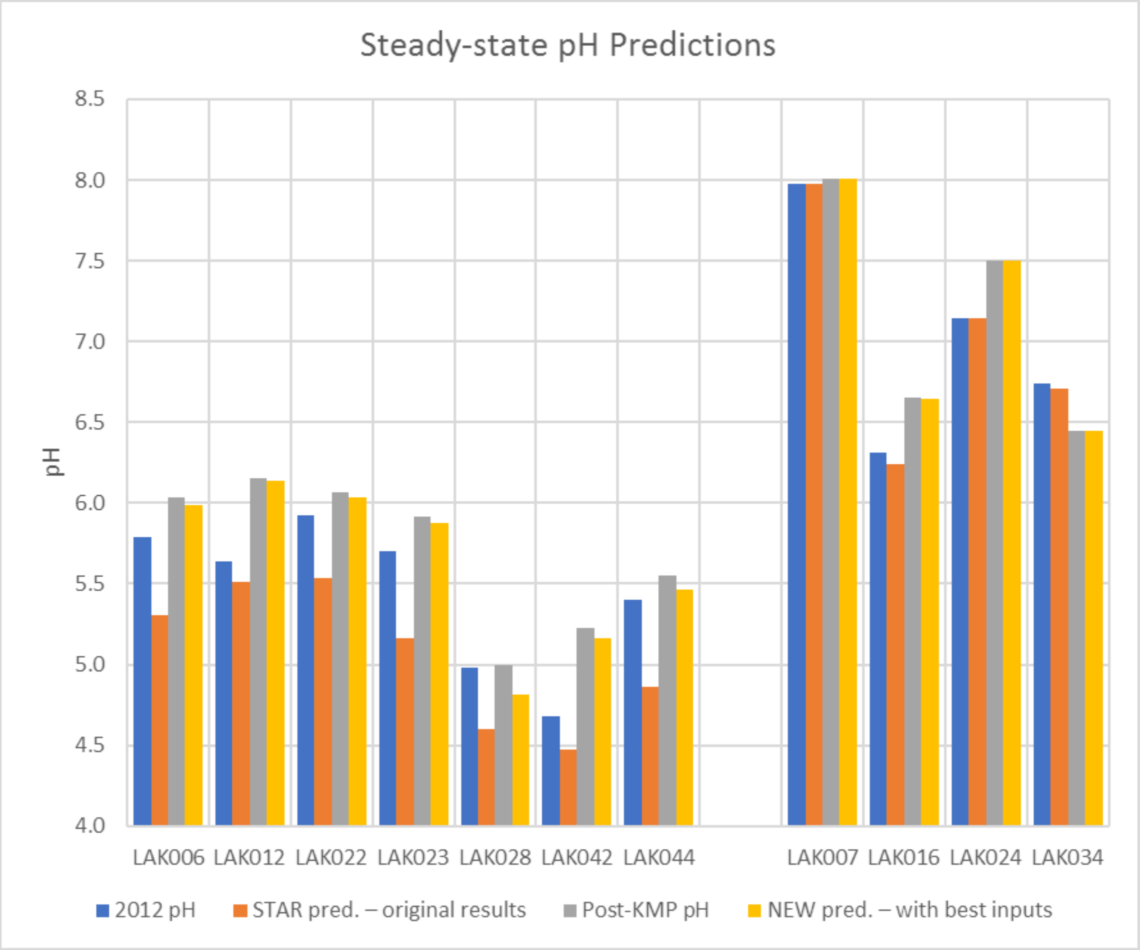

Figure 3-5.Observed pH and predicted steady-state pH for all of the EEM lakes. The STAR predictions were based on the change in deposition from the "pre-KMP" to the "post-KMP" modeled deposition. The new predictions are based on the increase in modeled deposition from current emissions (29.3 tpd) to the maximum future emissions level (42 tpd).

3.5.2.2 Sensitivity Analyses

The results of the sensitivity analyses on predictions of steady-state pH and calculated change from 2012 pH for all the EEM lakes are shown in Table 3-3 and Figure 3-6.

The sensitivity analyses show that the predicted steady-state pH and thus the calculated change from 2012 pH are generally not sensitive to the changes in the model inputs tested. LAK028 is the only lake that shows some variation among the sensitivity analyses performed, particularly with respect to the revised F-factor. As discussed at greater length, LAK028 is the only lake for which the revised estimation of the F-factor results in a meaningfully different value. Furthermore, given that LAK028 has experienced the highest levels of deposition and largest changes in lake chemistry, its results should be sensitive to the value of the F-factor.

Across all sensitivity analyses, LAK034 has a predicted decrease of 0.3 pH units relative to 2012. However, as described earlier the predicted pH change from current conditions is zero but its current pH is already 0.3 pH units below 2012 (as described in the evidentiary framework, this decline is unrelated to the smelter because sulphate has declined over the same period).

The sensitivity analyses on the broader set of all STAR lakes (Section 3.5.1) showed that using the revised runoff had a notable effect of on prediction greater decreases in pH. However, the new predictions of steady-state pH show negligible sensitivity to the revised runoff, which indicates that the effect of reduced run-off more than offset by the much lower changes in deposition from the new emissions modeling (i.e., the STAR predictions were based on much higher increases in deposition than predicted by the new emissions modeling)

Table 3-3. New predictions and sensitivity analyses of steady-state pH and resultant change in pH from 2012 for all EEM lakes, plus original predictions from the STAR. The STAR predictions were based on the change in deposition from the "pre-KMP" to the "post-KMP" modeled deposition. The new predictions are based on the increase in modeled deposition from current emissions (29.3 tpd) to the maximum future emissions level (42 tpd).

Lake	Empirical Observations		ORIGINAL: STAR predictions		NEW: Best Prediction		SENSITIVITY: Revised Runoff		SENSITIVITY: Revised F-factor		SENSITIVITY: Original pH-ANC curve	
	2012 pH	Post-KMP pH	pH$_\infty$	Δ pH (2012)	pH$_\infty$	Δ pH (2012)	pH$_\infty$	Δ pH (2012)	pH$_\infty$	Δ pH (2012)	pH$_\infty$	Δ pH (2012)
EEM Sensitive Lakes												
LAK006	5.8	6.0	5.3	-0.5	6.0	0.2	6.0	0.2	6.0	0.2	6.0	0.2
LAK012	5.6	6.2	5.5	-0.1	6.1	0.5	6.1	0.5	6.1	0.5	6.1	0.5
LAK022	5.9	6.1	5.5	-0.4	6.0	0.1	6.0	0.1	6.0	0.1	6.0	0.1
LAK023	5.7	5.9	5.2	-0.5	5.9	0.2	5.9	0.2	5.9	0.2	5.9	0.2
LAK028	5.0	5.0	4.6	-0.4	4.8	-0.2	4.8	-0.2	4.9	-0.1	4.8	-0.2
LAK042	4.7	5.2	4.5	-0.2	5.2	0.5	5.2	0.5	5.2	0.5	5.2	0.5
LAK044	5.4	5.6	4.9	-0.5	5.5	0.1	5.5	0.1	5.5	0.1	5.5	0.1
EEM Less Sensitive Lakes												
LAK007	8.0	8.0	8.0	0.0	8.0	0.0	8.0	0.0	8.0	0.0	8.0	0.0
LAK016	6.3	6.7	6.2	-0.1	6.6	0.3	6.6	0.3	6.6	0.3	6.6	0.3
LAK024	7.1	7.5	7.1	0.0	7.5	0.4	7.5	0.4	7.5	0.4	7.5	0.4
LAK034	6.7	6.4	6.7	0.0	6.4	-0.3	6.4	-0.3	6.4	-0.3	6.4	-0.3

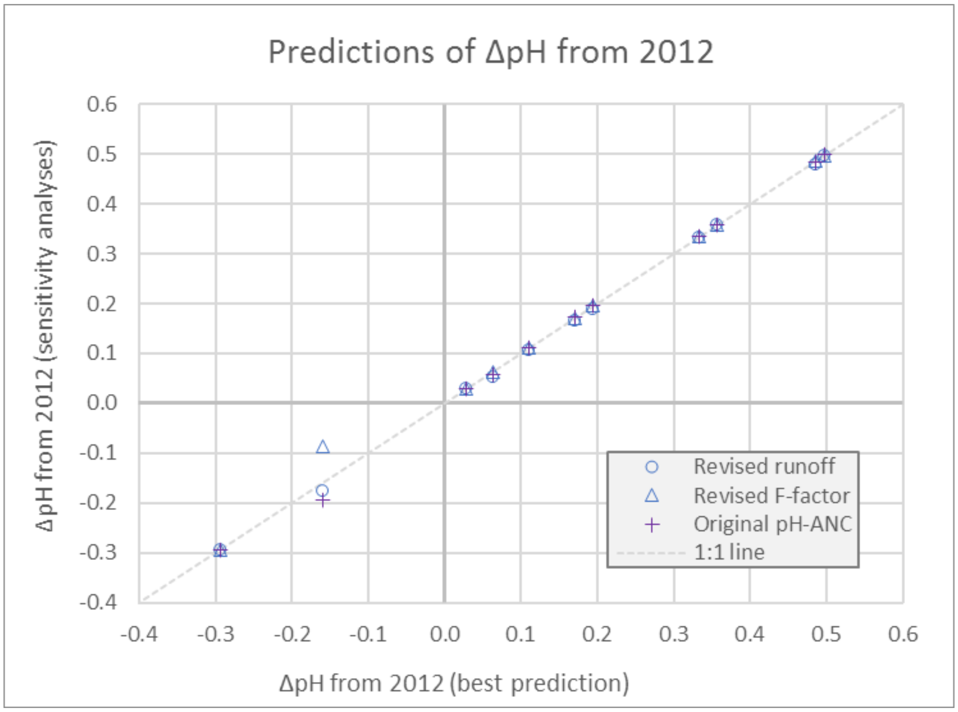

Figure 3-6. Predicted changes in pH (from 2012 to steady-state) based on the sensitivity analyses relative to the "best case" prediction. These predictions are based on the increase in modeled deposition from current emissions (29.3 tpd) to the maximum future emissions level (42 tpd).

3.5.3 Predictions of ANC_∞ for EEM lakes only

The ESSA-DFO model includes a prediction of the change in Gran ANC that will occur under a particular level of deposition. Table 3-4 shows the Gran ANC predicted to occur under steady-state conditions with deposition associated with the 42 tpd emissions scenario. None of the sensitive EEM lakes are predicted to decline below their lake-specific thresholds identified from the analyses of the titration data (Figure 3-7). LAK007 is predicted below its lake-specific threshold but this is not a significant or concerning result because it has a very high Gran ANC (over an order of magnitude greater than other lakes) and its pH is not predicted to change at all even under maximum future deposition levels.

Table 3-4. Predicted future Gran ANC and resultant change in Gran ANC from 2012 with best inputs for ESSA-DFO model under modeled deposition from 42 tpd emissions scenario.

			NEW pred. – with best inputs		
	2012 Gran ANC	post-KMP Gran ANC (2016-2018)	Gran ANC ∞	∆ Gran ANC (2012)	∆ Gran ANC (2012) Threshold
EEM Sensitive Lakes					
LAK006	25.7	27.7	24.7	-1.0	-10.8
LAK012	57.0	58.3	56.0	-1.0	-16.3
LAK022	27.8	33.0	30.4	2.6	-11.5
LAK023	19.8	26.4	23.8	4.0	-10.5
LAK028	-4.0	-3.5	-9.3	-5.3	-13.4
LAK042	-20.4	5.6	4.2	24.6	-24.4
LAK044	1.3	5.0	2.8	1.5	-6.2
EEM Sensitive Lakes					
LAK007	1437.6	1385.9	1385.9	-51.6	-50.6
LAK016	68.7	89.8	88.0	19.4	-25.6
LAK024	299.5	463.2	463.2	163.7	-60.4
LAK034	99.4	139.6	138.7	39.3	-22.0

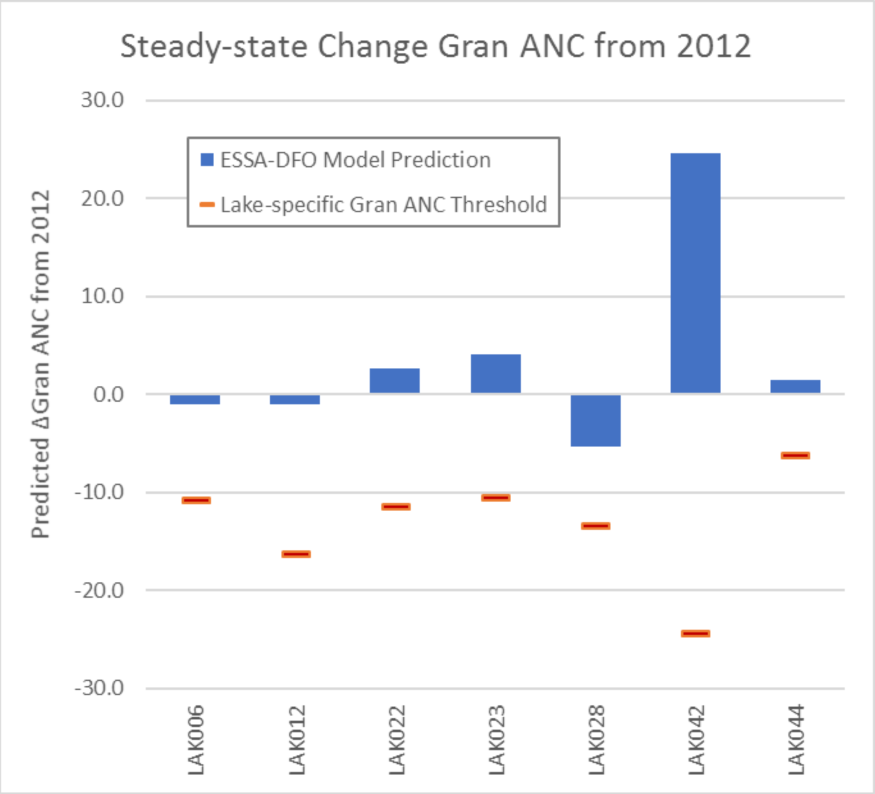

Figure 3-7. Predicted future Gran ANC using ESSA-DFO model under 42 tpd emissions scenario, compared against the lake-specific thresholds. The Gran ANC thresholds were developed from analysis of the lab titration data in order to determine the magnitude of change in Gran ANC equivalent to a 0.3 unit decrease in pH.

3.5.4 Sensitivity Analyses on CALPUFF Modeled Deposition Estimates

The results of the sensitivity analyses on the uncertainty in the CALPUFF deposition estimates are shown in Table 3-5 and Figure 3-8.

LAK028 is the only lake that shows a sensitivity to a change in deposition assumptions. If deposition under the 42 tpd emissions scenarios is assumed to be 50% of the CALPUFF model estimates, then the predicted change in pH from 2012 levels would no longer exceed a 0.1 unit decrease. If deposition under the 42 tpd emissions scenarios is assumed to be 200% of the CALPUFF model estimates, then the predicted change in pH from 2012 levels would increase to greater than a 0.3 unit decrease. The other sensitive lakes show slight changes that are visible in Figure 3 8 but are predominantly too small to show up in Table 3 5 where results are rounded to a single decimal place.

The steady-state pH predictions for the less sensitive lakes are completely insensitive to the halving or doubling of the CALPUFF deposition estimates.

LAK034 shows a decline of approximately 0.3 pH units (actual value is slightly less) from 2012 pH values under all of the tested deposition levels because this decline has already occurred (which is unrelated to the smelter as explained by the evidentiary framework) and the ESSA-DFO model does not actually predict any change in pH from current levels, even when the deposition estimate is doubled.

Table 3-5. Sensitivity analyses on uncertainty in CALPUFF modeled estimates of deposition. Yellow and red cells indicate decreases in pH greater than 0.1 and 0.3 pH units, respectively. Note that the already observed pH decline in LAK034 (zero change predicted from post-KMP pH) is unrelated to the smelter, as explained in the evidentiary framework.

	Baseline Lake Chemistry (2012)		**Post-KMP Lake Chemistry (2016-2018)**		**0.5x Deposition**		**1.0x Deposition**		**2.0x Deposition**	
	pH	**Gran ANC**	**pH**	**Gran ANC**	**pH∞**	**∆ pH (2012)**	**pH∞**	**∆ pH (2012)**	**pH∞**	**∆ pH (2012)**
EEM Sensitive Lakes										
LAK006	5.8	25.7	6.0	27.7	6.0	0.2	6.0	0.2	5.9	0.1
LAK012	5.6	57.0	6.2	58.3	6.1	0.5	6.1	0.5	6.1	0.5
LAK022	5.9	27.8	6.1	33.0	6.1	0.1	6.0	0.1	6.0	0.1
LAK023	5.7	19.8	5.9	26.4	5.9	0.2	5.9	0.2	5.8	0.1
LAK028	5.0	-4.0	5.0	-3.5	4.9	-0.1	4.8	-0.2	4.7	-0.3
LAK042	4.7	-20.4	5.2	5.6	5.2	0.5	5.2	0.5	5.1	0.4
LAK044	5.4	1.3	5.6	5.0	5.5	0.1	5.5	0.1	5.4	0.0
EEM Less Sensitive Lakes										
LAK007	8.0	1437.6	8.0	1385.9	8.0	0.0	8.0	0.0	8.0	0.0
LAK016	6.3	68.7	6.7	89.8	6.6	0.3	6.6	0.3	6.6	0.3
LAK024	7.1	299.5	7.5	463.2	7.5	0.4	7.5	0.4	7.5	0.4
LAK034	6.7	99.4	6.4	139.6	6.4	-0.3	6.4	-0.3	6.4	-0.3

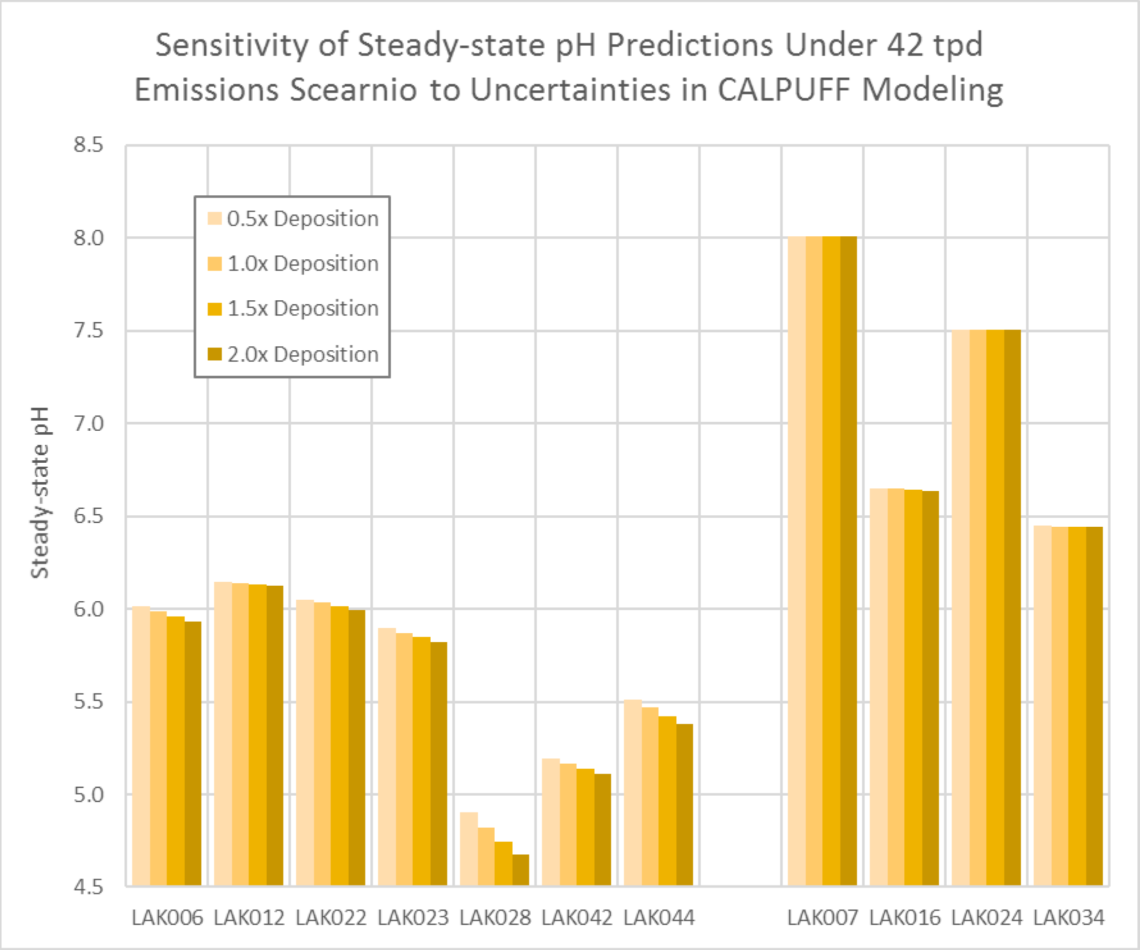

Figure 3-8. Sensitivity of steady-state pH predictions for EEM lakes to uncertainty in the CALPUFF modeled estimates of deposition.

4 Key Results

4.1 Critical Loads and Steady-state pH for EEM Lakes

The results from the "best case" analyses of the critical loads and steady-state pH for the EEM lakes are shown in Table 4-1. To be most conservative, these forward-looking analyses have been performed assuming the maximum level of emissions allowed under the permit (i.e., 42 tpd scenario). For each of the key metrics of interest (i.e., exceedances of critical loads, predicted changes in pH relative to the 2012 baseline, and predicted changes in Gran ANC thresholds relative to the 2012 baseline), there is only one lake that exceeds the reference threshold (as defined in the table caption):

Exceedance of critical loads

LAK044 has a critical load of zero and therefore shows a positive exceedance under all deposition scenarios. None of the other EEM lakes are predicted to show an exceedance of their critical loads (i.e., revised estimates based on the best data inputs) under the maximum predicted deposition levels (i.e., 42 tpd emissions scenario).

Future changes in pH from baseline conditions

LAK034 is shown to have a predicted future pH that is 0.3 pH units below its 2012 level; however, this decline is unrelated to the smelter because sulphate has also decreased during the same period (as explained by the evidentiary framework). In fact, LAK034 is predicted to have zero change in pH from current (2016-18) levels, but these levels are already below 2012.

Future changes in Gran ANC from baseline conditions

LAK007 is shown to have a predicted change in Gran ANC that is greater than its lake-specific threshold; however, this result is an artifact of a change that has already occurred and is unrelated to the smelter. Gran ANC has declined since 2012 but because sulphate is also lower than 2012, the decline must not be driven by smelter emission (as per the evidentiary framework). LAK007 is highly insensitive to acidic deposition – it has very high Gran ANC and is predicted to have zero change in Gran ANC from current levels with higher deposition (even under the sensitivity analyses of 200% deposition). Furthermore, its pH has not changed since 2012 and is not predicted to change under any deposition scenario or sensitivity analysis.

Table 4-1. Summary of the estimated critical loads and the predicted exceedances, pH and Gran ANC under the 42 tpd emissions scenarios. Red cells indicate critical loads of zero, positive exceedances, predicted declines in pH of greater than 0.3 pH units, or predicted declines in Gran ANC that exceed the lake-specific threshold. Yellow cells indicate predicted declines in pH of greater than 0.1 pH units (but less than 0.3 pH units). The changes in LAK007 and LAK034 are unrelated to the smelter, as per the evidentiary framework and further explained in the text.

	CALPUFF results		**SSWC Model Results**		**ESSA-DFO Model Results**								
	S Deposition (42tpd)		**Critical load**	**Ex(A)**	**pH**				**Gran ANC (µeq/L)**				
LAKE	**meq/ m^2/yr**	**kg/ha/ yr**	**meq/ m^2/yr**	**meq/ m^2/yr**	**Baseline (2012)**	**Post-KMP (2016-18)**	**Future (steady-state)**	**∆pH (from 2012)**	**Baseline (2012)**	**Post-KMP (2016-18)**	**Future (steady-state)**	**∆ANC (from 2012)**	**ANC threshold**
EEM Sensitive Lakes													
LAK006	12.2	5.9	29.4	-8.9	5.8	6.0	6.0	0.2	25.7	27.7	24.7	-1.0	-10.8
LAK012	11.8	5.7	68.1	-48.3	5.6	6.2	6.1	0.5	57.0	58.3	56.0	-1.0	-16.3
LAK022	11.2	5.4	58.3	-39.3	5.9	6.1	6.0	0.1	27.8	33.0	30.4	2.6	-11.5
LAK023	11.1	5.3	33.3	-13.9	5.7	5.9	5.9	0.2	19.8	26.4	23.8	4.0	-10.5
LAK028	63.6	30.5	81.1	-8.5	5.0	5.0	4.8	-0.2	-4.0	-3.5	-9.3	-5.3	-13.4
LAK042	3.4	1.6	17.4	-6.3	4.7	5.2	5.2	0.5	-20.4	5.6	4.2	24.6	-24.4
LAK044	3.6	1.7	0.0	11.4	5.4	5.6	5.5	0.1	1.3	5.0	2.8	1.5	-6.2
EEM Less Sensitive Lakes													
LAK007	22.1	10.6	1383.4	-1353.5	8.0	8.0	8.0	0.0	1437.6	1385.9	1385.9	-51.6	-50.6
LAK016	13.2	6.4	118.1	-96.7	6.3	6.7	6.6	0.3	68.7	89.8	88.0	19.4	-25.6
LAK024	11.8	5.7	551.6	-531.4	7.1	7.5	7.5	0.4	299.5	463.2	463.2	163.7	-60.4
LAK034	4.7	2.2	138.4	-126.0	6.7	6.4	6.4	-0.3	99.4	139.6	138.7	39.3	-22.0

4.2 STAR Criteria for Inclusion in EEM

As shown Figure 4-1, the STAR identified lakes with low pH (<6.0 pH units) and/or predicted exceedances of their critical loads and/or predicted declines in pH of greater than 0.1 pH units. The seven lakes identified for inclusion in the EEM program were those with a predicted pH decline of greater than 0.1 pH units. Lakes with existing pH<6.0 that did not have a predicted pH decline greater than 0.1 pH units were not included. Lakes with a positive exceedance and pH>6.0 would have been considered for inclusion but none of the STAR lakes met those criteria.

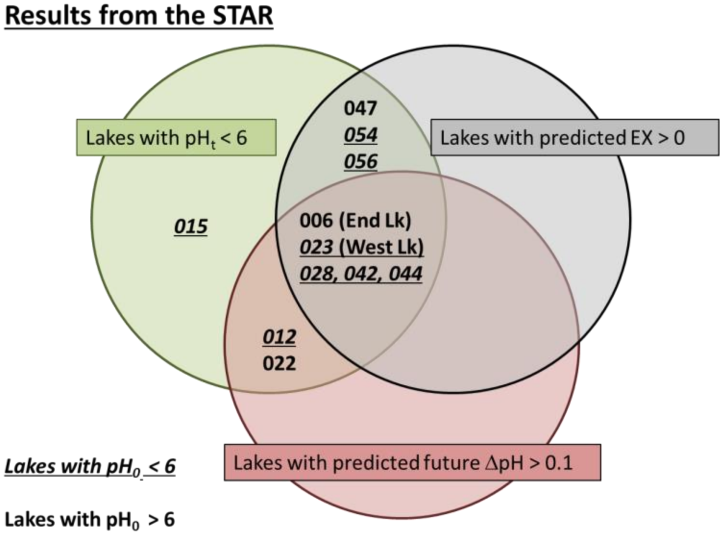

Figure 4-1. STAR classification of lakes with low pH, predicted exceedances of critical loads and/or predicted declines in pH greater 0.1 pH units. The EEM program selected the lakes with predicted pH decline >0.1 pH units.

We used the same criteria from the STAR to position the lakes within the study area (Figure 4-2). The updated classification shows that of the seven lakes previously predicted to have a future pH decline greater than 0.1 pH units relative to 2012, only one of the lakes (LAK028) remains in that classification. Furthermore, of the eight lakes previously predicted to have an exceedance under the maximum level of emissions, only four of those lakes remain in that classification and all those lakes are lakes with critical loads of zero. It should be noted that for Two KAA lakes added to the present study (but outside the boundaries of the STAR study area) also have exceedances predicted but similarly they also both have critical loads of zero, pre-KMP pH (i.e., 2013) less than 6.0 and also original pre-industrial pH less than 6.0 – therefore, had these lakes been included in the original STAR, they would have been identified as naturally acidic lakes with a negligible predicted change in pH and thus excluded for consideration as EEM lakes.

The results of the updated analyses of critical loads, exceedances and future pH, the results suggest that the STAR did not omit any lakes that should have been considered for inclusion in the EEM. Additionally, it suggests that many of the lakes included in the EEM no longer match the inclusion criteria initially applied.

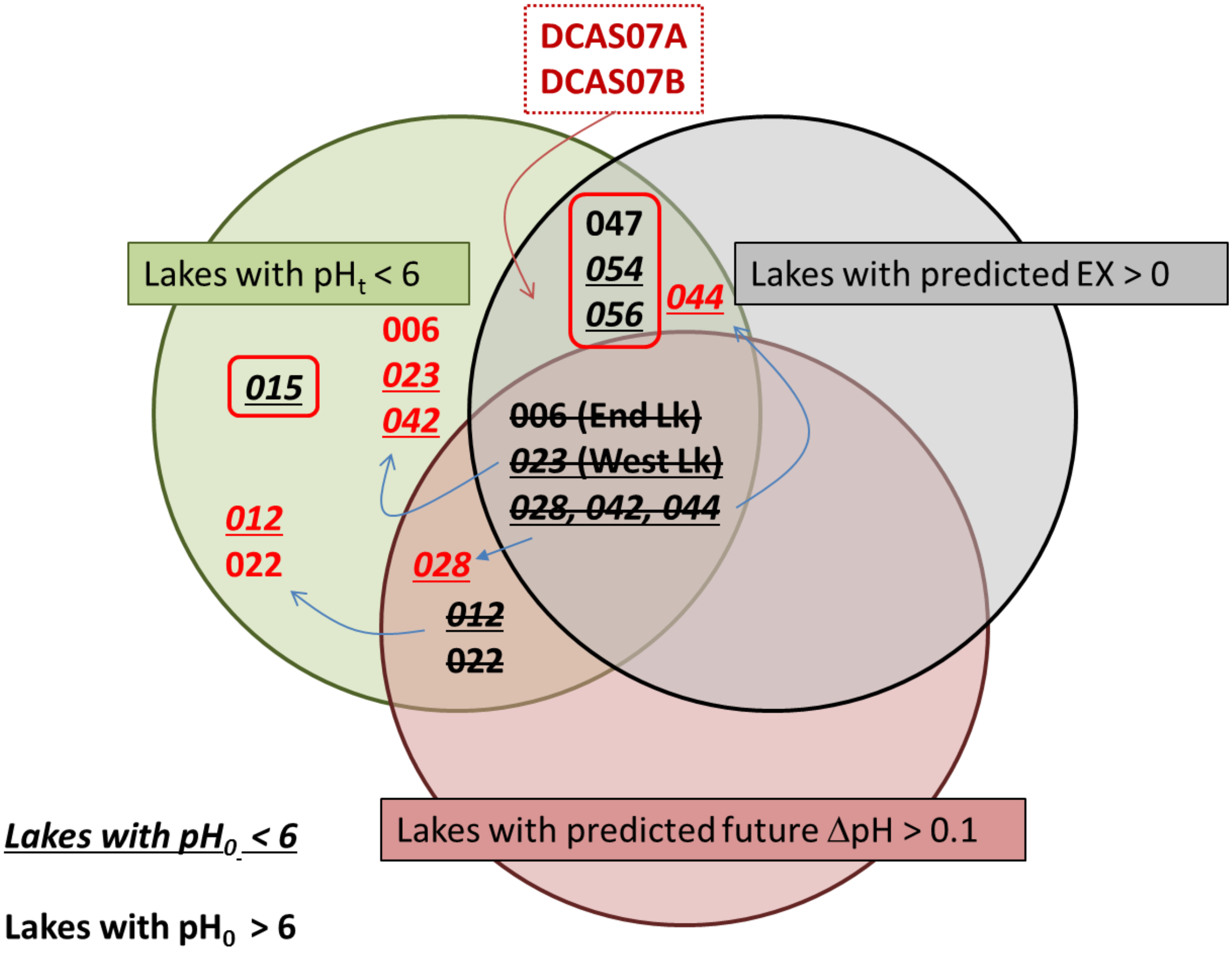

Figure 4-2. Application of the STAR criteria for identifying potential lakes for further monitoring using the new results available. Black font indicates original STAR position, strikethrough font indicates that the position has changed, red text indicates the new position, and red outline indicates that the position remained the same. Current pH (pH_t) and predicted change in pH are relative to 2012. DCAS07A and DCAS07B were from the KAA, therefore a) they were not included in the STAR classification, b) pH_t refers to 2013, and c) they do not have estimates of ΔpH (due to lacking deposition data for comparable emissions scenarios to the STAR). The results for LAK015, LAK047, LAK054, and LAK056 are based on their critical loads from the STAR (and do not have updated predictions of steady-state pH, as discussed elsewhere), whereas the results of LAK006, LAK012, LAK022, LAK023, LAK028, LAK042 and LAK044 (i.e., the EEM lakes) are based on the analyses using the most recent data.

7.8 Aquatic Appendix H: Kitimat River Water Quality

The following water quality sampling was conducted at the Rio Tinto intake from the Kitimat River during 2017 and 2018.

Water quality sampling results at Rio Tinto intake from Kitimat River during 2017

Parameter	Units	BC Drinking Water Quality Guidelines	Sampling date					
			26-Jun-17	31-Aug-17	30-Sep-17	9-Oct-17	30-Nov-17	31-Dec-17
Dissolved Sulphate (SO_4)	mg/l	**500**		2.04	1.85	1.95		3.94
Fluoride (F)	mg/l	**1.5**	0.032	0.028	0.036	0.037	0.041	0.017
Nitrate plus Nitrite (N)	mg/l			0.04	0.049	0.049	0.085	0.11
Total Suspended Solids	mg/l		<4.0	<4.0	8.5	53.8		
Dissolved Calcium (Ca)	mg/l		4.02	3.75	5.27	5.03	4.88	7.34
Dissolved Magnesium (Mg)	mg/l		0.384	0.398	0.588	0.598	0.579	0.883
Dissolved Hardness (CaCO3)	mg/l			11	15.6	15	14.6	22
pH			7.33	7.45	7.56	7.32	7.28	7.41
Dissolved Chloride (Cl)	mg/L							
Dissolved Aluminum (Al)	mg/l	**9.5**	0.0217	0.0225	0.0452	0.054	0.0931	0.0234
Dissolved Antimony (Sb)	mg/l		<0.00050		<0.00050	<0.00050	<0.00050	<0.00050
Dissolved Arsenic (As)	mg/l	**0.01**	<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Barium (Ba)	mg/l		0.0081		0.0113	0.0108	0.0108	0.0153
Dissolved Beryllium (Be)	mg/l		<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Bismuth (Bi)	mg/l		<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Boron (B)	mg/l		<0.050		<0.050	<0.050	<0.050	<0.050
Dissolved Cadmium (Cd)	mg/l	**0.005**	<0.000010		<0.000010	<0.000010	<0.000010	<0.000010
Dissolved Chromium (Cr)	mg/l		<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Cobalt (Co)	mg/l		<0.00020		<0.00020	<0.00020	<0.00020	<0.00020
Dissolved Copper (Cu)	mg/l	**1**	0.00312		0.0143	0.00727	0.0114	0.0042
Dissolved Iron (Fe)	mg/l	**0.3**	0.0427		0.0837	0.088	0.128	0.115
Dissolved Lead (Pb)	mg/l	**0.01**	<0.00020		<0.00020	<0.00020	<0.00020	<0.00020
Dissolved Lithium (Li)	mg/l		<0.0020		<0.0020	<0.0020	<0.0020	<0.0020
Dissolved Manganese (Mn)	mg/l	**0.05**	0.004		0.0068	0.0047	0.0148	0.0219
Dissolved Mercury (Hg)	mg/l	**0.001**	<0.000050					
Dissolved Molybdenum (Mo)	mg/l	**0.25**	<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Nickel (Ni)	mg/l		<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Selenium (Se)	mg/l	**0.01**	<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Silicon (Si)	mg/l		1.58		2.39	2.01	2.55	3.2
Dissolved Silver (Ag)	mg/l		<0.000020		<0.000020	<0.000020	<0.000020	<0.000020
Dissolved Strontium (Sr)	mg/l		0.0235		0.0322	0.0312	0.0281	0.0425
Dissolved Thallium (Tl)	mg/l		<0.000010		<0.000010	<0.000010	<0.000010	<0.000010
Dissolved Tin (Sn)	mg/l		<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Titanium (Ti)	mg/l		<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Uranium (U)	mg/l		<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Vanadium (V)	mg/l		<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zinc (Zn)	mg/l	**5**	<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zirconium (Zr)	mg/l		<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Potassium (K)	mg/l		0.354		0.605	0.548	0.429	0.658
Dissolved Sodium (Na)	mg/l		0.807		1.27	1.13	1.29	2.7
Dissolved Sulphur (S)	mg/l		<3.0		<3.0	<3.0	<3.0	<3.0

Water quality sampling results at Rio Tinto intake from Kitimat River during January to June 2018

Parameter	Units	BC Drinking Water Quality Guidelines	Sampling date				
			1-Jan-18	19-Mar-18	25-Apr-18	31-May-18	4-Jun-18
Dissolved Sulphate (SO_4)	mg/l	**500**	3.72	<0.50	2.09	1.86	2.31
Fluoride (F)	mg/l	**1.5**	0.045	0.045	0.049	0.035	0.036
Nitrate plus Nitrite (N)	mg/l		0.105	0.109	0.101	0.062	0.052
Total Suspended Solids	mg/l					4.5	<4.0
Dissolved Calcium (Ca)	mg/l		6.55	6.98	5.1	4.18	4.62
Dissolved Magnesium (Mg)	mg/l		0.731	0.86	0.561	0.484	0.469
Dissolved Hardness (CaCO3)	mg/l		19.4	21	15	12.4	13.5
pH			7.31	7.39	7.29	7.33	7.5
Dissolved Chloride (Cl)	mg/l					0.89	0.75
Dissolved Aluminum (Al)	mg/l	**9.5**	0.0436	0.0271	0.0731	0.041	0.0265
Dissolved Antimony (Sb)	mg/l		<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Dissolved Arsenic (As)	mg/l	**0.01**	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Barium (Ba)	mg/l		0.0127	0.0155	0.0108	0.0095	0.0095
Dissolved Beryllium (Be)	mg/l		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Bismuth (Bi)	mg/l		<0.001	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Boron (B)	mg/l		<0.050	<0.050	<0.050	<0.050	<0.050
Dissolved Cadmium (Cd)	mg/l	**0.005**	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Dissolved Chromium (Cr)	mg/l		<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Cobalt (Co)	mg/l		<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Dissolved Copper (Cu)	mg/l	**1**	0.00415	0.0166	0.00356	0.00438	0.0047
Dissolved Iron (Fe)	mg/l	**0.3**	0.118	0.153	0.0833	0.055	0.0523
Dissolved Lead (Pb)	mg/l	**0.01**	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Dissolved Lithium (Li)	mg/l		<0.002	<0.0020	<0.0020	<0.0020	<0.0020
Dissolved Manganese (Mn)	mg/l	**0.05**	0.0163	0.0084	0.0069	0.0066	0.0061
Dissolved Mercury (Hg)	mg/l	**0.001**					
Dissolved Molybdenum (Mo)	mg/l	**0.25**	<0.001	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Nickel (Ni)	mg/l		<0.001	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Selenium (Se)	mg/l	**0.01**	0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Silicon (Si)	mg/l		2.97	2.79	2.55	1.91	1.88
Dissolved Silver (Ag)	mg/l		<0.00002	<0.00002	<0.00002	<0.00002	<0.00002
Dissolved Strontium (Sr)	mg/l		0.0359	0.0471	0.0298	0.0308	0.0281
Dissolved Thallium (Tl)	mg/l		<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Dissolved Tin (Sn)	mg/l		<0.005	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Titanium (Ti)	mg/l		<0.005	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Uranium (U)	mg/l		<0.0001	<0.0001	0.0001	<0.0001	<0.0001
Dissolved Vanadium (V)	mg/l		<0.005	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zinc (Zn)	mg/l	**5**	<0.005	0.006	<0.0050	<0.0050	<0.0050
Dissolved Zirconium (Zr)	mg/l		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Potassium (K)	mg/l		0.539	0.548	0.423	0.401	0.396
Dissolved Sodium (Na)	mg/l		1.79	2.43	1.22	0.963	1.03
Dissolved Sulphur (S)	mg/l		<3.0	<3.0	<3.0	<3.0	<3.0

Water quality sampling results at Rio Tinto intake from Kitimat River during July to December 2018

Parameter	Units	BC Drinking Water Quality Guidelines	Sampling date					
			4-Jul-18	31-Aug-18	17-Sep-18	31-Oct-18	6-Nov-18	4-Dec-18
Dissolved Sulphate (SO_4)	mg/l	**500**	2.27	2.91	4.13	2.78	1.64	3.16
Fluoride (F)	mg/l	**1.5**	0.031	0.036	0.035	0.045	0.044	0.045
Nitrate plus Nitrite (N)	mg/l		0.036	0.027	0.051	0.122	0.129	0.136
Total Suspended Solids	mg/l		<4.0	<4.0	<4.0	<4.0	45.7	<4.0
Dissolved Calcium (Ca)	mg/l		4.34	5.07	6.08	4.44	4.77	6.32
Dissolved Magnesium (Mg)	mg/l		0.434	0.524	0.698	0.581	0.544	0.727
Dissolved Hardness (CaCO3)	mg/l		12.6	14.8	18.1	16.2	14.2	18.8
pH			6.99	7.68	7.68	7.22	7.16	7.47
Dissolved Chloride (Cl)	mg/l		0.88	1.1	1.8	1.3	0.83	1.5
Dissolved Aluminum (Al)	mg/l	**9.5**	0.0242	0.0106	0.0105	0.0519	0.0518	0.0312
Dissolved Antimony (Sb)	mg/l		<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Dissolved Arsenic (As)	mg/l	**0.01**	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Barium (Ba)	mg/l		0.0093	0.0110	0.0136	0.0114	0.0107	0.0134
Dissolved Beryllium (Be)	mg/l		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Bismuth (Bi)	mg/l		<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Boron (B)	mg/l		<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
Dissolved Cadmium (Cd)	mg/l	**0.005**	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Dissolved Chromium (Cr)	mg/l		<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Cobalt (Co)	mg/l		<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Dissolved Copper (Cu)	mg/l	**1**	0.00335	0.0004	0.00327	0.00561	0.00559	0.00399
Dissolved Iron (Fe)	mg/l	**0.3**	0.0339	0.0278	0.0592	0.0742	0.0705	0.11
Dissolved Lead (Pb)	mg/l	**0.01**	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Dissolved Lithium (Li)	mg/l		<0.0020	<0.0020	<0.0020	<0.0020	<0.0020	<0.0020
Dissolved Manganese (Mn)	mg/l	**0.05**	0.0049	<0.0010	0.0121	0.0024	0.0075	0.0151
Dissolved Mercury (Hg)	mg/l	**0.001**		<0.0020				
Dissolved Molybdenum (Mo)	mg/l	**0.25**	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Nickel (Ni)	mg/l		<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Selenium (Se)	mg/l	**0.01**	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Silicon (Si)	mg/l		1.64	1.71	2.09	2.26	1.84	2.79
Dissolved Silver (Ag)	mg/l		<0.00002	<0.00002	<0.00002	<0.00002	<0.00002	<0.00002
Dissolved Strontium (Sr)	mg/l		0.0260	0.0305	0.0370	0.0317	0.0282	0.0364
Dissolved Thallium (Tl)	mg/l		<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Dissolved Tin (Sn)	mg/l		<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Titanium (Ti)	mg/l		<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Uranium (U)	mg/l		<0.0001	<0.0001	<0.0001	0.00011	0.00011	<0.0001
Dissolved Vanadium (V)	mg/l		<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zinc (Zn)	mg/l	**5**	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zirconium (Zr)	mg/l		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Dissolved Potassium (K)	mg/l		0.496	0.584	0.603	0.522	0.477	0.582
Dissolved Sodium (Na)	mg/l		0.974	1.48	2.06	1.24	1.12	1.93
Dissolved Sulphur (S)	mg/l		<3.0	<3.0	<3.0	<3.0	<3.0	<3.0

7.9 Aquatic Appendix I: Sensitivity Analyses with Alternative Baseline

7.9.1 Introduction

7.9.1.1 Purpose of Appendix

The aquatic analyses presented in the Comprehensive Review use the lake chemistry data for 2012 as the pre-KMP baseline. The purpose of this appendix is to present and discuss sensitivity analyses that we conducted using an alternate baseline based on the transition period of 2012-2014. The rationale for using 2012 alone for the pre-KMP baseline, along with acknowledgement of the inherent concerns of doing so, are presented in the main report (Section 7.3.2.2) and reiterated below. However, the reviewers of the draft Comprehensive Review expressed a strong interest in understanding the potential impacts that using an alternatively defined baseline could have on the reported results.

7.9.1.2 Structure of Appendix

This appendix includes the results of the sensitivity analyses as applied to three sets of analyses in the Comprehensive Review for which the definition of the baseline is relevant: the deterministic analyses of the empirical data (i.e., main report Section 7.3.1 and Aquatic Appendix A, the statistical analyses (i.e., main report Section 7.3.2.3 and Aquatic Appendix F), and the predicted future steady-state pH (main report Section 7.3.2.5 and Aquatic Appendix G).

For all three sets, the results of the sensitivity analyses using an alternative baseline are presented in this appendix only, which is briefly referenced in the main report.

7.9.1.3 Baselines

This section provides a brief summary of the history of baselines in the EEM Plan, Program and Comprehensive Report.

7.9.1.3.1 EEM Plan

In the EEM Plan, the aquatic KPI was defined based on observed changes in pH relative to the “mean baseline pH level measured pre-KMP”. The EEM Plan also provided further details on how it was anticipated that the pre-KMP baseline should be defined:

> *“For water quality parameters which show statistically or biologically significant differences between summer 2012 and fall 2013/2014 values, the mean baseline pre-KMP values will be defined as the mean of the fall index samples in 2013 and 2014. For parameters which showed no statistically or biologically significant differences between summer 2012 and fall 2013 samples, the mean baseline pre-KMP values will be defined as the mean of summer 2012, fall 2013 and fall 2014 values.”* (EEM Plan, Section 6.2.1, p. 36)

The EEM Annual Reports for 2015, 2016 and 2017 focused on reporting and interpreting inter-annual changes. These annual reports also reported the observed change over the period of record (i.e., 2012 to 201x) but did not explicitly examine pre-/post-KMP changes (due to the limited number of years of post-KMP data and deference to the upcoming Comprehensive Review).

7.9.1.3.2 EEM Program

The decision to use 2012 as the baseline emerged over several years during implementation of the EEM program, and completion of the Comprehensive Report. The statistical power analyses (EEM 2016 Technical Memo W04) sought to determine the ability to detect changes in lake chemistry, and therefore used all of the data available at that time (i.e., a 2012-14 baseline):

> *"The lake chemistry model starts with the baseline lake chemistry observations, adds a defined hypothetical KMP effect, and then adds assumed variability over a 20-year period. We defined the baseline conditions as the average of the observed values in 2012-2014. This period does not represent an ideal, stable baseline because KMP emissions were already declining during this period (and for several years previously), and therefore were lower than longer-term pre-KMP baseline conditions. Given the pre-KMP data available, alternate baselines could have included the average of 2013-2014 (i.e., only use fall samples) or just 2014 (i.e., the last year prior to KMP); however, both of these options would reduce the number of pre-KMP observations and decrease the power to detect changes in the primary metrics. We opted to utilize all of the pre-KMP data in defining the baseline."* (EEM 2016 Technical Memo W04, "Summary Report on Power Analyses", p. 9)

Over time, we realized that the period from 2012-2014 was better described as a *transition period* with the decommissioning of the old smelter, and not as a pre-KMP baseline. For the Comprehensive Report, we were faced with two less than ideal options: using a single observation from August 2012 as a pre-KMP baseline; and using observations from the 2012-2014 transition period with potential confounding from the decommissioning of the old smelter and its influences on lake chemistry. As described in Section 7.3.2.2 of the main report, we chose to use 2012 as the baseline for pH and Gran ANC. Using the 2012-2014 transition period as a baseline for pH and Gran ANC would have increased the risk of Type I error (a false positive) in testing for exceedances of thresholds for ΔpH and ΔANC. In general, the pH and Gran ANC of the EEM sensitive lakes increased during the 2012-2014 period as SO_2 emissions from the old smelter declined (Sections 7.6.2.1.2 and 7.6.2.1.3 of Aquatic Appendix F). Including pH and ANC observations from 2013 and 2014 in the estimates of mean pre-KMP pH and mean pre-KMP Gran ANC would increase those metrics to a level that is not representative of the pre-KMP period prior to and including 2012, and increase the risk of a false exceedance of the thresholds for changes in pH and Gran ANC. Changes in lake [SO_4] are an important part of the simplified and full evidentiary frameworks (main report Section 7.3.4.5). Using 2012-2014 as a baseline also could increase the risk of a false positive for detecting an increase in lake [SO_4], if a lake's [SO_4] decreased during 2013-3014 due to the decommissioning of the old smelter and reduced emissions of SO_2. Therefore, both the draft Comprehensive Report and the 2018 EEM Report used 2012 as a baseline for comparison.

In the following sections, we use the transition period from 2012-2014 as a baseline, either with unadjusted EEM thresholds (Section 7.9.2 and Analysis A in Section 7.9.3) or using adjusted thresholds that consider changes in lake chemistry between 2012 and 2014 (Analysis B in Section 7.9.3). As noted in Table 7.80:

- Analysis A may overestimate smelter impacts relative to the pre-KMP condition, as values of lake pH and Gran ANC, may have increased during 2012-14 due to the decommissioning of the old smelter and associated declines in SO_2 emissions. Since 2012-14 was a transition period rather than a pre-KMP period, Analysis A has a higher risk of false positives.

- Analysis B may under-estimate smelter impacts since it assumes that any increases in lake pH or Gran ANC from 2012 to 2014 were due to declining emissions during decommissioning of the old smelter, and adjusts pH and ANC thresholds accordingly. Analysis B therefore has a higher risk of false negatives.

7.9.2 Deterministic Analyses of Empirical Data

This section of the sensitivity analysis simply computes the mean values of pH, Gran ANC and SO_4 for each of the two alternative baselines: the 2012 pre-KMP year and the 2012-2014 transition period. We then calculate the average values of these parameters for the 2016-2018 post-KMP period, and the changes relative to each of the two alternative baselines. These comparisons do not apply any statistical methods. Statistical analyses are included in Section 7.9.3 of this appendix.

One caveat is that the lake-specific thresholds for ΔGran ANC were based on processing data from laboratory titrations at Trent University, to determine how much change in Gran ANC corresponded to a 0.3 unit change in pH from the 2012 pH. We did not go through the laborious process of estimating how much change in Gran ANC would correspond to a 0.3 unit change in pH from the mean pH during 2012-2014.

7.9.2.1 Changes in pH, Gran ANC and SO_4 against pre-KMP and transition period baselines

Table 7.76 demonstrates that comparing post-KMP values during 2016-2018 to the 2012-2014 baseline generates estimates of ΔpH and ΔANC that are more negative than using a 2012 baseline (e.g., LAK028 shows a -0.2 unit change in pH relative to the 2012-2014 baseline, and a 0.0 unit pH change relative to the 2012 baseline). This is to be expected given that 10 out of the 11 lakes had higher 2012-2014 mean values for pH than their estimates from 2012; the only exception was LAK007 for which the mean pH for 2012-2014 is the same as its 2012 value (8.0; Table 7.76). All 11 lakes had higher 2012-2014 mean values for Gran ANC than their 2012 value (Table 7.76). The control lakes are not included in Table 7.76 since the only pre-KMP measurement was for 2013, and it therefore is not possible to compare the two alternative baselines.

Eight of the 11 lakes had higher 2012-2014 mean values for SO_4 than their 2012 measurement. This general increase in SO_4 was not expected since average SO_2 emissions from the smelter declined from 16.1 tpd in 2012 to 11.6 tpd between 2012 and 2014. The pattern of changes in SO_4 suggested that there may have been some hydrologic changes across 2012-2014 (e.g., less precipitation could cause less dilution and higher concentrations of both SO_4 and Gran ANC, and higher pH values). We therefore explored the correlations between lake chemistry and levels of precipitation in the 2 months prior to lake sampling (Appendix I Section 7.9.3.5), and the effects of including precipitation (and lake sensitivity) on statistical analyses of a smelter effect (Appendix I Section 7.9.3.6).

Table 7.77 compares the two estimates of ΔpH from the two baselines to the EEM threshold of 0.3 pH units. None of lakes show an exceedance of the pH threshold under either baseline. A similar conclusion is found for Gran ANC (Table 7.78). The only exception is for LAK034, where application of the 2012-2014 baseline results in an exceedance of the threshold for ΔGran ANC. As indicated in the footnote to Table 7.78, the decrease in Gran ANC in LAK034 cannot be associated with sulphur-driven acidification from the smelter because the concentration of SO_4

decreased to zero during the monitoring period. Table 7.79 shows that 9 of the 11 lakes generated the same direction of change in lake SO_4 under the two different baselines.

Table 7.76. Mean values of pH, Gran ANC and SO_4 for two different baselines (2012 and 2012-14), the 2016-2018 post-KMP period , the changes between these two periods, and the EEM thresholds.

	pH						Gran ANC (µeq/L)						SO_4^{2-}*(µeq/L)				
	Baseline		Post-KMP	ΔpH			Baseline		Post-KMP	ΔANC			Baseline		Post-KMP	ΔSO_4^{2-*}	
EEM sensitive lakes	2012	2012-14	2016-18	vs. 2012	vs. 2012-14	EEM Threshold	2012	2012-14	2016-18	vs. 2012	vs. 2012-14	Threshold †	2012	2012-14	2016-18	vs. 2012	vs. 2012-14
LAK006	5.8	6.0	6.0	0.2	0.0	-0.3	25.7	31.2	27.7	2.0	-3.5	-10.8	11.4	12.6	14.0	2.5	1.3
LAK012	5.6	6.0	6.2	0.5	0.2	-0.3	57.0	63.1	58.3	1.3	-4.8	-16.3	6.1	11.1	12.9	6.8	1.8
LAK022	5.9	6.1	6.1	0.1	0.0	-0.3	27.8	37.0	33.0	5.1	-4.1	-11.5	30.2	38.4	38.8	8.6	0.4
LAK023	5.7	5.9	5.9	0.2	0.1	-0.3	19.8	25.2	26.4	6.7	1.2	-10.5	19.0	20.7	12.3	-6.7	-8.4
LAK028	5.0	5.2	5.0	0.0	-0.2	-0.3	-4.0	7.8	-3.5	0.5	-11.3	-13.4	56.9	93.1	128.4	71.5	35.3
LAK042	4.7	5.1	5.2	0.5	0.1	-0.3	-20.4	4.4	5.6	26.1	1.3	-24.4	6.2	5.3	5.4	-0.8	0.1
LAK044	5.4	5.6	5.6	0.2	-0.1	-0.3	1.3	5.2	5.0	3.7	-0.2	-6.2	6.2	5.7	4.4	-1.9	-1.3
Total lakes with increase				**7**	**4**					**7**	**2**					**4**	**5**
Total lakes with decrease				**0**	**3**					**0**	**5**					**3**	**2**

EEM less sensitive lakes	2012	2012-14	2016-18	vs .2012	vs. 2012-14	EEM Threshold	2012	2012-14	2016-18	vs. 2012	vs. 2012-14	Threshold †	2012	2012-14	2016-18	vs. 2012	vs. 2012-14
LAK007	8.0	8.0	8.0	0.0	0.0	-0.3	1437.6	1448.5	1385.9	-51.6	-62.5	-50.6	51.4	49.6	47.0	-4.4	-2.6
LAK016	6.3	6.6	6.7	0.3	0.1	-0.3	68.7	90.4	89.8	21.1	-0.6	-25.6	39.0	48.0	44.5	5.4	-3.6
LAK024	7.1	7.4	7.5	0.4	0.1	-0.3	299.5	385.8	463.2	163.7	77.4	-60.4	24.8	31.0	38.9	14.1	7.9
LAK034	6.7	6.8	6.4	-0.3	-0.3	-0.3	99.4	171.6	139.6	40.2	-32.0	-22.0	24.1	26.4	0.1	-24.0	-26.3
Total lakes with increase				**3**	**3**					**3**	**1**					**2**	**1**
Total lakes with decrease				**1**	**1**					**1**	**3**					**2**	**3**

† The Gran ANC threshold was determined (based on analysis of the titration data) as the magnitude of change in Gran ANC equivalent to a 0.3 pH unit decline *from the 2012 pH value.*

Table 7.77. Comparisons of ΔpH versus 0.3 threshold for the 2012 and 2012-2014 baselines.

	pH								
	Baseline		Post-KMP	ΔpH			Observed post-KMP change in pH relative to threshold based on empirical data		
EEM sensitive lakes	2012	2012-14	2016-18	vs. 2012	vs. 2012-14	EEM Threshold	vs. 2012	vs. 2012-14	Does the alternate baseline change the conclusion for this metric?
LAK006	5.8	6.0	6.0	0.2	0.0	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK012	5.6	6.0	6.2	0.5	0.2	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK022	5.9	6.1	6.1	0.1	0.0	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK023	5.7	5.9	5.9	0.2	0.1	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK028	5.0	5.2	5.0	0.0	-0.2	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK042	4.7	5.1	5.2	0.5	0.1	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK044	5.4	5.6	5.6	0.2	-0.1	-0.3	Does not exceed threshold	Does not exceed threshold	No
Total lakes with increase				**7**	**4**				
Total lakes with decrease				**0**	**3**				

EEM less sensitive lakes	2012	2012-14	2016-18	vs .2012	vs. 2012-14	EEM Threshold	vs. 2012	vs. 2012-14	Does the alternate baseline change the conclusion for this metric?
LAK007	8.0	8.0	8.0	0.0	0.0	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK016	6.3	6.6	6.7	0.3	0.1	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK024	7.1	7.4	7.5	0.4	0.1	-0.3	Does not exceed threshold	Does not exceed threshold	No
LAK034	6.7	6.8	6.4	-0.3	-0.3	-0.3	Magnitude of change equivalent to threshold †	Magnitude of change equivalent to threshold †	No
Total lakes with increase				**3**	**3**				
Total lakes with decrease				**1**	**1**				

† The decrease in pH in LAK034 cannot be associated with sulphur-driven acidification from the smelter because the concentration of SO_4 decreased to zero during the monitoring period.

Table 7.78. Empirical comparisons of ΔGran ANC versus lake-specific thresholds for the 2012 and 2012-2014 baselines.

	Gran ANC (μeq/L)								
	Baseline		Post-KMP	ΔANC			Observed post-KMP change in Gran ANC relative to threshold based on empirical data		
EEM sensitive lakes	**2012**	**2012-14**	**2016-18**		**vs. 2012-14**	**Threshold †**	**vs. 2012**	**vs. 2012-14**	**Does the alternate baseline change the conclusion for this metric?**
LAK006	25.7	31.2	27.7	2.0	-3.5	-10.8	Does not exceed threshold	Does not exceed threshold	No
LAK012	57.0	63.1	58.3	1.3	-4.8	-16.3	Does not exceed threshold	Does not exceed threshold	No
LAK022	27.8	37.0	33.0	5.1	-4.1	-11.5	Does not exceed threshold	Does not exceed threshold	No
LAK023	19.8	25.2	26.4	6.7	1.2	-10.5	Does not exceed threshold	Does not exceed threshold	No
LAK028	-4.0	7.8	-3.5	0.5	-11.3	-13.4	Does not exceed threshold	Does not exceed threshold	No
LAK042	-20.4	4.4	5.6	26.1	1.3	-24.4	Does not exceed threshold	Does not exceed threshold	No
LAK044	1.3	5.2	5.0	3.7	-0.2	-6.2	Does not exceed threshold	Does not exceed threshold	No
Total lakes with increase				**7**	**2**				
Total lakes with decrease				**0**	**5**				

EEM less sensitive lakes	**2012**	**2012-14**	**2016-18**	**vs. 2012**	**vs. 2012-14**	**Threshold †**	**vs. 2012**	**vs. 2012-14**	**Does the alternate baseline change the conclusion for this metric?**
LAK007	1437.6	1448.5	1385.9	-51.6	-62.5	-50.6	Exceeds threshold	Exceeds threshold	No
LAK016	68.7	90.4	89.8	21.1	-0.6	-25.6	Does not exceed threshold	Does not exceed threshold	No
LAK024	299.5	385.8	463.2	163.7	77.4	-60.4	Does not exceed threshold	Does not exceed threshold	No
LAK034	99.4	171.6	139.6	40.2	-32.0	-22.0	Does not exceed threshold	Exceeds threshold	**Yes***
Total lakes with increase				**3**	**1**				
Total lakes with decrease				**1**	**3**				

† The Gran ANC threshold was determined (based on analysis of the titration data) as the magnitude of change in Gran ANC equivalent to a 0.3 pH unit decline *from the 2012 pH value.*

* The decrease in Gran ANC in LAK034 cannot be associated with sulphur-driven acidification from the smelter because the concentration of SO_4 decreased to zero during the monitoring period.

Table 7.79. Comparisons of ΔSO_4 versus for the 2012 and 2012-2014 baselines.

	SO_4^{2-*}(µeq/L)							
	Baseline		Post-KMP	ΔSO_4^{2-*}		Observed post-KMP change in SO_4 based on empirical data		
EEM sensitive lakes	2012	2012-14	2016-18	vs. 2012	vs. 2012-14	vs. 2012	vs. 2012-14	Does the alternate baseline change the conclusion for this metric?
LAK006	11.4	12.6	14.0	2.5	1.3	SO_4 increased	SO_4 increased	No
LAK012	6.1	11.1	12.9	6.8	1.8	SO_4 increased	SO_4 increased	No
LAK022	30.2	38.4	38.8	8.6	0.4	SO_4 increased	SO_4 increased	No
LAK023	19.0	20.7	12.3	-6.7	-8.4	SO_4 decreased	SO_4 decreased	No
LAK028	56.9	93.1	128.4	71.5	35.3	SO_4 increased	SO_4 increased	No
LAK042	6.2	5.3	5.4	-0.8	0.1	SO_4 decreased	SO_4 increased	Yes (but difference is negligible)
LAK044	6.2	5.7	4.4	-1.9	-1.3	SO_4 decreased	SO_4 decreased	No
Total lakes with increase				4	5			
Total lakes with decrease				3	2			

EEM less sensitive lakes	2012	2012-14	2016-18	vs. 2012	vs. 2012-14	vs. 2012	vs. 2012-14	Does the alternate baseline change the conclusion for this metric?
LAK007	51.4	49.6	47.0	-4.4	-2.6	SO_4 decreased	SO_4 decreased	No
LAK016	39.0	48.0	44.5	5.4	-3.6	SO_4 increased	SO_4 decreased	Yes
LAK024	24.8	31.0	38.9	14.1	7.9	SO_4 increased	SO_4 increased	No
LAK034	24.1	26.4	0.1	-24.0	-26.3	SO_4 decreased	SO_4 decreased	No
Total lakes with increase				2	1			
Total lakes with decrease				2	3			

7.9.3 Statistical Analyses

Based on feedback from reviewers of the draft Comprehensive Report, we completed four sensitivity analyses of selected statistical analyses in Aquatic Appendix F, as described in Table 7.80. As explained at the end of Section 7.9.1, and in Table 7.80, we completed two analyses (A and B), which were designed to bracket the potential effects of the smelter on lake chemistry: Analysis A (2012-14 baseline, EEM thresholds) is more likely to over-estimate the effects of the smelter on lake chemistry, while Analysis B (2012-14 baseline, adjusted thresholds) is more likely to under-estimate these effects. The adjusted thresholds for ΔpH (Table 7.81) are 0.3 + (Mean $pH_{2012\text{-}14} - pH_{2012}$). The adjusted thresholds for ΔGran ANC (Table 7.81) are the EEM lake-specific threshold + (Mean Gran $ANC_{2012\text{-}14} - GranANC_{2012}$). Analyses A and B can be illustrated for LAK028, which had a pH of 5.0 in 2012, and a mean pH of 5.2 over 2012-14 (i.e., an increase of 0.2 pH units over the 2012 value). In applying analysis A to LAK028, we used a mean pH of 5.2 as the 2012-14 baseline, and the EEM threshold of 0.3 pH units. In applying analysis B to LAK028, we also used a mean pH of 5.2 as the 2012-14 baseline, but applied an adjusted EEM threshold of 0.5 pH units (i.e., the 0.3 unit threshold from the EEM Plan, plus the 0.2 pH unit difference between the 2012 measurement and the 2012-14 mean value).

Table 7.80. Sensitivity analyses to explore effects of alternate baseline periods and additional covariates.

Analysis Code	Question Addressed	Methods / Assumptions	Interpretation
A	*How are conclusions on the % belief in changes in SO_4, Gran ANC and pH altered if the statistical analysis uses 2012-2014 as a baseline rather than 2012, and keeps the same thresholds for ΔpH and ΔGran ANC? (Section 7.9.3.1 to Section 7.9.3.4)*	Repeat the Bayesian analyses of chemical changes, using a 2012-2014 baseline with the same thresholds for ΔpH and ΔGran ANC (i.e., 0.3 pH units and corresponding threshold for ΔGran ANC).	Analysis A may overestimate smelter impacts relative to the pre-KMP condition, as values of lake pH and Gran ANC may have increased during 2012-14 due to the decommissioning of the old smelter and associated declines in SO_2 emissions. Since 2012-14 was a transition period rather than a pre-KMP period, Analysis A has a higher risk of false positives.
B	*How are conclusions on the % belief in changes in Gran ANC and pH altered if the statistical analysis uses 2012-2014 as a baseline rather than 2012, and the thresholds for pH and Gran ANC are adjusted?*	Repeat the Bayesian analyses of chemical changes, using a 2012-2014 baseline, and use larger thresholds for ΔpH and ΔGran ANC, based on the difference between the 2013-2014 mean value and the 2012 value.	Analysis B may under-estimate smelter impacts since it assumes that any increases in lake pH or Gran ANC from 2012 to 2014 were due to declining emissions during decommissioning of the old smelter, and adjusts pH and ANC thresholds accordingly. Analysis B therefore has a higher risk of false negatives.
C	*To what extent are changes in lake chemistry correlated with seasonal changes in precipitation? (Section 7.9.3.5)*	Linear regressions between pH, ANC, SO_4 and total precipitation in the 2 months prior to sampling[19]. Previous analyses in Appendix F (Section 7.6.2.2) looked at correlations over much shorter time periods (3 days and 14 days), to assess the effects of storm events.	If seasonal changes in precipitation affect water chemistry (e.g., lower values of SO_4, Gran ANC, and pH after relatively wet periods due to dilution effects), then precipitation should be used as a covariate in all statistical analyses.
D	*To what extent are the results of the Before-After-Control-Impact (BACI) analysis altered if precipitation and lake sensitivity are included as covariates? (Section 7.9.3.6)*	Include seasonal precipitation in the prior 2 months (analysis C) and each lake's F-factor in the statistical analysis. This BACI sensitivity analysis adds two covariates (seasonal precipitation and lake sensitivity) to the BACI analyses done previously.	If either of these covariates are statistically significant it indicates that lake chemistry is correlated with changes in that covariate, which might alter the evidence for a smelter effect in the BACI analysis.

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[19] Computed by averaging the monthly precipitation at the Kitimat Townsite and Terrace monitoring stations for each month, and then summing those averages for the two months prior to sampling: June-July for August 2012 sampling; and August-Sept for 2013-2018 October sampling.

Table 7.81. EEM thresholds and adjusted thresholds for ΔpH and ΔGran ANC. See text for explanation of computation.

	pH				Gran ANC (μeq/L)			
	Baseline		ΔpH		Baseline		ΔANC	
EEM sensitive lakes	2012	2012-14	EEM Threshold	Adjusted Threshold	2012	2012-14	EEM Threshold	Adjusted Threshold
LAK006	5.8	6.0	-0.3	-0.52	25.7	31.2	-10.8	-16.3
LAK012	5.6	6.0	-0.3	-0.64	57.0	63.1	-16.3	-22.4
LAK022	5.9	6.1	-0.3	-0.49	27.8	37.0	-11.5	-20.7
LAK023	5.7	5.9	-0.3	-0.45	19.8	25.2	-10.5	-16.0
LAK028	5.0	5.2	-0.3	-0.5	-4.0	7.8	-13.4	-25.2
LAK042	4.7	5.1	-0.3	-0.7	-20.4	4.4	-24.4	-49.2
LAK044	5.4	5.6	-0.3	-0.5	1.3	5.2	-6.2	-10.2

EEM less sensitive lakes	2012	2012-14	EEM Threshold	Adjusted Threshold	2012	2012-14	EEM Threshold	Adjusted Threshold
LAK007	8.0	8.0	-0.3	-0.32	1437.6	1448.5	-50.6	-61.5
LAK016	6.3	6.6	-0.3	-0.57	68.7	90.4	-25.6	-47.4
LAK024	7.1	7.4	-0.3	-0.55	299.5	385.8	-60.4	-146.7
LAK034	6.7	6.8	-0.3	-0.34	99.4	171.6	-22.0	-94.2

7.9.3.1 Effects of alternative baseline on estimated ΔSO_4

We are interested if application of the alternative baseline changes the overall level of support for an increase in concentrations of lake SO_4, which is the first step in the evidentiary framework (Figure 7-10 in main report). A % belief greater than 80% is considered strong support, 20-80% is considered intermediate support, and less than 20% is considered weak support.

Including the transition period in the baseline (2012-2014; Analysis A from Table 7.80) *decreased* the % belief of a SO_4 increase in three of the sensitive lakes, from high (>80%) to intermediate (20-80%), and did not change the level of support for an increase in sulphate in the other four sensitive lakes. The overall conclusion is that there is *less* of an effect of SO_2 emissions on lake sulphate concentrations in the sensitive lakes (Figure 7.142). The statistical analysis reflects the fact that the mean concentration of SO_4 over 2012-14 was higher than the 2012 concentration in 4 of the 7 sensitive lakes (LAK006, LAK012, LAK022, LAK028), as shown in Table 7.76.

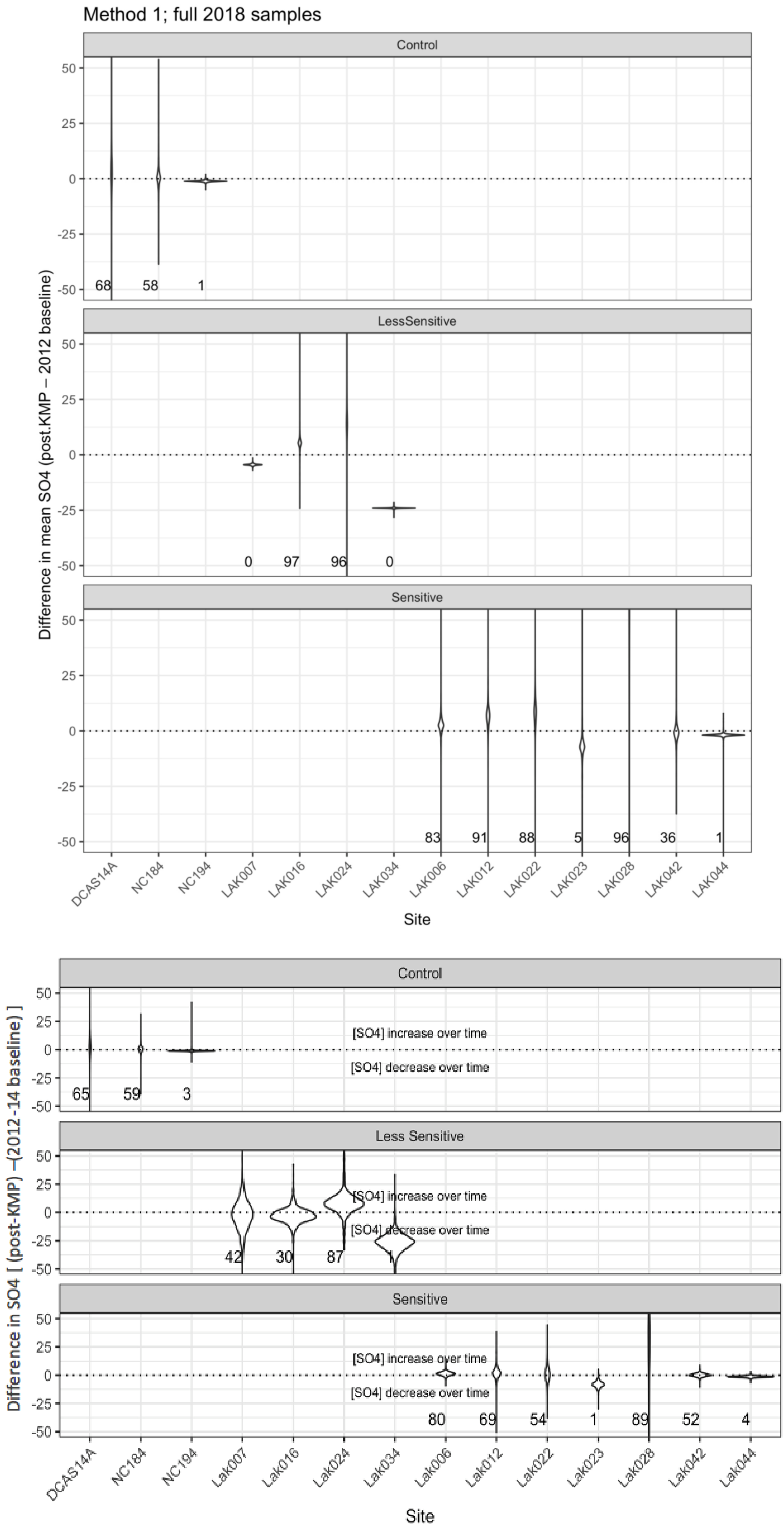


Figure 7.142. Percent belief in lake-specific change in sulphate given: 1) original baseline period of 2012 (upper figure; Figure 7.115, Aquatic Appendix F); and 2) an alternate baseline period of 2012-2014 (lower). The number at the base of each plot indicates the percent belief in an *increase* in sulphate.

7.9.3.2 Effects of alternative baseline on estimated ΔpH

The purpose of this analysis is to determine if there is a change in the level of support for a decline of beyond the KPI threshold of 0.3 pH units (Analysis A), or an adjusted threshold (Analysis B), when using the transition period baseline (2012-2014).

Using the transition period baseline (2012-2014; Analysis A) there is an *increase* in the % belief (from 10% to 20%, still considered ‘low’) that pH declined by 0.3 pH units in LAK028. Though there are 1-5% changes in the % belief in eight of the other lakes, and one larger change (31% in LAK034) these shifts do not affect the category of support (i.e., low < 20%, intermediate 20-80%, high > 80%) for a 0.3 pH decline (Figure 7.143).

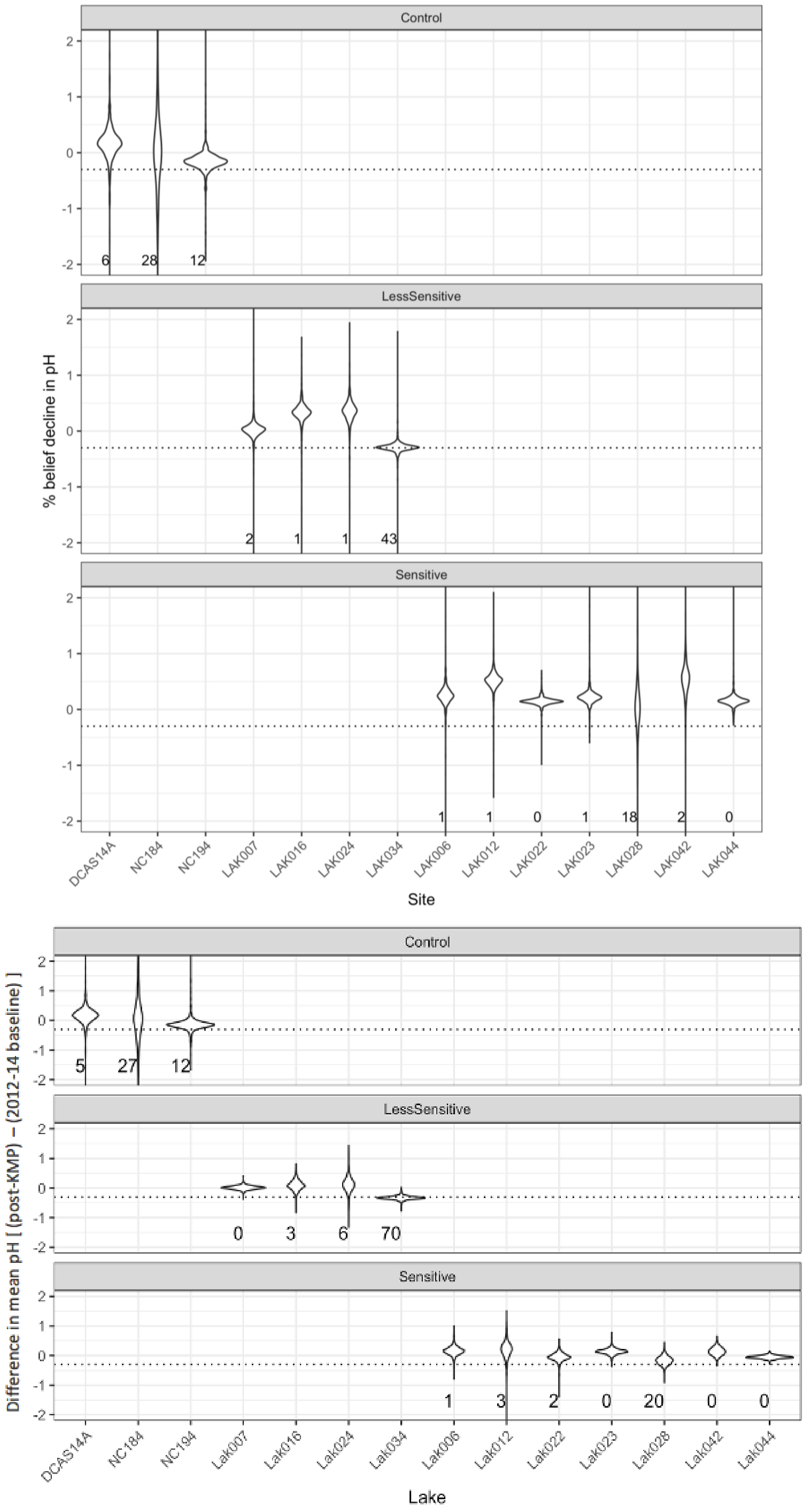


Figure 7.143. Percent belief in lake-specific ΔpH > 0.3 given: 1) original baseline period of 2012 (upper figure; Figure 7.127, Aquatic Appendix F); and 2) alternate baseline period of 2012-2014 (lower figure). The number at the base of each plot indicates the percent belief in a decline in pH greater than the threshold of 0.3 pH units.

When considering the adjusted threshold in addition to the transition baseline (Analysis B), there is generally a *decrease* in the % belief that pH has declined beyond the threshold (Figure 7.144).

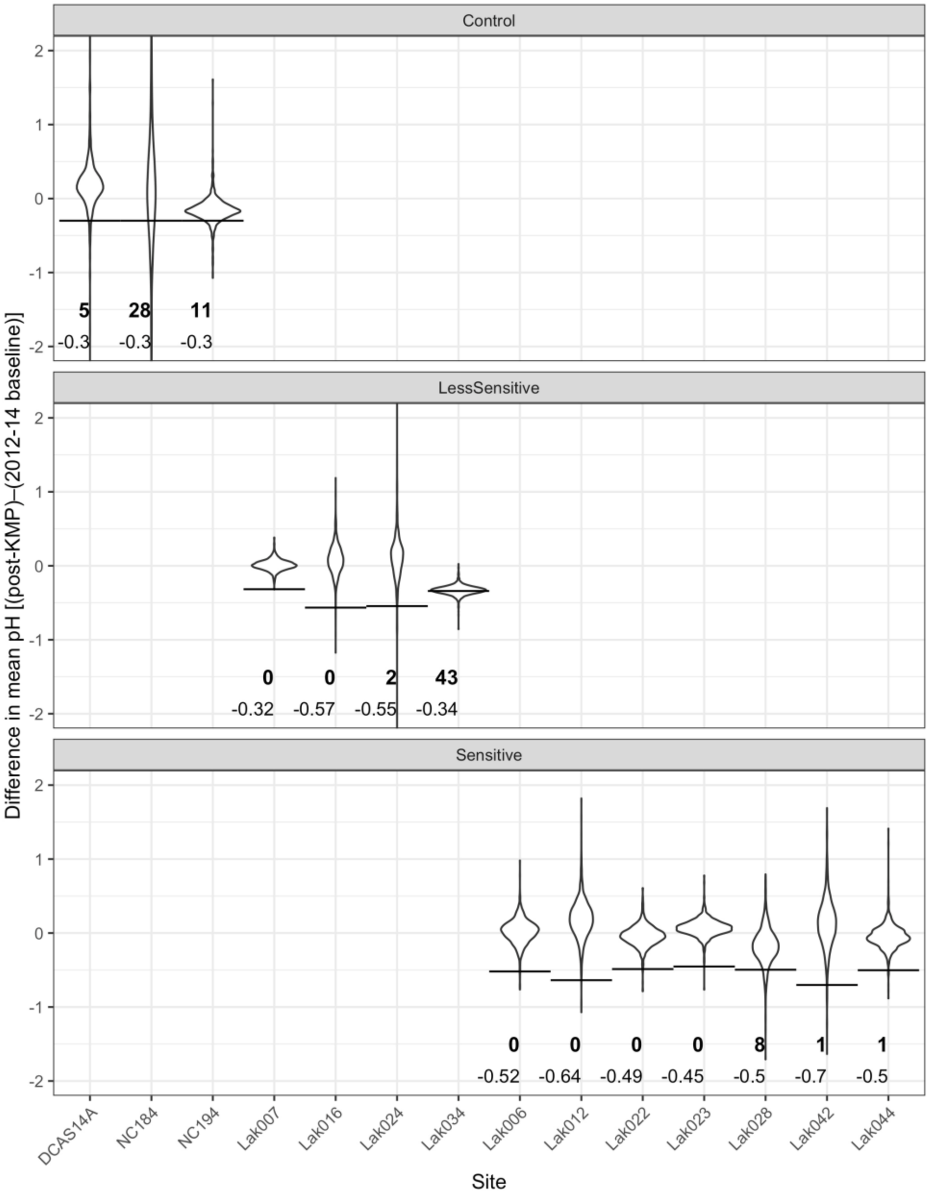


Figure 7.144. Percent belief in lake-specific decline in pH beyond the adjusted threshold using the alternate baseline period of 2012-2014. The % belief value is shown in bold and the value of the adjusted threshold for each lake is shown below the bolded value. Values for percent belief can be compared to the top graph in Figure 7.143.

7.9.3.3 Effects of alternative baseline on estimated ΔANC

The purpose of this analysis is to determine if there is a change in the level of support for a decline in Gran ANC beyond the lake-specific thresholds (Analysis A), or adjusted thresholds (Analysis B), when using the transition period baseline (2012-2014).

LAK028 is the only sensitive lake that showed an *increase* in the category of % belief (from 2% to 33%, low to intermediate level of support) that Gran ANC declined beyond the KPI threshold when using the alternate 2012-2014 baseline (Analysis A in Table 7.80). All other sensitive lakes showed the essentially same % belief (Figure 7.145).

The four less sensitive lakes all showed increases in the % belief that Gran ANC declined beyond the KPI threshold (Figure 7.145). Two of these increases were small (LAK016 (5%) and LAK024 (8%)), one was moderate (LAK034 (59%)), and one was large (LAK007 (76%)). The shift in % belief in LAK034 was large enough to change the level of support for exceedance of the ANC threshold from low to intermediate, and to moderate for LAK007, though as discussed previously the declines in lake pH and ANC in LAK034 were unrelated to the smelter, as lake [SO_4] declined relative to both the 2012 and 2012-14 baselines (Table 7.76).

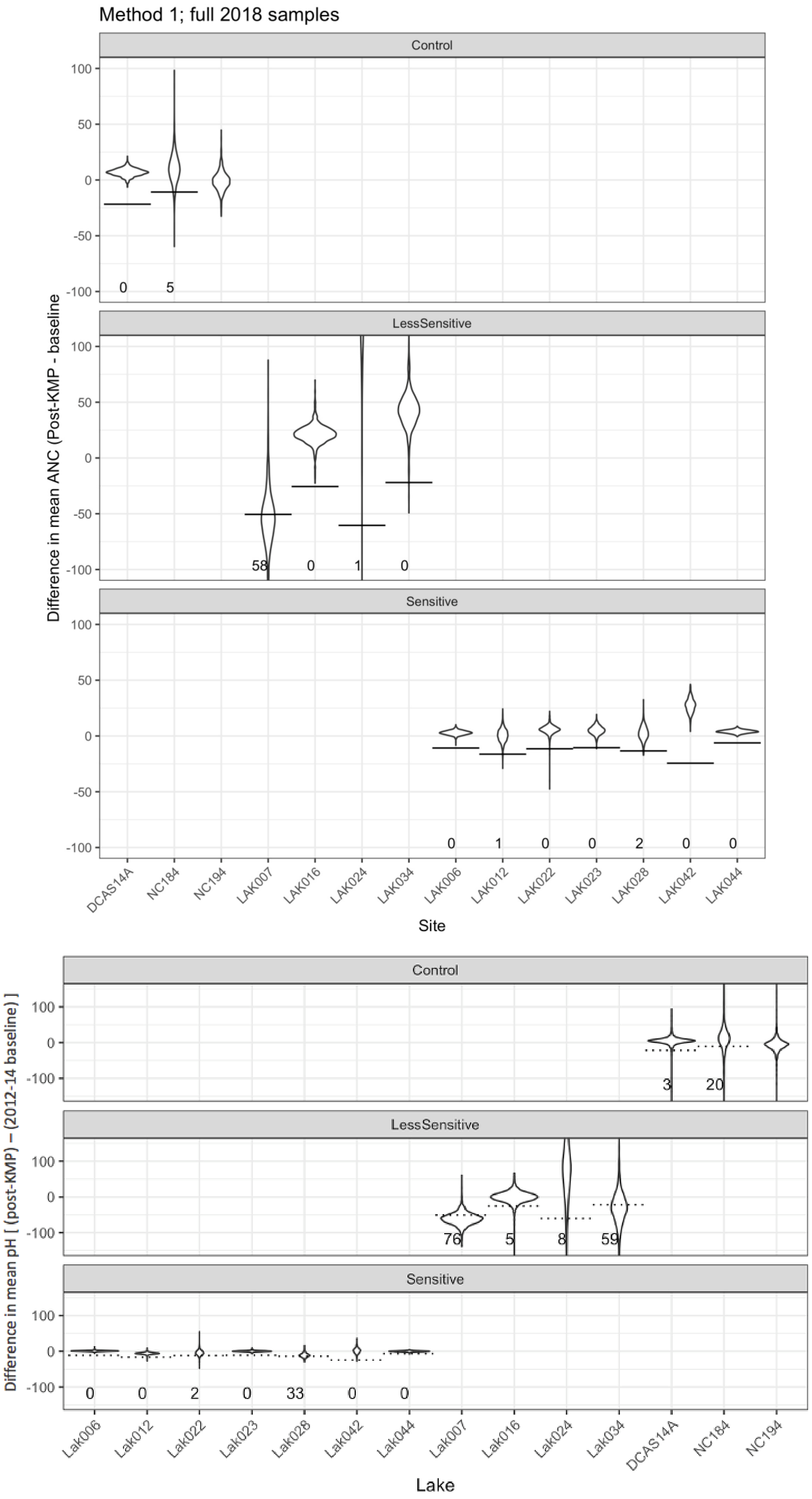


Figure 7.145. Percent belief in lake-specific decline in ANC beyond lake-specific threshold that corresponds to a change in pH of 0.3 pH units given: 1) baseline of 2012 (top graph, Figure 7.135, Aquatic Appendix F) or 2) alternate baseline period of 2012-2014 (Analysis A).

The thresholds of change in Gran ANC which correspond to a change in 0.3 pH units were based on laboratory titration curves using the 2012 data as the baseline. The titration data would have to be re-processed with the alternate baseline data to generate the appropriate thresholds for each lake with respect to a 2012-2014 baseline. This represents a significant amount of work and is not recommended at this time as it is unlikely to change the results of the sensitivity analysis. Instead, the adjusted thresholds for Analysis B simply modify the existing thresholds based on the difference between the mean Gran ANC in 2012-2014 and the 2012 value, as shown in Table 7.81. Using an adjusted Gran ANC threshold (Analysis B in Table 7.80) resulted in either a *decreased* or similar percent belief in an ANC change beyond the threshold relative to the original analysis for all lakes except the less sensitive LAK034 (which showed only a low level of support for exceeding its adjusted Gran ANC threshold).

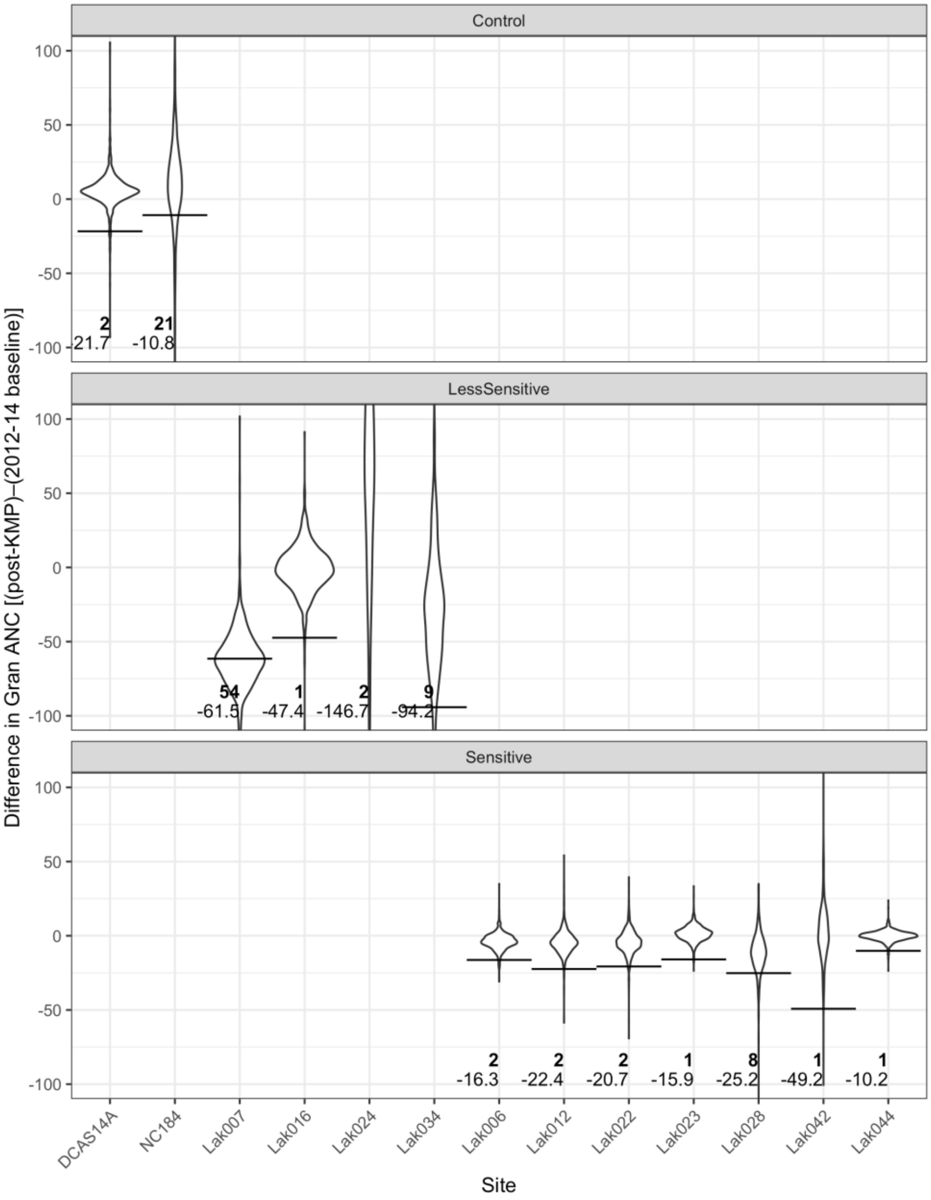


Figure 7.146. Percent belief in lake-specific decline in ANC beyond adjusted lake-specific threshold (Analysis B in Table 7.80). The % belief value is shown in bold and the adjusted ANC threshold for each lake is shown below the bolded value. This graph can be compared to the original analysis in the top graph of Figure 7.145.

7.9.3.4 *Synthesis of Results for SO_4, ANC and pH*

The simplified evidentiary framework (Figure 7-3 in main report) requires knowledge of the strength of evidence for *any* change in SO_4, pH and ANC, as well as evidence of whether or not the change in pH and Gran ANC has exceeded the EEM thresholds. Table 7.82 helps address the first question, while Table 7.83addresses the second question. Table 7.82 tabulates percent belief values for the 2012-14 baseline, summarizing analyses completed for this Appendix (violin plots exist, but have not been included to save space). Table 7.82 shows that application of the 2012-

2014 baseline increases the percent belief that there has been a decline in pH and ANC. The 2012-14 mean values of pH and ANC are higher than the 2012 values (possibly affected by the decommissioning of the old smelter), which increases the baseline value, and results in a higher % belief that values have declined from this higher baseline.

Table 7.82. Percent belief in pH and ANC decline > 0 with 2012 vs 2012-2014 baseline. These % belief statistics do not apply the EEM thresholds, but rather a threshold of 0. Percent belief values < 20% are shown in green, those from 20% to 80% are shown in yellow, and those > 80% are shown in bolded red.

	pH						Gran ANC (µeq/L)					
	Baseline		Post-KMP	ΔpH			Baseline		Post-KMP	ΔANC		
EEM sensitive lakes	2012	2012-14	2016-18	vs. 2012 [% belief in pH decline]	vs. 2012-14 [% belief in pH decline]		2012	2012-14	2016-18	vs. 2012 [% belief in ANC decline]	vs. 2012-14 [% belief in ANC decline]	
LAK006	5.8	6.0	6.0	0.2 [1%]	0.0 [24%]		25.7	31.2	27.7	2.0 [0%]	-3.5 [6%]	
LAK012	5.6	6.0	6.2	0.5 [1%]	0.2 [6%]		57.0	63.1	58.3	1.3 [1%]	-4.8 **[46%]**	
LAK022	5.9	6.1	6.1	0.1 [0%]	0.0 [57%]		27.8	37.0	33.0	5.1 [0%]	-4.1 [6%]	
LAK023	5.7	5.9	5.9	0.2 [1%]	0.1 [16%]		19.8	25.2	26.4	6.7 [0%]	1.2 [8%]	
LAK028	5.0	5.2	5.0	0.0 [18%]	-0.2 **73%]**		-4.0	7.8	-3.5	0.5 [2%]	-11.3 **[34%]**	
LAK042	4.7	5.1	5.2	0.5 [2%]	0.1 [10%]		-20.4	4.4	5.6	26.1 [0%]	1.3 [0%]	
LAK044	5.4	5.6	5.6	0.2 [0%]	-0.1 **[55%]**		1.3	5.2	5.0	3.7 [0%]	-0.2 [0%]	
EEM less sensitive lakes	2012	2012-14	2016-18	vs .2012	vs. 2012-14		2012	2012-14	2016-18	vs. 2012	vs. 2012-14	
LAK007	8.0	8.0	8.0	0.0 [2%]	0.0 [64%]		1437.6	1448.5	1385.9	-51.6 **[58%]**	-62.5 **[97%]**	
LAK016	6.3	6.6	6.7	0.3 [1%]	0.1 [24%]		68.7	90.4	89.8	21.1 [50%]	-0.6 [1%]	
LAK024	7.1	7.4	7.5	0.4 1%]	0.1 [31%]		299.5	385.8	463.2	163.7 [1%]	77.4 [2%]	
LAK034	6.7	6.8	6.4	-0.3 **[43%]**	-0.3 **[100%]**		99.4	171.6	139.6	40.2 [0%]	-32.0 [2%]	

Table 7.83 shows that the sensitivity analyses using a baseline of 2012-2014 do not change the overall conclusions for any of the lakes. There is less evidence of a smelter effect on sulphate in three of the sensitive lakes (LAK006, LAK012 and LAK022). There is somewhat more evidence of a smelter effect on pH and ANC in LAK028 (though not sufficiently to change the previous conclusion, which acknowledged that pre-KMP conditions in LAK028 were potentially damaging to biota and have remained so in the post-KMP period).

Figure 7.147 compares the application of the simplified evidentiary framework in the main report (Figure 7-10) with the results from Analysis A (i.e., assuming a 2012-14 baseline and no change in thresholds). As noted in Table 7.80, Analysis A is more likely to over-estimate the impacts of the smelter, since the period from 2012 to 2014 was a transition period with decommissioning of the old smelter and not a representative pre-KMP period. In applying the simplified evidentiary framework, it is important to examine not only the % belief statistics in Table 7.81, but also the actual changes in mean values described in Section 7.9.2.1, and the time series of changes in Aquatic Appendix C. This is because the Bayesian analysis may in some cases show an intermediate or high % belief in a magnitude of change that is of no significance chemically or biologically, particularly for less sensitive lakes and control lakes with less frequent sampling. Issues like this are highlighted in some of the footnotes to Table 7.81.

The Bayesian analysis takes into account the variability in water chemistry measurements both within and between years, and computes the percent belief in a [SO_4] increase based on the entire distribution of estimates for changes in [SO_4] (as shown in Figure 7.142). There can sometimes be a considerable shift in the percent belief in an increase in [SO_4] for a very small change in the estimates of [SO_4] for each time period. For example, using the 2012 baseline, LAK007 had only a 1% belief in an increase in [SO_4], as shown in Table 7.84. The actual change in [SO_4] between 2012 and 2016-18 was a *decrease* of 4.4 μeq/L (Section 7.9.2.1, Table 7.76), and only 1% of the distribution of credible estimates for Δ[SO_4] was positive. When applying the 2012-14 baseline, LAK007 shows a 42% belief in an increase in [SO_4], because 42% of the distribution of credible estimates for Δ[SO_4] was positive. However, the actual change in mean values of [SO_4] between 2012-14 and 2016-18 was still a decrease, now of 2.6 μeq/L, a very small change (Section 7.9.2.1). Therefore, in the reapplication of the simplified evidentiary framework (Figure 7.147), LAK007 is still classified as a lake not showing evidence of an increase in [SO_4]. For the control lakes, which have only five years of observations (2013, 2015, 2016-18), we also take into account the fact that they are far outside the plume from the smelter.

Figure 7.147 shows that application of the 2012-14 baseline (relative to the 2012 baseline) results in little change in the first blue decision box *[Has lake [SO_4] increased since the pre-KMP period?]*. The only change relative to the draft Comprehensive Report is that LAK016 shows much less support for an increase in lake [SO_4] when the 2012-14 baseline is used, as compared to using the 2012 baseline (Table 7.83). At the second decision box *[Has lake pH or Gran ANC decreased since pre-KMP period?]*, there is stronger evidence for declines in pH and ANC relative to the 2012-14 baseline (lower figure) than occurred with the 2012 baseline, as evident in Table 7.82. Five sensitive lakes (lakes 006, 012, 022, 028 and 042) therefore proceed to the third blue decision box *[Is ΔpH or ΔGran ANC greater than the thresholds?]*. As shown in Table 7.83, none of these five sensitive lakes are likely to have exceeded the pH or Gran ANC thresholds. When compared to the 2012-14 baseline, LAK028 shows a 20% belief in exceeding the pH threshold, and a 33% belief of exceeding the Gran ANC threshold. Those would be considered low to low-intermediate levels of support.

Table 7.83. Results of sensitivity analyses on alternative baseline (2012-2014) compared to results with original baseline (2012), based on Method 1 of the Bayesian analysis. Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red. Results of using the alternative baseline are shown in blue text, and in *italics* for alternative thresholds. Results for original baseline are in Table 7-10 of the main report and Table 7.71 of Aquatic Appendix F. "*[Same]*" in last column means that the sensitivity analysis has the same overall conclusion as the results in the draft comprehensive report with the original baseline.

LAKE	**Changes in SO_4** (% belief in SO_4 increase / decrease from Bayesian analysis - Method 1 violin plot) [A. 2012-2014 baseline]	**Changes in Gran ANC** (% belief that ANC threshold exceeded, from Bayesian analysis - Method 1) [A. 2012-2014 baseline & original thresholds; *B. 2012-2014 & adjusted thresholds*]	**Changes in pH** (% belief pH threshold exceeded, from Bayesian analysis - Method 1) [A. 2012-2014 baseline & original thresholds; *B. 2012-2014 & adjusted thresholds*]	**OVERALL INTERPRETATION for 2012 BASELINE** ***[OVERALL INTERPRETATION for 2012-2014 BASELINE]***
Sensitive Lakes				
LAK006	91% belief in increase [80%]	0% [0%; *2%*]	0% [1%; *0%*]	SO_4 increase *[weaker]*; no evidence of S-induced acidification ***[Same]***
LAK012	99% belief in increase [69%]	8% [0%; *2%*]	0% [3%; *0%*]	SO_4 increase *[weaker evidence]*; no consistent evidence for S-induced acidification. ***[Less evidence of smelter effect]***
LAK022	88% belief in increase [54%]	1% [2%; *2%*]	0% [2%; *0%*]	SO_4 increase *[weaker evidence]*; no evidence of S-induced acidification ***[Less evidence of smelter effect]***
LAK023	1% belief in increase [1%]	13% [0%; *1%*]	0% [0%; *0%*]	SO_4 decrease; no evidence of S-induced acidification ***[Same]***
LAK028	100% belief in increase [89%]	13% [33%; *8%*]	10% [20%; *8%*]	SO_4 increase; some evidence of S-induced acidification; low *[to intermediate]* belief in exceeding pH and ANC thresholds; conditions potentially damaging to biota pre-KMP and have remained so. ***[Same]***
LAK042	32% belief in increase [52%]	1% [0%; *1%*]	0% [0%; *1%*]	No clear change in SO_4; no evidence of S-induced acidification ***[Same]***
LAK044	0% belief in increase [4%]	18% [0%; *1%*]	0% [0%;*1%*]	SO_4 decrease; no evidence of S-induced acidification ***[Same]***
Less Sensitive Lakes				
LAK007	1% belief in increase [42%][e]	53% [76%; 54%]	3% [0%; *0%*]	SO_4 decrease *[or no change]*; no evidence of S-induced acidification ***[Same]***
LAK016	98% belief in increase [30%]	1% [5%; *1%*]	1% [3%; *0%*]	SO_4 increase; no evidence of S-induced acidification ***[Same]***
LAK024	96% belief in increase [87%]	3% [8%; *2%*]	2% [6%; *2%*]	SO_4 increase; no evidence of S-induced acidification ***[Same]***
LAK034	0% belief in increase [1%]	1% [59%; 9%]	39% [b] [70%; *43%*]	SO_4 decrease; no evidence of S-induced acidification ***[Same]***
Control Lakes				
DCAS14A	68% belief in increase[c] [65%]	4% [3%; *2%*]	5% [5%; *5%*]	No clear change in SO_4; no evidence of S-induced acidification ***[Same]***
NC184	59% belief in increase [c] [59%]	19% [20%; 21%]	26%[a] [27%; *28%*]	No clear change in SO_4; no evidence of S-induced acidification ***[Same]***
NC194	1% belief in increase [3%]	TBD[d]	14% [a] [12%;*11%*]	SO_4 decrease; no evidence of S-induced acidification ***[Same]***

[a] Mean pH in NC184 changed from ~5.7 (2013) to ~5.8 (2016-18); Mean pH in NC194 changed from ~6.6 (2013) to ~6.4 (2016-18).

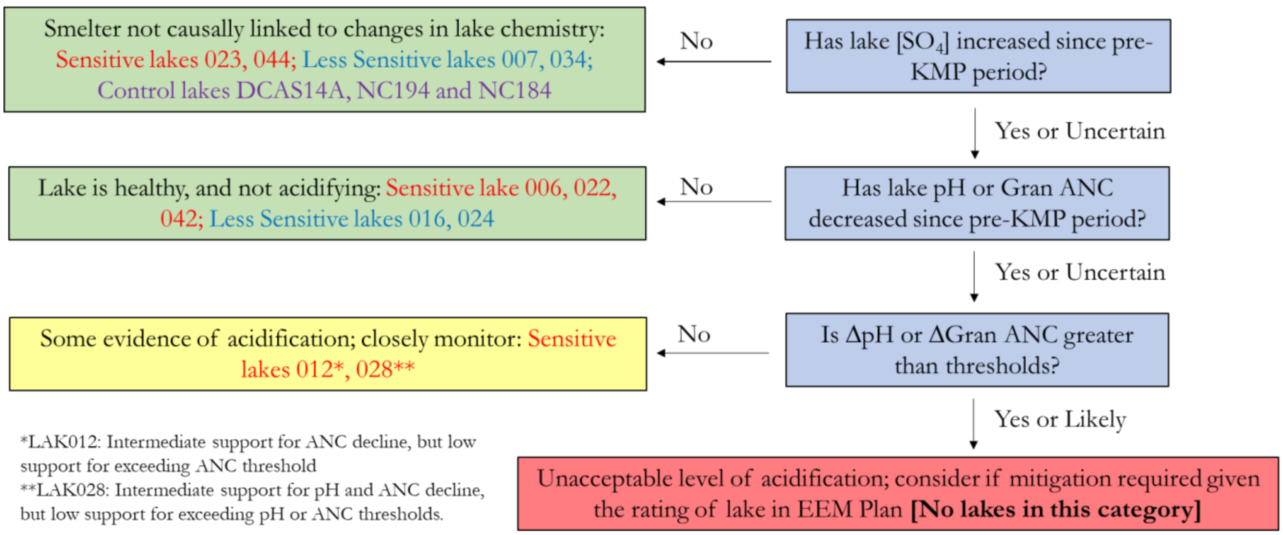
[b] Not related to S deposition as lake SO_4 has declined in LAK034.

[c] Magnitude of increase in [SO_4] between 2013 and 2016-2018 is very small in NC184 (0.5 µeq/L) and DCAS14A (3 µeq/L); only 4 samples available for statistical analysis.

[d] Lake NC194 did not have a lab titration from which we could determine an ANC threshold. It had a 6 µeq/L ANC decline between 2013 and 2016-2018, but ANC decline not related to SO_4.

[e] LAK007 mean [SO_4] showed little change between 2012-14 (49.5 µeq/L) and 2016-18 (48.0 µeq/L).

Grouping of lakes by evidentiary framework in draft Comprehensive Report (2012 baseline)



Has lake [SO_4] increased since pre-KMP period?

No → Smelter not causally linked to changes in lake chemistry: Sensitive lakes 023, 044; Less Sensitive lakes 007, 034; Control lakes DCAS14A, NC194 and NC184

Yes or Uncertain ↓

Has lake pH or Gran ANC decreased since pre-KMP period?

No → Lake is healthy, and not acidifying: Sensitive lake 006, 022, 042; Less Sensitive lakes 016, 024

Yes or Uncertain ↓

Is ΔpH or ΔGran ANC greater than thresholds?

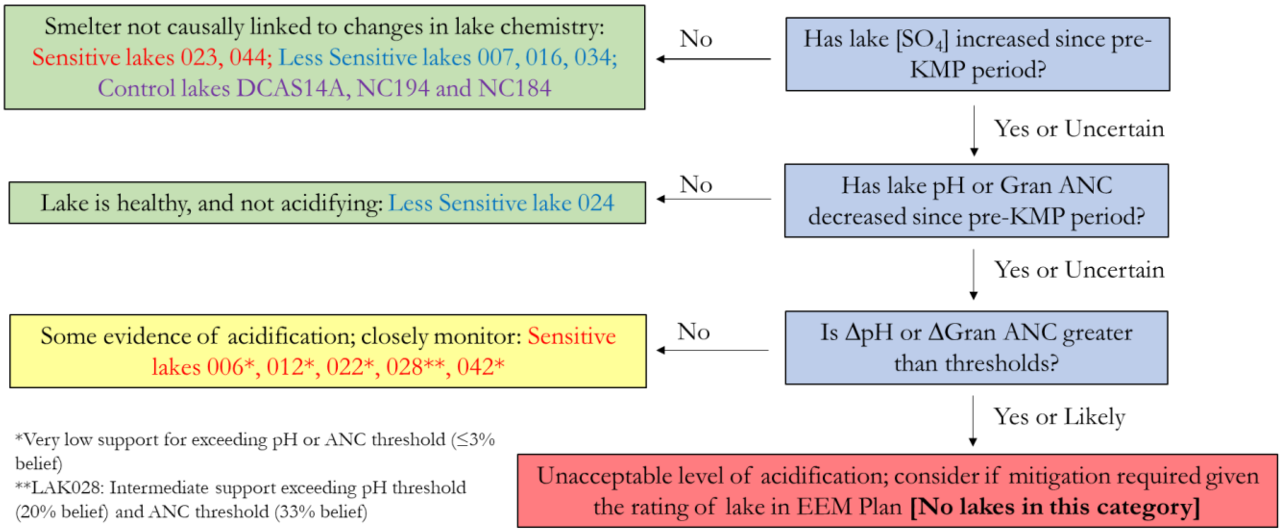
No → Some evidence of acidification; closely monitor: Sensitive lakes 012*, 028**

Yes or Likely ↓

Unacceptable level of acidification; consider if mitigation required given the rating of lake in EEM Plan **[No lakes in this category]**

*LAK012: Intermediate support for ANC decline, but low support for exceeding ANC threshold
**LAK028: Intermediate support for pH and ANC decline, but low support for exceeding pH or ANC thresholds.

Grouping of lakes by evidentiary framework in sensitivity analysis using 2012-14 baseline



Has lake [SO_4] increased since pre-KMP period?

No → Smelter not causally linked to changes in lake chemistry: Sensitive lakes 023, 044; Less Sensitive lakes 007, 016, 034; Control lakes DCAS14A, NC194 and NC184

Yes or Uncertain ↓

Has lake pH or Gran ANC decreased since pre-KMP period?

No → Lake is healthy, and not acidifying: Less Sensitive lake 024

Yes or Uncertain ↓

Is ΔpH or ΔGran ANC greater than thresholds?

No → Some evidence of acidification; closely monitor: Sensitive lakes 006*, 012*, 022*, 028**, 042*

Yes or Likely ↓

Unacceptable level of acidification; consider if mitigation required given the rating of lake in EEM Plan **[No lakes in this category]**

*Very low support for exceeding pH or ANC threshold (≤3% belief)
**LAK028: Intermediate support exceeding pH threshold (20% belief) and ANC threshold (33% belief)

Figure 7.147. Original application of the evidentiary framework (main report Figure 7-10, top) and revised application based on the results using a 2012-2014 baseline (as shown in Table 7.81 of this appendix).

7.9.3.5 Correlations with 2-month precipitation

Lakes were analyzed by linear regression individually and all together for correlations between response variables (SO_4, pH, Gran ANC) and the cumulative precipitation over the 2-month period prior to sampling (i.e., June plus July for the August 2012 sampling, and August plus September for the October sampling in 2013-2018); see Table 7.84. No significant correlations (at alpha value of 0.01) were detected for any of the response variables whether lakes were analyzed individually or combined (Table 7.85, Figure 7.148, Figure 7.149, Figure 7.150), despite approximately a 4-fold variation in seasonal precipitation.

Table 7.84. Estimated values for seasonal precipitation.

Year	2 Months Included in Average	Total Precipitation over these 2 months (mm)
2012	July, August	122
2013	August, September	159
2014	August, September	121
2015	August, September	303
2016	August, September	280
2017	August, September	242
2018	August, September	69

Table 7.85. Results of the linear regression analyses between response variables (SO_4, pH, Gran ANC) and the cumulative amount of precipitation in the 2 months prior to sampling. No significant correlations were detected at p<0.01. Results for all lakes combined are bolded.

Lake	Response	Estimate	Std. Error	P.value	Adj-R2
Lak006	SO_4	-0.003	0.007	0.701	-0.162
Lak007	SO_4	-0.001	0.040	0.990	-0.200
Lak012	SO_4	0.008	0.015	0.616	-0.135
Lak016	SO_4	-0.013	0.022	0.567	-0.116
Lak022	SO_4	-0.013	0.022	0.572	-0.118
Lak023	SO_4	-0.024	0.014	0.150	0.239
Lak024	SO_4	-0.002	0.024	0.945	-0.248
Lak028	SO_4	0.121	0.115	0.341	0.017
Lak034	SO_4	-0.063	0.051	0.277	0.075
Lak042	SO_4	-0.002	0.005	0.740	-0.171
Lak044	SO_4	-0.004	0.003	0.292	0.061
DCAS14A	SO_4	-0.022	0.012	0.162	0.375
NC184	SO_4	-0.010	0.003	0.057	0.670
NC194	SO_4	-0.002	0.002	0.421	-0.034
COMBINED	**SO_4**	**-0.007**	**0.028**	**0.797**	**-0.010**
Lak006	pH	0.000	0.000	0.631	-0.140
Lak007	pH	0.000	0.000	0.338	0.020
Lak012	pH	0.000	0.001	0.775	-0.179

Lake	Response	Estimate	Std. Error	P.value	Adj-R2
Lak016	pH	0.000	0.001	0.750	-0.173
Lak022	pH	0.000	0.000	0.714	-0.165
Lak023	pH	0.000	0.000	0.897	-0.196
Lak024	pH	0.000	0.001	0.795	-0.226
Lak028	pH	-0.001	0.001	0.055	0.465
Lak034	pH	-0.001	0.001	0.288	0.065
Lak042	pH	0.001	0.001	0.301	0.052
DCAS14A	pH	0.000	0.001	0.406	-0.018
Lak044	pH	0.000	0.000	0.672	-0.153
NC184	pH	-0.002	0.001	0.033	0.766
NC194	pH	0.000	0.000	0.221	0.256
COMBINED	**pH**	**0.000**	**0.001**	**0.798**	**-0.010**
Lak006	ANC	-0.006	0.017	0.741	-0.171
Lak007	ANC	-0.005	0.251	0.985	-0.200
Lak012	ANC	0.016	0.023	0.532	-0.101
Lak016	ANC	0.012	0.056	0.838	-0.189
Lak022	ANC	0.000	0.023	0.986	-0.200
Lak023	ANC	0.018	0.015	0.268	0.084
Lak024	ANC	-0.031	0.288	0.919	-0.246
Lak028	ANC	-0.042	0.038	0.312	0.042
Lak034	ANC	-0.002	0.156	0.991	-0.200
Lak042	ANC	0.029	0.051	0.592	-0.126
Lak044	ANC	0.008	0.009	0.408	-0.032
DCAS14A	ANC	0.925	1.819	0.646	-0.227
NC184	ANC	-0.081	0.039	0.130	0.452
NC194	ANC	-0.026	0.033	0.490	-0.107
COMBINED	**ANC**	**0.015**	**0.374**	**0.969**	**-0.011**

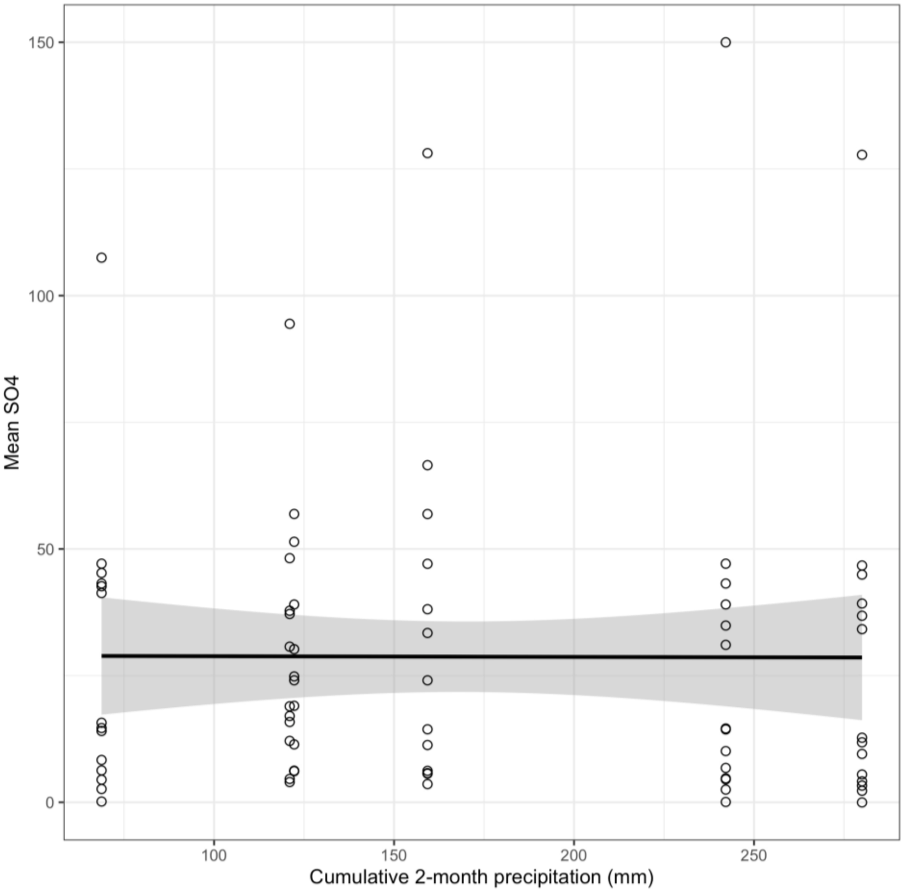


Figure 7.148. Linear regression with annual mean SO_4 and 2-month precipitation for all lakes. The grey shaded area is the 95% confidence interval.

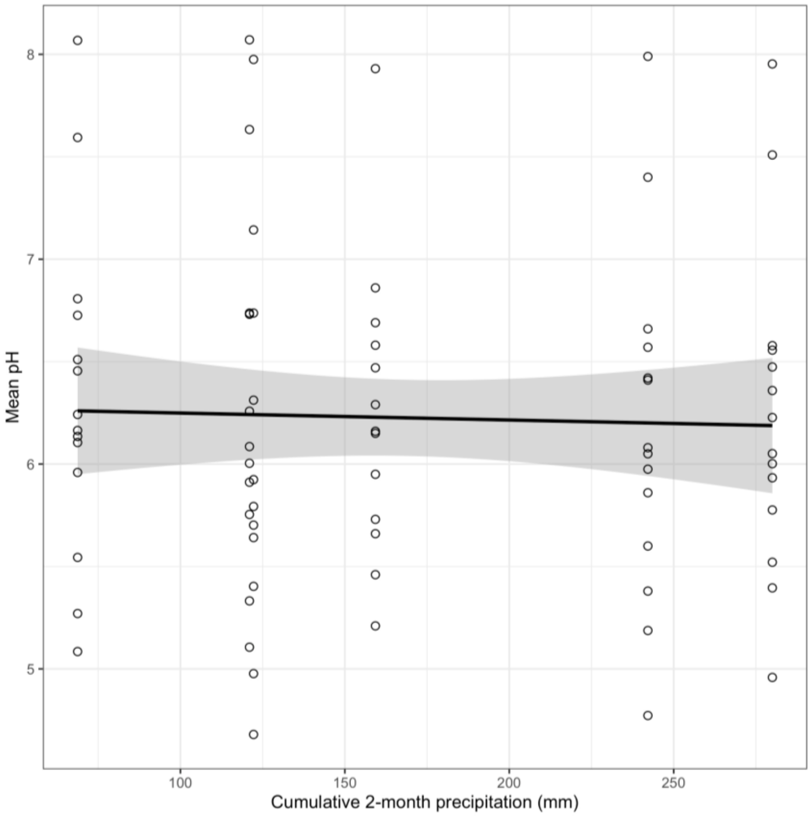


Figure 7.149. Linear regression with annual mean pH and 2-month precipitation for all lakes. The grey shaded area is the 95% confidence interval.

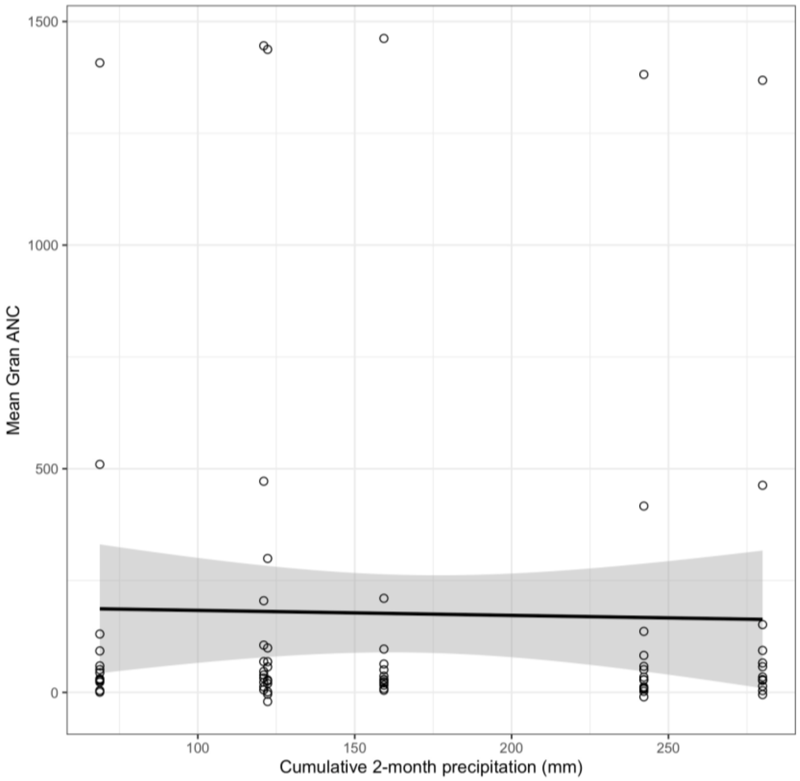


Figure 7.150. Linear regression with annual mean Gran ANC and 2-month precipitation for all lakes. The grey shaded area is the 95% confidence interval.

7.9.3.6 BACI with 2-month precipitation and F-Factor

A suite of three additional BACI analyses that use the 2012-2014 baseline were run for each response variable (SO_4, pH, Gran ANC) with all lakes combined. Each suite of models includes a model with just the BACI contrast, a model with the BACI contrast and the 2-month precipitation covariate, and a model with the BACI contrast, the 2-month precipitation and F-Factor covariates (in response to a reviewer's suggestion to include lake sensitivity). Compared to previous BACI analyses in Appendix F, these analyses add one or two additional covariates (seasonal precipitation and lake sensitivity). Annual average emissions were used as a covariate in the previous BACI analyses in Appendix F, but were removed since the BACI contrast is intended to test for a smelter effect; including emissions as a covariate is redundant. No significant BACI contrast, 2-month precipitation effect or significant F-Factor were identified for any of the response variables (Table 7.84).

Table 7.86. The results of the additional BACI analyses with the 2012-2014 baseline for each response variable (pH, ANC, SO_4). No significant BACI contrast, or effect of precipitation or F-Factor was identified in any analysis. Models 1, 4, and 7 include the BACI contrast as well as the 2-month precipitation and F-Factor covariates. Models 2, 5, and 8 include the BACI contrast and only the 2-month precipitation covariate. Models 3, 6, and 9 only include the BACI contrast.

Model No.	term	Response	estimate	SE	p.value	Precip	F.Factor
1	baci	pH	0.075	0.109	0.496	Yes	Yes
1	PRECIP	pH	0.000	0.001	0.720	Yes	Yes
1	F.FACTOR	pH	-0.221	1.147	0.854	Yes	Yes
2	baci	pH	0.146	0.093	0.120	Yes	No
3	baci	pH	0.144	0.093	0.126	No	No
4	baci	ANC	7.309	4.969	0.144	Yes	Yes
4	PRECIP	ANC	0.000	0.030	0.998	Yes	Yes
4	F.FACTOR	ANC	50.840	45.800	0.309	Yes	Yes
5	baci	ANC	8.238	4.208	0.053	Yes	No
6	baci	ANC	8.190	4.199	0.054	No	No
7	baci	SO_4	0.595	8.345	0.943	Yes	Yes
7	PRECIP	SO_4	0.017	0.022	0.516	Yes	Yes
7	F.FACTOR	SO_4	133.345	82.442	0.157	Yes	Yes
8	baci	SO_4	1.704	7.085	0.810	Yes	No
9	baci	SO_4	1.184	7.004	0.866	No	No

7.9.4 Steady State Future pH

7.9.4.1 Future pH

Average pH levels over the 2012-2014 period were consistently higher than 2012 pH levels (first two columns under Empirical Observations in Table 7.87). Post-KMP mean pH levels (third column under Empirical Observations) have remained equal to, or higher than, the 2012-2014 mean values in nine of the eleven lakes. The two exceptions are LAK028 (decline of 0.2 pH units relative to the 2012-14 mean, see Table 7.83 for more detailed analysis) and LAK034 (decline of 0.4 pH units, unrelated to the smelter, as SO_4 concentrations have declined, see Table 7.83). The next part of Table 7.87 lists the predicted steady state pH (pH_∞), and the predicted change in pH from 2012 levels, under an emission scenario of 42 tpd, as reported in the STAR. In the STAR, all of the sensitive lakes were predicted to have a pH decline of 0.1 pH units or more (which is what led to their inclusion in the EEM program). Revised predictions of steady state pH included in Table 7-11 of the Comprehensive Report ("NEW: Best Prediction" in Table 7.87) are considerably higher that the predictions in the STAR, for several reasons (i.e., emissions have been ~30 tpd, not 42 tpd; most lakes have shown less change in SO_4 than predicted even after accounting for lower emissions; and lakes with evidence of SO_4 change have been less acid-sensitive than predicted). When expressed relative to the 2012-14 baseline ("ΔpH (2012-14)"), the predicted ΔpH is less positive (or more negative) compared to being expressed relative to the 2012 baseline.

Table 7.87. Predicted change in steady state pH relative to both a 2012 baseline and a 2012-2014 baseline. Revision of Table 7.83 in this appendix, and the pH component of Table 7-11 in the main report.

Lake	Empirical Observations			ORIGINAL: STAR predictions		NEW: Best Prediction			Effect of Alternate Baseline on Predicted Steady-state pH
	2012 pH	2012-14 pH	Post-KMP pH	pH_∞	Δ pH (2012)	pH_∞	Δ pH (2012)	Δ pH (2012-14)	
EEM Sensitive Lakes									
LAK006	5.8	6.0	6.0	5.3	-0.5	6.0	0.2	0.0	Predicted increase decreases to zero
LAK012	5.6	6.0	6.2	5.5	-0.1	6.1	0.5	0.2	Predicted increase declines from 0.5 to 0.2
LAK022	5.9	6.1	6.1	5.5	-0.4	6.0	0.1	-0.1	Small increase becomes small decrease
LAK023	5.7	5.9	5.9	5.2	-0.5	5.9	0.2	0.0	Predicted increase decreases to zero
LAK028	5.0	5.2	5.0	4.6	-0.4	4.8	-0.2	-0.4	**Predicted decrease exceeds threshold**
LAK042	4.7	5.1	5.2	4.5	-0.2	5.2	0.5	0.1	Predicted increase declines from 0.5 to 0.1
LAK044	5.4	5.6	5.6	4.9	-0.5	5.5	0.1	-0.1	Small increase becomes small decrease
EEM Less Sensitive Lakes									
LAK007	8.0	8.0	8.0	8.0	0.0	8.0	0.0	0.0	No change
LAK016	6.3	6.6	6.7	6.2	-0.1	6.6	0.3	0.1	Predicted increase declines from 0.3 to 0.1
LAK024	7.1	7.4	7.5	7.1	0.0	7.5	0.4	0.1	Predicted increase declines from 0.4 to 0.1
LAK034	6.7	6.8	6.4	6.7	0.0	6.4	-0.3	-0.3	Negligible change (-0.29 vs. -0.33).

*Not related to S deposition as lake SO_4 has declined in LAK034

7.9.4.2 Future ANC

Average Gran ANC levels over the 2012-2014 period were consistently higher than 2012 pH levels (first two columns under Empirical Observations in Table 7.87). Post KMP mean Gran ANC levels (third column under Empirical Observations) have remained higher than the 2012-2014 mean values in three lakes, decreased relative to the 2012-2014 mean in five lakes, and have shown no change (< 1 µeq/l) in two lakes; see Table 7.83 for a more detailed analysis. The next part of Table 7.87 lists the predicted steady state Gran ANC (Gran ANC_∞), and the predicted change in Gran ANC relative to both 2012 levels and the mean ANC from 2012-2014, under an emission scenario of 42 tpd. When expressed relative to the 2012-14 baseline ("ΔGran ANC (2012-14)"), the predicted ΔGran ANC is less positive (or more negative) compared to being expressed relative to the 2012 baseline. Relative to the 2012-14 baseline, two lakes (LAK028 and LAK034) are predicted to eventually exceed their reference thresholds for changes in Gran ANC. As noted above, changes in the pH and Gran ANC of LAK034 are unrelated to the smelter.

Table 7.88. Predicted change in steady state Gran ANC relative to both a 2012 baseline and a 2012-2014 baseline. Revision of Table 7.84 in this appendix, and the ANC component of Table 7-11 in the main report.

	Empirical Observations of Gran ANC (µeq/L)			NEW prediction – with best inputs				Effect of Alternate Baseline on Predicted Steady-state pH
Lake	2012 Gran ANC	2012-14 Gran ANC	post-KMP Gran ANC (2016-2018)	Gran ANC_{∞}	Δ Gran ANC (2012)	Δ Gran ANC (2012-14)	Δ Gran ANC (2012) Threshold †	
EEM Sensitive Lakes								
LAK006	25.7	31.2	27.7	24.7	-1.0	-6.5	-10.8	Larger decrease; still above reference threshold †
LAK012	57.0	63.1	58.3	56.0	-1.0	-7.1	-16.3	Larger decrease; still above reference threshold †
LAK022	27.8	37.0	33.0	30.4	2.6	-6.6	-11.5	Larger decrease; still above reference threshold †
LAK023	19.8	25.2	26.4	23.8	4.0	-1.4	-10.5	Larger decrease; still above reference threshold †
LAK028	-4.0	7.8	-3.5	-9.3	-5.3	-17.1	-13.4	**Larger decrease, exceeds reference threshold †**
LAK042	-20.4	4.4	5.6	4.2	24.6	-0.2	-24.4	Predicted increase decreases to approx. zero
LAK044	1.3	5.2	5.0	2.8	1.5	-2.5	-6.2	Larger decrease; still above reference threshold †
EEM Sensitive Lakes								
LAK007	1437.6	1448.5	1385.9	1385.9	-51.6	-62.5	-50.6	Larger decrease; still exceeds reference threshold †
LAK016	68.7	90.4	89.8	88.0	19.4	-2.4	-25.6	Predicted increase → small decrease; still above threshold †
LAK024	299.5	385.8	463.2	463.2	163.7	77.4	-60.4	Predicted increase decreases
LAK034	99.4	171.6	139.6	138.7	39.3	-32.9	-22.0	**Predicted increase → decrease; exceeds reference threshold †**

† The Gran ANC threshold was determined (based on analysis of the titration data) as the magnitude of change in Gran ANC equivalent to a 0.3 pH unit decline *from the 2012 pH value* and due to the non-linear relationship between pH and Gran ANC, this threshold does **not** necessarily represent a 0.3 pH unit decline *from the average 2012-14 pH value.* The Gran ANC threshold therefore only applies directly to the changes calculated from the 2012 baseline but is included for approximate reference.

7.10 Aquatic Appendix J: Cited References for Aquatic Receptor Chapter and Appendices

Baker, J.P., D.P. Bernard, S.W. Christensen, M.J. Sale, J. Freda, K. Heltcher, D. Marmorek, L. Rowe, P. Scanlon, G. Suter, W. Warren-Hicks, and P. Welbourn. 1990. Biological Effects of Changes in Surface Water Acid-Base Chemistry. NAPAP Report 13. In: National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology. Volume II, 1990.

Baker, L.A., P. R. Kaufmann, A.T. Herlihy, J.M. Eilers. 1991. Current Status of Acid Base Chemistry (Rep 9), NAPAP State of Science and Technology, NAPAP, Washington, DC. 383 pp.

Baldigo B.P., G.B. Lawrence, R.W. Bode, H.A. Simonin, K.M. Roy, A.J. Smith. 2009. Impacts of acidification on macroinvertebrate communities in streams of the western Adirondack Mountains, New York, USA. *Ecological Indicators* 9: 226–239

Bennett, S. and C.J. Perrin. 2017. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lakes in 2016. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 40pp. plus appendices.

Bennett, S. and C.J. Perrin. 2018. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lakes in 2017. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 49pp. plus appendices.

Driscoll, C.T., M.D. Kehtinen and T.J. Sullivan. 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. Water Res. Research. 30 (2): 297-306.

Dupont, J., T.A. Clair, C. Gagnon, D.S. Jeffries, J.S. Kahl, S.J. Nelson, and J.M. Peckenham. 2005. Estimation of critical loads of acidity for lakes in northeastern United States and eastern Canada. Environmental Monitoring and Assessment 109: 275-291.

ESSA Technologies Ltd. 2018. Literature Review on Acidification Risk to Amphibians. Draft prepared for Rio Tinto, BC Works B.C. 29 pp.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants, and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Volume 2: Final Technical Report. Prepared for Rio Tinto Alcan, Kitimat, B.C. 450 pp.

ESSA Technologies, J. Laurence, Risk Sciences International, Trent University, and Trinity Consultants. 2014. Kitimat Airshed Emissions Effects Assessment. Report prepared for BC Ministry of Environment, Smithers, BC. 205 pp. + appendices.

Evans, C.D., R. Harriman, D.T. Monteith and A. Jenkins. 2001. Assessing the suitability of acid neutralizing capacity as a measure of long-term trends in acidic waters based on two parallel datasets. Water, Air and Soil Pollution 130: 1541-1546.

Fölster, J., C. Andrén, K. Bishop, I. Buffam, N. Cory, W. Goedkoop, K. Holmgren, R. Johnson, H. Laudon, and A. Wilander. 2007. A Novel Environmental Quality Criterion for Acidification in Swedish Lakes – An Application of Studies on the Relationship Between Biota and Water Chemistry. Water Air Soil Pollut: Focus 7, 331-338.

Hemond, H.F. 1990. Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids. Environmental Science and Technology 24: 1486-1489.

Henriksen A., P.J. Dillon, and J. Aherne. 2002. Critical loads of acidity for surface waters in south-central Ontario, Canada: regional application of the steady-state water chemistry (SSWC) model. Canadian Journal of Fisheries and Aquatic Sciences 59: 1287-1295.

Henriksen, A., and M. Posch. 2001. Steady-state models for calculating critical loads of acidity for surface waters. Water, Air and Soil Pollution: Focus 1(1-2): 375–398.

Hesthagen T., P. Fiske, and R. Saksgård. 2016. Recovery of young brown trout (Salmo trutta) in acidified streams: What are the critical values for acid-neutralizing capacity? *Atmospheric Environment* 146: 236-244

Holt, C.A., N.D. Yan, and K.M. Somers. 2003. pH 6 as the threshold to use in critical load modeling for zooplankton community change with acidification in lakes of south-central Ontario: accounting for morphometry and geography. Can. J. Fish. Aquat. Sci. 60:151-158.

Hruska, J., H. Laudon, C.E. Johnson, S. Kohler and K. Bishop. 2001. Acid/base character of organic acids in a boreal stream during snowmelt. Water Res. Research 37 (4): 1043-1056.

Kilgour, B.W., K.M. Sommers, D.E. Matthews. 1998. Using the normal range as a criterion for ecological significance in environmental monitoring and assessment. Ecoscience 5(4): 542-550.

Kruschke 2013. BEST - Bayesian Estimation Supersedes T-Test , J Exp Psychol Gen. 142(2): 573-603.

Lawrence, G. B.; Sutherland, J. W.; Boylen, C. W.; Nierzwicki-Bauer, S. A.; Momen, B.; Baldigo, B. P.; Simonin, H. A. Acid rain effects on aluminum mobilization clarified by inclusion of strong organic acids. Environ. Sci. Technol. 2007, 41 (1), 93−98.

Lawrence, G.B., J. E. Dukett, N. Houck, P. Snyder, and S. Capone. 2013. Increases in dissolved organic carbon accelerate loss of toxic Al in Adirondack lakes recovering from acidification. Environ. Sci. Technol. 2013, 47, 7095−7100. dx.doi.org/10.1021/es4004763.

Lien, L., G.G. Raddum, A. Fjellheim, A. Henriksen. 1996. A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. Science of the Total Environment 177: 173-193.

Limnotek. 2016. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of water and aquatic Biota in 2015. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 66p.

Limnotek. 2019. Rio Tinto Kitimat Modernization Project: Environmental effects monitoring of lakes and streams in 2018. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Ltd. 84pp. plus appendices.

Lydersen, E., T. Larssen, E. Fjeld. 2004. The influence of total organic carbon (TOC) on the relationship between acid neutralizing capacity (ANC) and fish status in Norwegian lakes. Science of the Total Environment 326 (2004) 63–69. doi:10.1016/j.scitotenv.2003.12.005.

Marmorek, D.R. and J. Korman. 1993. The use of zooplankton in a biomonitoring program to detect lake acidification and recovery. Water, Air, and Soil Pollution 69: 223-241.

Marmorek, D.R., M.L. Jones, C.K. Minns, and F.C. Elder. 1990. Assessing the Potential Extent of Damage to Inland Lakes in Eastern Canada due to Acidic Deposition. I. Development and Evaluation of a Simple "Site" Model. Canadian Journal of Fisheries and Aquatic Sciences 47: 55-66.

Marmorek, D.R., R.M. MacQueen, C.H.R. Wedeles, J. Korman, P.J. Blancher, and D.K. McNicol. 1996. Improving pH and alkalinity estimates for regional-scale acidification models: incorporation of dissolved organic carbon. Canadian Journal of Fisheries and Aquatic Sciences 53: 1602-1608.

Morgan, M.D. 1985. Photosynthetically elevated pH in acid waters with high nutrient content and its significance for the zooplankton community. Hydrobiologia 128 (3): 239–247.

Oliver, B.G., E.M. Thurman, and R.L., Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim*. Acta 47, 2031.

Perrin, C.J and S. Bennett 2015. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lake water quality in 2014. Data report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 20p.

Perrin, C.J., E. Parkinson and S. Bennett 2013. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of water and aquatic Biota in 2013. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 41p.

Robertson-Bryan Inc., 2004. Technical Memorandum: pH Requirements of Freshwater Aquatic Life. 13 pp. https://www.waterboards.ca.gov/centralvalley/water_issues/basin_plans/ph_turbidity/ph_turbidity_04phreq.pdf.

Small, M.J., and M.C. Sutton. 1986. A Regional pH-Alkalinity Relationship. Water Research 20(3): 335-343.

Skjelkvåle, B.L., J.L. Stoddard, D.S. Jeffries, K. Tørseth, T. Høgåsen, J. Bowman, J. Mannio, D.T. Monteith, R. Mosello, M. Rogora, D. Rzychon, J. Vesely, J. Wieting, A. Wilander, and A. Worsztynowicz. 2005.Regional scale evidence for improvements in surface water chemistry 1990-2001. Environmental Pollution 137:165-176.

Stoddard, J. L., A. D. Newell, N. S. Urquhart, and D. Kugler. 1996. The TIME project design: II. Detection of regional acidification trends. Water Resources Research 32:2529-2538.

Stoddard, J.L., C.T. Driscoll, J.S. Kahl, and J.H. Kellogg. 1998. A regional analysis of lake acidification trends for the northeastern U.S. 1982-1994.

Stoddard, J.L., J.S. Kahl, F.A. Deviney, D.R. DeWalle, C.T. Driscoll, A.T. Herlihy, J.H. Kellogg, P.S. Murdoch, J.R. Webb, and K.E. Webster. 2003. Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990. EPA 620/R-03/001. US Environmental Protection Agency, Office of Research and Development. National Health and Environmental Effects Research Laboratory, Research Triangle Park, NC 27711. 92 pp.

United Nations Economic Commission for Europe (UNECE). 2004. Mapping Manual 2004: Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends. UNECE Convention on Long-range Transboundary Air Pollution, ICP Modelling and Mapping. 254 pp.

Wiens, J.A. and K.R. Parker. 1995. Analyzing the Effects of Accidental Environmental Impacts: Approaches and Assumptions. Ecol. Applications 5 (4): 1069-1083. https://doi.org/10.2307/2269355

Wigington, Jr. P.J., D. R. DeWalle, P. S. Murdoch, W. A. Kretser, H. A. Simonin,J. Van Sickle, J. P. Baker. 1996. Episodic Acidification of Small Streams in the Northeastern United States: Ionic Controls of Episodes. Ecological Applications, Vol. 6, No. 2 (May, 1996), pp. 389-407 URL: http://www.jstor.org/stable/2269378 .

Yan, N.D., W. Keller, N.M. Scully, D.R.S. Lean, and P.J. Dillon. 1996. Increased UV-B penetration in a lake owing to drought-induced acidification. Nature 381:141-143