B.C. Works'
Sulphur Dioxide Environmental Effects Monitoring Program

2022 Annual Report, Draft V.2

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Version Tracking Table

No.	Date	Summary of content /changes
V.1	June 8, 2023	Draft for review by Rio Tinto
V.2	June 21, 2023	Draft for review by B.C. Ministry of Environment and Climate Change Strategy (B.C. ENV)
V.3		Draft for review by Rio Tinto with edits per ENV comments
V.4		Final for B.C. ENV

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Executive Summary

ATMOSPHERIC PATHWAYS

The atmospheric pathways activities implemented in 2022 were:

- continuous SO_2 monitoring and analysis
- revisions to the Phase 2 network optimization report for continuous network,
- passive SO_2 sampling and analysis, and
- analyses of sulphur deposition.

All **continuous SO_2 analyzers** passed B.C. ENV's audits and had greater than 90% data capture for SO_2 in 2022. However, the 2022 datasets have not yet been validated by B.C. ENV. Therefore all 2022 relevant datasets are considered preliminarily valid for comparisons to the 1-hour and annual average SO_2 Canadian Ambient Air Quality Standards (CAAQS).

Generally, Haul Road concentrations trend closely with SO_2 emissions from the smelter, while stations farther from the smelter change more noticeably due to seasonal weather patterns than to changes in SO_2 emissions. When smelter SO_2 emissions decreased drastically in August 2021, concentrations at Riverlodge, Whitesail, Kitamaat Village, Lakelse Lake, and Terrace were not substantially lower than concentrations during previous years' fall and winter months. Similarly, when SO_2 emissions from the smelter steadily increased from August 2022 through December 2022, most of these stations showed a decrease in concentrations consistent with seasonal weather patterns.

As in prior years, ambient concentrations of SO_2 remain low (below 4 ppb) most of the time, and higher concentrations occur infrequently.

Annual average monitored concentrations aligned closely with model results in 2022. The 1-hour 99th percentile of monitored concentrations also align with model results for all stations other than Haul Road (which measured over double the regional-scale modelled concentration and nearly double the local-scale modelled concentration). Overall, these comparisons are consistent with the discussion in the 2019 Comprehensive Review that predicted modelled concentrations in most areas are higher than measured concentrations, resulting in cautious risk assessments. However, model underpredictions at Haul Road in 2022 differed from the patterns observed in 2020 and 2021 (when model predictions were greater or equal to monitored values). This is likely an artifact of the model scaling method during these two years with several months at very low SO_2 emission levels rather than the possibility that the model's relationship to monitored data has changed meaningfully.

The network of **passive samplers** was redeployed in the Kitimat Valley during 2022 following the same procedures as in 2016-2021. Deployment started in April 2022 at 22 sites within the Kitimat Valley, primarily focused along the Wedeene and Bish roads to capture the plume path. Over 150 sample exposures were collected and analysed. The 2022 results are similar to the 2021 observations, although concentrations in 2022 are slightly lower as expected during the low emission levels from the smelter in 2022. Higher concentrations were monitored later during the 2022 year due to the restart and increased smelting capacity coming on-line. The spatial pattern is consistent with previous years.

Continued deployments are recommended during 2023 to further define the plume throughout the restart and into the transition to normal operation.

Preliminary data **sulphur wet deposition** monitoring in 2022 show that average annual precipitation volume was consistently higher at Haul Road compared to levels at Lakelse Lake during 2014–2022. During 2022, precipitation volume at Haul Road (2207 mm) and at Lakelse Lake (1493 mm) were slightly lower than the nine-year average, and the relationship between the two stations was consistent with past years. Higher weekly sulphate concentration (mg/L) and lower pH was observed at Haul Road compared with Lakelse Lake. The higher SO_4 and lower pH in rainfall at Haul Road are caused by the higher atmospheric concentration of SO_2 and corresponding higher S deposition at Haul Road. Higher rainfall volume and higher sulphate concentration observed at Haul Road combines to result in a more pronounced wet S deposition difference compared with Lakelse Lake on an annual and weekly basis.

Total mass of **SO_2 dry deposition** was calculated based on modelled dry deposition velocity and measured ambient SO_2 concentrations. The 'big-leaf' model was used to estimate hourly species-specific dry deposition velocity at four stations in the Kitimat Valley (Haul Road, Whitesail, Lakelse Lake, and Terrace Airport [YXT]) using 2022 meteorological data. Total mass of SO_2 dry deposition tended to be more heavily influenced by monitored SO_2 concentration at each site versus changes in SO_2 deposition velocity. This difference in SO_2 concentrations is clearly the reason for elevated dry deposition mass at Haul Road compared to other sites. Similarly, dry deposition rates at all sites are lower in 2022 compared to 2021 due to the lower SO_2 concentrations and lower SO_2 emission rates from the smelter in 2022. Similar ratios of wet versus dry S deposition occur during each year from 2016 – 2022 at Haul Road.

There is no **KPI** for atmospheric pathways. The results from analyses of the atmospheric pathways line of evidence are inputs to the KPIs for the human health, terrestrial ecosystems, and aquatic ecosystems lines of evidence.

HUMAN HEALTH

Starting January 1, 2020, the SO_2 health KPI implemented the SO_2 Canadian Ambient Air Quality Standards (CAAQS). In 2022 the CAAQS value was 70 ppb, and in 2025 the CAAQS value changes to 65 ppb. The SO_2 health KPI is used to assess residential SO_2 ambient air quality. The SO_2 Health KPI for 2022 is a threshold for residential SO_2 ambient air concentration of 70 ppb and is evaluated as defined in the B.C. Air Quality Objectives.

For 2022 the **KPI** is calculated as the 3-year average of the annual 99th percentile of the D1HM (maximum daily 1-hour concentrations of SO_2) using validated data for years 2020 and 2021 and preliminary data for year 2022. The 2022 KPI calculation results for Kitamaat Village, Riverlodge and Whitesail were all well below the KPI (CAAQS value of 70 ppb) and, as such, demonstrate attainment of the KPI. The KPI will be calculated for the Service Centre in 2023, when three years of data have been collected.

TERRESTRIAL ECOSYSTEMS

Most of the terrestrial ecosystems work done in 2022 was under the **Vascular Plant and Cyanolichen Biodiversity Monitoring Program (PCMP)**. This included first assessment of 12 of the total 33 Kitimat Valley sites, identifying two additional reference sites to be assessed in the Kemano Valley, additional reconnaissance for a minimum of six new “alternate” sites in the Kitimat Valley, soil sampling for all sites, and (at the Kemano long-term acidification plots) inspection/repair/replacement of plot stakes and the tagging and measurement of tree diameter-at-breast-height (DBH).

A review of wind direction data in 2022 indicated that corrections were required for the deposition model. As the design of the PCMP plots was originally developed using previous deposition modelling data, the PCMP was reviewed in 2022 using the corrected deposition modeling results, and the deposition category of three established PCMP plots has subsequently changed.

Activities for the vegetation component of the SO_2 EEM Program in 2022 included the assessment of the second set of PCMP field plots, and analysis and presentation of results in the December submission of the second annual report for the PCMP. . An assessment of vegetation health was undertaken at plot locations in the Kitimat-Terrace valley that included all established plots that could be visited during the June-July timeframe. We also undertook reconnaissance and establishment of eight new plots in the Kitimat Valley and two new reference plots in the Kemano Valley.

Vegetation health inspections were undertaken at both newly established Kemano plots, and all twelve fully assessed plots in the Kitimat Valley in 2022. Opportunistic vegetation health inspections were made at previously established sites in the Kitimat Valley undertaken during soil sampling whenever timing allowed. This resulted in ten additional inspections, for a total of 24 vegetation health inspections completed as part of the PCMP in 2022. Cyanolichen health inspections are part of the cyanolichen assessment portion of the PCMP, and these inspections were made at the 14 primary plots assessed in 2022. Overall, no patterns related to plant or cyanolichen health and deposition category were noted based on these inspections.

A major component of biodiversity is species richness, which was assessed during 2022 for plants in the low shrub and herb layers. As expected, no trends between deposition zones are noted in initial plant species richness results. These data generally show that cyanolichen diversity is inversely proportional to increasing deposition zone (largely as an historical artifact of fluoride emissions); however, the data also demonstrate the stochastic nature of this metric (e.g., if a host tree is lost from a plot, a dramatic shift in recorded cyanolichen diversity may occur).

In 2022 soil samples were collected at all established sites as part of the PCMP field session except one. This includes all previously established and accessible sites for which samples could be obtained, as well as the two new Kemano sites, and the eight newly established sites in the Kitimat Valley. Composite mineral soil samples were subsequently analysed for pH, exchangeable cations and exchangeable acidity. In analysed samples, pH ranged from 4.03 to 6.10, and averaged 4.84. Cation Exchange Capacity ranged from 4.8 to 65.0, and averaged 29.6 meq/100g. Of exchangeable cations, potassium and sodium were below detection limits in all samples; calcium ranged from undetectable to 2120 mg/kg, averaging 520.63 mg/kg; and magnesium ranged from undetectable to 173 mg/kg, averaging 100.79 mg/kg.

In addition, the two permanent, long-term soil acidification plots in Kemano were visited in 2022. At each plot, the stakes were inspected and replaced, as needed, and the trees within each were tagged and their DBH measured and recorded.

The **KPI** of Critical Load Exceedance from modelled atmospheric S deposition will not be assessed for attainment during Phase III of the EEM Program (as noted in the Phase III Plan). The Phase III Comprehensive Review will assess if a KPI can be established for the plant biodiversity component of the terrestrial ecosystems line of evidence.

AQUATIC ECOSYSTEMS

The year 2022 was exceptional in the 11-year history of the SO_2 EEM Program because emissions from the smelter were dramatically less than in any previous year. Emissions during the 12 months prior to 2022 fall sampling were 21% of the levels in 2020 and 17% of the 2016-2018 period applied in the 2019 Comprehensive Review. The prolonged reduction in emissions after August 2021 could alter lake chemistry, especially since the estimated water residence time is less than a year for most of the sensitive EEM lakes.

The dominant responses in the 2022 data were generally consistent with our expectations (with a few exceptions): concentrations of SO_4 declined in all sensitive lakes (except LAK028); Gran ANC went up in all lakes; CBANC increased in 4 of the sensitive EEM lakes (but decreased in 3 of them); pH increased by 0.2-0.8 pH units in all 11 lakes, with the same range across the sensitive EEM lakes alone); and base cations dropped in all sensitive EEM lakes except LAK028. The changes observed from 2021 to 2022 generally countered the changes of the previous year (e.g., pH declined in all 11 lakes from 2020 to 2021 related to high levels of precipitation prior to sampling in the fall of 2021, and pH increased in all 11 lakes from 2021 to 2022). An important net result is that these "reversals" of the previous year's anomalous changes tended to reduce the estimated magnitude of long-term change (i.e., post-KMP 3-year average of an indicator minus the pre-KMP baseline value), compared to the results reported last year.

Of the two lakes showing a long-term decline in CBANC in last year's report, only LAK028 continues to show a long-term decline, albeit a smaller magnitude (-2.9 µeq/L now vs. -7.9 µeq/L last year). Two lakes (LAK012 and LAK028) still show long-term declines in BCS compared to 2012, though the magnitudes of these declines are smaller than in last year's report. LAK022 continues to be the only lake with a decline in Gran ANC relative to the 2012 baseline, though the magnitude is small and only slightly greater than previously reported. LAK022 also continues to be the only lake with a decline in pH relative to pre-KMP conditions. LAK022 is the only sensitive lake which is sampled just once per year; the other 6 lakes are sampled 4 times during the fall index period.

We recommend sampling LAK027 again in 2023. In 2021, the widely-observed storm-driven dilution event negated the ability of the sampling data to provide a meaningful comparison against the initial STAR data as intended. In 2022, the combination of exceptionally low deposition and particularly dry hydrologic conditions again negated the ability to provide the intended comparison.

The mean values of CBANC for the post-KMP period indicate **KPI** attainment, meaning that there have been no exceedances of the KPI thresholds.

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1 Introduction

The purpose of the SO_2 Environmental Effects Monitoring (EEM) Program is to monitor effects of SO_2 on human health, terrestrial ecosystems, and aquatic ecosystems. Results from the SO_2 EEM Program will inform decisions regarding the need for changes to the scale or intensity of monitoring, as well as decisions regarding the need for mitigation. The SO_2 EEM Program includes impact threshold criteria either for emission reduction or other mitigations that, when exceeded, would trigger emission reduction and/or other mitigation.

The SO_2 EEM Program is structured around the conceptual model shown in Figure 1-1.

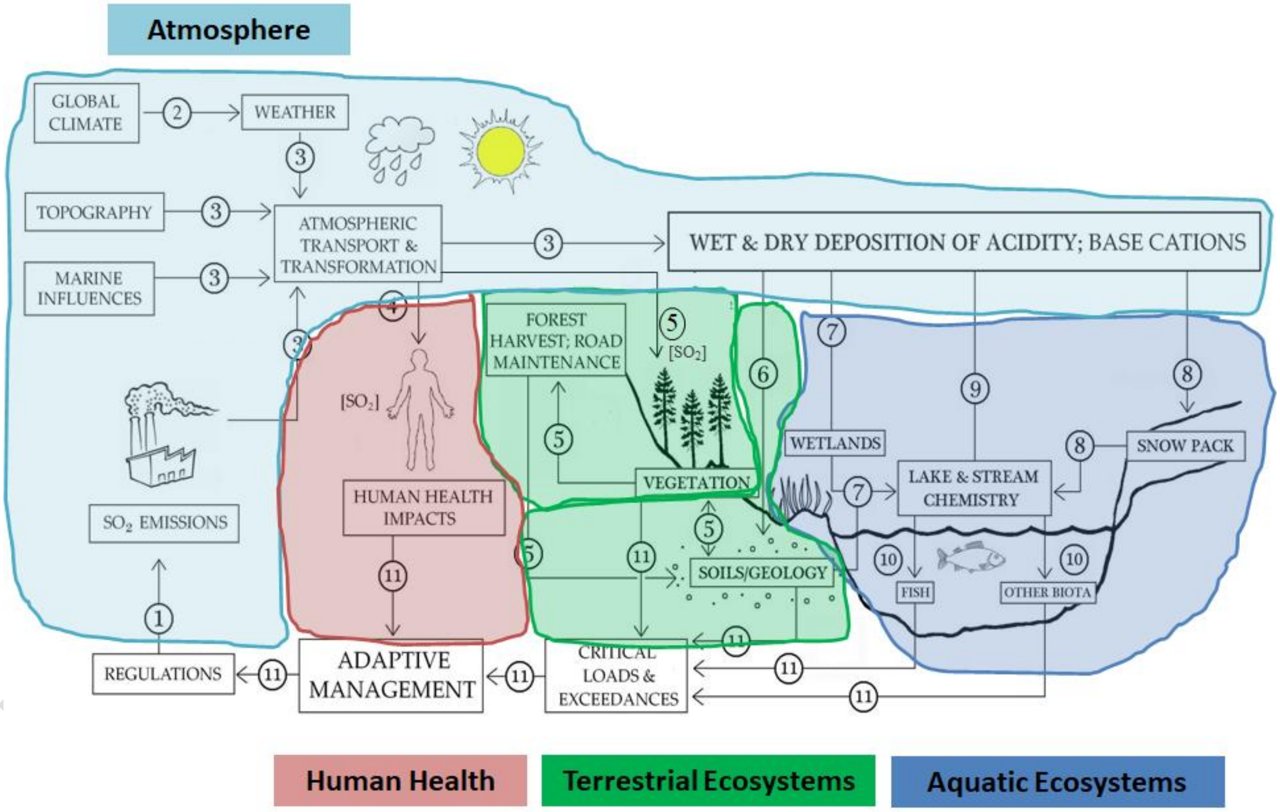


Figure 1-1. Conceptual (source-pathway-receptor) model of SO_2 emissions in the environment, showing linkages between sources and receptors. Source: Figure 1-1 from ESSA et al., 2020a.

This document comprises the SO_2 EEM Program 2022 Annual Report. It is organized into sections according to the pathway and receptor lines of evidence depicted Figure 1-2. The SO_2 EEM Program Annual Report for 2023 will be prepared in the spring of 2024.

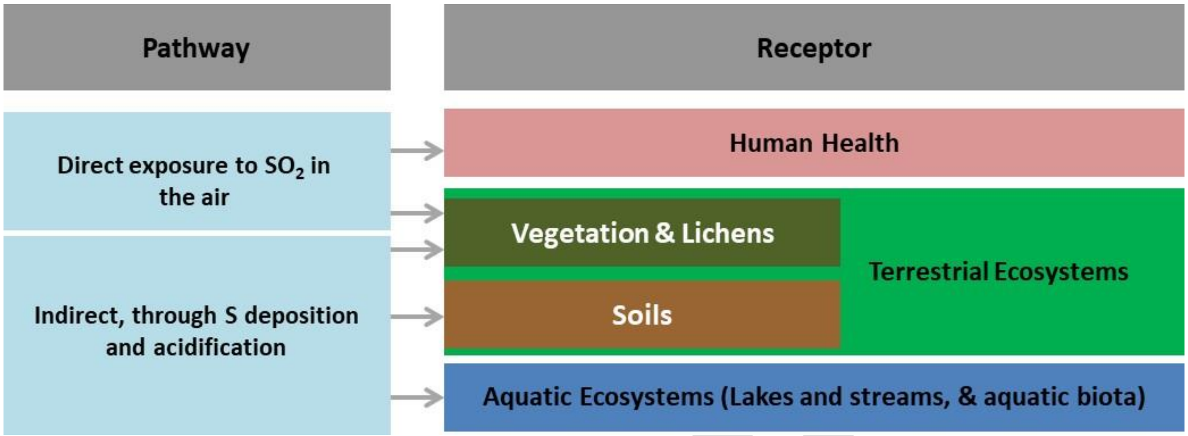
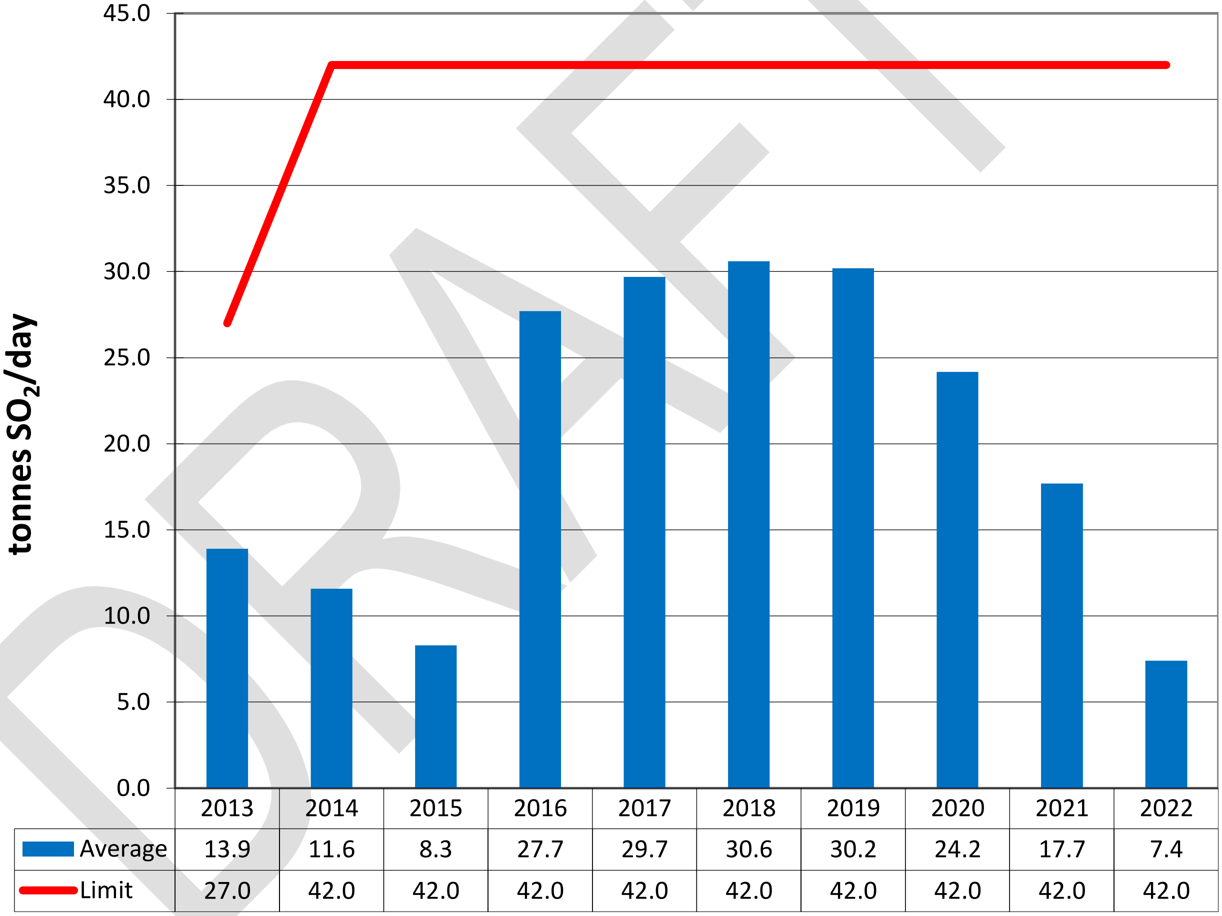


Figure 1-2. Organization of the five lines of evidence in the SO_2 EEM Program.

2 Facility Emissions

Average annual emissions of SO_2 from the Kitimat smelter decreased from the 17.7 t/d average rate in 2021 to an average rate of 7.4 t/d in 20221 (Figure 2-1). SO_2 emissions in 2022 remained below the 42 t/d permit limit. SO_2 emissions were below the normal emission range due to the process for restarting the smelter after the 2021 labour disruption. SO_2 emissions started to ramp-up with the restart of the anode baking furnace and the restarts of the aluminium smelting pots (an average of 0.75 pot start per day). As pots were being brought online, SO_2 emissions increased proportionally with the increased consumption of anode carbon (Figure 2-2).



	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
■ Average	13.9	11.6	8.3	27.7	29.7	30.6	30.2	24.2	17.7	7.4
▬ Limit	27.0	42.0	42.0	42.0	42.0	42.0	42.0	42.0	42.0	42.0

Figure 2-1. Annual SO_2 emissions from the Kitimat smelter from 2013 to 2022. (Source: Rio Tinto)

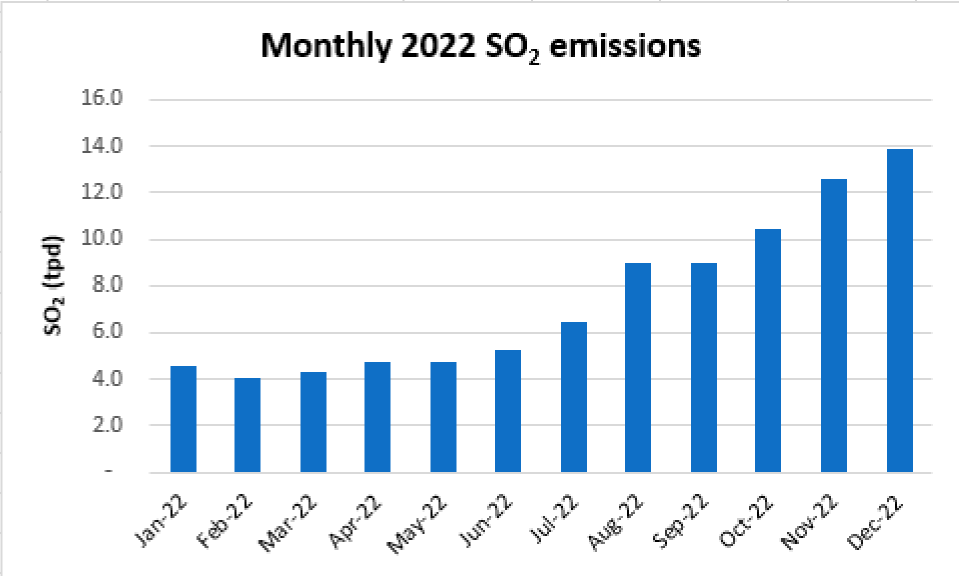


Figure 2-2. Average monthly SO_2 emissions from the Kitimat smelter throughout 2022. (Source: Rio Tinto)

3 EEM Activities

3.1 Atmospheric Pathways

3.1.1 SO_2 Concentrations – Continuous Monitoring

Continuous SO_2 monitoring data were collected from six existing continuous analysers: Haul Road (fenceline), Riverlodge (lower Kitimat), Whitesail (upper Kitimat), Kitamaat Village, Lakelse Lake[1], and Industrial Avenue (Figure 3-1). A seventh station (not pictured) was established in 2015 by the B.C. Ministry of Environment and Climate Change Strategy (B.C. ENV) in Terrace that can also be used to help assess SO_2 emissions from the smelter. The continuous SO_2 monitoring station was established in Service Centre (Industrial Avenue) in May 2020. The newest continuous air quality monitoring stations record hourly observations of SO_2. They provide information on air quality in the area on an ongoing basis, and will provide important data for many EEM activities over the next several years.

All SO_2 analyzers passed B.C. ENV's[2] audits and had greater than 90% data capture for SO_2 in 2022. However, validated continuous SO_2 data are not available from the B.C. ENV until late in the following year. Therefore, all 2022 relevant datasets are considered preliminarily valid for comparisons to the 1-hour and annual average SO_2 Canadian Ambient Air Quality Standards (CAAQS). The continuous SO_2 data summarized in this report include final, post-validated data for 2021 and prior years and preliminary data for 2022.

Figure 3-2 shows the pattern of the monthly average SO_2 concentrations at the seven continuous monitoring stations from 2013 through 2022, along with monthly SO_2 emissions over the same period. Figure 3-3 presents the same data without the Haul Road and Industrial Avenue stations in order to show the detailed changes at the lower concentrations. Figure 3-2 shows that the Haul Road concentrations generally trend closely with SO_2 emissions from the smelter. Figure 3-3 (without Haul Road) shows that stations farther from the smelter change more noticeably due to seasonal weather patterns than due to changes related to SO_2 emission levels. Even when smelter SO_2 emissions decreased drastically in August 2021, concentrations at Riverlodge, Whitesail, Kitamaat Village, Lakelse Lake, and Terrace were not substantially lower than concentrations during previous years' fall and winter months. Similarly, when SO_2 emissions from the smelter steadily increased from August 2022 through December 2022, most[3] of these stations showed a decrease in concentrations consistent with seasonal weather patterns.

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[1] The sole purpose of the Lakelse SO_2 analyzer is for estimating dry deposition and is not included in air quality monitoring network for British Columbia.

[2] B.C. Ministry of Environment and Climate Change Strategy (ENV) conducts audits on all monitoring stations within the network; however, since the Lakelse Lake monitor's purpose is for estimating dry deposition, it is not within the network and not audited by ENV.

[3] The pre-validated Whitesail station is the only station in Figure 3-3 that appeared to measure increasing concentrations over the August – December 2022 period. However, this trend may be an artifact of sensor drift, in which case, the post-validated 2022 Whitesail data would not show the increasing trend.

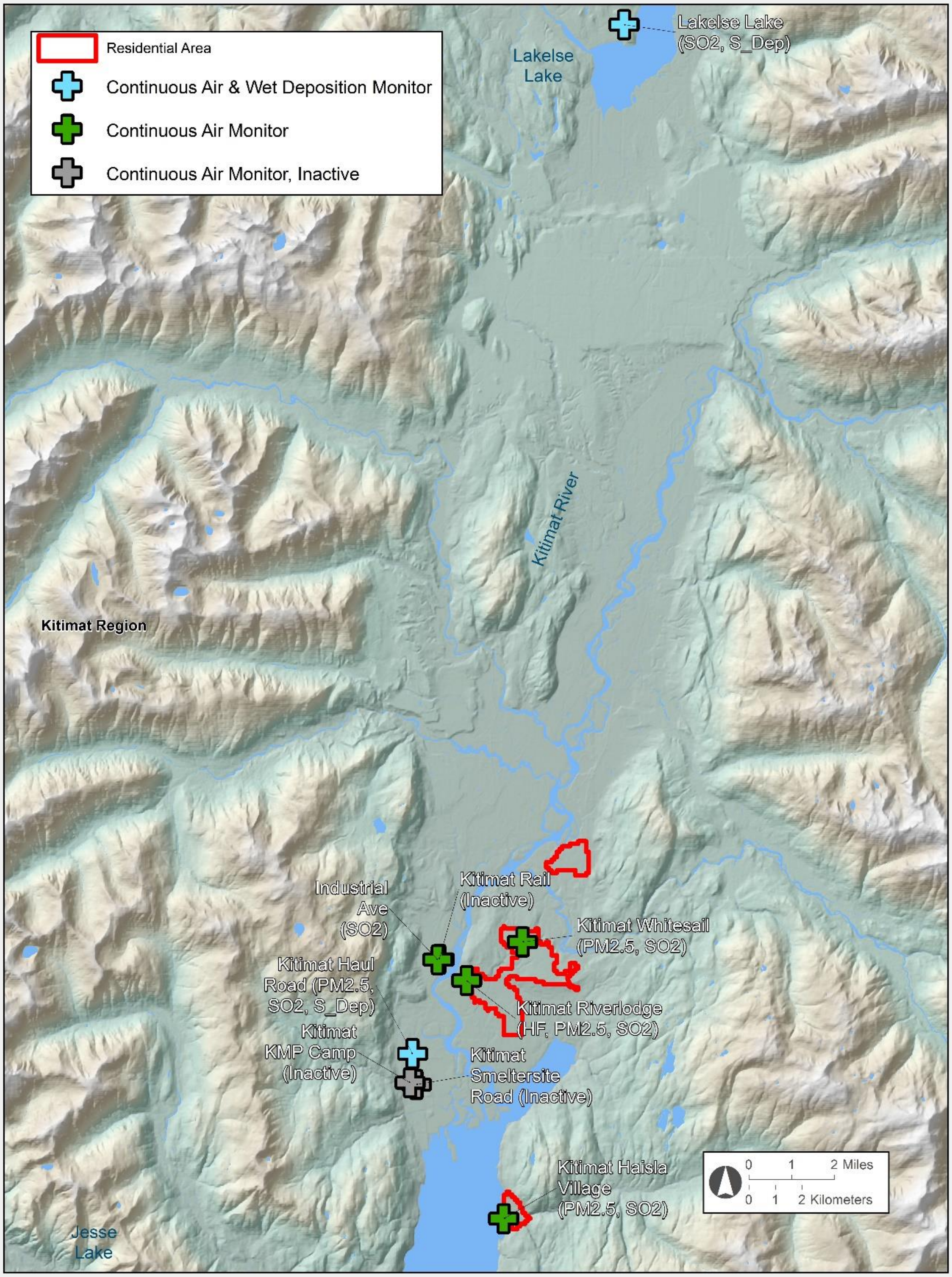

Figure 3-1. Locations of the six Rio Tinto continuous SO_2 analysers (Haul Road, Whitesail, Riverlodge, Kitamaat Village, Industrial Ave, Lakelse Lake).

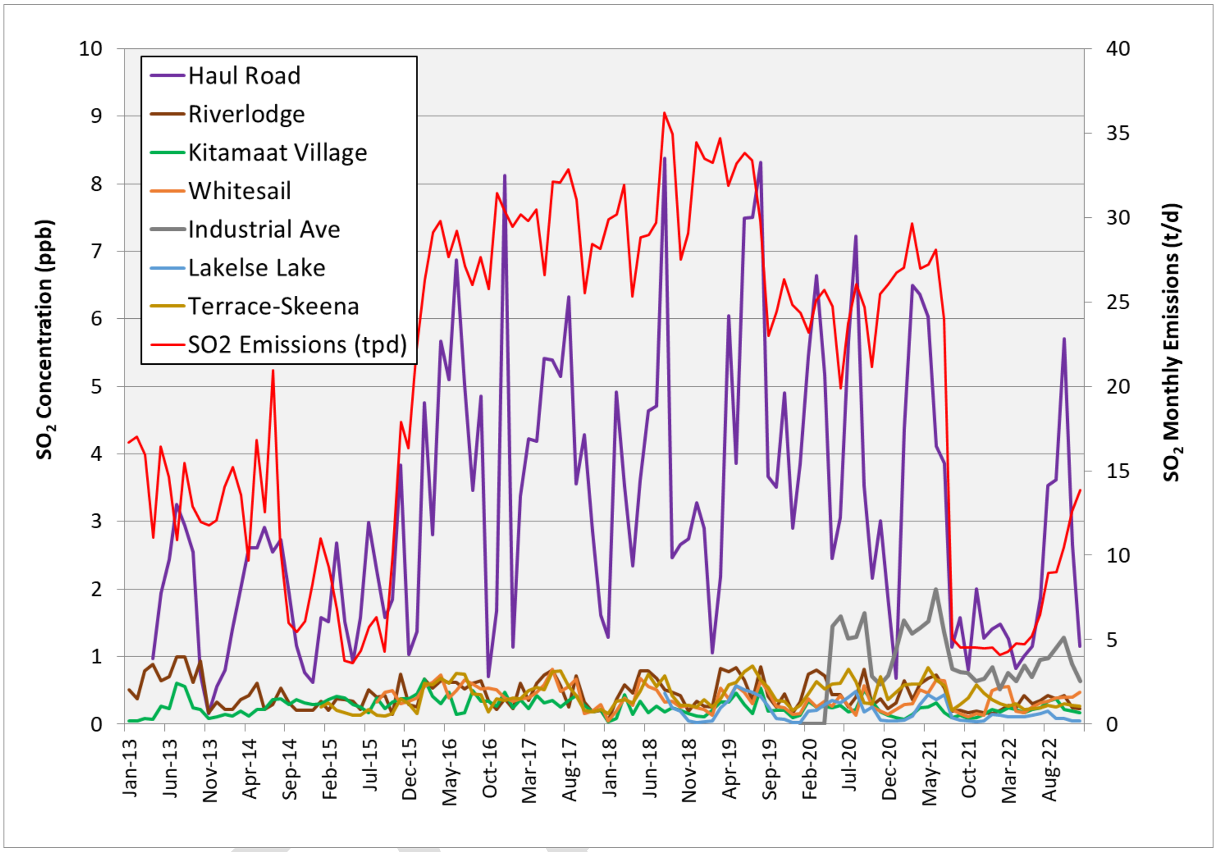

Figure 3-2. Monthly SO₂ emissions (red line) and monthly average ambient SO₂ concentrations at the seven continuous monitoring stations (purple, brown, green. orange, grey, blue and gold lines) for 2013 to 2022. (Source: Rio Tinto and Envista database)

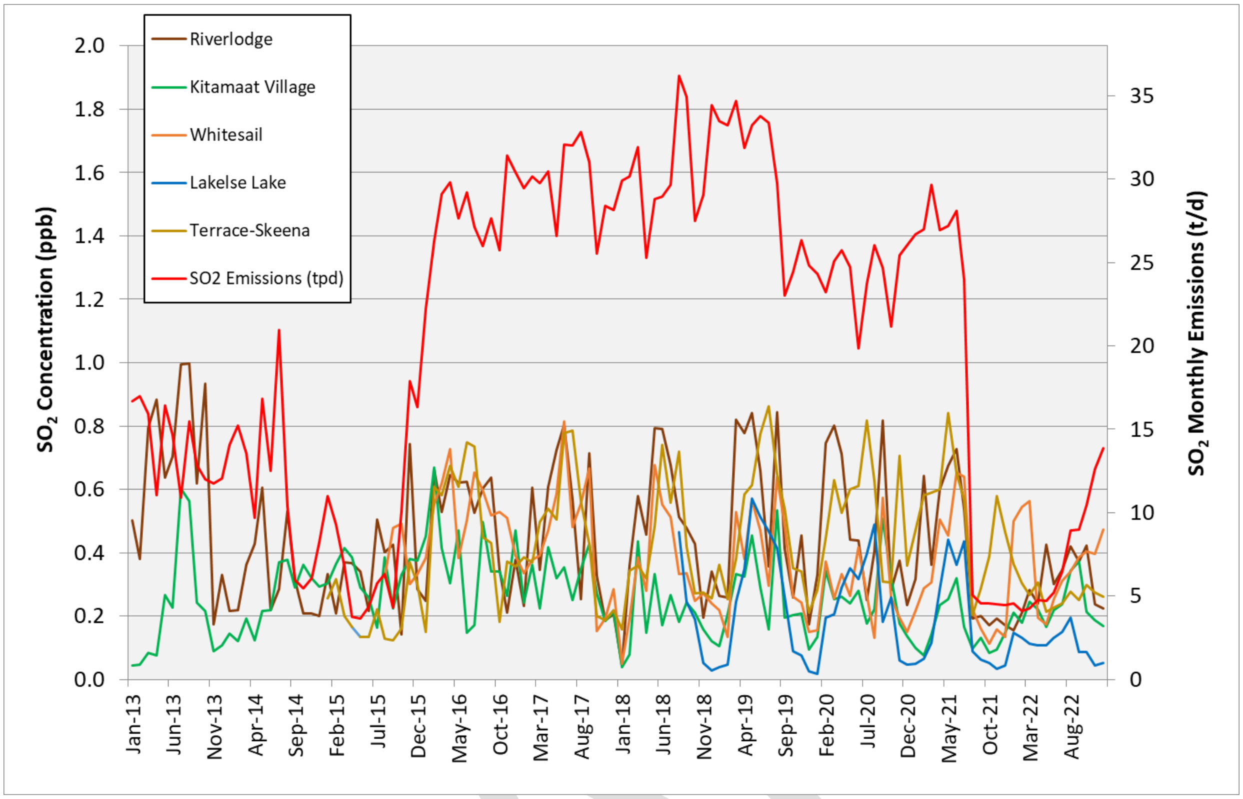

Figure 3-3. The same monthly SO_2 emissions (red line) and monthly average ambient SO_2 concentrations data as in Figure 3-2 but excluding the Haul Road and Industrial Avenue stations in order to show the detailed changes at the lower concentrations. (Source: Rio Tinto and Envista database)

Figure 3-4 shows a histogram depicting the relative frequency of hourly averaged concentrations of SO_2 at Haul Road (fenceline), Riverlodge (lower Kitimat), Whitesail (upper Kitimat), Kitamaat Village, and Industrial Avenue (Service Centre).[4] Low concentrations (below 4 ppb) occur most of the time (high frequency), and higher concentrations occur infrequently.

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[4] The sole purpose of the Lakelse SO_2 analyzer is for estimating dry deposition and is not included in air quality monitoring network for British Columbia nor in Figure 3-4.

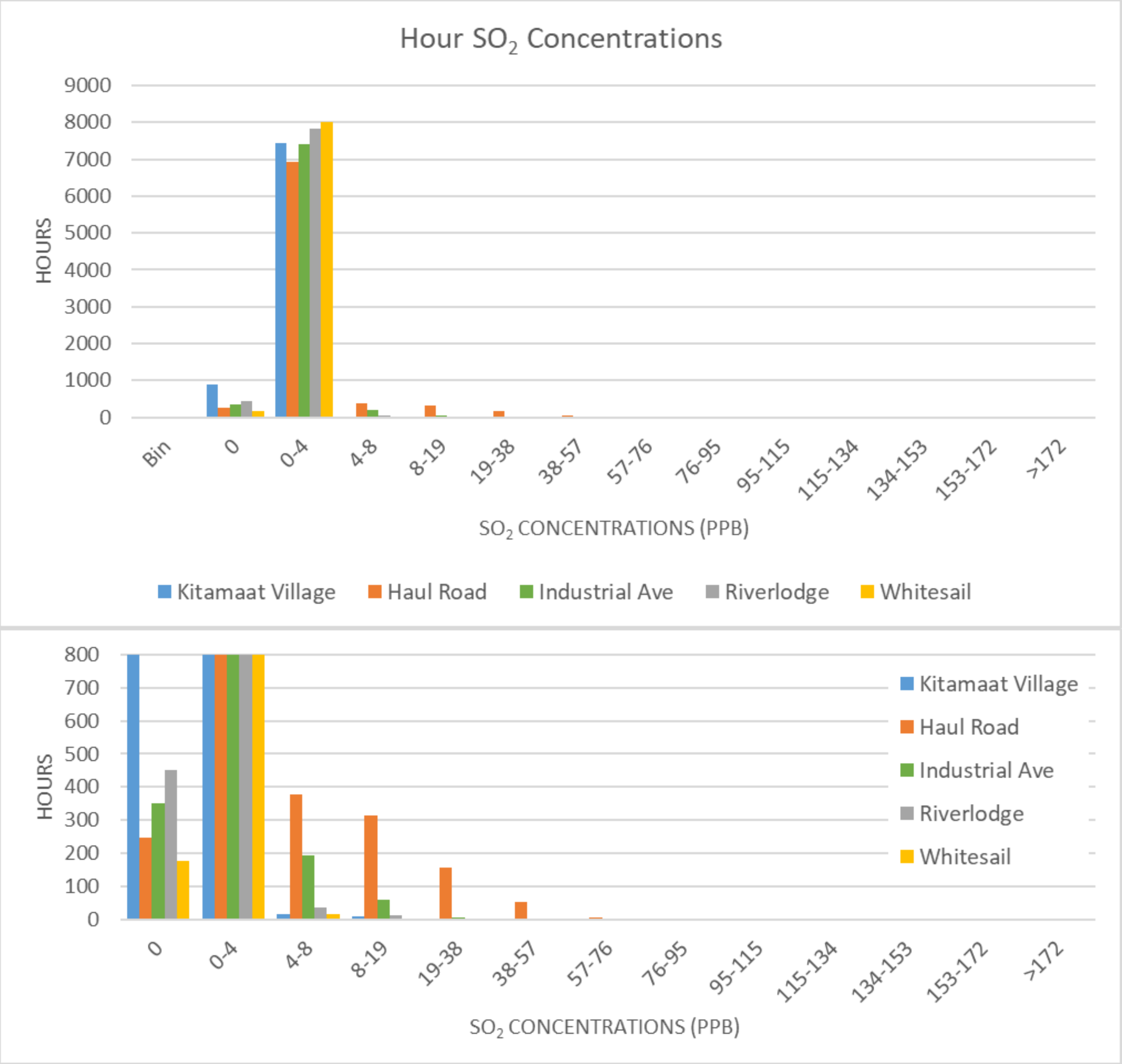

Figure 3-4. SO_2 hourly concentrations in 2022 at the Kitamaat Village, Haul Road, Industrial Avenue, Riverlodge, and Whitesail continuous monitoring stations (top graph). The bottom graph zooms in on the subset of the data showing lower frequencies (800 hours and less) of higher concentrations. (Source: Rio Tinto)

Comparison to the Model Output

Monitoring data collected at the four[5] monitor stations are compared to the air dispersion modelling results prepared for the EEM 2019 Comprehensive Review (ESSA et al., 2020a). The model comparisons in this section reflect the updated CALPUFF model results using corrected CALMET wind data.[6] Table 3-1, Figure 3-5 and Figure 3-6 show the comparison between monitored concentrations in 2021 and the predicted SO_2 concentrations from the air dispersion modelling analysis for 99th% 1-hour daily max and annual averaging periods. All results are in the form of the Canadian Ambient Air Quality Standards (CAAQS), which are used as the BC Air Quality Objectives for SO_2. Note that the predicted concentrations from the air dispersion modelling analysis include the more realistic background concentrations (the same background concentrations that were applied in the 2019 Comprehensive Review for the model evaluation).

As shown in Table 3-1, annual average monitored concentrations align closely with model results in 2022, ranging from approximately half of the modelled concentrations (42% at Riverlodge for both scales) to 118% (Haul Road for regional-scale). The 1-hour monitored concentrations also align with model results for all stations other than Haul Road (which measured over double the regional-scale modelled concentration and nearly double the local-scale modelled concentration) and Kitamaat Village regional-scale (monitored is nearly double regional scale model). The remaining 1-hour monitor to model comparisons range from 44% (Whitesail local scale) to 96% (Riverlodge regional scale). These model results represent actual emissions applying a more realistic background used for model performance evaluation. The Service Centre station is not included in the comparison as the station was added after the modelling was completed.

Overall, these comparisons are consistent with the discussion in the 2019 Comprehensive Review that predicted modelled concentrations in most areas are higher than measured concentrations, resulting in cautious risk assessments. However, while the comparison in 2021 continues to support the 2019 Comprehensive Review conclusions related to model performance and general overprediction, comparisons for 2021 and 2022 show lower magnitude and fewer instances of overprediction and larger magnitude and more instances of underprediction than the same comparisons for historic years. The measured concentrations at Haul Road compared to scaled model results shows an inverse relationship compared to most years (when monitored concentrations are slightly lower than scaled

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[5] The four stations with complete data used for model evaluation in the 2019 Comprehensive Review are used for model comparison in this section. Other stations either have incomplete data or are too distant for comparison.

[6] CALPUFF results revised for wind corrections for all years. ENV and Trinity reviewed wind direction data in 2021 and determined that the Whitesail station was aligned to magnetic north rather than true north prior to August 2018 and that the Yacht Club station wind direction was also misaligned historically and realigned to true north in early 2019. Therefore, the wind directions recorded at these two stations needed correcting for most or all of the Comprehensive Review CALPUFF model period. In addition, Yacht Club wind speed data was be invalidated by ENV for most of 2018. Trinity conducted a study for the full CALPUFF period (2016 through 2018) using the corrected wind data. An addendum to the Comprehensive Review report (ESSA et. al., 2022) evaluated the corrected CALPUFF results for each line of evidence in order to determine if the post-correction CALPUFF results are meaningfully different than the results from the original Comprehensive Review report and whether use of the post-corrected results would lead to different conclusions in the Comprehensive Review.

model results). Comparisons for 2016 through 2020 showed corrected CALPUFF[6] generally predicting about the same to double of measured concentrations, with 4 of the 80 comparisons showing slight underprediction (two for annual and six for 1-hour). This change in comparison is likely an artifact of the model scaling method during these two years with several months at very low SO_2 emission levels rather than the possibility that the model's relationship to monitored data has changed meaningfully. The annual average and 1-hour model results were scaled based on annual average emission rates (2022 averaged 7.4 tpd compared to the actual scenario of about 30 tpd), but the emission levels in August through December of 2022 averaged 11 tpd.

Table 3-1. 2022 Monitored Data Compared to Modelled Concentrations.

Site	Averaging Period[a] / Model	Monitored Concentration (ppb)	Modelled Concentration[b] (ppb)	Monitored Concentration (ppb)	Modelled Concentration[b] (ppb)
		2022		3-Year Average	
Haul Road	Annual/Local	2.17	2.11	3.21	4.34
Kitamaat Village	Annual/Local	0.23	0.37	0.23	0.49
Riverlodge	Annual/Local	0.30	0.73	0.40	1.30
Whitesail	Annual/Local	0.38	0.47	0.33	0.72
Haul Road	Annual/Regional	2.17	1.84	3.21	3.75
Kitamaat Village	Annual/Regional	0.23	0.33	0.23	0.41
Riverlodge	Annual/Regional	0.30	0.72	0.40	1.27
Whitesail	Annual/Regional	0.38	0.50	0.33	0.79
Haul Road	99% 1HDM/Local	58	31	67	66
Kitamaat Village	99% 1HDM/Local	10	10	13	20
Riverlodge	99% 1HDM/Local	10	12	19	25
Whitesail	99% 1HDM/Local	6	13	12	27
Haul Road	99% 1HDM/Rgnl	58	26	67	56
Kitamaat Village	99% 1HDM/Rgnl	10	6	13	10
Riverlodge	99% 1HDM/Rgnl	10	11	19	23
Whitesail	99% 1HDM/Rgnl	6	9	12	18

[a] Averaging periods and forms of results correspond to the CAAQS. 1HDM = 1-hour averaging period, daily maximum

[b] Modelled concentrations are based on results from the actual scenario using actual emissions for 2016, 2017, 2018, based on updated model from wind correction performed in 2021. For 2019 forward, the 3-year average actual model results are scaled from 2016-2018 average emissions to current year emission.

The following background value from Williams Lake is added to account for non-modelled sources of SO_2 (for 2019 forward, note the background is added after scaling model results).

Annual Average	0.26	ppb
99th% 1-hour Daily Max	1.80	ppb

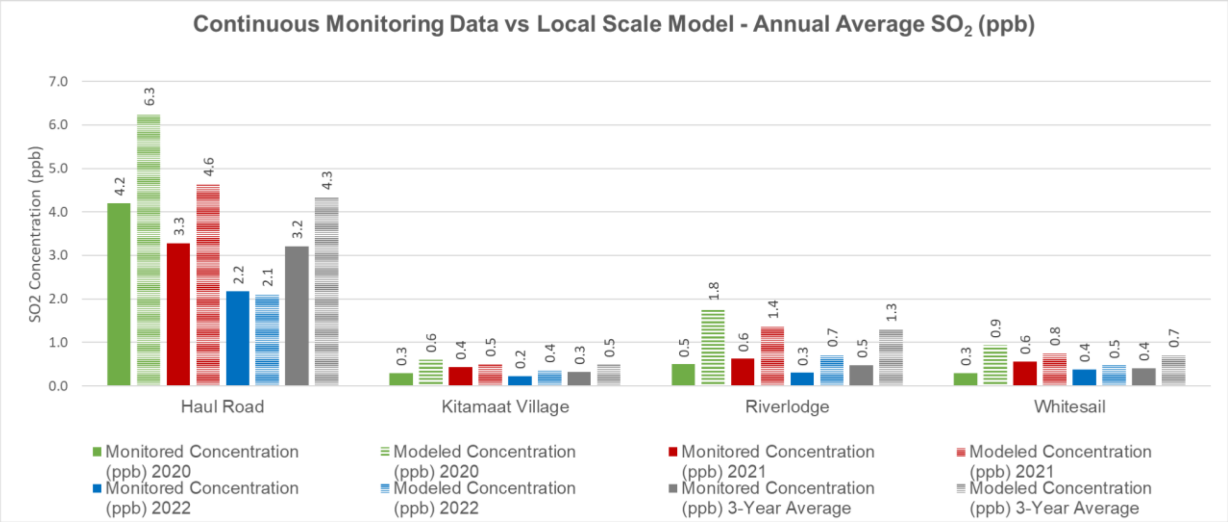

Figure 3-5. 2022 Monitored annual average data compared to modelled concentrations.

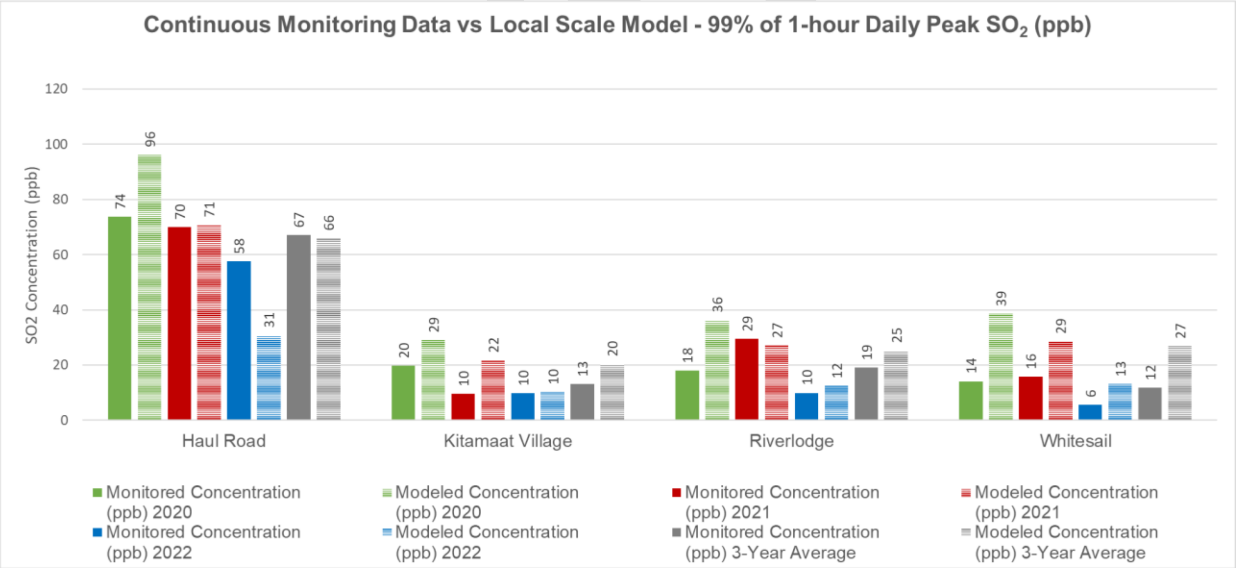

Figure 3-6. 2022 Monitored 1-hour data compared to modelled concentrations.

Network Optimization

Rio Tinto revised Phase 2 of the network optimization to incorporate the updated CALPUFF model results[6] and it is currently under review by B.C. ENV. The Terms of Reference (TOR) for the SO_2 network optimization incorporating the latest monitoring data and the 2019 Comprehensive Review model results was approved by B.C. ENV in December of 2020. The draft Phase 2 network optimization report was submitted to B.C. ENV in December 2021 and the revised version for corrected CALPUFF model results was submitted to B.C. ENV in December 2022.

3.1.2 SO_2 Concentrations – Passive Sampling

The network of passive samplers was redeployed in the Kitimat Valley during 2022 following the same procedures as in 2016-2021 (ESSA et al., 2020a). The network was deployed starting April 27, 2022[7], at 22 sites within the Kitimat Valley (Figure 3-7), primarily focused along the Wedeene and Bish roads to capture the plume path. This network is referred to as the plume path network and historically referred to as the valley network.[8]

Based on the 2020 passive sampling plan (Trinity 2020), a detailed site evaluation was conducted and documented during the 2020 deployment. The original 15 sites deployed in 2020 were deployed in 2022. In addition, the six sites added in 2021 based on reconnaissance performed in early 2021 were also deployed in 2022.[9] Location A05 (Kitamaat Village) was added in 2022 to understand the extent of the plume to the southeast and for another site to compare with continuous ambient SO_2 monitoring.

As detailed in the Phase III EEM work plan's 2021-Specific Work Plan for Passive Sampling (ESSA et. al., 2021), the network changed from employing IVL SO_2 passive samplers to Bureau Veritas (BV) All-Season Passive Air Sampling System (PASS) and laboratory. All 2022 sample analysis was performed using the BV PASS system.

Six deployments, with an approximate exposure time of one-month (27–34 days), were carried out under the plume path network between April and November 2022. Lake 28 sampling had five deployments from June – November 2022.

In 2022, there were 155 sample exposures across the plume path network collected and analysed during the six deployments. These included replicate samplers deployed approximately 18% of the time (28 duplicate exposures) and 23 blank samples (approximately four per sampling period).

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[7] The Lake 28 sampler was deployed later than the other sites, on June 13, 2022.

[8] A second network of passive samplers deployed in the urban and residential areas of Kitimat was in continuous operation from June 2018 through December 2019. The urban network study concluded in 2019 (before the time period of this report).

[9] Three of the six new 2021 sites (V17, V18/V18b, and V20) were added east and west of V01 to create an east-west transect to better understand the eastern and western boundaries of the plume path. The remaining three new 2021 sites (V21, V22, and V23) were added farther north near Terrace to better understand the northern boundary of the plume path (and to verify where the plume is not).

The observed data show elevated atmospheric SO_2 along the plume path (Figure 3-7). Results shown in Figure 3-7 and listed in Table 3-2 are uncalibrated because the BV PASS results need to undergo a new calibration analysis (different from the historic calibration based on IVL sampler data). The BV PASS calibration analysis will be performed in 2023 after sufficient data have been collected from BV PASS samplers co-located at continuous monitoring stations. The 2022 results within the plume path network are similar to the 2021 observations, although concentrations in 2022 are slightly lower as expected during the low emission levels from the smelter in 2022. Higher concentrations were monitored later during the 2022 year due to the restart and increased smelting capacity coming on-line. The spatial pattern is consistent with previous years. It is recommended that deployments be continued during 2023 to further define the plume throughout the restart and into the transition to normal operation.

Additional information can be found in Technical Memo P06, provided in Appendix A.

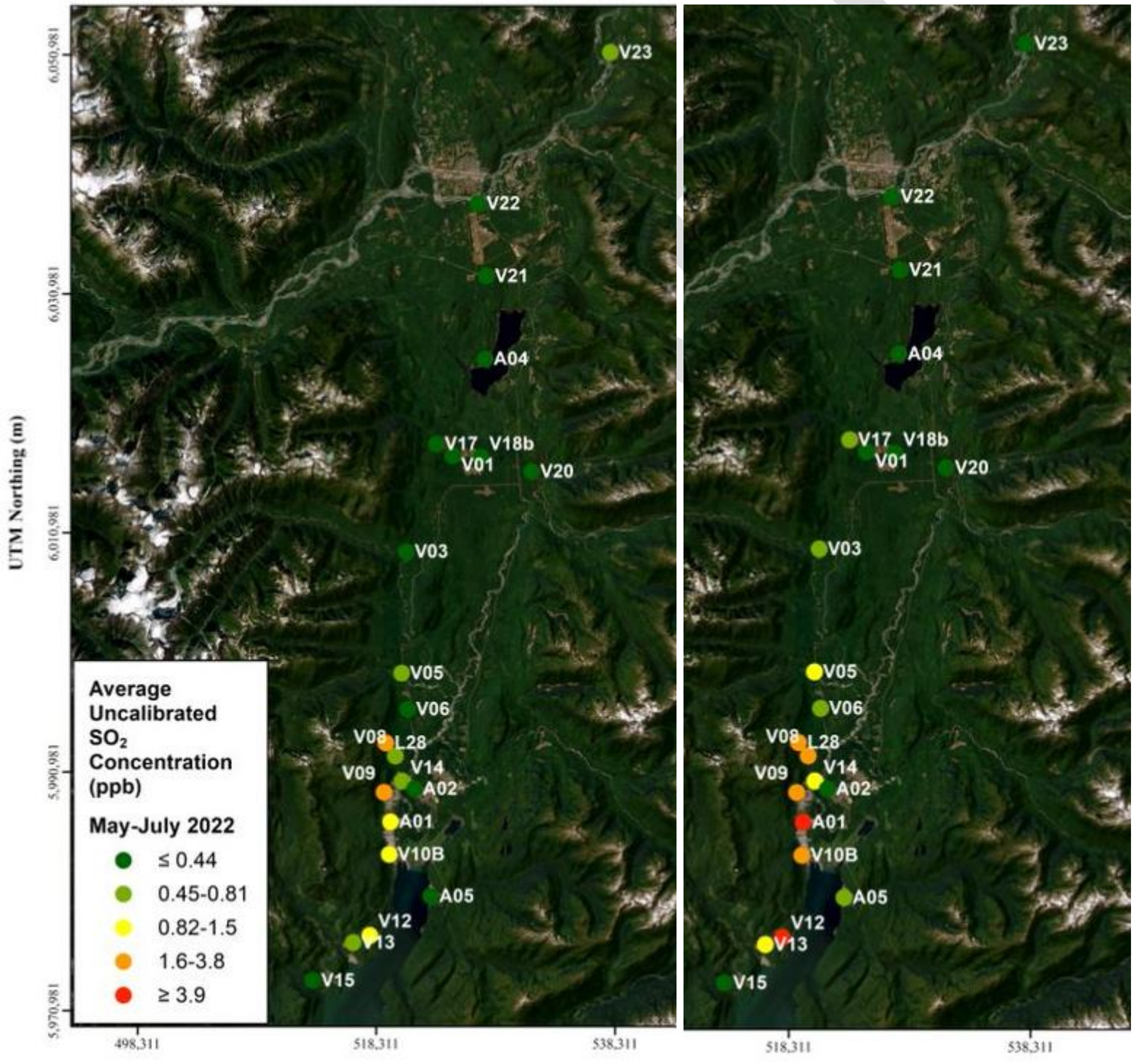

Figure 3-7. Average atmospheric sulphur dioxide (SO_2) concentration during May to July 2022 (left) and during August to October (right) in the Kitimat Valley passive diffusive monitoring networks (uncalibrated).

Table 3-2. Monthly concentration of SO_2 (ppb) from passive samplers in the SO_2 network during the 2022 sampling season.

ID	Site Name	UTM E	UTM N	May-22	Jun-22	Jul-22	Aug-22	Sep-22	Oct-22
A01	Haul Road Station	519527	5986823	1.1	1.4	1.8	3.9	5.2	7.0
A02	Riverlodge Station	521538	5989580	0.3	0.2	0.2	0.3	0.3	0.4
A04	Lakelse Lake NADP Station	527457	6025573	0.2	0.1	0.2	0.2	0.2	0.1
A05	Kitamaat Village Station	522907	5980600	0.2	0.2	0.3	0.5	0.5	0.5
V01	Onion Lake Ski Trail North	524757	6017435	0.2	0.1	0.3	0.5	0.3*	0.3
V03	Mound TKTP92	520853	6009407	N/C	0.3	0.5	0.7	0.5*	0.5
V05	LNG Muster Station	520457	5999250	N/C	0.6	0.8	1.1	0.9	0.7
V06	Sand Pit	520970	5996240	0.4	0.4	0.6	0.8	0.7	0.7
V08	Claque Mountain Trail at Powerline	519938	5992329	0.7	0.8	0.9	2.2	1.2*	1.7
V09	Sand Hill at Powerline	518985	5989292	1.5	1.6	2.8	3.6*	3.2	3.9
V10B	Pullout before Bish FSR	519425	5984090	0.6	1.7	1.2	3.3	4.0	2.8
V12	Bish Road Pullout 4	517790	5977294	0.6	1.6	0.9	2.3	5.4	5.1
V13	Bish Road at Chevron LNG	516389	5976708	0.4	0.7	0.4	0.8	1.6*	1.7
V14	Industrial Area Kitimat Hotel	520490	5990236	0.7	0.4	0.4	0.6	0.9*	1.1
V15	Bish Mainline	512994	5973534	0.2	0.3	0.2	0.3	0.4	0.3*
V17	West Lake	523359	6018434	N/C	0.3	0.5	0.9	0.6	0.9
V18B	Wedeene mainline	527088	6017351	0.2	0.1	0.1	0.2	0.2	0.2
V20	Pipeline laydown	531354	6016121	0.2	<0.1	0.1	0.2	0.1	0.2
V21	South of airport	527566	6032493	0.2	<0.1	0.2	0.2	0.2	0.2
V22	Kitselas Development	526862	6038551	0.1	<0.1	0.1	0.2	0.3	0.2
V23	Gitaus water tower	537941	6051192	1.5	<0.1	<0.1	0.1	<0.1	0.1
L28	Lake 28	519139	5993425	N/C	1.6	2.4	3.4	2.0	2.0

1. Data are uncalibrated because the passive sampling technology changed to BV PASS in 2021 and have not collected sufficient co-located data to determine a reliable calibration coefficient.
2. Dates are the end month of each sampling period (for deployments that started and ended near the end of the month), except for L28, dates are listed month-beginning (because L28 deployments began near the beginning of the month).
3. N/C means not collected; * means sample had seeds, insect eggs, or webs in the PASS assembly during the sampling period.

3.1.3 Sulphur Wet and Dry Deposition

3.1.3.1 Wet Deposition (Precipitation Chemistry)

Validated annual wet deposition data values are not available from the National Atmospheric Deposition Program (NADP) until late in the following year. Therefore, annual deposition values are estimated for the reporting year using *preliminary* weekly datasets. The data summarized below include final, post-validated data for 2021 and prior years, and preliminary data for 2022.[10,11]

Figure 3-8 compares the amount of annual precipitation (mm) Haul Road and Lakelse Lake precipitation chemistry monitoring stations during 2013 to 2022. Note that because the Lakelse Lake station was only in operation for part of 2013, data from that location are only shown for 2014 to 2022. Average annual precipitation volume was consistently higher at Haul Road compared to levels at Lakelse Lake during 2014–2022 (48% to 80% higher), averaging 2441 mm and 1507 mm, respectively. During 2022, precipitation volume at Haul Road (2207 mm) and at Lakelse Lake (1493 mm) were slightly lower than the nine-year average, and the relationship between the two stations was consistent with past years (48% higher at Haul Road compared to Lakelse Lake).

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[10] January through September 20, 2022 data from NADP are weekly validated. September 20 through December 31, 2022 data are preliminary not yet validated.

[11] Similarly, the 2021 report showed final data for 2020 and prior and preliminary data for 2021. As a comparison point, the weekly 2021 data at Haul Road yielded an estimated annual SO_4 deposition rate of 40.6 kg SO_4^{2-}/ha/yr compared to the post-validated annual NADP value of 39.8 kg SO_4^{2-}/ha/yr (both marine-adjusted).

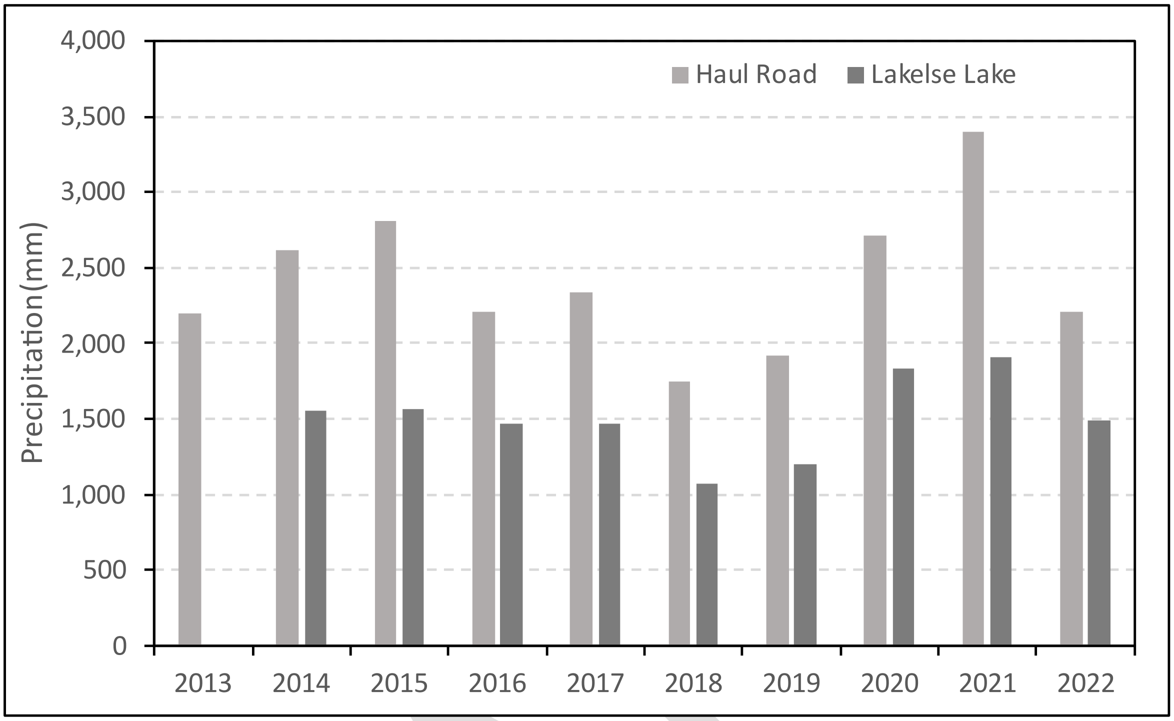


Figure 3-8. Annual precipitation volume (mm) from 2013 to 2022 at the Haul Road and Lakelse Lake precipitation chemistry monitoring stations. (Source: NADP [URL: https://nadp.slh.wisc.edu/precipitation/])

Weekly precipitation volume (mm) at the two stations (operated by the NADP) during the same nine-year period showed a highly synchronous pattern but with generally higher volume at Haul Road (Figure 3-9). Higher volume was recorded at Lakelse Lake for only approximately 7% of the observation on average and 14% of observations in 2022. In addition, higher weekly sulphate concentration (mg/L) and lower pH was observed at Haul Road compared with Lakelse Lake (Figure 3-9). The higher SO_4 and lower pH in rainfall at Haul Road are caused by the higher atmospheric concentration of SO_2 and corresponding higher S deposition at Haul Road.

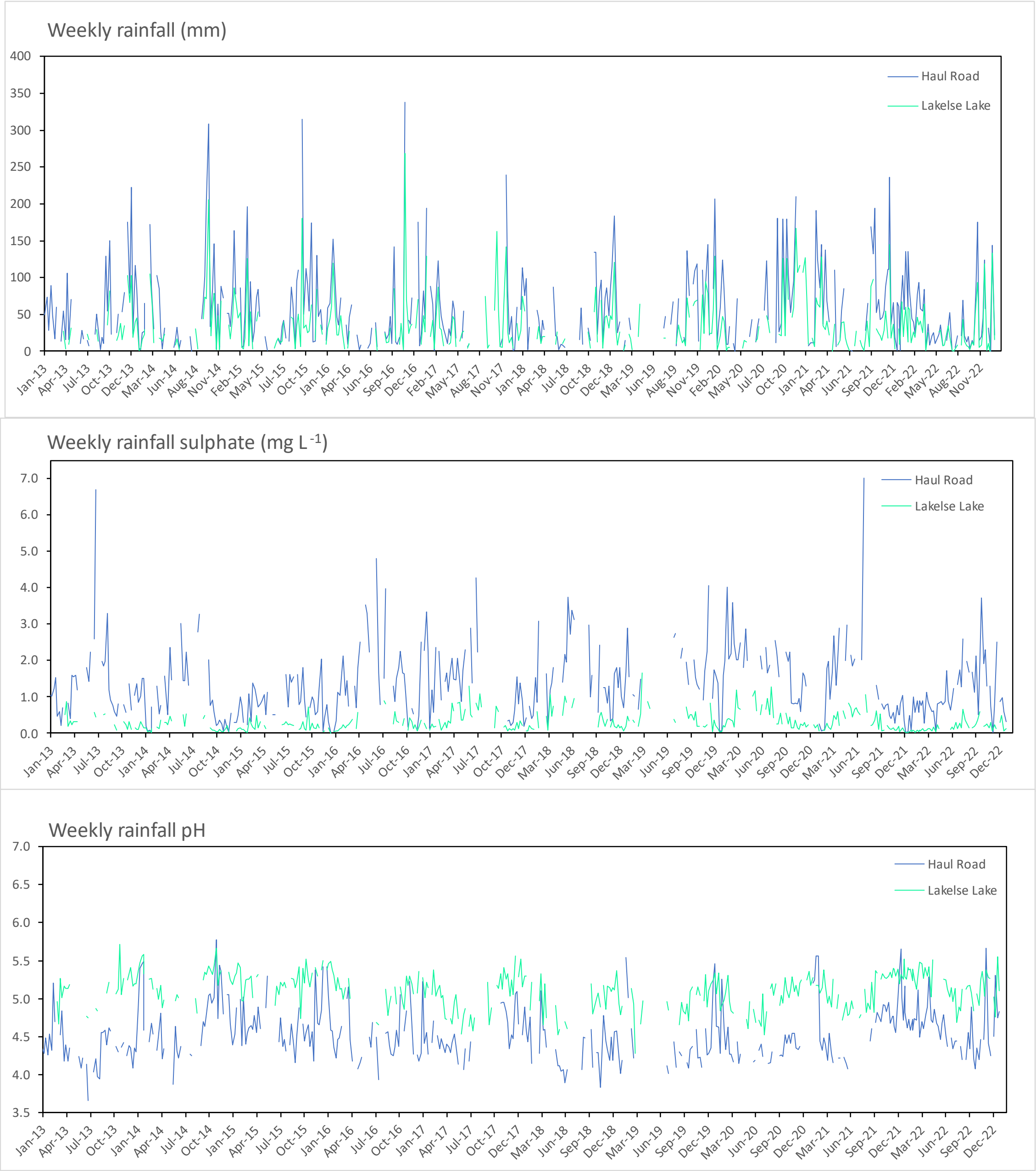


Figure 3-9. Weekly precipitation volume (mm) and chemistry (mg/L) at Haul Road (January 2013 to December 2022) and Lakelse Lake (April 2013–December 2022) showing inter-annual variation in precipitation volume (upper graph), sulphate concentration (middle graph) and precipitation pH (lower graph).

Higher rainfall volume and higher sulphate concentration observed at Haul Road combines to result in a more pronounced wet S deposition difference compared with Lakelse Lake on an annual (Figure 3-10) and weekly basis (Figure 3-11).

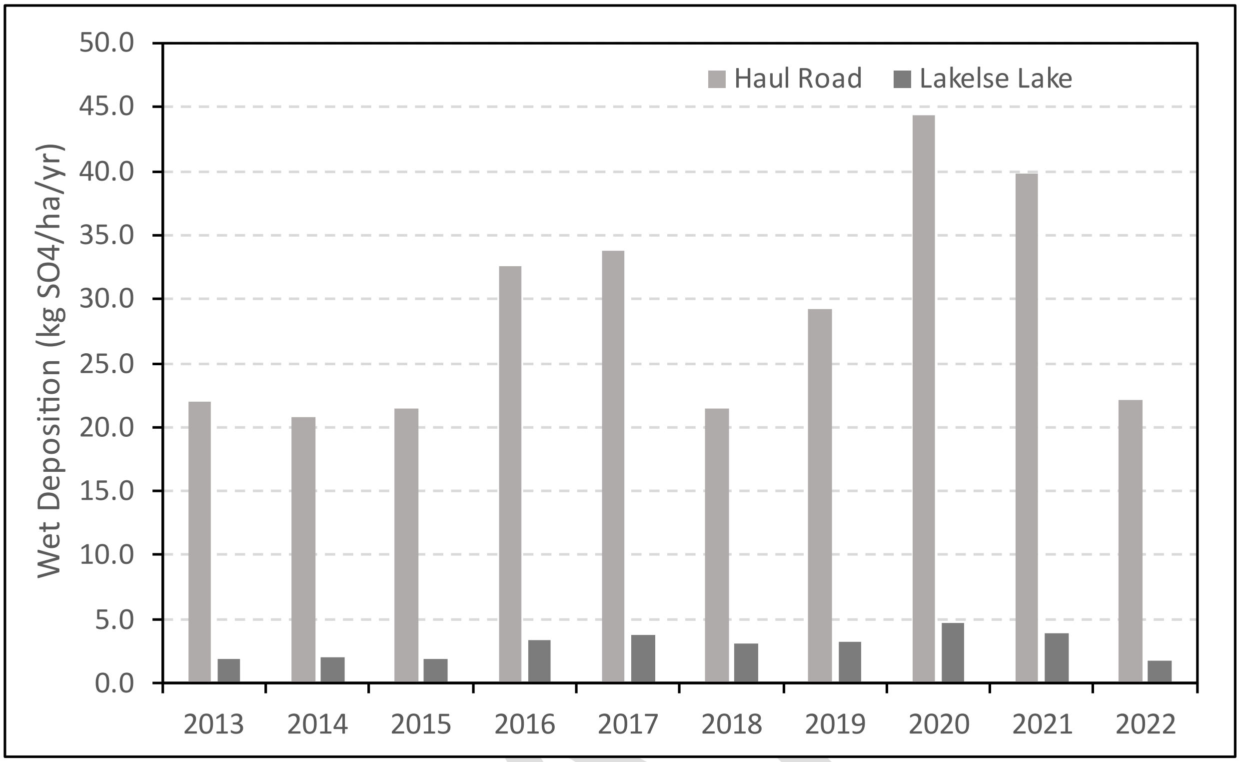


Figure 3-10. Annual wet deposition (kg SO_4/ha/yr) from 2013 to 2022 at the Haul Road and Lakelse Lake precipitation chemistry monitoring stations. (Source: NADP [URL: https://nadp.slh.wisc.edu/precipitation/])

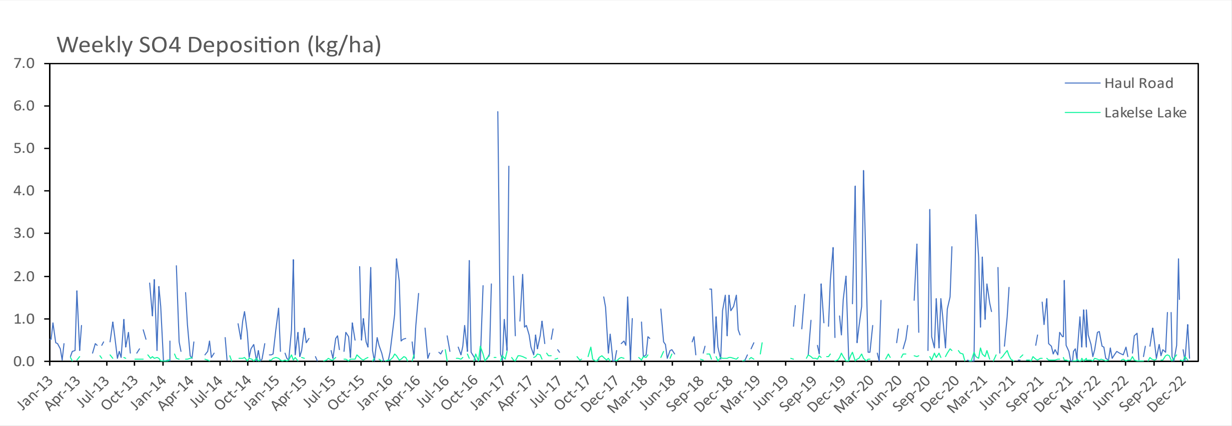


Figure 3-11. Weekly wet deposition (kg SO_4/ha/yr) from 2013 to 2022 at the Haul Road and Lakelse Lake precipitation chemistry monitoring stations. (Source: NADP [URL: https://nadp.slh.wisc.edu/precipitation/])

3.1.3.2 Dry deposition modelling methods

Dry deposition measurements are difficult and rarely conducted because of the requirements for highly sophisticated methods and instrumentation (Wesely and Hicks 2000). In general, dry deposition is modelled from air concentrations of gaseous and particulate species (e.g., SO_2 and p SO_4^{2-}) multiplied by a species-specific dry deposition velocity estimated using modelling techniques, i.e., 'inferential' models (Vet et al., 2014).

$$F = C \times V_d$$

Where:
F is the dry deposition flux,
C is the measured ambient air concentration, and
V_d is the deposition velocity, which is influenced by factors such as wind speed, height of observation, heat flux, moisture availability, vegetation, and surface roughness (Wesely and Hicks 2000).

The 'big-leaf' model developed by Environment and Climate Change Canada (Zhang et al., 2001, 2003a, 2003b; Zhang and He 2014) was used to estimate hourly species-specific V_d at four stations in the Kitimat Valley (Haul Road, Whitesail, Lakelse Lake, and Terrace Airport [YXT]). The V_d model required meteorological forcing variables on an hourly resolution for the period of interest (calendar year 2022). The data sources for the big-leaf dry deposition velocity model at four stations are shown in Table 3-3. The model also requires site-specific variables, such as latitude and land cover; deposition velocities were estimated for coniferous land cover only. For further details on the big-leaf model see Technical Memo D01 (2016) and Technical Memo D02 (2018).

Table 3-3. Data sources for meteorological variables required to model deposition velocity at Haul Road, Whitesail, Lakelse Lake and Terrace Airport.

Variable	Kitimat: Haul Road	Kitimat: Whitesail	Lakelse Lake	Terrace Airport
Temperature	Haul Road hourly	Whitesail hourly	Terrace Airport hourly	Terrace Airport hourly
Wind speed	Haul Road hourly	Whitesail hourly	Terrace Airport hourly	Terrace Airport hourly
Relative humidity	Whitesail hourly	Whitesail hourly	Terrace Airport hourly	Terrace Airport hourly
Solar irradiance	Modelled from maximum and minimum daily temperature using Hargreaves method	Modelled from maximum and minimum daily temperature using Hargreaves method	Modelled from maximum and minimum daily temperature using Hargreaves method	Modelled from maximum and minimum daily temperature using Hargreaves method
Precipitation rate	NADP Haul Road, obtained from University of Wisconsin	Haul Road	NADP Lakelse Lake, obtained from University of Wisconsin	Terrace Airport daily data, disaggregated by NADP Lakelse Lake hourly data
Surface pressure	Haul Road hourly	Whitesail hourly	Terrace Airport hourly	Terrace Airport hourly

Variable	Kitimat: Haul Road	Kitimat: Whitesail	Lakelse Lake	Terrace Airport
Snow depth	Environment Canada, Kitimat Hatchery, daily data applied to all hours	Environment Canada, Kitimat Hatchery, daily data applied to all hours	Terrace A / Terrace PCC daily snow depth, applied to all hours	Terrace A / Terrace PCC daily snow depth, applied to all hours
Cloud fraction	Environment Canada, Terrace Airport hourly	Environment Canada, Terrace Airport hourly	Environment Canada, Terrace Airport hourly	Environment Canada, Terrace Airport hourly

3.1.3.3 Dry deposition modelling results

Annual modelled dry deposition velocity (V_d) for SO_2 ranged between 0.03 – 4.66 cm/s for Haul Road, 0.05 – 4.55 cm/s for Whitesail, 0.03 – 4.79 cm/s for Lakelse Lake, and <0.01 – 4.32 cm/s for Terrace Airport. Figure 3-12 shows the annual distribution of modelled V_d for SO_2 at each location. The V_d for Lakelse Lake is first modelled for reporting year 2022 and was also modelled using data back to 2020. Dry sulphur deposition calculations based on SO_2 measured at Lakelse Lake for periods prior to 2020 (starting August 2018 when the Lakelse Lake SO_2 monitor was established) have applied modelled V_d from the Terrace Airport.

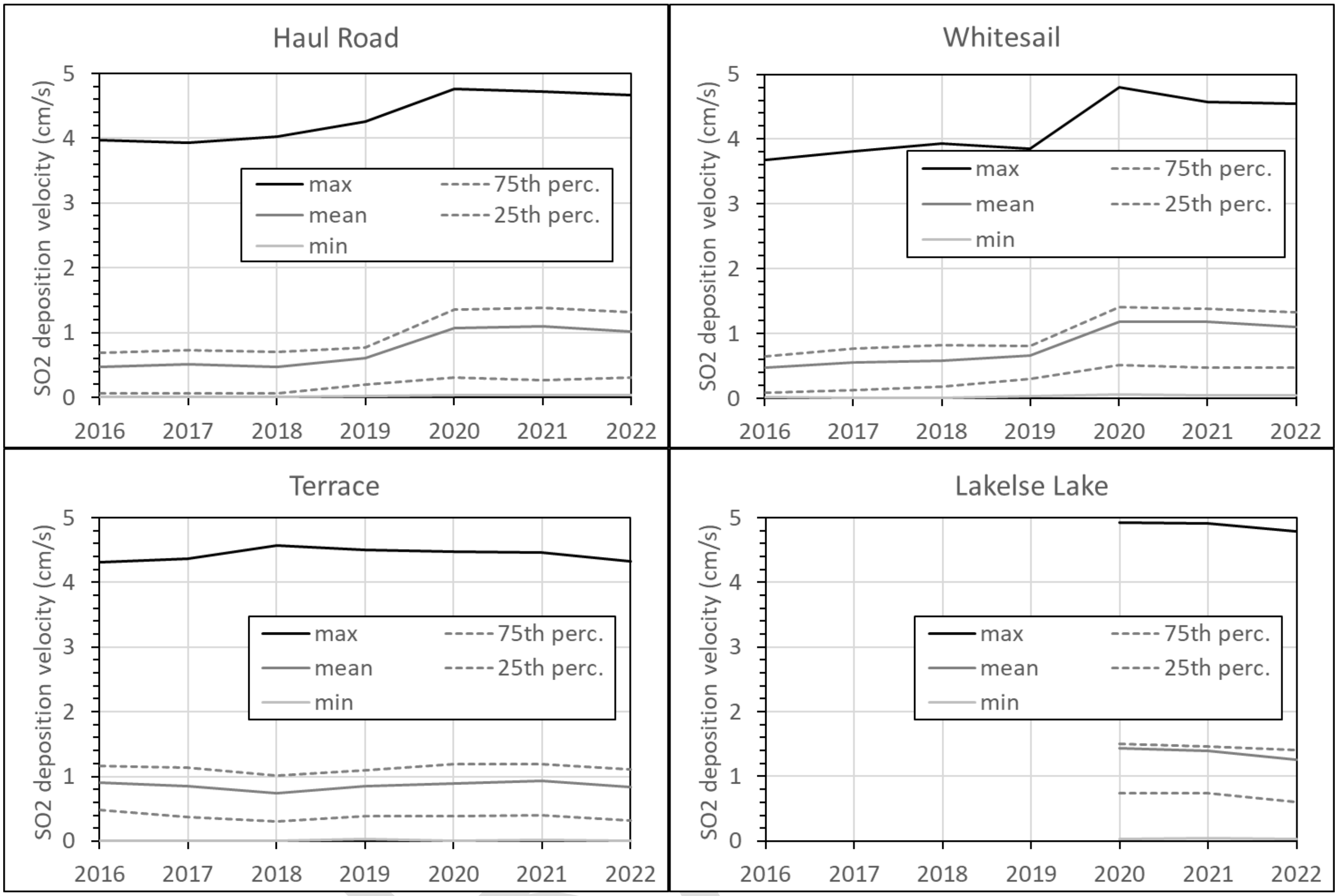
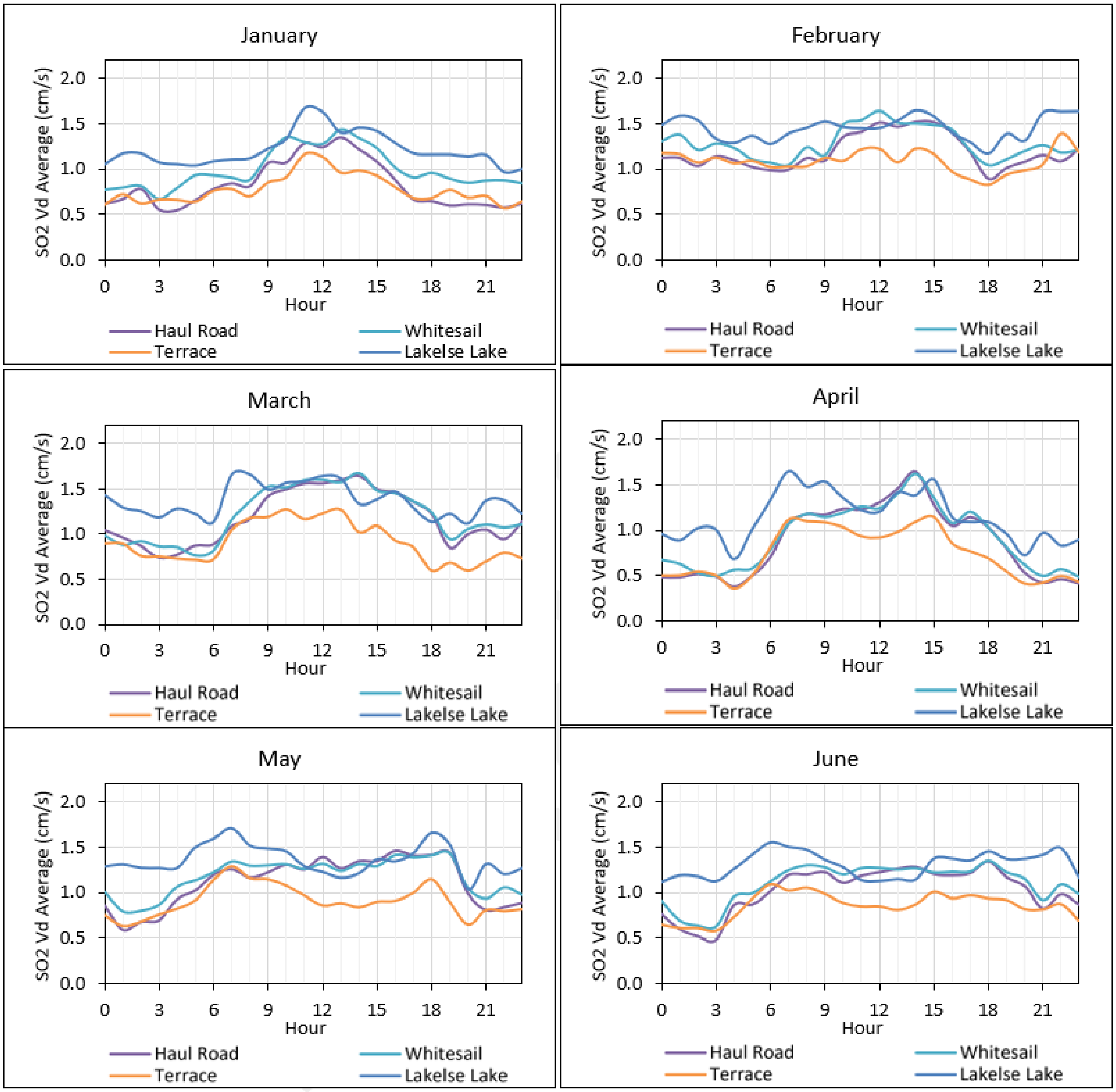


Figure 3-12. Annual distribution of SO_2 V_d for 2016 – 2022.

The annual distribution of SO_2 V_d was similar among all years 2016-2022, with a slight increase in overall magnitude during 2020 for Haul Road and Whitesail. This analysis also investigated trends in variable SO_2 V_d on a daily and seasonal basis. Figure 3-13 demonstrates the 2022 diurnal behavior of SO_2 V_d showing that SO_2 V_d is higher during daytime hours aligning similarly with trends in daily temperature and solar irradiance.


January
February
March
April
May
June
SO2 Vd Average (cm/s)
0.0
0.5
1.0
1.5
2.0
Hour
0
3
6
9
12
15
18
21
Haul Road
Whitesail
Terrace
Lakelse Lake

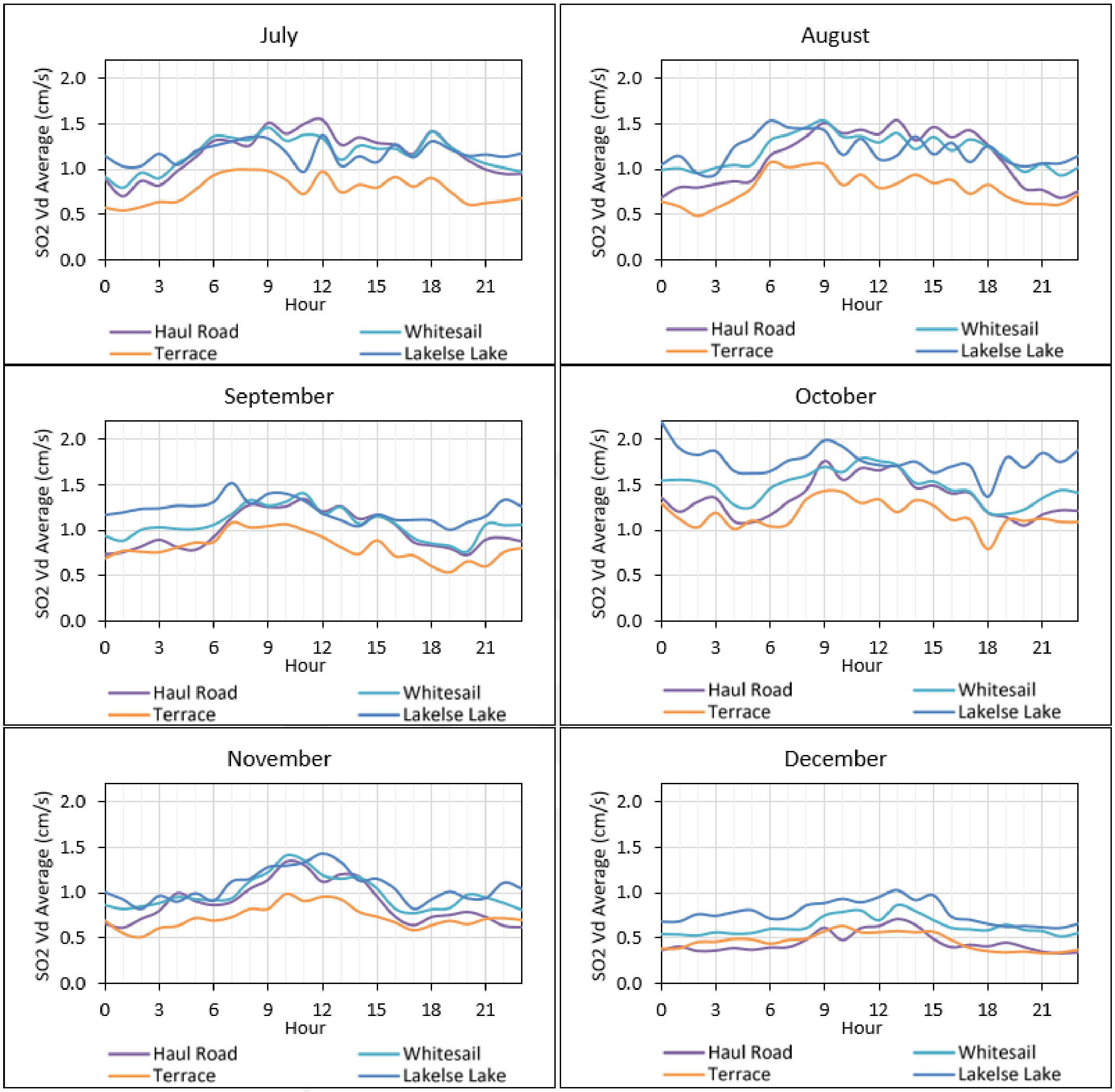


Figure 3-13. Diurnal behavior of SO_2 V_d in 2022.

Hourly SO_2 V_d was multiplied by the preliminary hourly monitored SO_2 concentrations to determine the total mass of SO_2 dry deposition in 2022. Dry deposition velocities were modelled at the Haul Road, Whitesail, and Lakelse Lake monitoring stations, using co-located SO_2 monitoring data and meteorological data (when available). The modelled dry deposition velocities for the Terrace airport were applied to the SO_2 monitoring data from the Terrace-Skeena Middle School. The total SO_2 dry deposition mass in 2022 was 33.2 kg/ha/yr for Haul Road, 3.3 kg/ha/yr for Whitesail, 0.9 kg/ha/yr for Lakelse Lake, and 2.0 kg/ha/yr for Terrace-Skeena Middle School. Figure 3-14 shows 2022 and prior years' SO_2 dry deposition mass.

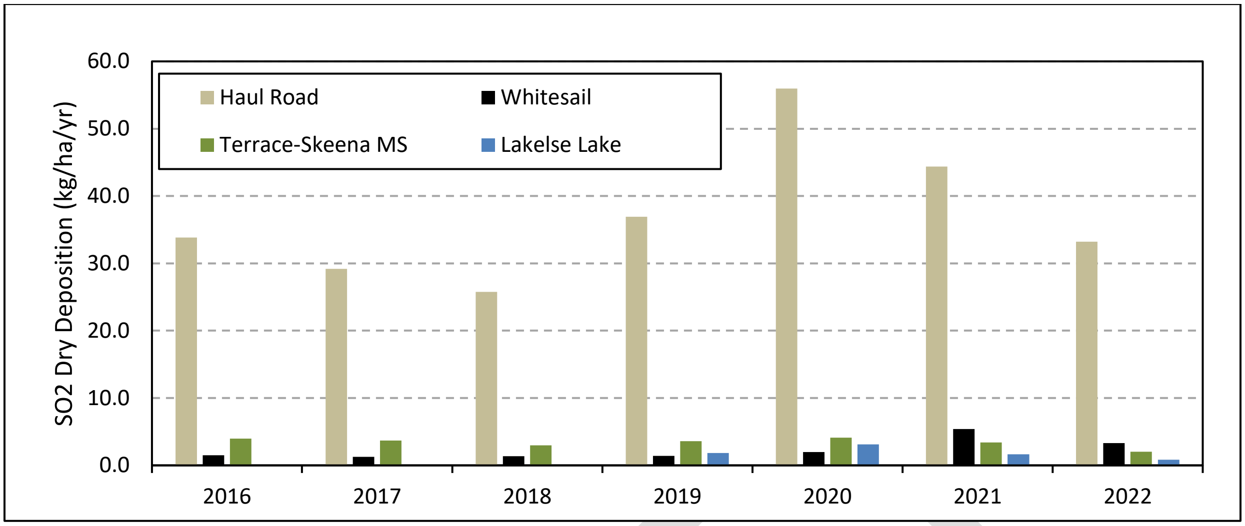


Figure 3-14. Annual SO_2 dry deposition mass 2016 – 2022.

Total mass of SO_2 dry deposition tended to be more heavily influenced by monitored SO_2 concentration at each site versus changes in SO_2 V_d. This difference in SO_2 concentrations is clearly the reason for elevated dry deposition mass at Haul Road compared to other sites. Similarly, dry deposition rates at all sites are lower in 2022 compared to 2021 due to the lower SO_2 concentrations and lower SO_2 emission rates from the smelter in 2022.

3.1.3.4 Total Sulphur Deposition

Figure 3-15 illustrates total mass of annual monitored wet deposition combined with modelled dry deposition at the Kitimat Haul Road location. Similar ratios of wet versus dry S deposition occur during each year from 2016 – 2022 at Haul Road.

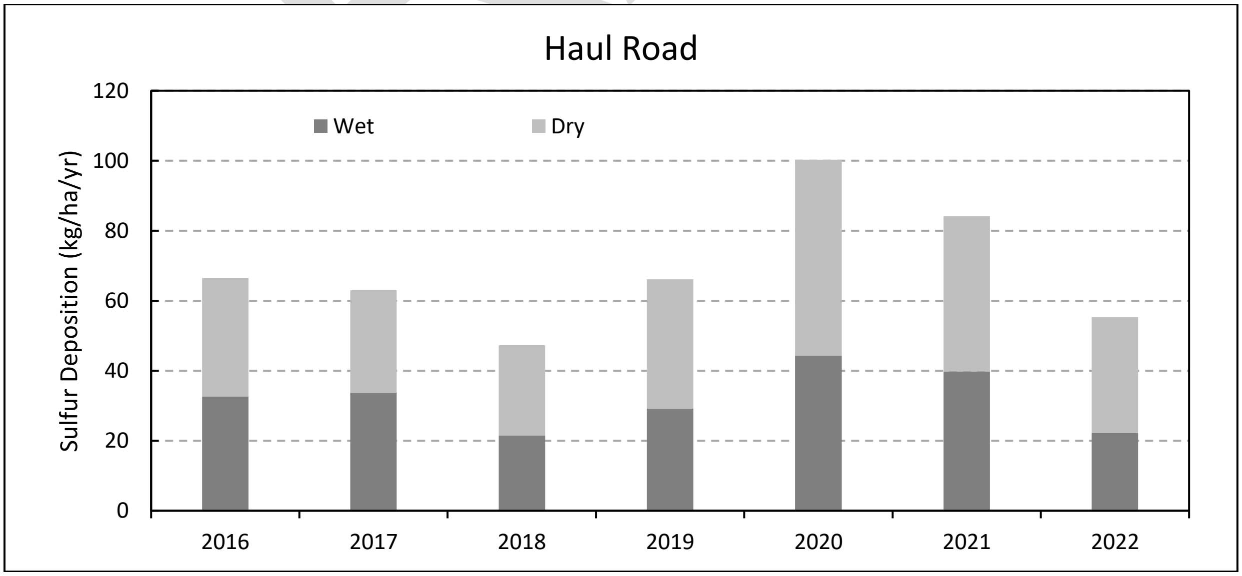


Figure 3-15. Haul Road wet and dry sulphur deposition annual total mass.

3.2 Human Health

B.C. ENV updated the province-wide interim SO$_2$ ambient air quality objective (IAAQO) in 2016, which became the SO$_2$ health KPI of the SO$_2$ EEM Program starting 2017. Starting January 1, 2020, the SO$_2$ health KPI implemented the SO$_2$ Canadian Ambient Air Quality Standards (CAAQS). In 2022, the CAAQS value was 70 ppb. In 2025 the CAAQS value changes to 65 ppb. The SO$_2$ health KPI is used to assess residential SO$_2$ ambient air quality. The SO$_2$ Health KPI for 2022 is a threshold for residential SO$_2$ ambient air concentration of 70 ppb and is evaluated through the following method as defined in the B.C. Air Quality Objectives:[12]

- *Achievement based on annual 99th percentile of daily 1-hour maximum (D1HM),*
- *averaged over three consecutive years,*
- *effective January 1, 2020;*
- *used to inform new air management decisions beginning January 1, 2017 and all air management decisions beginning January 1, 2020.*

Table 3-4 provides the KPI results for 2022, using the 3-year average of the 99th percentile of the D1HM for 2020 – 2022. The "Human Health KPI Calculations for 2022" memorandum is provided in Appendix B. The 2022 KPI calculation results for Kitamaat Village, Riverlodge and Whitesail were all well below the KPI (CAAQS value of 70 ppb) and, as such, demonstrate attainment of the KPI. The KPI will be calculated for the Service Centre in 2023, when three years of data have been collected.

Table 3-4. Calculation method and results for the SO$_2$ Health KPI in 2022.[a]

Station	99th percentile D1HM [b] SO$_2$ (ppb)			SO$_2$ Health KPI (ppb) (3-year average of 99th percentile D1HM[b])	KPI Attainment / Non-Attainment
	2020	2021	2022		
Kitamaat Village	19.8	9.1	9.8	12.9	Attainment
Riverlodge	18.0	29.2	9.9	19.0	Attainment
Whitesail	14.1	15.6	5.7	11.8	Attainment

[a] Data for this table were extracted from the Envista database of B.C. ENV in May 2023, Verification of 2022 data by B.C. ENV was not confirmed as of the date of the download. Therefore, the 2022 dataset is *preliminary*.
[b] Daily 1-hour average maximum

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[12] BC air quality objectives (https://www2.gov.bc.ca/assets/gov/environment/air-land-water/air/reports-pub/aqotable.pdf), footnote 18.

3.3 Terrestrial Ecosystems

This section contains a condensed summary of the major actions and knowledge gained in 2022 with respect to Terrestrial Ecosystems, including the Informative Indicators of soils, biodiversity and plant health.

For 2022, most Terrestrial Ecosystems subsections fall under the umbrella of the Vascular Plant and Cyanolichen Biodiversity Monitoring Program ("PCMP"). The PCMP plan was agreed to and finalized in November 2020 (Laurence et al., 2020), and the field manual to support its implementation finalized and agreed to in June 2021 (Coosemans and Laurence 2021), prior to commencing field activities. As described in the 2022 update to the Work Plan and Schedule for Terrestrial Ecosystems (Coosemans 2022), field activities scheduled for 2022 as part of the EEM Phase III included the following tasks:

- first assessment of 12 of the total 33 Kitimat Valley sites;
- two additional reference sites to be identified and assessed in the Kemano Valley;
- additional reconnaissance for a minimum of six new "alternate" sites in the Kitimat Valley;
- soil sampling for all sites—including the 10-20cm mineral soil layer, as separate samples, wherever possible; and
- the inspection/repair/replacement of plot stakes and the tagging and measurement of tree DBH at the Kemano long-term acidification plots.

Monitoring for the 33 Kitimat Valley sites is conducted using a 3-year rotating panel method, thus all 33 total Kitimat Valley sites will have been monitored for the first time at the end of the 2023 field season. Further detail on the 2022 assessments is provided in the following subsections, and in the *Vascular Plant and Cyanolichen Biodiversity Monitoring Program First Annual Report* (Coosemans, Doyle and Grossmann 2021).

Few deviations from the schedule of activities for 2022 were made:

- One site (B13) was dropped from the program owing to active bear use combined with poor visual sight lines and difficult egress, as well as the prevalence of fragile, overlapping vegetation that would be impossible to avoid impacting during assessments. Site B13 was replaced with another previously established site, so that the total of 12 sites to be assessed during 2022 was still achieved.
- As an extra layer of monitoring relating to the smelter restart, additional/opportunistic vegetation health assessments were also conducted at pre-established PCMP sites whenever possible.
- While not technically a deviation from the 2022 Work Plan, it is noted that, while attempts were made to opportunistically collect *Lobaria oregana* samples at/near all biodiversity monitoring plots where sufficient quantities are present to allow sampling without impacting plot data, no such sites were found to be available, and thus no samples were collected or analysed in 2022.

Of note in 2022 is that a review of wind direction data by B.C. ENV and Trinity Consultants indicated that corrections were required for the deposition model. As the design of the PCMP plots was originally developed using previous deposition modelling data, the Program was reviewed in 2022 using the corrected modeling results, and the deposition category of three established PCMP plots has subsequently changed. As a result, we will continue to review the identification of deposition zones to ensure the right balance of monitoring plots is maintained—particularly with respect to the selection of sites to be assessed in 2023.

2022 also saw the restart of the smelter following the labour dispute in 2021, and with it an amendment to the P2-00001 Multimedia Waste Discharge Permit (the "P2 Permit"). The P2 Permit included the conditions that a Monthly Program (MP) and Vegetation Monitoring Program (VMP) be resumed during 2022, wherein monthly vegetation health inspections were required to be conducted at 20 pre-established and agreed-upon sites, and western hemlock sampling for F and paired vegetation health inspections were required at 11 pre-established and agreed-upon sites, respectively (and among which were 7 sites that overlapped both programs). VMP activities and results for 2022 are detailed in Coosemans and Grossmann (2023a), which includes a detailed addendum (Coosemans and Grossmann 2023b) for one of the MP sites. Note that these activities were directly related to the P2 Permit, as they are no longer part of the SO_2 environmental effects monitoring program (SO_2 EEM Program), and thus are not part of the Work Plan and Schedule for Terrestrial Ecosystems (Coosemans 2022; ESSA et al., 2023), and are not reported on further here.

3.3.1 Plant and Cyanolichen Biodiversity and Plant Health

Activities in 2022 centered around the continued implementation of the PCMP (begun in 2021), which replaces the vegetation component of the SO_2 EEM Program from previous years. In the Comprehensive Review (ESSA et al., 2020a), recommendations were made to transition vegetation sampling and analysis of western hemlock needles for S and assessment of visible injury to a more ecologically-based program designed to detect subtle changes in the occurrence and abundance of plants and cyanolichens. This recommendation was based on air dispersion modelling that showed air concentrations of SO_2 to be well below those that would cause visible injury to sensitive vegetation, and the lack of any such injury during the first phase of the SO_2 EEM Program. In addition, the concentrations of S (and fluoride) in western hemlock needles were at or near background concentrations reported in the scientific literature. Therefore, emphasis was shifted to changes in biodiversity and health of plants and cyanolichens that might be mediated through long term deposition of SO_4^{2-} and potential changes in soil chemistry.

Scheduled activities for the vegetation component of the SO_2 EEM Program in 2022 included the assessment of the second set of PCMP field plots (Figure 3-16) between June 18th and July 8th; and the analysis and presentation of results in the December submission of the Vascular Plant and Cyanolichen Biodiversity Monitoring Program Second Annual Report (Coosemans and Grossmann 2022). As part of the PCMP field program, a concomitant assessment of vegetation health was undertaken at plot locations in the Kitimat-Terrace valley—for 2022, including all established plots that could be visited during the June-July timeframe. In addition, reconnaissance and establishment of eight new plots in the Kitimat Valley was undertaken (these sites, B36-B42, were roughly established with plot corners, and soil samples were collected and analysed), as well as the reconnaissance, establishment and assessment of two new reference plots in the Kemano Valley (K33 and K34; Figure 3-17). As a result of the reconnaissance activities, the total number of sites now established and integrated into the Program (including alternate sites) is currently 37.

Vegetation health inspections are a component of PCMP plot field work, and were undertaken at both newly established Kemano plots (June 18-19), and all twelve fully assessed plots in the Kitimat Valley (June 27 to July 8) in 2022. In addition, opportunistic vegetation health inspections were made at previously established sites in the Kitimat Valley undertaken during soil sampling whenever timing allowed (i.e., if soils were sampled during the early summer period up to July 8th).

This resulted in ten (10) additional inspections, for a total of 24 vegetation health inspections completed as part of the PCMP in 2022. Cyanolichen health inspections are part of the cyanolichen assessment portion of the PCMP, and these inspections were made at the 14 primary plots assessed in 2022 (i.e., twelve (12) in the Kitimat Valley and two (2) in the Kemano Valley).

Weather during these health assessments was relatively typical for the region for the time of year, without any major heat stress or drought. While there was a prominence and prevalence of feeding insects (notably caterpillars) and fungal damage noted across most plots (and throughout the region) during 2022, irrespective of their location in the valley, we noted that vegetation otherwise appeared to be healthy/thriving. A single observation was made of a lichen appearing stressed: The tripartite cyanolichen, *Lobaria linita*, had significant areas of colonies that appeared stressed/dying at a single, medium deposition site (B07). Overall, no patterns related to plant or cyanolichen health and deposition category were noted based on these inspections.

3.3.1.1 Vascular plant and cyanolichen biodiversity monitoring

The PCMP was designed to detect potential changes in the biodiversity (species richness and abundance) trends of vascular plants in the low shrub and forb layers, and of cyanolichens, in forest ecosystems of the Kitimat Valley (including the Lakelse Watershed). The Program focuses on detecting mid- to long- term effects on plants and cyanolichens associated with acidification due to emissions of SO_2 from Rio Tinto BC Works. As such, initial differences between vegetation and cyanolichen biodiversity between sites are expected—the data collected from plots are not "baseline," but simply "initial." Data from each site will ultimately (once assessed at least twice as part of the PCMP) be compared with itself, to determine if differential changes (i.e., trends) are occurring over the mid- to long- term based on deposition zone. Only once plots have been re-assessed will it be possible to extract initial trend data from the assessment results.

The Program was implemented largely as planned in the summer of 2022; however, a plot was lost owing primarily to safety considerations (active bear presence) as well as the potential for negative impacts to plot vegetation, as described at the beginning of Section 3.3. Furthermore, several minor variations were made to the PCMP in 2022 as field-based experiences identified need. This included, for example, the combining of two species that could not be reliably distinguished when sterile (*Streptopus amplexifolius* and *Maianthemum dilatatus*) in cover estimates at one site in Kemano. Details of these variations (as well as cumulative adjustments to the PCMP) can be found in Coosemans and Grossmann (2022).

A major component of biodiversity is species richness—the number of species present/observed—which can be readily summarized and presented: Table 3-5 provides species richness assessed during 2022 for plants in the low shrub and herb layers. As expected, no trends between deposition zones are noted in initial plant species richness results. Table 3-6 summarizes species richness assessed for cyanolichens at all plots that have been assessed as part of the PCMP up to and including 2022, and include the data provided for those sites previously established by B.C. ENV (Williston 2020): As expected, these data generally show that cyanolichen diversity is inversely proportional to increasing deposition zone (largely as an historical artifact of fluoride emissions); however, the data also demonstrate the stochastic nature of this metric (e.g., if a host tree is lost from a plot, a dramatic shift in recorded cyanolichen diversity may occur).

Table 3-5. Species Richness in the low shrub (B2) and herb (C) layers at each plot (blueberry species combined).

Plot	# Tree Species in B2 Layer	# Non-Tree Shrub Species in B2 Layer	# Herb Species (C Layer)	Total Richness in B2 & C Layers
B01AC22	4	13	14	31
B02AC22	3	3	3	9
B03AC22	1	9	14	24
B05AC22	2	4	6	12
B07AC22	3	5	15	23
B08AC22	1	7	14	22
B15AC22	3	3	8	14
B21AC22	3	5	14	22
B24AC22	3	5	15	23
B25AC22	3	5	10	18
B28AC22	2	7	5	14
B29AC22	2	3	10	15
K33AC22	2	3	11	16
K34AC22	0	3	10	13

Table 3-6. Cyanolichen richness recorded at assessed sites 2016-2022.

Site	Cyanolichen Richness 2016/17*	Cyanolichen Richness 2020*	Cyanolichen Richness 2021 Pcmp	Cyanolichen Richness 2022 Pcmp
B01	12	14	N/a	5
B02	5	6	N/a	2
B03	9	6	N/a	4
B04	6	7	6	N/a
B05	2	2	N/a	1
B07	3	3	N/a	1
B08	5	6	N/a	4
B09	0	0	0	N/a
B10	4	4	5	N/a
B12	2	2	4**	N/a
B15	8	N/a	N/a	5
B17	0	0	0	N/a
B20	10	6	10	N/a
B21	12	10	N/a	4
B22	5	2	2	N/a
B24	2	3	N/a	1
B25	0	0	N/a	0
B26	0	0	0	N/a
B28	0	0	N/a	0
B29	5	9	N/a	3
B30	6	10	4	N/a
B32	2	2	0	N/a
K33	N/a	N/a	N/a	4
K34	N/a	N/a	N/a	4

*from Williston (2020); **B12 was moved from the original B.C. ENV plot to another area in the same stand.

3.3.1.2 Visual inspection and assessment of plant health as part of biodiversity monitoring

2020 was the final year of the previous VMP, wherein the health of vegetation at 23 sites in the vicinity of the smelter was assessed. Visual assessment of plant health continues to be an important activity in the Terrestrial Ecosystem Line of Evidence. New protocols were developed as part of the program design to assure that the assessment of plant health continues. The methods are described in Coosemans and Laurence (2021). Beginning in 2021, vegetation health is now primarily monitored through visual inspection of vegetation at PCMP plots whenever each is assessed (on a three-year, rotating basis); however, as described above, in 2022 Rio Tinto volunteered to also inspect vegetation, opportunistically, at other established PCMP plots should timing allow.

In all, 24 sites were visually inspected between June 18 and July 7, as part of the PCMP in 2022 in the Kitimat and Kemano Valleys. Symptoms of visible injury were not noted at any of the plots (e.g., due to either gaseous fluoride or sulphur dioxide). There did not appear to be patterns or substantial differences in the degree of insect feeding or the incidence and severity of plant diseases related to the location of the sites in relation to deposition zones, and the level of insect activity and plant diseases appeared typical for the region in recent years.

3.3.1.3 S and F content in western hemlock needles

Based on the results of the Comprehensive Review, 2020 was the final year of regularly scheduled sampling of foliage for S and F as the program transitions to a more ecological focus, and it is thus no longer part of the SO_2 EEM Program. We do refer the reader, however, to Coosemans and Grossmann (2023; 2023a) for background and results of the VMP, related not to the EMP, but to the P2 Permit conditions associated with the restart of the smelter following the labour disruption of 2021.

3.3.2 Soils

Per the 2022 schedule, soil samples were collected at all established sites as part of the PCMP field session—with the exception of Site B06, for which soil sampling was attempted but could not be obtained owing to the presence of deep organic layers, for a total of 36 of the 37 sites: This total includes all previously established and accessible sites for which samples could be obtained (26), as well as the two (2) new Kemano sites, and the eight (8) newly established sites in the Kitimat Valley. Composite mineral soil samples, collected at 0-10cm and 10-20cm depths near the four outer corners of each PCMP field plot, were subsequently analysed for pH, exchangeable cations and exchangeable acidity.

In analysed samples, pH ranged from 4.03 (B40 0-10cm sample) to 6.10 (B23 0-10cm sample), and averaged 4.84. CEC ranged from 4.8 (B23 0-10cm sample) to 65.0 (B24 0-10cm sample), and averaged 29.6 meq/100g. Of exchangeable cations, potassium and sodium were below detection limits in all samples; calcium ranged from undetectable to 2120 mg/kg (B08 0-10cm sample), averaging 520.63 mg/kg; and magnesium ranged from undetectable to 173 mg/kg (B36 0-10cm sample), averaging 100.79 mg/kg.

In addition, the two (one primary and one alternate) permanent, long-term soil acidification plots in Kemano were visited in 2022 during the course of PCMP activities in that valley. At each plot, the stakes were inspected and replaced, as needed, and the trees within each were tagged and their DBH measured and recorded.

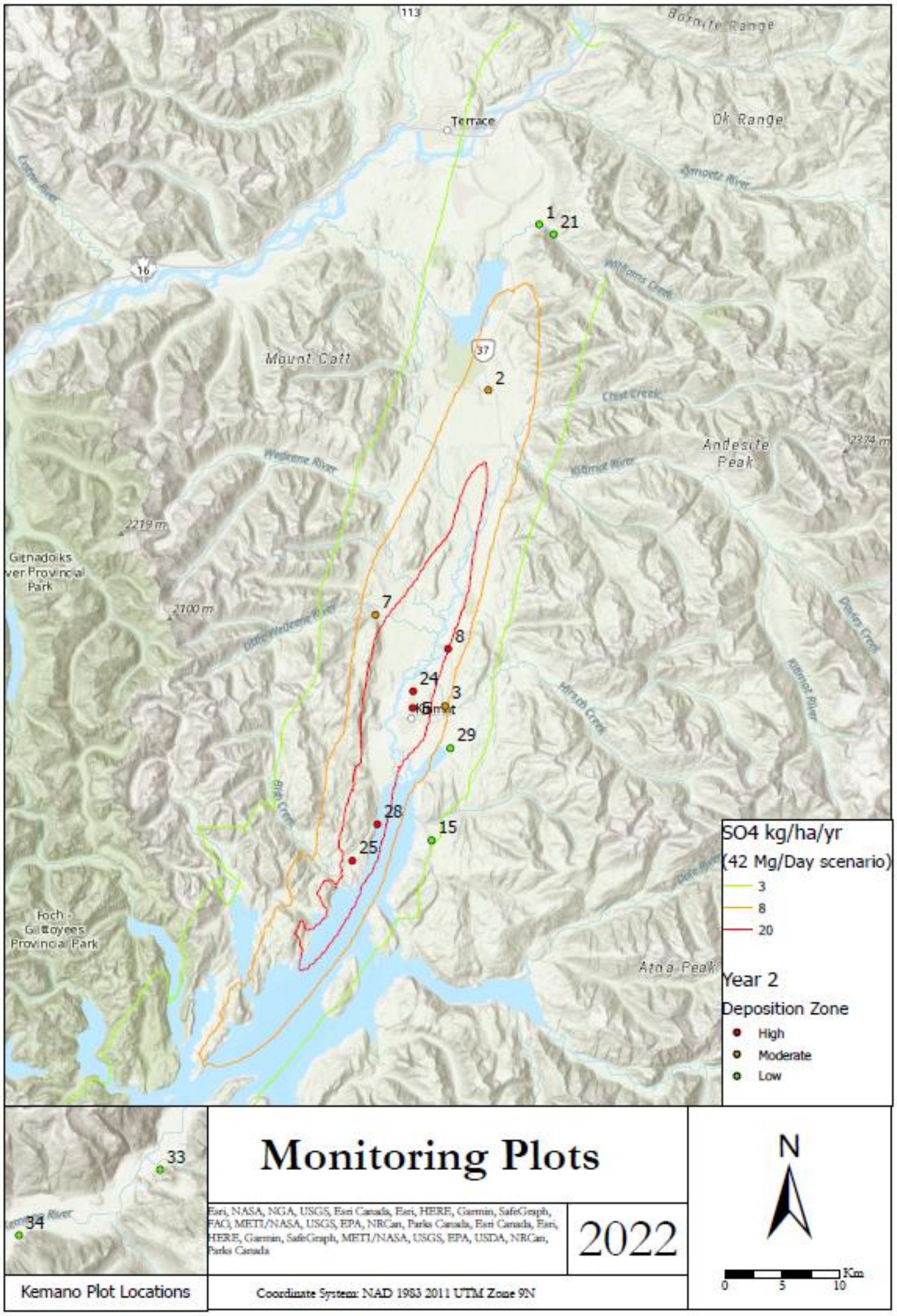
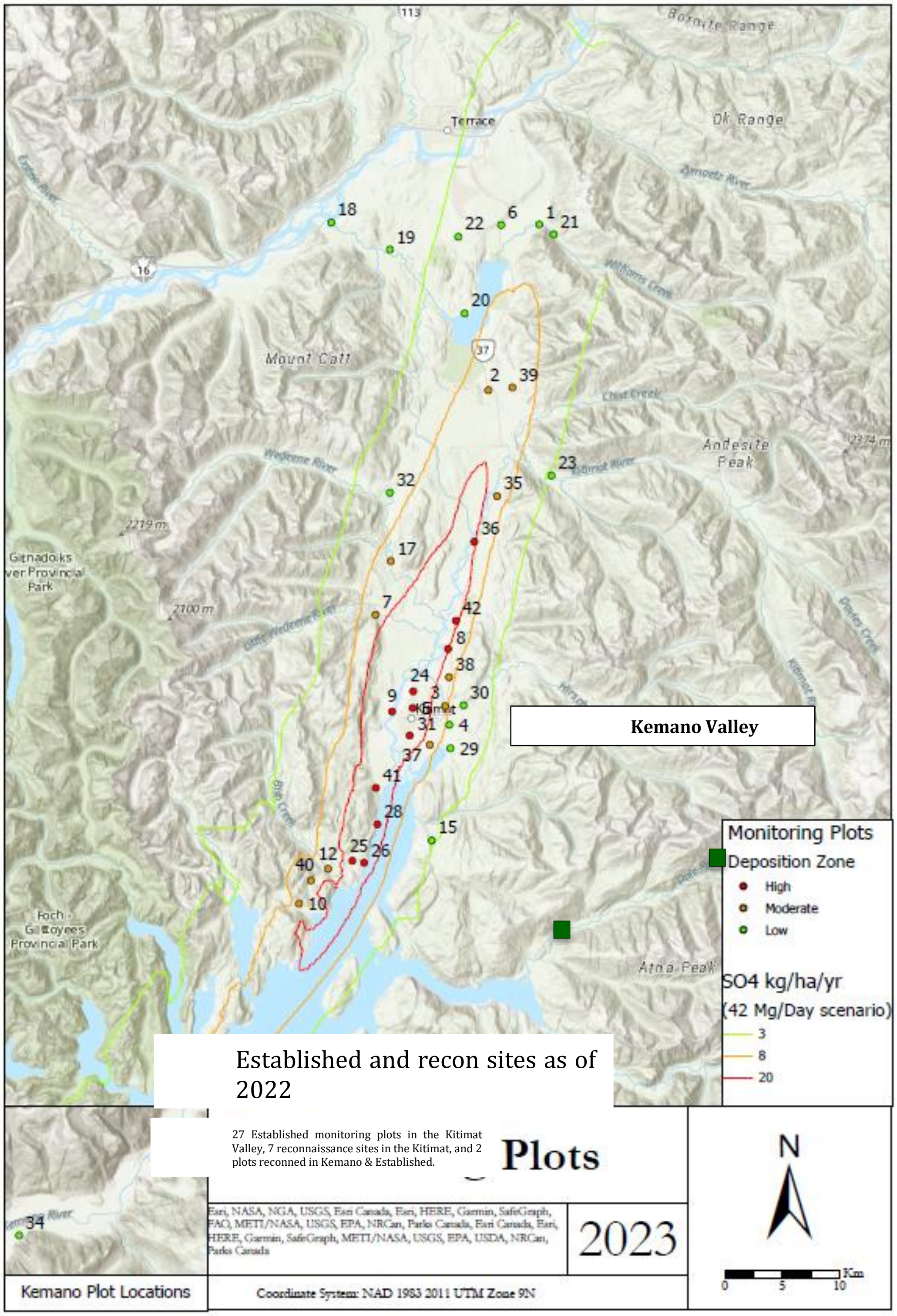


Figure 3-16. Map showing sites fully assessed during 2022 in relation to sulphate Deposition Zones.



Established and recon sites as of 2022

27 Established monitoring plots in the Kitimat Valley, 7 reconnaissance sites in the Kitimat, and 2 plots reconned in Kemano & Established.

Esri, NASA, NGA, USGS, Esri Canada, Esri, HERE, Garmin, SafeGraph, FAO, METI/NASA, USGS, EPA, NRCan, Parks Canada, Esri Canada, Esri, HERE, Garmin, SafeGraph, METI/NASA, USGS, EPA, USDA, NRCan, Parks Canada

Coordinate System: NAD 1983 2011 UTM Zone 9N

Figure 3-17. Map showing all previously existing and newly established sites in the Kitimat & Kemano Valleys (new sites from 2022 reconnaissance that have not yet been fully assessed shown in lighter green).

3.4 Aquatic Ecosystems (Lakes, Streams and Aquatic Biota)

This section contains a condensed summary of the major actions and knowledge gained in 2022 with respect to the Aquatic Ecosystems receptor. Further detail can be found in the Aquatic Ecosystems Actions and Analyses Technical Memo W11 (provided in Appendix C) and the Technical Report of Lake Monitoring in 2022 (provided in Appendix D).

3.4.1 Major Actions Taken in 2022

The Phase III EEM sampling plan includes eleven lakes: seven sensitive lakes, one less sensitive lake, and three control lakes (ESSA et al., 2023). The three control lakes (NC184, NC194 and DCAS14A) are all located outside of the zone of sulphur deposition from B.C. Works, and have pre-KMP baseline data for 2013 from sampling as part of the KAA (ESSA et al., 2014). Sampling of these eleven EEM lakes was conducted in accordance with the EEM Phase III Plan.

LAK027 was added for one-time sampling in 2021, as agreed to by B.C. ENV and Rio Tinto in May 2021. The intent was to resample one of the STAR lakes located relatively close to the smelter to check the validity of the conclusions made in the STAR, based on sampling completed in 2012, nine years prior to 2021. LAK027 was chosen because it was the only candidate that was moderately sensitive, whereas all the other lakes in the southern portion of the Kitimat Valley were determined to be insensitive based on the sampling during the STAR (except for LAK028, which was included in the SO_2 EEM Program because of its sensitivity). LAK027 was sampled again in 2022, as per the recommendation in the SO_2 EEM Program 2021 Annual Report that *"the widely-observed storm-driven dilution event [in fall 2021] negated the ability of this year's sampling to provide a meaningful comparison against the initial STAR data as intended."*

We examined the empirical changes in water chemistry between the pre-KMP baseline (2012) and the post-KMP period (2020-2022), especially with respect to the KPI thresholds. We also conducted statistical analyses on the changes between these two periods, repeating two sets of analyses applied in the 2019 Comprehensive Review with the more recent years of data: 1) the Bayesian "Method 1" to assess the % belief that any of the lakes had exceeded their KPI or informative indicator thresholds; and 2) the "Method 3" before-after control-impact (BACI) analyses of the differential trends between the sensitive EEM lakes and the control lakes.

We also evaluated differential trends between the sensitive lakes and the control lakes using the before-after control-impact (BACI) analysis methods described in the 2019 Comprehensive Review (i.e., Method 3: BACI using mean values). Using this method, we evaluated the sensitive lakes individually and as a group, for both CBANC (as an informative method, as the KPI is not based on this statistical approach) and the pH informative indicator.

In 2020, we expanded the simplified evidentiary framework put forth in the 2019 Comprehensive Review to be aligned with the two-threshold structure of the KPI and acidification informative indicators in the EEM Phase III Plan. We applied this same framework with the new results from the statistical analyses. This revision and rationale are described in Section 2.6 of Technical Memo W09.

3.4.2 Knowledge Gained from Actions taken in 2022

3.4.2.1 Exceptional Annual Context – Low Emissions in 2022

The year 2022 was exceptional in the 11-year history of the SO_2 EEM Program. Emissions from the smelter were dramatically less than in any previous year of the SO_2 EEM Program. In August 2021, emissions dropped by approximately 83%, from 27.1 tpd during January to June 2021, to 4.6 tpd during August to December 2021. As discussed in the SO_2 EEM Program 2021 Annual Report, we did not expect to see much influence on lake chemistry in the 2021 data because: a) the drop in emissions happened only 1-2 months before the lakes were sampled in October 2021; and b) any small response to that change in emissions would have been swamped by the dominant influence of exceptionally wet hydrologic conditions in September and October 2021 (discussed last year).

Smelter emissions remained low into 2022 and started to increase very gradually only starting in the summer of 2022. As a result, the average emissions from September 2021 to August 2022 (i.e., the 12 months prior to the fall sampling period in 2022) were 5.1 tpd. Emissions during the 12 months prior to 2022 fall sampling were 21% of the levels in 2020 and 17% of the 2016-2018 period applied in the 2019 Comprehensive Review (ESSA et al., 2020a).

The prolonged reduction in emissions after August 2021 could alter lake chemistry, especially since the estimated water residence time is less than a year for most of the sensitive EEM lakes (less than nine months for 5 out of 7 sensitive EEM lakes, 1.4 years for LAK006, and 2.1 years for LAK044 (see 2019 Comprehensive Review, Technical Appendix 7, Table 7.19; ESSA et al., 2020b)). We expected that the decline in SO_2 emissions would cause a decline in lake [SO_4], and possibly an increase in CBANC, Gran ANC and pH, in at least the 5 sensitive EEM lakes with short water residence times. Increases in lake [SO_4] are generally associated with increases in lake base cations, due to cation exchange processes in the watershed. The converse also holds: decreases in lake [SO_4] would be expected to result in lower base cation concentrations.

The dominant responses in the 2022 data were generally consistent with our expectations:

- [SO_4] declined in all sensitive lakes except LAK028 (+3.5 μeq/L); some of the decreases were quite substantial
- Gran ANC went up in ALL lakes
- CBANC showed an increase in 4 of the sensitive EEM lakes, a limited decrease in 2 of them, and LAK042 (far north of the study area) decreased by 9.7 μeq/L
- pH increased by 0.2-0.8 pH units in all 11 lakes, with the same range across the sensitive EEM lakes alone
- base cations dropped in all sensitive EEM lakes except LAK028 (+9.9 μeq/L)

The changes observed in 2022 *generally* countered the changes of the previous year:

- Across all lakes ~80% of the annual changes observed over 2021-2022 for CBANC, Gran ANC, BCS, pH, and SO_4 were in the opposite direction of the changes observed over 2020-2021
- For CBANC, this general pattern was less consistent - two lakes showed decreases for two years in a row (LAK023, LAK042) and two lakes showed increases for two years in a row (LAK016, LAK028)

- For pH, this general pattern was universally observed - all 11 lakes decreased in pH over 2020-2021 and increased in pH over 2021-2022
- The combined result from the two annual changes (i.e., the net change from 2020 to 2022) was more variable – that is, in some cases the changes in 2022 only partially offset the significant changes in 2021 and in other cases they more than offset the previous year's changes

An important net result is that these "reversals" of the previous year's anomalous changes tended to reduce the estimated magnitude of long-term change (i.e., post-KMP 3-year average of an indicator minus the pre-KMP baseline value), compared to the results reported last year.

3.4.2.2 Empirical Changes in Water Chemistry

Empirical changes in CBANC, pH, Gran ANC, SO_4^{2-}, DOC, sum of base cations, chloride, and calcium are shown in Table 3-7. Changes are reported in terms of the difference between the post-KMP average (2020-2022) and the pre-KMP baseline (2012 for the sensitive and less sensitive lakes; 2013 for the control lakes). The sensitive EEM lakes and less sensitive EEM lakes are presented separately within each of the tables. The inter-annual changes presented in this report use the mean annual values whenever multiple within-season samples were acquired from a given lake in a given year.

The mean values of CBANC for the post-KMP period indicate that there have been no exceedances of the KPI thresholds.

To protect aquatic ecosystems in the sensitive lakes, we want to avoid declines in recent measurements of CBANC, Gran ANC, BCS, and pH (i.e., the KPI and other acidification informative indicators) compared to the pre-KMP 2012 baseline. We use the average of the last 3 years to dampen the effects of an unusual year. Results of our analyses indicate a general recovery of lake chemistry in most of the sensitive lakes from the changes observed in 2021. The estimated changes since 2012 for CBANC, Gran ANC and BCS became more positive in 5 to 6 of the 7 sensitive lakes, as compared to the 2021 EEM report (see Table 3-1 in Technical Memo W11). Relative to the 2021 EEM report, all seven sensitive lakes showed reductions in the estimated change in [SO_4] since 2012, consistent with the reductions in SO_2 emissions since August 2021. In addition, all seven lakes showed an increase in the estimated long-term change in base cations since 2012. The only exception to this general pattern of recovery is that the estimated change in pH since 2012 remained the same for 6 of the 7 sensitive lakes.

Of the two lakes showing a long-term decline in CBANC in last year's report, only LAK028 continues to show a long-term decline, albeit a smaller magnitude (-2.9 μeq/L now vs. -7.9 μeq/L last year). Two lakes still show long-term declines in BCS compared to 2012 (LAK012 and LAK028), though the magnitudes of these declines are smaller than in last year's report. LAK022 continues to be the only lake with a decline in Gran ANC relative to the 2012 baseline, though the magnitude is small and only slightly greater than previously reported (-1.6 μeq/L now vs. -0.9 μeq/L last year). LAK022 also continues to be the only lake with a decline in pH relative to pre-KMP conditions (-0.16 in this report vs -0.15 last year, a negligible difference). LAK022 is the only sensitive lake which is sampled just once per year; the other 6 lakes are sampled 4 times during the fall index period.

In LAK028 (the lake closest to the smelter with the highest deposition) mean [SO_4^{2-}] is estimated to have increased by 58.5 μeq/L since 2012, and total base cations (ΣBC*) increased by 56.6 μeq/L (both lower magnitudes than shown in last year's Annual Report). The changes in ΣBC* and SO_4^{2-} largely explain the observed change in CBANC, a decline of 2.9 μeq/L. CBANC equals the sum of base cations minus the sum of strong acid anions, and ΔΣBC* - Δ[SO_4^{2-}] = 56.6 – 58.5 = – 1.9, close to the 2.9 μeq/L decline in CBANC. Gran ANC shows a long-term increase (5.4 μeq/L) in LAK028 and there continues to be no change in mean pH, similar to last year. LAK028 showed a decline in Base Cation Surplus (BCS) since the pre-KMP period, though BCS has shown considerable variation in LAK028, with its lowest value in 2013.

For the CBANC KPI, only 2 of the 7 sensitive lakes (LAK028 and LAK044) have post-KMP values below the *level of protection* threshold. Both of those lakes were already below that threshold in 2012 (and the alternate, transition period baseline) and neither of those lakes have exceeded the *change limit* threshold. None of the 7 sensitive lakes exceeded the *change limit* threshold and only one lake (LAK028) shows any long-term decrease in CBANC. In the sensitivity analyses with the alternate, transition period baseline (2012-2014), there are no lakes with an estimated long-term decrease in CBANC. The empirical data therefore indicate that none of the lakes exceeded the KPI.

For the pH informative indicator (highlighted here due to being the former KPI in Phase II), 5 of the 7 sensitive lakes (LAK022, LAK023, LAK028, LAK042, and LAK044) have post-KMP values below the *level of protection* threshold (a pH of 6.0). All 7 lakes were already below that threshold in 2012, and 4 of the 5 lakes currently below the threshold have been at or below that threshold throughout the entire period of record. None of the sensitive lakes have exceeded the *change limit* threshold. Only one lake (LAK022) shows any decrease in pH relative to 2012. The empirical data therefore indicate that none of the lakes have exceeded the pH informative indicator.

Resampling of LAK027

The results for LAK027 are shown in Table 3-4 in Technical Memo W11. LAK027 was resampled for a second year in 2022 due to the influence of anomalous hydrologic conditions in fall 2021 across all of the lakes. We compared conditions in 2022 to those in 2012 to achieve the original intent of resampling this lake. CBANC, Gran ANC, and BCS all increased substantially, whereas pH declined by 0.1 pH units. There were also substantial increases in both ΣBC* (123.9 μeq/L) and SO_4^{2-} (63.9 μeq/L) and the relative difference between those increases explains the increase in CBANC (i.e., 123.9 – 63.9 = 60.0 μeq/L).

Table 3-7. Empirical changes in CBANC, Gran ANC, BCS, pH, SO_4^{2-}, DOC, base cations, chloride, and calcium for EEM lakes. These values represent the difference between the average of the post-KMP period (2020-2022) and the 2012 baseline. Numbers shown are the value in the later period minus the value in the earlier year. Increases are shaded in green; decreases are shaded in red. The Gran ANC and pH values are based on the "integrated" time series (i.e., values from the Trent University laboratory from 2012 to 2019 with the 2020, 2021, and 2022 values imputed from the values measured by the BASL laboratory ("integ"); see details in Section 2.1 of Technical Memo W11).

SITE	CBANC (µeq/L)	Gran ANC (integ) (µeq/L)	BCS (µeq/L)	pH (integ)	SO4* (µeq/L)	DOC (mg/L)	∑ BC* (µeq/L)	Cl (µeq/L)	Ca* (µeq/L)
Lak006	20.2	11.6	14.2	0.2	3.5	1.2	23.9	0.6	13.6
LAK012	4.1	11.3	-7.9	0.3	9.0	2.4	13.4	3.0	6.9
LAK022	4.1	-1.6	1.5	-0.2	6.5	0.5	10.8	0.3	5.7
LAK023	12.0	3.8	3.8	0.1	-2.0	1.6	10.5	0.3	7.3
LAK028	-2.9	5.4	-17.9	0.0	58.5	3.0	56.6	2.9	41.7
LAK042	17.7	18.5	10.6	0.2	2.0	1.4	19.8	-0.5	11.2
LAK044	8.1	3.0	7.0	0.2	-2.1	0.2	6.2	0.5	1.9
Total ↑	**6**	**6**	**5**	**5**	**5**	**7**	**7**	**6**	**7**
Total ↓	**1**	**1**	**2**	**2**	**2**	**0**	**0**	**1**	**0**
LAK016	12.5	23.0	-1.5	0.0	11.6	2.8	25.0	1.4	16.3
Total ↑	**1**	**1**	**0**	**0**	**1**	**1**	**1**	**1**	**1**
Total ↓	**0**	**0**	**1**	**1**	**0**	**0**	**0**	**0**	**0**
DCAS14A	13.8	1.3	11.6	-0.3	-3.8	0.5	7.8	-2.6	3.5
NC184	-7.2	-1.2	-4.7	-0.3	-1.7	-0.5	-9.0	-6.9	-4.7
NC194	0.3	-3.6	-1.2	-0.5	-1.6	0.3	-1.2	-2.1	-0.6
Total ↑	**2**	**1**	**1**	**0**	**0**	**2**	**1**	**0**	**1**
Total ↓	**1**	**2**	**2**	**3**	**3**	**1**	**2**	**3**	**2**

3.4.2.3 Statistical Analyses of Changes in Water Chemistry

We have summarized the key results of the statistical analyses of changes in lake chemistry in Table 3-8 and Figure 3-18. These results applied Bayesian Method 1, described in Appendix F of the 2019 Comprehensive Review (ESSA et al., 2020b).

We evaluated the KPI and the informative indicators using the two-threshold structure (Table 3-8). None of the 11 EEM lakes have a high % belief in exceedance of either the KPI or any of the informative indicators. None of the 11 EEM lakes have even a moderate % belief in exceedance of the KPI – all lakes show a low % belief in exceedance of the CBANC KPI. However, three sensitive EEM lakes and two control lakes show moderate % belief of one or two of the informative indicators:

- LAK022 shows moderate % belief in exceedance of Gran ANC and pH
- LAK028 shows moderate % belief in exceedance of BCS
- LAK042 shows moderate % belief in exceedance of BCS and pH
- NC184 shows moderate % belief in exceedance of Gran ANC and pH
- NC194 shows moderate % belief in exceedance of pH

The only two changes in classification (across all lakes and metrics) from last year are the changes from low to moderate for LAK042 BCS and NC194 pH. All other results are the same as last year in terms of final classification.

This is only the third year that the Bayesian analyses were performed on CBANC. Despite the widespread changes in numerous water chemistry metrics observed in both 2021 and 2022, the CBANC results remain remarkably similar to the 2020 results for almost all of the lakes, possibly providing an indication of the robustness of the CBANC metric to anomalous conditions.

This is the fifth year that the Bayesian analyses were performed for Gran ANC and pH. That length of time provides an opportunity to see how the results have changed since these analyses were first implemented in the 2019 Comprehensive Review. For Gran ANC, there are only two lakes that have showed a change in category over the five years of repeating the analyses – LAK022 and NC194 increases from low to moderate, albeit still at the low end of the moderate range (~30% belief). For pH, 2 sensitive lakes, 1 less sensitive lake, and all 3 control lakes have showed a change in category – from low to moderate in all cases. In all cases, the shift occurred with the 2021 results (driven by high precipitation in September 2021) and the 2022 results remained quite similar[13]. LAK042 and LAK016 have been only in the low end of the moderate category. LAK022, DCAS14A and NC184 have been in the mid-range of the moderate category and only NC194 has been at the top end. However, decreases in pH in the control lakes must be driven by factors other than the smelter because they are well outside the deposition plume, and all three control lakes have a low percent belief in any sulphate increase.

The key outcomes from the BACI analyses include:

- For CBANC, Gran ANC and BCS, 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)
- For pH, one of the lakes (LAK012) showed a statistically significant effect, but for a change in pH that was *more positive* than in the control lakes, which is evidence against acidification
- When analysed as a group with all seven sensitive EEM lakes combined:
  - Changes in CBANC, Gran ANC, and BCS were not statistically significant
  - Changes in pH were significantly *more positive* than in the control lakes, which is evidence against acidification.

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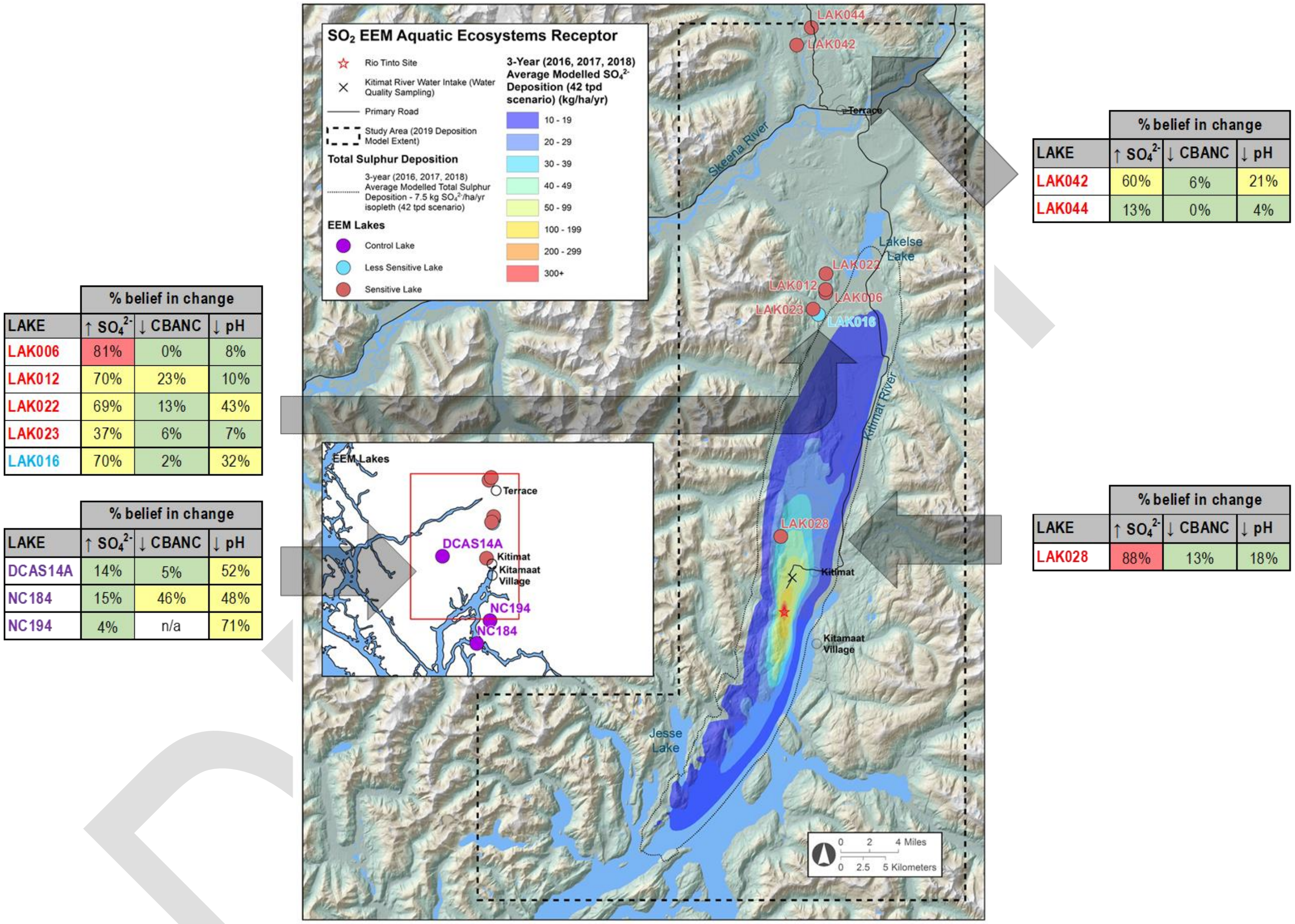
[13] Note: 4 out of these 5 lakes were not sampled in 2020, meaning the 2020 results were based only on 2018-2019, and therefore it is not actually possible to determine whether the shifts that show up in the 2021 results reflect changes in lake chemistry in 2020, 2021 or both.

Table 3-8. Summary of findings across all lakes monitored in the SO_2 EEM Program. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review (ESSA et al., 2020b). Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red.

	Changes in SO_4	Exceedance of *CHANGE LIMIT*				Exceedance of *LEVEL OF PROTECTION*				KPI and Informative Indicator Evaluation			
	(% belief that threshold exceeded; from Bayesian analysis method 1)	(% belief that metric value has decreased by more than the threshold; from Bayesian analysis method 1)				(% belief that metric value is below threshold; from Bayesian analysis method 1)				(Classification of % belief that both the change limit and level of protections thresholds are exceeded)			
Metric	**SO_4**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**
Threshold	Increase > 0	Lake-spec.	Lake-spec.	Δ 13 ueq/L	Δ 0.3 pH units	20 ueq/L	30.7 ueq/L	0 ueq/L	6.0 pH units	KPI	Inform. Indic.	Inform. Indic.	Inform. Indic.
LAK006	81%	0%	0%	1%	8%	0%	0%	0%	70%	LOW	LOW	LOW	LOW
LAK012	70%	23%	14%	42%	10%	0%	0%	0%	77%	LOW	LOW	LOW	LOW
LAK022	69%	13%	30%	9%	43%	0%	80%	0%	84%	LOW	MOD	LOW	MOD
LAK023	37%	6%	2%	3%	7%	0%	100%	0%	100%	LOW	LOW	LOW	LOW
LAK028	88%	13%	8%	62%	18%	100%	100%	100%	100%	LOW	LOW	MOD	LOW
LAK042	60%	6%	6%	20%	21%	0%	100%	80%	100%	LOW	LOW	MOD	MOD
LAK044	13%	0%	4%	1%	4%	100%	100%	0%	100%	LOW	LOW	LOW	LOW
LAK016	70%	2%	7%	33%	32%	0%	0%	0%	1%	LOW	LOW	LOW	LOW
DCAS14A	14%	5%	7%	13%	52%	0%	0%	0%	10%	LOW	LOW	LOW	LOW
NC184	15%	46%	30%	43%	48%	0%	100%	1%	97%	LOW	MOD	LOW	MOD
NC194	4%	▨	▨	4%	71%	0%	100%	0%	33%	▨	▨	LOW	MOD



LAKE	% belief in change ↑ SO_4^{2-}	↓ CBANC	↓ pH
LAK042	60%	6%	21%
LAK044	13%	0%	4%

LAKE	% belief in change ↑ SO_4^{2-}	↓ CBANC	↓ pH
LAK006	81%	0%	8%
LAK012	70%	23%	10%
LAK022	69%	13%	43%
LAK023	37%	6%	7%
LAK016	70%	2%	32%

LAKE	% belief in change ↑ SO_4^{2-}	↓ CBANC	↓ pH
LAK028	88%	13%	18%

LAKE	% belief in change ↑ SO_4^{2-}	↓ CBANC	↓ pH
DCAS14A	14%	5%	52%
NC184	15%	46%	48%
NC194	4%	n/a	71%

Figure 3-18. Spatial distribution of percent belief in chemical change. Numbers show % belief in: a) SO_4 increase [no threshold], b) CBANC decrease below lake-specific threshold, and c) pH decrease below 0.3 threshold. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review (ESSA et al., 2020b). NC194 does not have an estimated ANC threshold because it did not have appropriate titration data available. NC194 does not have an estimated ANC threshold because it did not have appropriate titration data available.

3.4.2.4 Application of the Evidentiary Framework

We applied the evidentiary framework using the updated results of the statistical analyses (Figure 3-19; detailed results in Table 4-2 of Technical Memo W11). Results show that: a) 1 sensitive lake and 3 control lakes[14] land within the first box, “smelter not causally linked to changes in lake chemistry”; b) 1 less sensitive lake lands within the second box, “lake is healthy, and not acidifying”; and c) 6 sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028 and LAK042) land within the third box, “some evidence of acidification, closely monitor”.

For LAK028, this classification is based on: a) average post-KMP values below the *level of protection* for both CBANC and pH, and b) moderate support for a decline in CBANC (66% belief) and pH (57% belief), but with low support for exceedance of either *change limit* threshold (13% belief for CBANC and 18% belief for pH). The overall result is similar to last year, but the level of support for declines in CBANC has decreased from strong to moderate.

For LAK006, LAK012, LAK022, LAK023, and LAK042, this classification is based on pH only. All five lakes have 0% belief in CBANC being below the *level of protection.*

LAK022 and LAK042 show: a) average post-KMP values below the *level of protection* for pH only, and b) moderate support for declines in pH (60% and 36% belief, respectively), with moderate support for exceedance of the *change limit* threshold (43% and 21% belief, respectively).

LAK023 shows: a) average post-KMP values below the *level of protection* for pH only, and b) moderate support for declines in pH (28% belief), but with low support for exceedance of the *change limit* threshold for pH (7%).

LAK006 and LAK012 show: a) a moderate belief in exceeding the *level of protection* for pH (70% and 77% belief, respectively), and b) moderate to low support for declines in pH (25% and 20% belief, respectively), with low support for exceedance of the *change limit* threshold (8% and 10% belief, respectively).

None of the lakes exceed the thresholds established for the KPI (CBANC) and the informative indicators (Gran ANC, pH, BCS; these thresholds are listed in Table 17 of the Phase III Plan, and are included below in Table 3-9 for ease of reference).

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[14] All of the control lakes are classified in the first box regardless of increases in sulphate because any such increases cannot be causally linked to the smelter due to their location well outside the smelter plume.

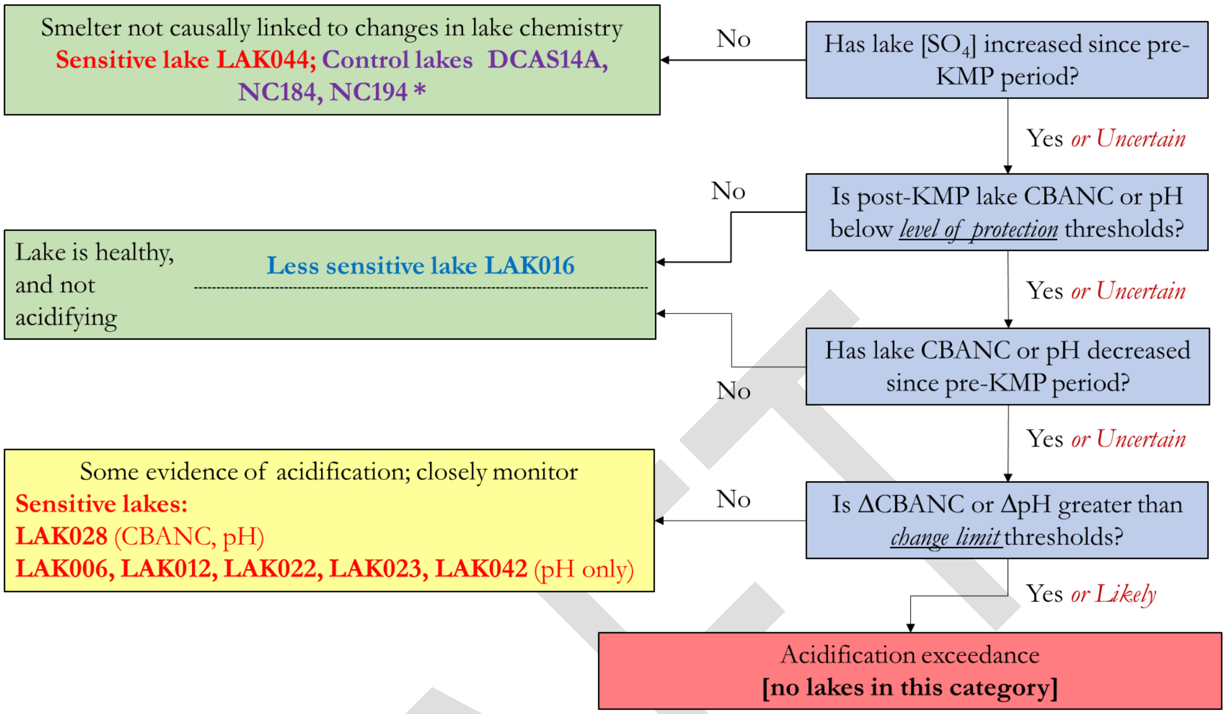


Figure 3-19. Classification of EEM lakes according to the simplified evidentiary framework. LAK028 has strong support for a decline in CBANC and moderate support for a decline in pH but low support for exceeding either *change limit* threshold. LAK006, LAK022, LAK023, and LAK042 have moderate support for declines pH with moderate to very low support for exceeding the *change limit* thresholds; however, they are all still above the CBANC *level of protection*. The control lakes (*) are all classified in the first box regardless of increases in sulphate because any such increases cannot be causally linked to the smelter due to their location well outside the smelter plume.

Table 3-9. Thresholds for level of protection and change limits for aquatic acidification KPI and informative indicators. Source: ESSA et al., 2023

Indicators	**Type**	**Level of Protection** (i.e., absolute threshold)	**Change Limit** (i.e., relative threshold)
CBANC	KPI	Decrease below 20 µeq/L	Decrease greater than lake-specific thresholds†
pH	Informative	Decrease below 6.0 pH units	Decrease ≥0.3 pH units
Gran ANC	Informative	Decrease below 30.7 µeq/L	Decrease greater than lake-specific thresholds†
BCS	Informative	Decrease below 0 µeq/L	Decrease greater than 13 µeq/L

† The lake-specific thresholds for CBANC and Gran ANC are shown in both Table 14 of the SO₂ EEM Phase III Plan (ESSA et al., 2023) and Appendix 5 of Technical Memo W11.

3.4.3 Recommendations for 2023

We recommend sampling LAK027 again in 2023. In 2021, the widely-observed storm-driven dilution event negated the ability of the sampling data to provide a meaningful comparison against the initial STAR data as intended. In 2022, the combination of exceptionally low deposition and particularly dry hydrologic conditions again negated the ability to provide the intended comparison.

We do not recommend any other changes or adjustments to next year's program.

4 Climate Change

The SO_2 EEM Program collects data that are of value for understanding and tracking the effects of climate change in the Kitimat Valley. Rio Tinto has volunteered to add the tracking of climate change indicators using some of the data currently collected by the SO_2 EEM Program and some additional new monitoring data.

The purpose of this chapter is to synthesize the SO_2 EEM collected monitoring data through the lens of climate change into indicators for tracking the changes in climate and the physical effects of the climatic change over time. The intent of adding climate change to the SO_2 EEM Program is to be able to provide an understanding of how the climate and environment are changing in the Kitimat Valley using the SO_2 EEM Program's monitoring data.

This chapter presents the climate indicators without analysis or interpretation of the indicators, as this scope will be undertaken in Comprehensive Review.

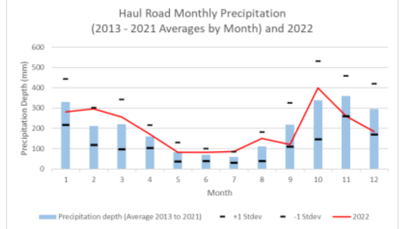
4.1 Activities Undertaken

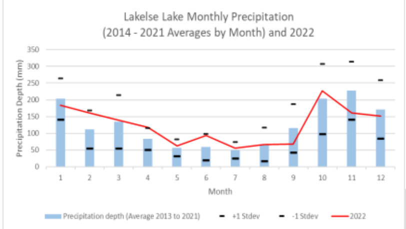
We have started to assemble data sets for the climate change indicators and review both the data quality and suitability of the data for supporting the indicators. We have also started to explore the specific statistics of the indicators. We have purchased solar irradiance monitors (Hukseflux ISO 9060 SR05) that were installed in May, 2023 at both the Lakelse Lake Deposition and Whitesail monitoring stations. We have also purchased soil moisture probes (HOBO MX Soil Moisture Data Loggers) that were installed in May 2023 at the primary Lakelse Lake Soil Plot. We also setup and measured new cyanolichen and vascular plant biodiversity monitoring plots in the Kemano Valley that will be used to understand the region changes due to the influence of climate change on the plant biodiversity in the Kitimat Valley.

4.2 Climate Change Trends

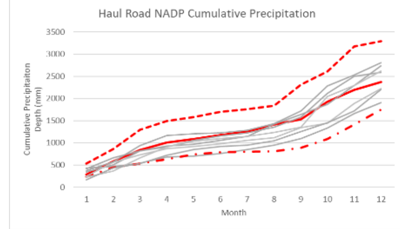
4.2.1 Meteorological Indicators

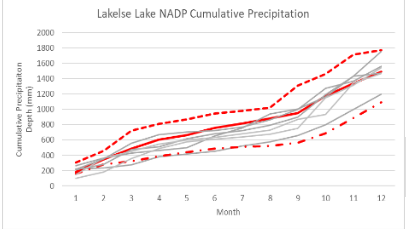
NADP Precipitation Annual Average Against Historical Normal





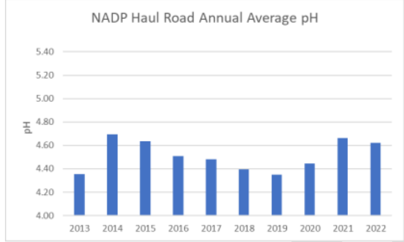
NADP Precipitation Patterns (cumulative and storm depths)

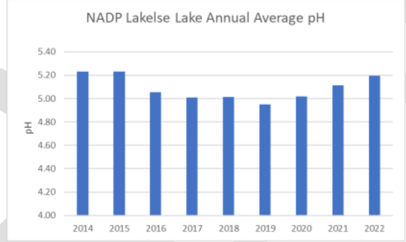




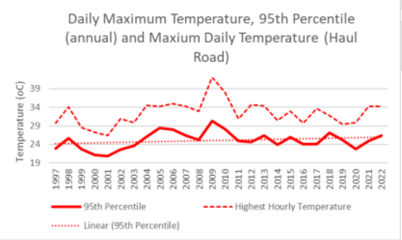
Storm patterns under development

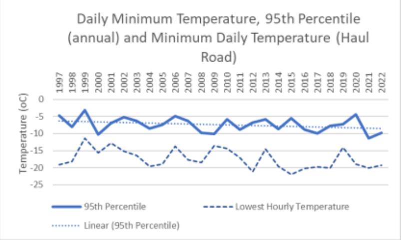
NADP Precipitation pH (weekly and annual average)

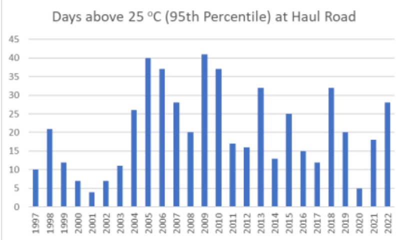




Air Temperature Against Historical Normal (seasonal, extremes and annual averages)







Air temperature data at the smeltersite (Haul Road, Yacht Club and the Kitimat 2 cooperative climate network station) was evaluated and the Haul road station was selected for the indicator based on the longer term history of avilable continuous data. Data from the Kitimat 2 station (1966 – 2020) will be evalualted to determine if the data set can be merged with the Haul Road station data to create a long term data set for the air temperature indicator.

Still Air Days (days with low windspeed)

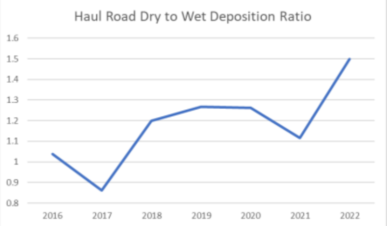
Data evaluation and analysis is in progress for assessing the potential for an indicator.

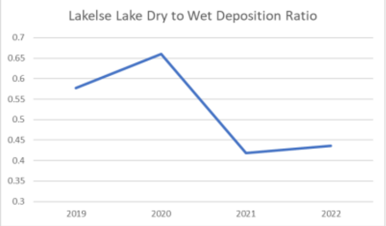
Solar Irradiance

Monitors installed and data collection is in progress for developing an indicator.

4.2.2 Effects Monitoring Indicators

SO_4 Deposition Rates and Ratios of Wet vs. Dry Deposition (seasonal and annual averages)





Deposition data is being analyzed to develop a seasonal deposition indicator

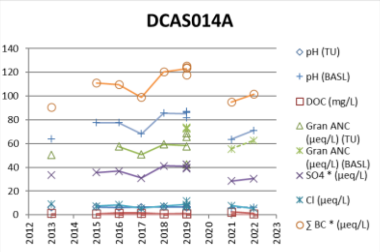
Soil Moisture at Lakelse Lake

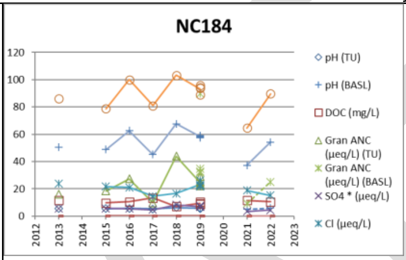
Monitors have been installed and data collection is in progress.

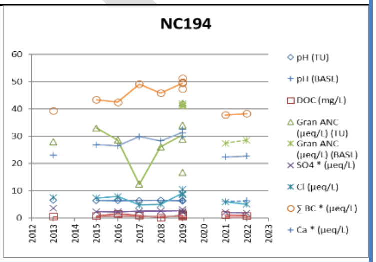
Vascular Plant Biodiversity

Monitoring plots were established in the Kemano Valley.

Lake Chemistry (Control Lakes DCAS14A, NC194 and NC184)







Water Temperature and Water Levels (Lak006 and Lak028)

Data evaluation and analysis is in progress for developing the indicator.

4.3 Additional Studies

A project will be sponsored under SO_2 EEM Phase III that will review and summarize the available predictions and literature for climate change in the Kitimat Valley and develop predictions for environmental responses. The intent of this project is to develop an understanding of the predicted climate changes that may occur in the Kitimat Valley and to develop an understanding of the potential effects of the changes.

This study will be completed between 2023 to 2025. No work was undertaken in 2022 for this project.

5 List of Cited Reports

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Zhang, L., J.R. Brook and R. Vet. 2003b. Evaluation of a non-stomatal resistance parameterization for SO$_2$ dry deposition. Atmospheric Environment, 37:21, 2941–2947.

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6 List of Cited EEM Technical Memos

The numbering of Technical Memos continues from the numbers in the previous Annual Reports. The Human Health KPI Calculations Memo for 2022 is provided in Appendix A, and Technical Memo W11 is provided in Appendix B.

Human Health KPI Calculations for 2022 (May 2023, Trinity Consultants.)

Technical Memo D01. Method for Estimating Dry Deposition, September 2016. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2017 Annual Report. ESSA Technologies Ltd, Vancouver, Canada.

Technical Memo D02. Atmospheric Sulphur Dioxide – Method for Estimating Dry Deposition: 2017 Update (June 2018, Trent University)

Technical Memo P06. Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: 2022 Results (June 2023, Trinity Consultants)

Technical Memo W09. Aquatic Ecosystems Actions and Analyses (July 2019, ESSA Technologies Ltd.)

Technical Memo W11. Aquatic Ecosystems Actions and Analyses (April 2023, ESSA Technologies Ltd.)

Appendix A: Technical Memo P06 – Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: 2022 Results

The following pages contain **B.C. Works SO_2 EEM Program Technical Memo P06**, in PDF format.

RioTinto

B.C. Works SO_2 EEM Program – Technical Memo P06

Atmospheric Sulphur Dioxide

Passive Diffusive Sampler Network: 2022 Results

June 2023

Prepared for:

Rio Tinto, BC Works
1 Smeltersite Road, P.O. Box 1800,
Kitimat, BC, Canada V8C 2H2

Prepared by:

Trinity Consultants
4525 Wasatch Blvd. Suite 200
Salt Lake City, UT 84124

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1 Introduction

The network of passive samplers was redeployed in the Kitimat Valley during 2022 following the same procedures that were utilized in previous years. The network was deployed at 22 sites within the Kitimat Valley (Figure 1), starting April 27, 2022[1]. The network was primarily focused along the Wedeene and Bish roads to capture the plume path. This network is referred to as the plume path network and historically referred to as the valley network.[2]

2 Overview

During 2022, the sulphur dioxide (SO_2) passive diffusive sampler network in the Kitimat Valley began monitoring on 27 April and finished on 28 October, following (approximately) six one-month exposures.

Based on Trinity Consultant's 2020 passive sampling plan, a detailed site evaluation was conducted and documented during the 2020 deployment. The original 15 sites deployed in 2020 were deployed in 2022. In addition, the six sites added in 2021 based on reconnaissance performed in early 2021 were also deployed in 2022.[3] Location A05 (Kitamaat Village) was added in 2022 to understand the extent of the plume to the southeast and for another site to compare with continuous ambient SO_2 monitoring.

As detailed in the Phase III EEM work plan's 2021-Specific Work Plan for Passive Sampling (ESSA et. al., 2021), the network changed from employing IVL SO_2 passive samplers to Bureau Veritas (BV) All-Season Passive Air Sampling System (PASS) and laboratory. All 2022 sample analysis was performed using the BV PASS system.

3 Study Design

Six deployments, with an approximate exposure time of one-month (27-34 days), were carried out under the plume path network between April and November 2022. Lake 28 sampling had five deployments from June – November 2022.

In 2022, there were 155 sample exposures across the plume path network collected and analyzed during the six deployments. These included replicate samplers deployed approximately 18% of the time (28 duplicate exposures) and 23 blank samples (approximately four per sampling period).

---

[1] The Lake 28 sampler was deployed later than the other sites, on June 13, 2022.

2 A second network of passive samplers deployed in the urban and residential areas of Kitimat was in continuous operation from June 2018 through December 2019. The urban network study concluded in 2019 (before the time period of this report).

3 Three of the six new 2021 sites (V17, V18/V18b, and V20) were added east and west of V01 create an east-west transect to better understand the eastern and western boundaries of the plume path. The remaining three new 2021 sites (V21, V22, and V23) were added farther north near Terrace to better understand the northern boundary of the plume path (and to verify where the plume is not).

4 Results

The observed data show elevated atmospheric SO_2 along the plume path (Figure 1). Results shown in Figure 1 are uncalibrated because the BV PASS results need to undergo a new calibration analysis (different from the historic calibration based on IVL sampler data). The BV PASS calibration analysis will be performed after sufficient data have been collected from BV PASS samplers co-located at continuous monitoring stations.

The 2022 results within the plume path network are similar to the 2021 observations, although concentrations in 2022 are slightly lower as expected during the low emission levels from the smelter in 2022. Higher concentrations were monitored later during the 2022 year due to the restart and increased smelting capacity coming on-line. The spatial pattern is consistent with previous years. It is recommended that deployments are continued during 2023 to further define the plume throughout the restart and into the transition to normal operation.

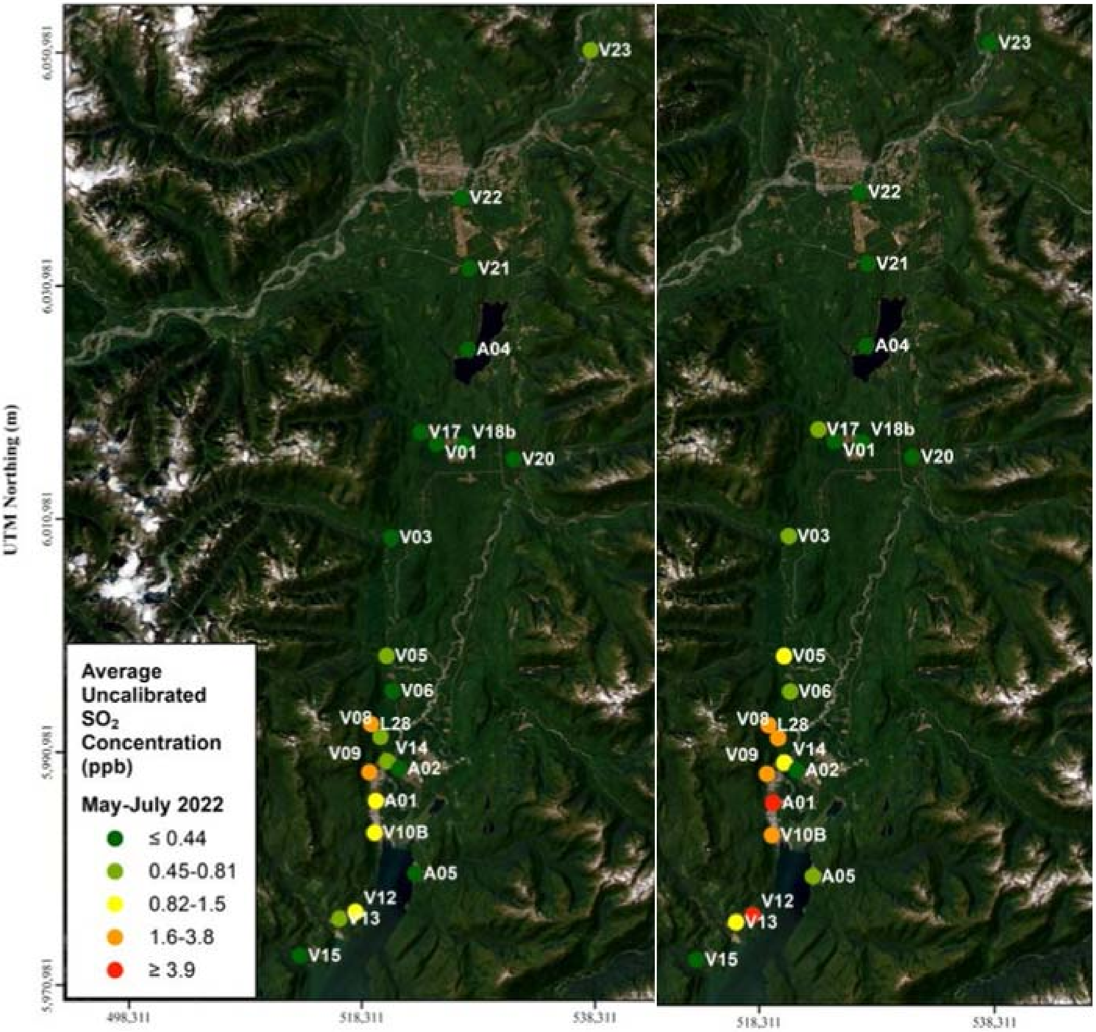

Figure 1. Average Atmospheric Sulphur Dioxide (SO_2) Concentration during May to July 2022 (left) and during August to October (right) in the Kitimat Valley Passive Diffusive Monitoring Network (uncalibrated).

Ambient SO_2 data were collected from the continuous SO_2 analyzers at Haul Road, Riverlodge, Lakelse, and Kitamaat Village were compared to the passive SO_2 sampling data to understand accuracy and precision of the passive method. In general, there was good correlation between passive and active at sites with higher concentrations however, correlation decreases at sites that have average passive concentrations below 1 ppb.

Tables 1 and 2 present a comparison of the ambient sampler results with the collocated passive SO_2 samples analyzed by Bureau Veritas laboratory collected for the Haul Road (AO1), Riverlodge (AO2), Lakelse (A04), and Kitamaat Village (A05) monitoring stations. SO_2 comparisons were made on a 30-day sampling basis.

Table 1 Comparison of SO_2 Passive Sampling Data to Ambient SO_2 Data at Station A01 and A02

	Haul Road (AO1)			Riverlodge (AO2)		
End Date (2022)	Bureau Veritas Passive (ppb)	Active (ppb)	Diff. (ppb)	Bureau Veritas Passive (ppb)	Active (ppb)	Diff. (ppb)
May	1.1	0.8	-0.3	0.2	0.3	0.1
June	1.35	1	0.35	0.2	0.2	0
July	1.8	1.7	0.1	0.2	0.2	0
August	3.9	3.4	0.5	0.2	0.3	0.1
Sept.	5.2	3.4	1.8	0.2	0.3	0.1
Oct	6.95	4.8	2.15	0.2	0.4	0.2
		Average	0.767		Average	0.083
		St. Dev.	0.895		St. Dev.	0.069

Table 2 Comparison of SO_2 Passive Sampling Data to Ambient SO_2 Data at Station A04 and A05

	Lakelse (AO4)			Kitimaat Village (AO5)		
End Date (2022)	Bureau Veritas Passive (ppb)	Active (ppb)	Diff. (ppb)	Bureau Veritas Passive (ppb)	Active (ppb)	Diff. (ppb)
May	0.2	0.0	0.2	0.2	0.2	0.1
June	0.2	0.0	0.2	0.1	0.1	0.1
July	0.3	0.0	0.3	0.2	0.2	0.1
August	0.5	0.2	0.3	0.2	0.2	0.0
Sept.	0.5	0.0	0.5	0.2	0.2	-0.2
Oct	0.5	0.0	0.5	0.1	0.1	0.0
		Average	0.302		Average	0.027
		St. Dev.	0.117		St. Dev.	0.095

The statistical differences between the active and passive monitors are shown below in Table 3. The averages column shows the average concentration difference between the active and passive monitors. The standard deviations and correlation coefficients (r^2) for the difference between active and passive monitors are also listed.

Table 3 Statistical Analysis of Active to Passive Concentrations

Statistic	Haul Road	Riverlodge	Lakelse	Kitamaat Village
Average (ppb)	0.77	0.08	0.30	0.02
Standard Deviation	0.90	0.07	0.12	0.09
r^2	0.96	0.00	0.19	0.21

The correlation coefficient for the Haul Road is high, but the correlation coefficients aremuch lower for the other locations. The passive and active sampling at the Haul Road show clear trends and provide similar results. The passive sampling appears to be biased high compared to the active sampling across all sites that have colocation. The Riverlodge specifically does not show a correlation between the passive and active sampling values. The Lakelse and Kitamaat Village colocation have a slight correlation but the results are not as significant as at the Haul Road location.

5 Conclusion

The 2022 results demonstrate a similar spatial pattern in SO_2 compared with 2021. Higher concentrations were monitored later during the 2022 year due to the restart and increased smelting capacity coming on-line.

In summary, the results from the 2022 network continue to support the use of passive samplers to provide empirical observations of atmospheric SO_2 concentrations to (a) assess spatial and temporal changes, (b) evaluate modelled concentration fields, and (c) estimate dry deposition of SO_2. It is recommended that deployments are continued during 2023.

Appendix A.

Table 4: Passive SO_2 Sampling Network Station Identifier, Name, and UTM Location

ID	Site Name	UTM E	UTM N
A01	Haul Road Station	519527	5986823
A02	Riverlodge Station	521538	5989580
A04	Lakelse Lake NADP Station	527457	6025573
A05	Kitamaat Village Station	522907	5980600
V01	Onion Lake Ski Trail North	524757	6017435
V03	Mound TKTP92	520853	6009407
V05	LNG Muster Station	520457	5999250
V06	Sand Pit	520970	5996240
V08	Claque Mountain Trail at Powerline	519938	5992329
V09	Sand Hill at Powerline	518985	5989292
V10B	Pullout before Bish FSR	519425	5984090
V12	Bish Road Pullout 4	517790	5977294
V13	Bish Road at Chevron LNG	516389	5976708
V14	Industrial Area Kitimat Hotel	520490	5990236
V15	Bish Mainline	512994	5973534
V17	West Lake	523359	6018434
V18B	Wedeene mainline	527088	6017351
V20	Pipeline laydown	531354	6016121
V21	South of airport	527566	6032493
V22	Kitselas Development	526862	6038551
V23	Gitaus water tower	537941	6051192

Table 5 Passive Sampling Results in ppb

Station	May (ppb)	June (ppb)	July (ppb)	August (ppb)	September (ppb)	October (ppb)
A01	1.1	1.4	1.8	3.9	5.2	7.0
A02	0.3	0.2	0.2	0.3	0.3	0.4
A04	0.2	0.1	0.2	0.2	0.2	0.1
A05	0.2	0.2	0.3	0.5	0.5	0.5
V01	0.2	0.1	0.3	0.5	0.3*	0.3
V03	Not Collected	0.3	0.5	0.7	0.5*	0.5
V05	Not Collected	0.6	0.8	1.1	0.9	0.7
V06	0.4	0.4	0.6	0.8	0.7	0.7
V08	0.7	0.8	0.9	2.2	1.2*	1.7
V09	1.5	1.6	2.8	3.6*	3.2	3.9
V10B	0.6	1.7	1.2	3.3	4.0	2.8
V12	0.6	1.6	0.9	2.3	5.4	5.1
V13	0.4	0.7	0.4	0.8	1.6*	1.7
V14	0.7	0.4	0.4	0.6	0.9*	1.1
V15	0.2	0.3	0.2	0.3	0.4	0.3*
V17	Not Collected	0.3	0.5	0.9	0.6	0.9
V18B	0.2	0.1	0.1	0.2	0.2	0.2
V20	0.2	<0.1	0.1	0.2	0.1	0.2
V21	0.2	<0.1	0.2	0.2	0.2	0.2
V22	0.1	<0.1	0.1	0.2	0.3	0.2
V23	1.5	<0.1	<0.1	0.1	<0.1	0.1
L28[1]	Not Collected	1.6	2.4	3.4	2.0	2.0

Green - Sample below reporting limit and reported as 1/2 RL.

[1] Dates are the end month of each sampling period (for deployments that started and ended near the end of the month), except for L28, dates are listed month-beginning (because L28 deployments began near the beginning of the month).

* Means sample had seeds, insect eggs, or webs in the PASS assembly during the sampling period

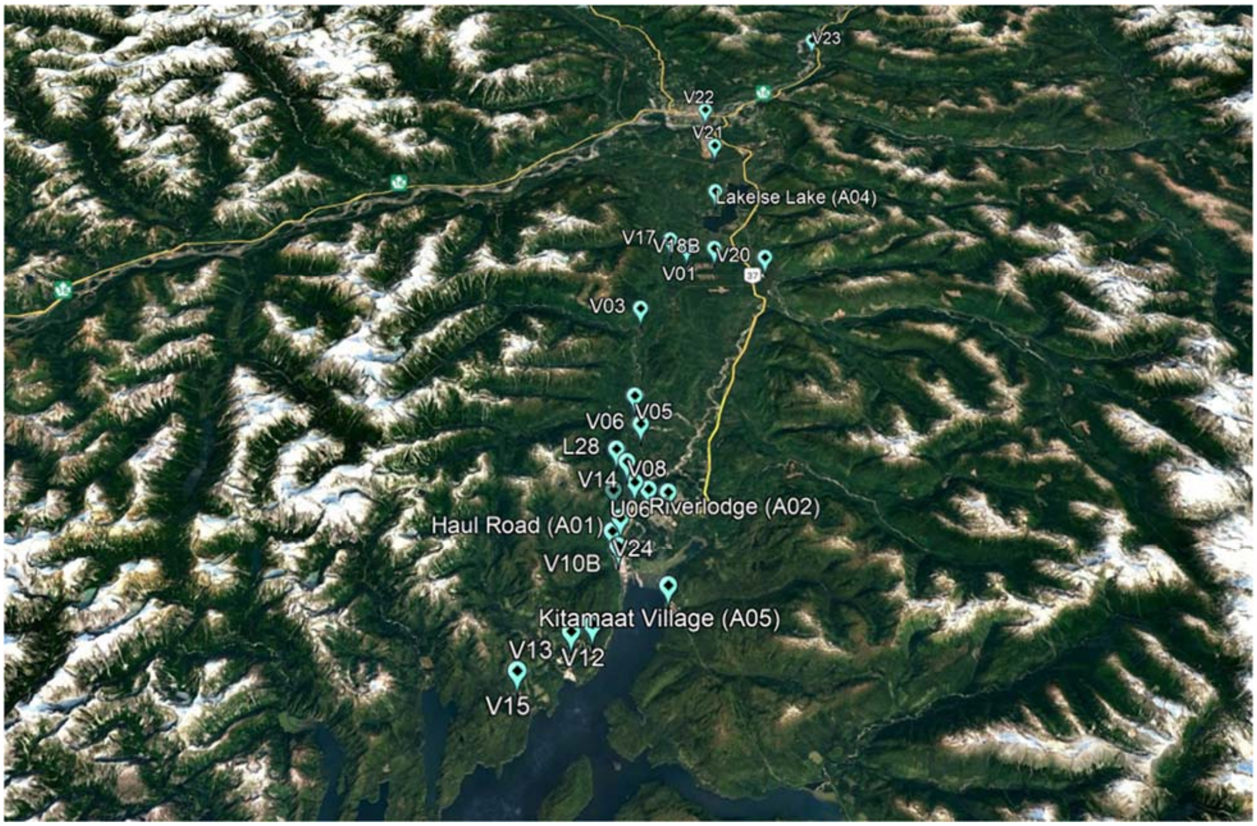

Figure 2 : Site Locations and IDs for the Kitimat Urban (U) and Ambient (A) Passive Diffusive Sampler Network; see Figure A1 and Table A1 for Further Details on Site Locations.

Appendix B: Human Health KPI Calculations Memorandum for 2022

The following pages contain the **Memorandum for the Human Health KPI Calculations for 2022**, in PDF format.

Trinity Consultants

MEMORANDUM

To: Shawn Zettler, Meagen Grossmann - Rio Tinto

From: Anna Henolson, Cara Keslar, Adrienne Kaul - Trinity Consultants

Date: May 19, 2023

RE: Human Health KPI Calculations for 2022

Introduction

The SO_2 Environmental Effects Monitoring (EEM) Program establishes Key Performance Indicators (KPIs) of various pathways in order to monitor effects of SO_2 from Rio Tinto's Kitimat aluminum smelter. This memorandum describes the SO_2 monitoring data collected in 2020 through 2022 in the Kitimat area and the method used in order to compare to the human health KPI for reporting year 2022.

Health KPI

British Columbia Ministry of Environment and Climate Change Strategy (B.C. ENV) updated the province-wide interim SO_2 ambient air quality objective (IAAQO) in 2016, which became the SO_2 health KPI of EEM Program starting 2017. Starting January 1, 2020, the SO_2 health KPI implemented the SO_2 Canadian Ambient Air Quality Standards (CAAQS). In 2022, the CAAQS value was 70 ppb. In 2025 the CAAQS value changes to 65 ppb. The SO_2 health KPI is used to assess residential SO_2 ambient air quality.

Exceptional Events

Exceptional events may occur from:

- Fire within the community that may emit SO_2;
- Emergency conditions at the facilities within the Kitimat airshed;
- Vandalism or corruption of data from other point sources such as vehicle emissions in close proximity to the ambient air monitoring station; and
- Temporary global events that impact SO_2 levels such as a volcano eruption.

These types of exceptional events could affect the determination of the health KPI.

The restarting of the smelter in 2022 is considered an exceptional event causing unusual SO_2 emission levels from the smelter. However, production and SO_2 levels remained low in all of 2022. As such, no exceptional events that caused unusually high levels of ambient SO_2 were identified in 2022.

Calculation Method

The monitoring data at residential areas in Kitimat is collected at three residential monitoring stations: Riverlodge, Whitesail, and Kitamaat Village[1]. The Industrial Avenue monitoring station (located in Service Centre) is also designated as a KPI attainment site per the decision issued by B.C. ENV on October 25,

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[1] Note that the BC ENV Envista database lists the Kitamaat Village monitoring station as the Haisla Village monitoring station.

2022.[2] However, the effective date listed in the decision is January 1, 2023. Therefore, 2022 data from the Industrial Avenue station is not used for the human health KPI calculations for 2022. The station began collecting data in May 2020. Following the January 1, 2023 effective date in the ENV decision, the station is collecting data for KPI attainment purposes beginning January 1, 2023.[3] Attainment with the KPI requires three years of data; therefore, the first reporting year with attainment status for Industrial avenue is expected to be 2025 (using years 2023, 2024, and 2025 to evaluate attainment status).

Ambient SO_2 monitors collect the SO_2 measurements continuously and hourly measurements are reported to BC ENV's Envista database[4]. The measurements at these monitor stations are reviewed and validated by BC ENV on an annual basis:

- Monitoring data for 2020 was validated as of March 5, 2022.
- Monitoring data for 2021 was validated as of January 20, 2023.
- Monitoring data for 2022 was not validated as of the date of this memorandum (May 2023)

The hourly measurements for calendar years 2020, 2021, and 2022 were downloaded from the Envista database after the validation was complete if possible, and then processed following the procedures described in *Guidance on Application of Provincial Air Quality Objectives for* SO_2[5] (the Guidance). Following the Guidance, the monitoring data was processed in the following steps:

1. Check daily data completeness and determine the daily 1-hour maximum concentration.
    - Daily measurements are the hourly readings from 1 AM to 12 AM marked for the same day.
    - A valid daily value is calculated as the maximum hourly reading from the day:
        - Where at least 18 hourly measurements are available in a day, the daily value is the maximum value from those readings in the same day; or
        - Where less than 18 hourly measurements are available in a day but at least one hourly measurement exceeds 70 ppb, the daily value is the maximum value from available readings in the same day.[6]
    - All values are reported to the nearest 0.1 ppb.
    - A summary of daily completeness is provided in Attachment A.

2. Check quarterly and annual data completeness. A summary of quarterly and annual data completeness is provided in Table 1.
    - The dataset is considered complete when there are at least 60% of all daily maximum 1-hour measurements in each quarter and at least 75% of all daily maximum 1-hour measurements in each year.
    - Periods which do not satisfy the data completeness criteria are flagged.

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[2] Letter from Douglas Hill (B.C. ENV) to Shawn Zettler (Rio Tinto). October 25, 2023. https://j200.gov.bc.ca/pub/ams/download.aspx?PosseObjectId=150676770

[3] The Janauary 1, 2023 effective date was based on the expectation that the smelter was expected to reach normal operations. As of May 2023, the smelter has not yet reached normal operation.

[4] BC Air Data Archive Website (Envista database), available at https://envistaweb.env.gov.bc.ca/.

[5] *Guidance on Application of Provincial Air Quality Objectives for* SO_2, BC ENV, Feburary 7, 2017, available at https://www2.gov.bc.ca/assets/gov/environment/air-land-water/air/reports-pub/so2_aqo-implementation_guide.pdf.

[6] In this case, there were no SO_2 readings higher than 70 ppb from the three monitoring stations in any day in 2020, 2021, and 2022.

Table 1. Quarterly and Annual Data Completeness

Period [a]	2020			2021			2022		
	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
Q1	100.0%	94.5%	100.0%	100.0%	100.0%	97.8%	100.0%	100.0%	98.9%
Q2	100.0%	100.0%	98.9%	100.0%	100.0%	98.9%	100.0%	100.0%	96.7%
Q3	97.8%	100.0%	58.7%	98.9%	98.9%	98.9%	98.9%	100.0%	95.7%
Q4	98.9%	98.9%	100.0%	97.8%	100.0%	97.8%	100.0%	98.9%	97.8%
Annual	99.2%	98.4%	89.3%	99.2%	99.7%	98.4%	99.7%	99.7%	97.3%

a. Q1 refers to January to March, Q2 refers to April to June, Q3 refers to July to September, and Q4 refers to October to December.

3. Calculate the 99th percentile value of daily 1-hour maximum values for each year at each station.
   - Firstly, all daily 1-hour maximum values for the year are sorted from highest to lowest. For example, there were 364 valid daily 1-hour maximum values at Kitamaat Village for 2022, and these 364 values were ordered from highest to lowest.
   - Secondly, count the number of valid daily values, and determine the corresponding rank for the annual 99th percentile value following Table I-1 of the Guidance. For example, the corresponding rank equivalent to annual 99th percentile is 4 for Kitamaat Village for 2022, as there were more than 300 daily values.
   - Lastly, report the value in the corresponding rank equivalent to annual 99th percentile of the daily 1-hour maximum values. The value is reported to the nearest 0.1 ppb.[7] For example, the 4th highest daily value is reported for Kitamaat Village for 2022 is 9.8 ppb.
4. Calculate the three-year average of annual 99th percentile of the daily 1-hour maximum values at each station.

The annual 99th percentile value of daily 1-hour maximum values for each year at each station and the three-year average values at each station are summarized in Table 2. The three-year average of annual 99th percentile of daily 1-hour maximum over 2020, 2021, and 2022 at all three monitor stations are also compared to the SO_2 CAAQS of 70 ppb, as shown in Table 2. Since all values are below 70 ppb, and since all hourly measurements in 2020, 2021, and 2022 are below 70 ppb, all three monitor stations are considered in the attained status regarding this human health KPI.

Table 2. Annual 99th Percentile and Three-Year Average

Monitor Station	Annual 99th Percentile of Daily 1-hour Maximum [a] (ppb)			Three-Year Average [a] (ppb)	Health KPI Attainment Status
	2020	2021	2022		
Kitamaat Village	19.8	9.1	9.8	12.9	Attained
Riverlodge	18.0	29.2	9.9	19.0	Attained
Whitesail	14.1	15.6	5.7	11.8	Attained

a. All values are reported with one decimal per comments from ENV (Memorandum P2-00001, dated June 4, 2020) rather than to the nearest 1 ppb (as listed in the *Guidance on Application of Provincial Air Quality Objectives for SO_2).*

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[7] All values are reported with one decimal per comments from ENV (Memorandum P2-00001, dated June 4, 2020) rather than to the nearest 1 ppb (as listed in the *Guidance on Application of Provincial Air Quality Objectives for SO_2).*

2022 AQHI plus SO_2 Monitoring Data Review

B.C. ENV began a pilot project in Kitimat to issue alerts when SO_2 levels equal or exceed 36 ppb. According to the ENV information page, “It is expected that 1-hour SO_2 levels of 35 ppb and lower will pose little or no additional health risk to even sensitive individuals.”[8] The periods of time in 2022 with elevated SO_2 concentrations at these three residential monitor stations were infrequent. There were no hourly SO_2 measurements equal to or higher than 36 ppb in 2022.

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[8] https://www2.gov.bc.ca/gov/content/environment/air-land-water/air/air-quality/measuring/kitimat-so2-alert-pilot-project

Attachment A
Daily 1-hour Maximum Concentrations and Completeness

Note: The daily completeness is calculated by the number of valid hourly measurements in the day divided by 24. Where the daily completeness is below 75% (less than 18 measurements), the daily 1-hr maximum value for the given day is not calculated unless the daily 1-hr maximum exceeds 75 ppb.

Table A1. Daily 1-hour Maximum Concentrations and Completeness Summary.

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
1/1/2022	0.3	0.7	1.1	95.8%	95.8%	91.7%
1/2/2022	0.3	0.2	0.5	95.8%	95.8%	95.8%
1/3/2022	0.3	0.3	0.7	95.8%	95.8%	95.8%
1/4/2022	0.3	0.2	0.6	95.8%	95.8%	95.8%
1/5/2022	0.3	0.2	0.6	95.8%	95.8%	95.8%
1/6/2022	0.3	0.3	0.7	95.8%	95.8%	95.8%
1/7/2022	0.2	0.3	0.6	95.8%	95.8%	95.8%
1/8/2022	0.2	0.3	0.6	95.8%	95.8%	95.8%
1/9/2022	0.9	0.5	0.6	95.8%	95.8%	95.8%
1/10/2022	0.3	0.6	0.6	95.8%	95.8%	95.8%
1/11/2022	0.4	0.2	0.9	95.8%	95.8%	95.8%
1/12/2022	0.4	1.6	0.7	95.8%	95.8%	95.8%
1/13/2022	0.6	1.4	0.5	95.8%	95.8%	95.8%
1/14/2022	0.3	1.3	0.7	95.8%	95.8%	95.8%
1/15/2022	0.3	0.2	0.5	95.8%	95.8%	95.8%
1/16/2022	0.3	0.3	0.5	91.7%	95.8%	95.8%
1/17/2022	0.3	0.4	0.5	95.8%	95.8%	95.8%
1/18/2022	0.3	0.3	0.5	95.8%	95.8%	95.8%
1/19/2022	0.9	0.4	0.5	95.8%	95.8%	95.8%
1/20/2022	1.4	0.4	1.1	95.8%	95.8%	95.8%
1/21/2022	0.3	0.3	0.5	95.8%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			**Daily Completeness**		
Date	**Kitamaat Village**	**Riverlodge**	**Whitesail**	**Kitamaat Village**	**Riverlodge**	**Whitesail**
1/22/2022	0.3	0.3	0.5	95.8%	91.7%	95.8%
1/23/2022	0.3	0.5	0.9	91.7%	95.8%	95.8%
1/24/2022	0.3	0.4	0.5	95.8%	79.2%	91.7%
1/25/2022	0.3	0.3	0.9	95.8%	95.8%	95.8%
1/26/2022	0.3	0.2	0.6	95.8%	95.8%	95.8%
1/27/2022	1.3	0.5	2.9	95.8%	95.8%	95.8%
1/28/2022	0.4	0.5	1.3	91.7%	91.7%	95.8%
1/29/2022	0.1	0.4	0.5	95.8%	95.8%	95.8%
1/30/2022	0.1	0.2	0.5	95.8%	95.8%	95.8%
1/31/2022	0.2	0.2	0.7	95.8%	95.8%	95.8%
2/1/2022	0.2	0.2	0.9	95.8%	95.8%	95.8%
2/2/2022	0.4	0.4	0.5	95.8%	95.8%	95.8%
2/3/2022	0.2	0.6	0.6	95.8%	95.8%	95.8%
2/4/2022	0.2	0.5	0.5	95.8%	95.8%	95.8%
2/5/2022	0.2	0.6	0.7	95.8%	95.8%	95.8%
2/6/2022	0.3	1.8	1.0	95.8%	95.8%	95.8%
2/7/2022	0.2	0.3	0.5	95.8%	95.8%	95.8%
2/8/2022	0.2	0.4	0.5	95.8%	95.8%	95.8%
2/9/2022	0.2	0.8	0.5	95.8%	95.8%	95.8%
2/10/2022	0.2	0.3	0.5	95.8%	95.8%	95.8%
2/11/2022	0.2	0.7	0.7	95.8%	95.8%	95.8%
2/12/2022	0.7	0.4	0.7	95.8%	95.8%	95.8%
2/13/2022	0.2	0.4	0.6	95.8%	95.8%	95.8%
2/14/2022	7.4	0.4	0.6	91.7%	87.5%	95.8%
2/15/2022	0.2	0.4	0.6	91.7%	95.8%	95.8%
2/16/2022	0.2	0.2	0.6	95.8%	95.8%	91.7%
2/17/2022	0.2	0.2	0.5	95.8%	95.8%	95.8%
2/18/2022	0.2	0.2	0.6	95.8%	95.8%	95.8%
2/19/2022	0.2	1.5	0.5	95.8%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
2/20/2022	0.8	2.2	1.8	95.8%	95.8%	95.8%
2/21/2022	0.2	0.2	0.6	95.8%	95.8%	95.8%
2/22/2022	0.2	0.2	0.7	95.8%	95.8%	95.8%
2/23/2022	0.5	1.7	1.0	95.8%	95.8%	95.8%
2/24/2022	0.9	0.9	1.8	95.8%	95.8%	95.8%
2/25/2022	2.0	1.3	1.3	95.8%	95.8%	95.8%
2/26/2022	0.3	0.4	0.6	95.8%	95.8%	95.8%
2/27/2022	0.5	0.8	1.2	95.8%	95.8%	95.8%
2/28/2022	0.5	1.0	0.6	95.8%	95.8%	95.8%
3/1/2022	0.5	0.9	1.8	95.8%	95.8%	95.8%
3/2/2022	0.3	1.0	1.0	95.8%	83.3%	95.8%
3/3/2022	0.6	1.6	1.4	87.5%	95.8%	87.5%
3/4/2022	0.9	4.0	4.6	95.8%	95.8%	95.8%
3/5/2022	1.2	1.6	1.2	95.8%	95.8%	95.8%
3/6/2022	0.6	0.7	1.0	95.8%	95.8%	95.8%
3/7/2022	0.3	0.3	0.6	95.8%	95.8%	95.8%
3/8/2022	0.4	0.3	0.5	95.8%	95.8%	95.8%
3/9/2022	0.5	1.3	1.2	95.8%	91.7%	95.8%
3/10/2022	0.2	0.3	0.6	91.7%	95.8%	95.8%
3/11/2022	0.2	0.3	0.6	95.8%	75.0%	91.7%
3/12/2022	0.8	1.7	1.6	95.8%	95.8%	95.8%
3/13/2022	4.5	3.4	3.6	95.8%	95.8%	95.8%
3/14/2022	0.3	0.3	0.6	95.8%	95.8%	95.8%
3/15/2022	0.3	0.2	0.5	95.8%	95.8%	95.8%
3/16/2022	0.2	0.7	1.3	95.8%	95.8%	91.7%
3/17/2022	0.3	0.4	0.6	95.8%	95.8%	95.8%
3/18/2022	0.9	0.5	1.3	95.8%	95.8%	87.5%
3/19/2022	0.2	0.6	0.8	95.8%	95.8%	75.0%
3/20/2022	2.1	0.3	0.7	95.8%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
3/21/2022	0.3	0.3	-	95.8%	75.0%	62.5%
3/22/2022	0.3	0.8	0.6	95.8%	95.8%	95.8%
3/23/2022	0.3	0.8	0.6	95.8%	95.8%	91.7%
3/24/2022	0.6	0.3	1.6	95.8%	87.5%	87.5%
3/25/2022	2.1	2.1	1.6	91.7%	95.8%	95.8%
3/26/2022	0.6	0.5	1.4	95.8%	95.8%	95.8%
3/27/2022	0.4	0.2	0.9	95.8%	95.8%	95.8%
3/28/2022	0.4	1.4	1.6	95.8%	95.8%	87.5%
3/29/2022	1.0	3.3	2.1	83.3%	83.3%	95.8%
3/30/2022	0.2	0.2	0.2	95.8%	95.8%	95.8%
3/31/2022	0.4	0.4	0.2	95.8%	95.8%	95.8%
4/1/2022	0.8	0.5	5.3	83.3%	91.7%	95.8%
4/2/2022	0.2	0.3	1.4	91.7%	95.8%	95.8%
4/3/2022	0.2	0.2	0.2	95.8%	95.8%	91.7%
4/4/2022	0.9	0.1	0.5	95.8%	95.8%	95.8%
4/5/2022	0.2	1.0	0.2	95.8%	95.8%	91.7%
4/6/2022	0.3	0.3	0.2	95.8%	95.8%	95.8%
4/7/2022	0.6	0.4	0.3	79.2%	95.8%	95.8%
4/8/2022	0.4	0.3	0.6	87.5%	95.8%	95.8%
4/9/2022	0.1	1.1	0.2	95.8%	95.8%	95.8%
4/10/2022	0.4	0.2	0.2	95.8%	95.8%	95.8%
4/11/2022	0.3	0.2	0.2	95.8%	95.8%	95.8%
4/12/2022	0.3	0.1	0.2	95.8%	95.8%	95.8%
4/13/2022	0.5	0.2	0.3	95.8%	95.8%	95.8%
4/14/2022	0.3	0.2	0.2	95.8%	91.7%	91.7%
4/15/2022	1.2	1.0	-	95.8%	79.2%	66.7%
4/16/2022	0.6	1.0	1.0	95.8%	95.8%	95.8%
4/17/2022	1.0	1.9	1.0	95.8%	95.8%	95.8%
4/18/2022	1.5	0.7	0.5	95.8%	95.8%	91.7%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
4/19/2022	0.8	1.3	0.5	95.8%	95.8%	95.8%
4/20/2022	0.4	0.3	0.1	95.8%	95.8%	95.8%
4/21/2022	0.4	0.5	0.6	95.8%	95.8%	95.8%
4/22/2022	0.4	1.0	1.3	95.8%	95.8%	95.8%
4/23/2022	2.3	0.8	0.2	95.8%	95.8%	95.8%
4/24/2022	0.4	0.1	0.5	95.8%	91.7%	95.8%
4/25/2022	0.1	0.7	0.6	91.7%	95.8%	95.8%
4/26/2022	0.5	2.2	2.1	95.8%	95.8%	91.7%
4/27/2022	1.7	2.0	1.3	95.8%	95.8%	95.8%
4/28/2022	3.6	1.2	1.0	95.8%	95.8%	95.8%
4/29/2022	0.5	5.5	1.7	95.8%	95.8%	95.8%
4/30/2022	0.2	1.1	0.2	95.8%	95.8%	95.8%
5/1/2022	0.1	1.0	0.8	95.8%	95.8%	95.8%
5/2/2022	0.3	1.4	2.9	95.8%	95.8%	91.7%
5/3/2022	0.1	3.1	0.4	95.8%	95.8%	95.8%
5/4/2022	0.1	0.4	0.1	95.8%	95.8%	95.8%
5/5/2022	0.1	1.1	0.2	95.8%	95.8%	95.8%
5/6/2022	0.1	1.3	0.2	95.8%	95.8%	95.8%
5/7/2022	0.1	0.5	0.5	95.8%	95.8%	95.8%
5/8/2022	0.1	0.3	0.2	95.8%	95.8%	95.8%
5/9/2022	0.2	0.3	0.2	95.8%	95.8%	95.8%
5/10/2022	0.2	1.4	1.0	95.8%	95.8%	95.8%
5/11/2022	2.3	1.6	1.0	95.8%	95.8%	95.8%
5/12/2022	1.6	1.1	0.3	95.8%	95.8%	95.8%
5/13/2022	0.1	1.4	0.8	95.8%	95.8%	95.8%
5/14/2022	1.0	3.2	1.7	95.8%	95.8%	91.7%
5/15/2022	1.2	2.6	1.9	91.7%	95.8%	95.8%
5/16/2022	0.2	1.8	0.7	95.8%	95.8%	95.8%
5/17/2022	2.8	4.1	4.1	95.8%	91.7%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	**Kitamaat Village**	**Riverlodge**	**Whitesail**	**Kitamaat Village**	**Riverlodge**	**Whitesail**
5/18/2022	0.3	0.4	0.3	91.7%	95.8%	95.8%
5/19/2022	0.3	6.3	3.0	95.8%	95.8%	91.7%
5/20/2022	0.5	1.0	0.6	95.8%	95.8%	95.8%
5/21/2022	0.4	2.1	1.2	95.8%	95.8%	95.8%
5/22/2022	2.1	2.4	1.5	100.0%	95.8%	95.8%
5/23/2022	0.2	0.3	0.1	100.0%	95.8%	95.8%
5/24/2022	0.2	4.6	1.3	91.7%	95.8%	91.7%
5/25/2022	0.7	1.5	0.6	95.8%	95.8%	91.7%
5/26/2022	0.7	5.0	1.8	95.8%	95.8%	95.8%
5/27/2022	0.6	1.6	0.8	95.8%	95.8%	95.8%
5/28/2022	0.2	1.6	0.6	95.8%	95.8%	95.8%
5/29/2022	0.2	0.3	0.1	95.8%	95.8%	95.8%
5/30/2022	0.9	0.5	0.3	95.8%	95.8%	95.8%
5/31/2022	1.8	0.9	0.6	95.8%	95.8%	95.8%
6/1/2022	0.8	1.0	0.2	95.8%	95.8%	95.8%
6/2/2022	0.4	0.3	0.3	95.8%	95.8%	95.8%
6/3/2022	0.2	0.3	0.1	95.8%	95.8%	79.2%
6/4/2022	1.1	5.3	4.9	95.8%	95.8%	95.8%
6/5/2022	0.2	0.3	0.1	95.8%	95.8%	95.8%
6/6/2022	0.3	0.7	0.6	95.8%	95.8%	95.8%
6/7/2022	0.4	3.5	3.7	95.8%	95.8%	95.8%
6/8/2022	0.3	1.4	1.0	95.8%	95.8%	95.8%
6/9/2022	0.3	0.7	0.3	95.8%	91.7%	95.8%
6/10/2022	0.5	0.5	0.4	79.2%	95.8%	95.8%
6/11/2022	0.3	0.3	0.2	95.8%	95.8%	91.7%
6/12/2022	0.3	0.3	0.2	95.8%	95.8%	95.8%
6/13/2022	0.5	0.3	0.2	87.5%	95.8%	95.8%
6/14/2022	0.3	0.4	0.8	95.8%	95.8%	95.8%
6/15/2022	0.6	2.2	-	95.8%	95.8%	37.5%

	Daily 1-hr Max Value (ppb)			**Daily Completeness**		
Date	**Kitamaat Village**	**Riverlodge**	**Whitesail**	**Kitamaat Village**	**Riverlodge**	**Whitesail**
6/16/2022	0.3	2.1	-	95.8%	95.8%	33.3%
6/17/2022	3.2	2.7	0.9	95.8%	91.7%	95.8%
6/18/2022	0.4	0.4	0.4	95.8%	95.8%	95.8%
6/19/2022	0.3	0.4	0.2	95.8%	95.8%	95.8%
6/20/2022	0.4	0.3	0.2	95.8%	91.7%	95.8%
6/21/2022	0.4	1.1	0.5	95.8%	95.8%	95.8%
6/22/2022	0.4	0.8	0.3	91.7%	95.8%	79.2%
6/23/2022	0.1	4.9	2.2	95.8%	95.8%	95.8%
6/24/2022	0.9	2.3	2.8	95.8%	83.3%	95.8%
6/25/2022	0.4	0.6	0.7	95.8%	95.8%	95.8%
6/26/2022	0.7	0.7	1.2	95.8%	95.8%	95.8%
6/27/2022	0.5	0.5	1.1	95.8%	95.8%	95.8%
6/28/2022	0.5	0.4	0.8	95.8%	95.8%	95.8%
6/29/2022	0.2	0.2	0.4	95.8%	95.8%	95.8%
6/30/2022	1.5	1.1	1.2	95.8%	91.7%	91.7%
7/1/2022	0.6	15.5	2.7	95.8%	95.8%	95.8%
7/2/2022	0.5	0.9	1.0	95.8%	91.7%	95.8%
7/3/2022	1.1	1.2	1.3	91.7%	95.8%	95.8%
7/4/2022	1.0	3.4	3.3	95.8%	95.8%	91.7%
7/5/2022	0.5	0.4	0.4	95.8%	95.8%	95.8%
7/6/2022	0.4	1.4	1.5	95.8%	95.8%	91.7%
7/7/2022	0.3	0.2	0.3	95.8%	95.8%	95.8%
7/8/2022	0.1	0.2	0.3	95.8%	95.8%	95.8%
7/9/2022	0.5	0.2	0.3	95.8%	95.8%	95.8%
7/10/2022	0.2	0.3	0.3	95.8%	95.8%	75.0%
7/11/2022	0.2	0.3	-	95.8%	95.8%	20.8%
7/12/2022	0.1	0.4	-	95.8%	95.8%	45.8%
7/13/2022	0.1	0.4	0.2	95.8%	95.8%	95.8%
7/14/2022	4.6	1.3	1.1	91.7%	91.7%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
7/15/2022	0.6	2.4	1.7	95.8%	95.8%	91.7%
7/16/2022	0.2	5.5	2.4	95.8%	95.8%	95.8%
7/17/2022	0.3	0.9	3.1	95.8%	95.8%	95.8%
7/18/2022	0.2	0.3	0.2	95.8%	95.8%	95.8%
7/19/2022	0.2	0.3	0.3	95.8%	95.8%	91.7%
7/20/2022	1.3	2.4	1.3	95.8%	95.8%	95.8%
7/21/2022	0.2	0.3	0.3	95.8%	95.8%	95.8%
7/22/2022	0.2	0.4	0.2	95.8%	95.8%	95.8%
7/23/2022	0.2	0.3	0.3	95.8%	95.8%	95.8%
7/24/2022	0.3	0.3	0.2	95.8%	95.8%	95.8%
7/25/2022	1.2	2.2	2.1	95.8%	91.7%	95.8%
7/26/2022	0.8	0.5	4.1	91.7%	95.8%	95.8%
7/27/2022	0.9	0.8	0.8	95.8%	95.8%	91.7%
7/28/2022	1.2	1.6	1.1	95.8%	95.8%	95.8%
7/29/2022	0.6	1.4	1.3	95.8%	95.8%	95.8%
7/30/2022	1.2	1.1	1.4	95.8%	95.8%	95.8%
7/31/2022	0.2	0.2	-	95.8%	95.8%	4.2%
8/1/2022	0.2	0.4	-	95.8%	95.8%	45.8%
8/2/2022	0.2	0.4	0.3	95.8%	95.8%	95.8%
8/3/2022	0.2	0.4	0.2	95.8%	95.8%	79.2%
8/4/2022	0.1	0.4	0.2	95.8%	95.8%	95.8%
8/5/2022	6.4	2.3	2.4	95.8%	95.8%	95.8%
8/6/2022	0.1	0.5	0.2	95.8%	95.8%	95.8%
8/7/2022	0.1	0.5	0.6	95.8%	95.8%	100.0%
8/8/2022	1.3	0.3	0.8	83.3%	95.8%	95.8%
8/9/2022	1.1	4.3	3.1	95.8%	95.8%	95.8%
8/10/2022	1.1	2.7	2.0	95.8%	95.8%	95.8%
8/11/2022	0.2	0.4	0.3	95.8%	95.8%	95.8%
8/12/2022	30.3	8.4	5.0	95.8%	95.8%	91.7%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
8/13/2022	0.1	0.3	0.2	95.8%	95.8%	95.8%
8/14/2022	0.4	9.5	5.2	95.8%	95.8%	95.8%
8/15/2022	0.2	0.7	0.3	95.8%	95.8%	95.8%
8/16/2022	0.2	1.0	2.5	95.8%	95.8%	95.8%
8/17/2022	1.3	1.3	1.1	95.8%	79.2%	95.8%
8/18/2022	1.4	1.8	2.0	91.7%	95.8%	95.8%
8/19/2022	2.2	0.9	1.1	95.8%	91.7%	83.3%
8/20/2022	1.7	2.2	1.7	95.8%	95.8%	95.8%
8/21/2022	1.3	1.4	1.5	95.8%	95.8%	95.8%
8/22/2022	0.3	0.4	0.3	95.8%	95.8%	95.8%
8/23/2022	16.5	4.8	3.1	95.8%	95.8%	95.8%
8/24/2022	2.3	1.8	2.6	95.8%	95.8%	95.8%
8/25/2022	0.3	0.3	0.4	95.8%	95.8%	95.8%
8/26/2022	0.3	0.3	0.3	95.8%	95.8%	95.8%
8/27/2022	0.3	0.7	0.3	95.8%	95.8%	95.8%
8/28/2022	0.3	0.4	0.8	95.8%	95.8%	95.8%
8/29/2022	0.3	0.4	0.4	95.8%	95.8%	95.8%
8/30/2022	0.3	0.4	0.4	95.8%	95.8%	95.8%
8/31/2022	0.3	1.0	0.7	95.8%	95.8%	95.8%
9/1/2022	1.4	1.4	1.5	95.8%	95.8%	95.8%
9/2/2022	0.1	0.1	0.3	95.8%	95.8%	91.7%
9/3/2022	3.8	1.0	0.9	95.8%	95.8%	95.8%
9/4/2022	0.2	0.6	0.4	95.8%	95.8%	95.8%
9/5/2022	0.2	0.2	0.3	95.8%	95.8%	95.8%
9/6/2022	0.3	1.2	0.4	95.8%	95.8%	91.7%
9/7/2022	0.2	0.9	0.3	95.8%	95.8%	95.8%
9/8/2022	4.4	2.0	3.4	95.8%	95.8%	95.8%
9/9/2022	2.2	0.1	0.6	95.8%	91.7%	95.8%
9/10/2022	1.3	0.2	0.3	91.7%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
9/11/2022	1.4	2.6	2.6	95.8%	95.8%	91.7%
9/12/2022	2.3	4.1	1.5	95.8%	95.8%	95.8%
9/13/2022	1.2	4.0	3.9	95.8%	95.8%	95.8%
9/14/2022	-	1.5	1.2	70.8%	87.5%	87.5%
9/15/2022	0.3	0.4	0.3	83.3%	95.8%	87.5%
9/16/2022	0.5	0.4	0.4	95.8%	95.8%	95.8%
9/17/2022	1.9	0.3	0.3	95.8%	95.8%	95.8%
9/18/2022	2.9	0.3	0.3	95.8%	95.8%	95.8%
9/19/2022	0.9	0.3	0.2	95.8%	95.8%	95.8%
9/20/2022	4.1	0.4	0.3	95.8%	95.8%	95.8%
9/21/2022	0.8	1.6	1.1	95.8%	95.8%	95.8%
9/22/2022	0.2	0.7	0.4	95.8%	95.8%	95.8%
9/23/2022	0.2	0.4	0.3	95.8%	95.8%	91.7%
9/24/2022	0.4	0.3	0.2	95.8%	95.8%	95.8%
9/25/2022	0.4	0.3	0.3	95.8%	91.7%	95.8%
9/26/2022	1.8	16.2	8.4	95.8%	95.8%	95.8%
9/27/2022	19.7	9.9	11.5	95.8%	95.8%	95.8%
9/28/2022	0.8	2.1	1.3	95.8%	95.8%	95.8%
9/29/2022	0.2	0.3	0.4	95.8%	91.7%	95.8%
9/30/2022	0.2	3.6	0.7	95.8%	95.8%	91.7%
10/1/2022	0.3	0.4	0.4	95.8%	95.8%	95.8%
10/2/2022	1.1	0.4	0.3	95.8%	91.7%	95.8%
10/3/2022	0.1	0.4	0.3	91.7%	95.8%	95.8%
10/4/2022	0.7	1.3	1.4	95.8%	95.8%	91.7%
10/5/2022	2.8	11.4	4.8	95.8%	95.8%	95.8%
10/6/2022	0.1	0.2	0.4	95.8%	95.8%	95.8%
10/7/2022	0.7	0.3	0.9	95.8%	95.8%	95.8%
10/8/2022	0.3	0.2	0.5	95.8%	95.8%	95.8%
10/9/2022	9.8	4.0	4.9	95.8%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
10/10/2022	0.2	6.1	0.4	95.8%	95.8%	95.8%
10/11/2022	0.1	0.2	0.3	95.8%	95.8%	95.8%
10/12/2022	0.4	0.2	0.4	95.8%	95.8%	95.8%
10/13/2022	0.1	0.4	0.8	95.8%	95.8%	95.8%
10/14/2022	0.9	5.0	5.7	95.8%	95.8%	95.8%
10/15/2022	1.0	0.3	1.0	95.8%	95.8%	95.8%
10/16/2022	0.3	0.2	0.4	95.8%	95.8%	95.8%
10/17/2022	0.2	0.3	0.4	95.8%	95.8%	95.8%
10/18/2022	0.2	1.8	0.7	95.8%	95.8%	95.8%
10/19/2022	0.2	9.2	0.5	95.8%	95.8%	95.8%
10/20/2022	0.3	1.7	0.8	95.8%	95.8%	95.8%
10/21/2022	0.4	1.5	0.4	95.8%	95.8%	95.8%
10/22/2022	3.1	4.3	6.6	95.8%	95.8%	95.8%
10/23/2022	0.7	1.9	2.4	95.8%	95.8%	95.8%
10/24/2022	0.3	7.6	0.5	95.8%	95.8%	95.8%
10/25/2022	4.1	5.6	0.7	95.8%	91.7%	95.8%
10/26/2022	0.2	1.9	0.3	91.7%	95.8%	95.8%
10/27/2022	1.4	0.7	1.0	79.2%	95.8%	91.7%
10/28/2022	0.2	2.5	2.7	95.8%	95.8%	95.8%
10/29/2022	0.3	1.7	1.0	95.8%	95.8%	95.8%
10/30/2022	0.3	4.5	1.2	95.8%	95.8%	95.8%
10/31/2022	0.3	4.8	0.9	83.3%	95.8%	95.8%
11/1/2022	0.3	0.4	-	95.8%	95.8%	70.8%
11/2/2022	0.5	0.4	-	95.8%	95.8%	41.7%
11/3/2022	0.8	0.3	0.6	95.8%	95.8%	75.0%
11/4/2022	0.2	-	0.3	95.8%	70.8%	95.8%
11/5/2022	0.9	8.8	1.6	95.8%	95.8%	95.8%
11/6/2022	0.2	0.2	0.4	95.8%	95.8%	95.8%
11/7/2022	0.3	0.4	0.6	95.8%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
11/8/2022	0.4	0.4	0.6	95.8%	95.8%	95.8%
11/9/2022	0.2	0.2	0.5	95.8%	95.8%	95.8%
11/10/2022	0.2	0.2	0.5	95.8%	95.8%	95.8%
11/11/2022	0.2	0.2	0.4	95.8%	95.8%	95.8%
11/12/2022	0.2	0.2	0.4	95.8%	95.8%	95.8%
11/13/2022	1.4	0.6	1.1	95.8%	95.8%	95.8%
11/14/2022	0.2	0.2	0.4	95.8%	95.8%	95.8%
11/15/2022	0.3	0.3	0.4	95.8%	95.8%	95.8%
11/16/2022	1.9	0.4	0.5	83.3%	95.8%	95.8%
11/17/2022	0.3	0.4	0.8	95.8%	91.7%	95.8%
11/18/2022	0.4	0.2	0.4	91.7%	95.8%	91.7%
11/19/2022	0.4	0.3	0.5	95.8%	95.8%	95.8%
11/20/2022	0.4	0.4	0.7	95.8%	95.8%	95.8%
11/21/2022	0.3	0.4	1.0	95.8%	95.8%	95.8%
11/22/2022	0.4	0.2	0.8	95.8%	95.8%	95.8%
11/23/2022	0.3	0.5	0.5	95.8%	95.8%	95.8%
11/24/2022	0.2	0.5	0.4	95.8%	95.8%	95.8%
11/25/2022	0.2	0.6	0.4	95.8%	95.8%	91.7%
11/26/2022	0.1	1.3	0.5	95.8%	95.8%	95.8%
11/27/2022	0.2	1.7	0.4	95.8%	95.8%	95.8%
11/28/2022	0.2	0.3	0.4	95.8%	95.8%	95.8%
11/29/2022	0.3	0.4	0.5	95.8%	95.8%	95.8%
11/30/2022	0.2	0.3	0.4	95.8%	95.8%	95.8%
12/1/2022	0.2	0.1	0.5	95.8%	95.8%	95.8%
12/2/2022	0.3	0.2	0.5	95.8%	95.8%	95.8%
12/3/2022	0.2	0.2	0.5	95.8%	95.8%	95.8%
12/4/2022	0.5	0.2	0.5	95.8%	95.8%	95.8%
12/5/2022	0.2	0.2	0.6	95.8%	95.8%	95.8%
12/6/2022	0.6	0.9	0.9	95.8%	95.8%	95.8%

	Daily 1-hr Max Value (ppb)			Daily Completeness		
Date	Kitamaat Village	Riverlodge	Whitesail	Kitamaat Village	Riverlodge	Whitesail
12/7/2022	0.3	0.4	0.5	95.8%	95.8%	95.8%
12/8/2022	0.4	0.8	2.1	95.8%	95.8%	95.8%
12/9/2022	0.3	0.5	0.5	95.8%	95.8%	95.8%
12/10/2022	0.2	0.4	0.4	95.8%	91.7%	95.8%
12/11/2022	0.3	0.5	0.4	91.7%	95.8%	91.7%
12/12/2022	0.1	0.4	0.6	95.8%	95.8%	87.5%
12/13/2022	0.4	0.7	1.1	95.8%	91.7%	95.8%
12/14/2022	0.1	0.4	0.5	95.8%	95.8%	95.8%
12/15/2022	0.2	0.3	0.5	91.7%	95.8%	95.8%
12/16/2022	0.8	0.7	1.4	95.8%	95.8%	95.8%
12/17/2022	0.5	0.5	0.6	95.8%	95.8%	95.8%
12/18/2022	0.2	0.2	0.5	95.8%	95.8%	95.8%
12/19/2022	0.1	0.3	0.5	95.8%	91.7%	95.8%
12/20/2022	0.5	0.3	0.6	95.8%	95.8%	95.8%
12/21/2022	1.2	0.3	0.6	95.8%	95.8%	95.8%
12/22/2022	0.6	0.2	0.6	95.8%	95.8%	95.8%
12/23/2022	0.3	0.2	0.6	95.8%	95.8%	95.8%
12/24/2022	0.3	0.2	0.6	95.8%	95.8%	95.8%
12/25/2022	0.3	0.3	0.5	95.8%	95.8%	95.8%
12/26/2022	0.2	0.3	0.6	95.8%	95.8%	95.8%
12/27/2022	0.3	0.4	0.4	95.8%	95.8%	95.8%
12/28/2022	0.3	0.4	0.4	95.8%	95.8%	95.8%
12/29/2022	0.3	0.4	0.4	95.8%	95.8%	95.8%
12/30/2022	0.2	0.3	0.4	95.8%	95.8%	95.8%
12/31/2022	1.1	0.4	2.6	95.8%	95.8%	95.8%

Appendix C: Technical Memo W11 – Aquatic Ecosystems Actions and Analyses

The following pages contain **B.C. Works SO_2 EEM Program Technical Memo W11**, in PDF format.

RioTinto

B.C. Works SO_2 EEM Program – Technical Memo W11

Aquatic Ecosystems Actions and Analyses

April 2023

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1 Introduction

This Technical Memo provides additional information on the data and analyses in support of the 2022 requirements for the Aquatic Ecosystems component of the B.C. Works' Sulphur Dioxide Environmental Effects Monitoring (EEM) Program (SO_2 EEM Phase III Plan, ESSA et al. 2023). These data and analyses thus provide the foundation for Section 3.4 in the SO_2 EEM Program 2022 Annual Report.

This Technical Memo applies methods and approaches that have already been described in detail in other relevant documents. Most of the methods follow those employed in the SO_2 Technical Assessment Report (STAR) (ESSA et al. 2013), the Kitimat Airshed Assessment (KAA) (ESSA et al. 2014a) and the 2019 EEM Comprehensive Review (ESSA et al. 2020a). Full details on the collection, processing and analysis of the water chemistry samples are reported in technical reports prepared by Limnotek for each year's sampling (Perrin et al. 2013; Perrin and Bennett 2015; Limnotek 2016; Bennett and Perrin 2017, 2018; Limnotek 2019, 2020, 2021, 2022, 2023). Wherever possible, the description of methods in this Technical Memo refers to these reports instead of repeating information that is already well-documented elsewhere.

The following four documents (as described above) are listed here because they are referenced throughout this Technical Memo, often without their full citation:

- The STAR (ESSA et al. 2013)
- The KAA (ESSA et al. 2014a)
- 2019 SO_2 EEM Comprehensive Review (ESSA et al. 2020a)
- The SO_2 EEM Phase III Plan (ESSA et al. 2023)

2 Methods

2.1 Water Chemistry Sampling

EEM Lakes

The SO_2 Phase III EEM Program sampling plan includes eleven lakes: seven sensitive lakes, one less sensitive lake, and three control lakes (ESSA et al. 2023). The three control lakes (NC184, NC194 and DCAS14A) are all located outside of the zone of sulphur deposition from B.C. Works, and have pre-KMP baseline data for 2013 from sampling as part of the KAA (ESSA et al. 2014a). The five lakes that were unable to be sampled in 2020 (due to COVID-related constraints on helicopter flights) were sampled again in 2021 and 2022 as per previous years.

LAK027 was added for one-time sampling in 2021, as agreed to by ENV and Rio Tinto in May 2021. The intent was to resample one of the STAR lakes located relatively close to the smelter to check the validity of the conclusions made in the STAR, based on sampling completed in 2012, nine years prior to 2021. LAK027 was chosen because it was the only candidate that was moderately sensitive, whereas all the other lakes in the southern portion of the Kitimat Valley were determined to be insensitive based on the sampling during the STAR (except for LAK028, which was included in the SO_2 EEM Program because of its sensitivity). LAK027 was sampled again in 2022, as per the recommendation in the SO_2 EEM Program 2021 EEM Annual Report:

> *We recommend sampling LAK027 again in 2022. The widely-observed storm-driven dilution event negated the ability of this year's sampling to provide a meaningful comparison against the initial STAR data as intended.*

In 2022, Limnotek sampled the eleven EEM lakes plus LAK027 according to the 2022 Aquatics Work Plan. The sampling methodology is described in detail in Limnotek (2023). Table 2-1 summarizes the sampling history of these 12 lakes. Figure 2-1 shows a map of the lakes sampled in 2022.

Table 2-1. Summary of sampling sites within the SO_2 EEM Phase III Program. The rationale for lakes included in the SO_2 EEM Phase III Program is described in ESSA et al. 2023.

Sample Site	Year of Sampling											
	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	
	STAR	EEM	EEM	EEM	EEM	EEM	EEM	EEM	EEM	EEM	EEM	
LAK006	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	EEM sensitive lake, included in Phase III
LAK012	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	EEM sensitive lake, included in Phase III
LAK022	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	EEM sensitive lake only accessible by helicopter, included in Phase III.
LAK023	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	EEM sensitive lake, included in Phase III
LAK028	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	EEM sensitive lake, included in Phase III
LAK042	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	EEM sensitive lake, included in Phase III
LAK044	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	EEM sensitive lake, included in Phase III
LAK016	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	EEM less sensitive lake, included in Phase III.
LAK027	✓									✓	✓	Resampling of STAR lake at southern end of valley.
NC184		✓†		✓	✓	✓	✓	✓		✓	✓	EEM control lakes added to EEM in 2015. Only accessible by helicopter, included in Phase III.
NC194		✓†		✓	✓	✓	✓	✓		✓	✓	
DCAS14A		✓†		✓	✓	✓	✓	✓		✓	✓	

† Sampled as part of the Kitimat Airshed Assessment (ESSA et al. 2014a).

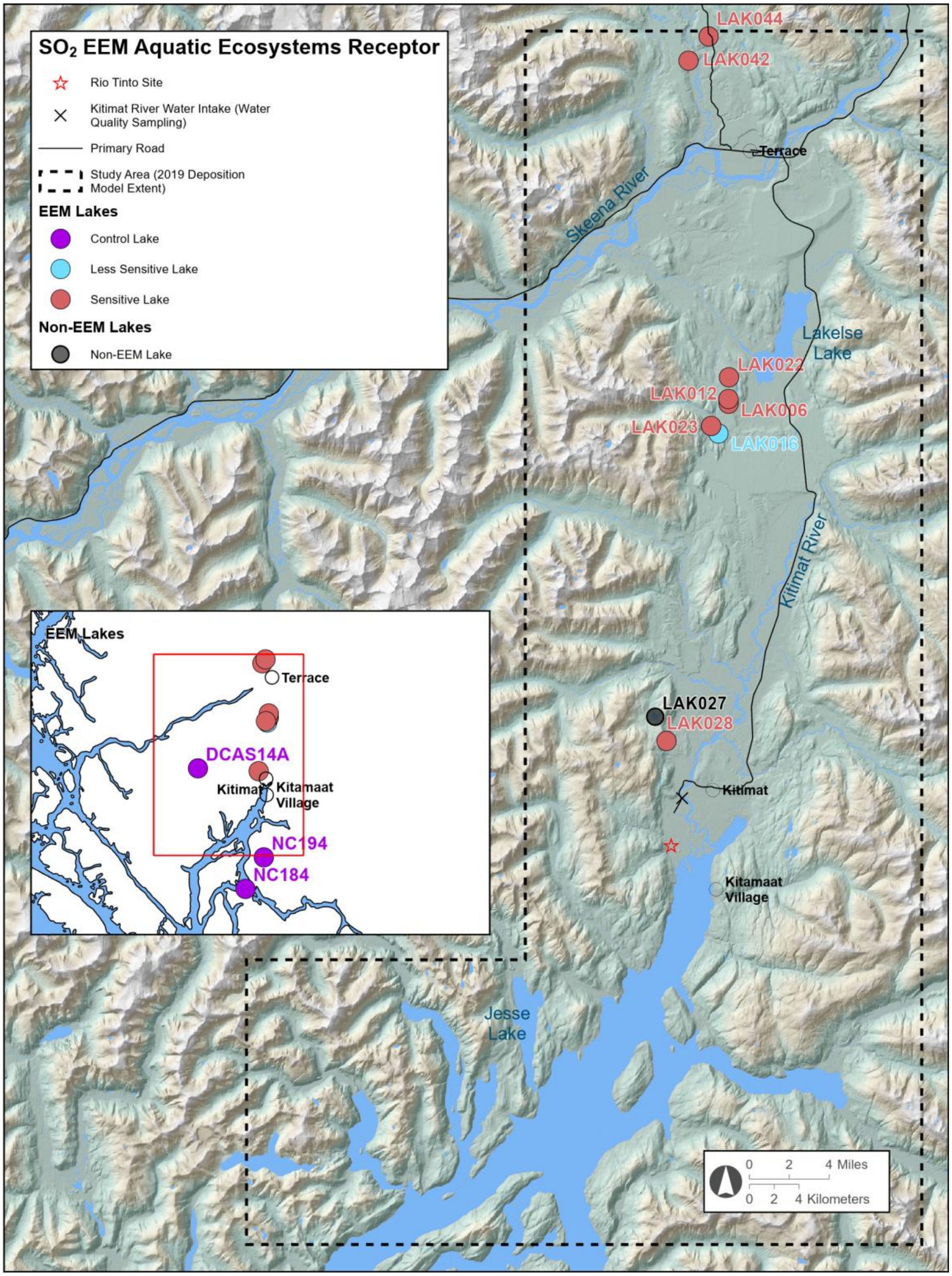

Figure 2-1. Location of the lakes in the EEM Program, including seven sensitive lakes (red), one less sensitive lake (blue) and three control lakes (purple). LAK027 was resampled in 2022 to compare with the STAR results.

Sampling frequency

Sampling frequency remained the same as last year:

- The sensitive lakes LAK006, LAK012, LAK023, LAK028, LAK042, and LAK044 on four occasions within the fall index period
- Sensitive lake LAK022, less sensitive lake LAK016, and the three control lakes were each sampled once during the Fall index period (as per previous years)
- LAK027 (not part of current SO_2 EEM Program) was sampled once
- LAK006 and LAK028 had five additional samples with full chemistry analysis taken over June through early September, to assess seasonal variability in lake chemistry

Continuous monitoring

Two lakes (LAK006, LAK028) had continuous monitoring of surface water pH, temperature and lake levels. LAK028 also had a similar instrument installed at depth. This work was planned, implemented and documented by Limnotek. The methods and results for 2022 are reported in Limnotek (2023).

Water chemistry data

There were no differences in the water chemistry analyses completed from the 2022 sampling compared to previous years. Continuing from 2020, analyses of Gran ANC are now *only* performed by the BASL facility (University of Alberta).

Al_{im} was not measured during this year's sampling season. In the SO_2 EEM Program 2020 Annual Report, we recommended discontinuing the measurement of Al_{im} going forward. These changes were not applied in the 2021 season because the field planning and purchasing was already in place for that year. This recommendation was therefore not implemented until 2022.

Integrating laboratory measurements of pH and Gran ANC from Trent and BASL laboratories

The planned transition of laboratory analysis of pH and Gran ANC from Trent University to the BASL laboratory at the University of Alberta was completed in 2020. In 2019, duplicate samples were sent to both laboratories to facilitate cross-laboratory comparisons (see Limnotek 2020).

To facilitate analyses over the entire period of record, we need an "integrated" data series for each of the two metrics. As in the SO_2 EEM Program 2020 Annual Report, we constructed an integrated time series by imputing Trent values for pH and Gran ANC for 2021 based on the regression of Trent values vs. BASL values from the 2019 data. This method was recommended and developed by Dr. Carl Schwarz (retired professor of statistics from Simon Fraser University) and is described in detail in the SO_2 EEM Program 2020 Annual Report.

2.2 Empirical Changes in Water Chemistry

The methods applied for examining empirical changes are the same as described in the last several years (except for the analysis of inorganic aluminum, which has been discontinued as it does not contribute novel information about lake chemistry).

2.3 Statistical Analyses of Changes in Water Chemistry

The 2019 Comprehensive Review performed an extensive series of statistical analyses of changes in water chemistry and concluded that the results from the Bayesian statistical analyses provided the greatest ability to assess the level of support for different hypotheses of chemical change. The 2019 Comprehensive Review further recommended that these analyses be re-run on an annual basis to assess status and detect any anomalous patterns. This annual report represents the fourth iteration of re-running those analyses with more recent monitoring data. These methods are described in detail in Appendix F of the 2019 Comprehensive Review (ESSA et al. 2020b) (see Bayesian Method 1 especially). The key metrics of interest are the differences in lake chemistry between the post-KMP average for the last three years (2020-2022) and the pre-KMP baseline (2012 for the sensitive and less sensitive lakes; 2013 for the control lakes). For the lakes that were not sampled in 2020, the post-KMP period used to compute average lake chemistry is still 2020-2022 and therefore only based on 2 years of data (2021 and 2022). Appendix 3 includes sensitivity analyses that examine the effect of using an alternative baseline representing the transition period as operations at the old smelter were wound down (2012-2014).

The results of the Bayesian statistical analyses are expressed in terms of: a) the % belief that the post-KMP values have exceeded the *level of protection* thresholds, and b) the % belief that the changes from the baseline period to the post-KMP period have exceeded the *change limit* thresholds. As applied in the 2019 Comprehensive Review, the % belief values are classified as low (< 20%), moderate (20% to <80%), or high (≥ 80%). This classification is done both for ease of interpretation, and to integrate the analyses for the two-threshold structure of the CBANC KPI and informative indicators into a single assessment for each indicator for each lake. As described in the Phase III Plan, the acidification indicators (CBANC, pH, Gran ANC and BCS) are only considered to be in exceedance if **both** thresholds are exceeded (i.e., the *level of protection* and the *change limit* thresholds). The single, integrated assessment of each of those indicators is determined according to the rules:

1. If the result for **either** threshold is **"low"**, then the overall assessment is **"low"**
2. The results for **both** thresholds must be **"high"** for an overall assessment of **"high"**
3. If result for **either** threshold is **"moderate"** and the results for the other threshold are "moderate" or "high", then the overall assessment is **"moderate"**.

As described in the SO_2 EEM Program Phase III Plan, the two-threshold structure avoids creating false positives by simultaneously considering the two dimensions of importance to aquatic organisms – the absolute level and the relative change in the water chemistry metrics used as acidification indicators.

Appendix 4 includes results of sensitivity analyses for the uncertainty associated with the imputation procedure associated with developing integrated data series for pH and Gran ANC following the transition of laboratories (details in Section 2.1).

We also evaluated differential trends between the sensitive lakes and the control lakes using the before-after control-impact (BACI) analysis methods described in the 2019 Comprehensive Review (i.e., Method 3: BACI using mean values). Using this method, we evaluated the sensitive lakes individually and as a group, for both CBANC (as an informative method, as the KPI is not based on this statistical approach) and the pH informative indicator.

2.4 Environmental Data

This section includes supplementary environmental observations or data utilized in the interpretation of the water chemistry results (see Section 4.3).

Providing the precipitation context for 2022 was more challenging this year than in previous years due to extensive missing data from climate stations. In past years, we have characterized precipitation patterns relevant to the interpretation of water chemistry sampling results by using the precipitation data for July to October from the Kitimat 2 and Terrace PCC climate stations. Those were the two stations in the valley with the most complete data as well as representing two different regions with the study area. But in 2022 (at the time of accessing the climate data[1]), the Terrace PCC station only has precipitation observations for 36% of the days within the July-October period, and the Kitimat 2 station only has precipitation observations for 22% of the period, including only two observations in September and zero observations in October. The extent of missing data rendered any comparisons with the precipitation data shown in previous years completely meaningless.

Instead, we are using the Terrace A station as an indicator of precipitation levels in the study area because it had 98% complete observation for July-October 2022. We have not used the Terrace A in previous years because it generally had a less complete record than the Terrace PCC station. For 2020, Terrace A has zero observations for July through the first few days of August, therefore we are using a comparison period of August 5 to October 31. We are excluding 2021 because the data coverage was still only 34% in this revised period, whereas it was 100%, 99%, and 98% for 2019, 2020, and 2022, respectively. In this approach, we have an apples-to-apples comparison of 2022 precipitation to at least 2019 and 2020, which were previously identified as being a significantly dry year and a significantly wet year. Having data only for Terrace and no appropriate data for Kitimat is a gap, albeit unavoidable.

Precipitation data from the Terrace A climate station shows that 2022 had similar total precipitation within the comparison period (August 5 to October 31) as 2019, which was a notably dry year (Table 2-2). However, the precipitation was significantly concentrated in October (~60%), making October notably wetter than either 2019 (dry year) or 2020 (wet year). By contrast, the total rainfall in September 2022 was 71 mm, which is 47% less than the 135 mm in 2020 and 28% less than the 99 mm in 2019.

During the two weeks prior to the annual sampling date on October 2, 2022 (i.e., the date in which all lakes are sampled), the Terrace A station measured only 21 mm of rainfall, compared to 118 mm and 67 mm in the 2-week periods before the 2020 and 2019 annual sampling dates, respectively. For reference, as reported in the SO_2 EEM Program 2021 Annual Report, the Kitimat 2 station measured 307 mm of rainfall and the Terrace PCC station measured 184 mm in the two weeks prior to the annual sampling date[2].

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[1] Source: Data accessed via Environment Canada's *Historical Climate DataClimate data extraction tool* web portal (https://climate-change.canada.ca/climate-data/#/http://climate.weather.gc.ca), Accessed: March 2023.

[2] Note that these are different stations than reported this year. Consistent station-to-station comparisons are not possible for 2021 versus 2022 for reasons discussed in the text.

Figure 2-2 shows that although the total summer-fall precipitation at the Terrace A station in 2022 was generally comparable to the dry year of 2019 (e.g., bottom row of Table 2-2), it was drier than 2019 when considering the period prior to lake sampling (first two rows of Table 2-2). The last of the lake chemistry samples were collected on October 20 and then 140 mm of rain (representing 74% of October rainfall and 44% of August-October rainfall) fell during October 23-31.

Table 2-2. Total Monthly Precipitation (mm) at Terrace A for 2019-2022.

	2019	2020	2021	2022
	Terrace A	Terrace A	Terrace A	Terrace A
August (5-31)	67.3	160.4	*Excluded due to excessive missing data*	60.6
September	99.4	142.8		71.0
October	138.6	134.8		189.9
Total	305.3	438.0	*n/a*	321.5

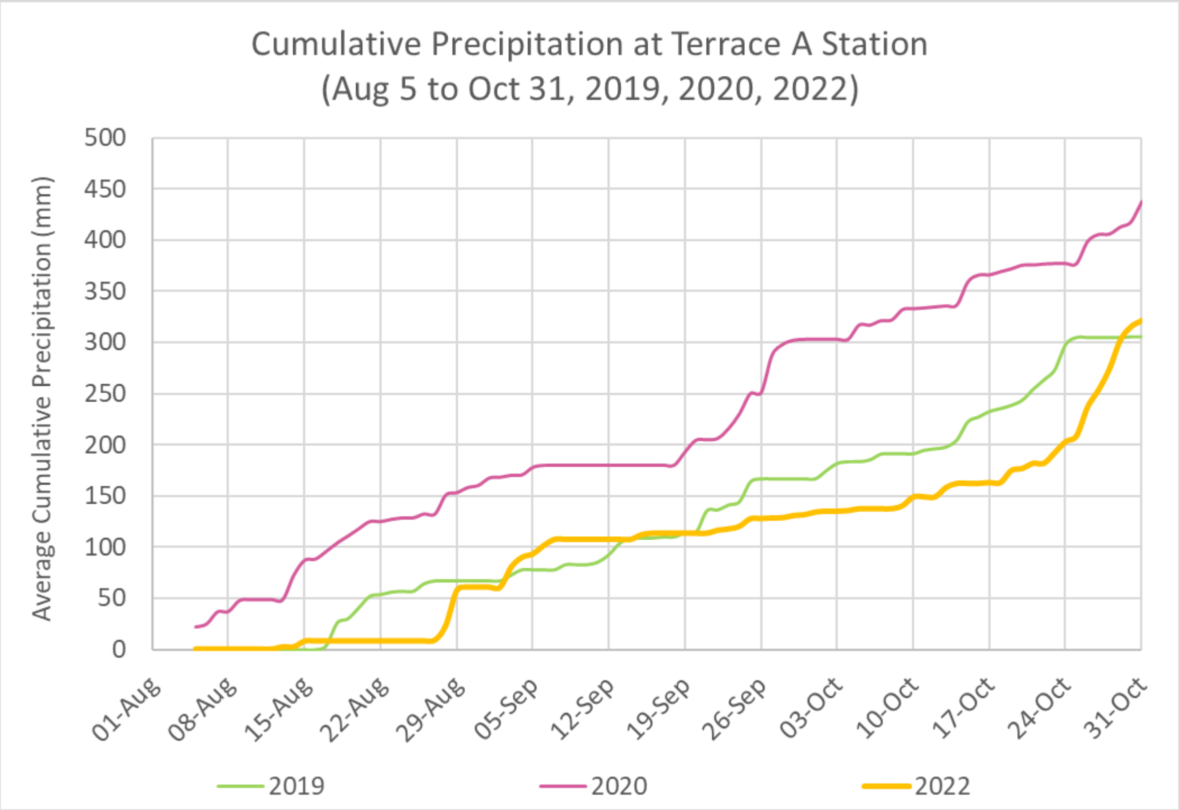

Figure 2-2. Cumulative precipitation at Terrace A station for August 5 to October 31 in 2019, 2020, and 2022.

2.5 Episodic Acidification

We reviewed the data record from the continuous pH monitors installed in LAK006 and LAK028 to identify any notable drops in pH. If any such changes were observed, we compared those results with the lake-level data to determine if they appeared to be correlated with high inflows to the lake.

2.6 Alignment of Evidentiary Framework with EEM Phase III Indicators

The “Simple Evidentiary Framework” developed in the 2019 Comprehensive Review and subsequently built into the SO_2 EEM Program Phase III Plan only considered post-KMP changes in pH and ANC[3] (relative to pre-KMP conditions), especially relative to the *change limit* thresholds, but did not consider the post-KMP state of either of those metrics with respect to the *level of protection* thresholds. The SO_2 EEM Program Phase III Plan made an important advance, moving to a two-threshold structure for the KPI and the pH and ANC informative indicators that consider both relative change and the absolute level of those indicators.

To be consistent with the SO_2 EEM Program Phase III Plan, we revised the Evidentiary Framework in the SO_2 EEM Program 2020 Annual Report by adding an assessment node associated with the *level of protection* threshold (Figure 2-3). The new node was inserted earlier in the logic sequence than the two nodes assessing the level of change. In the two-threshold structure for the KPI and informative indicators, neither of the thresholds takes precedence – an exceedance of the indicator requires that both thresholds are exceeded with a high percent belief. Therefore, there is no inherent sequence between evaluating the *change* limit and *level of protection* thresholds. However, in the Evidentiary Framework, there is an additional node that considers whether there has been any change in the indicator prior to assessing against the *change limit* threshold, which makes the framework more precautionary, so we believe it made more sense to have the *level of protection* node earlier in the sequence than the two change-based nodes.

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[3] Gran ANC in the 2019 Comprehensive Review; CBANC in the SO_2 EEM Program Phase III Plan (consistent with the revised KPI).

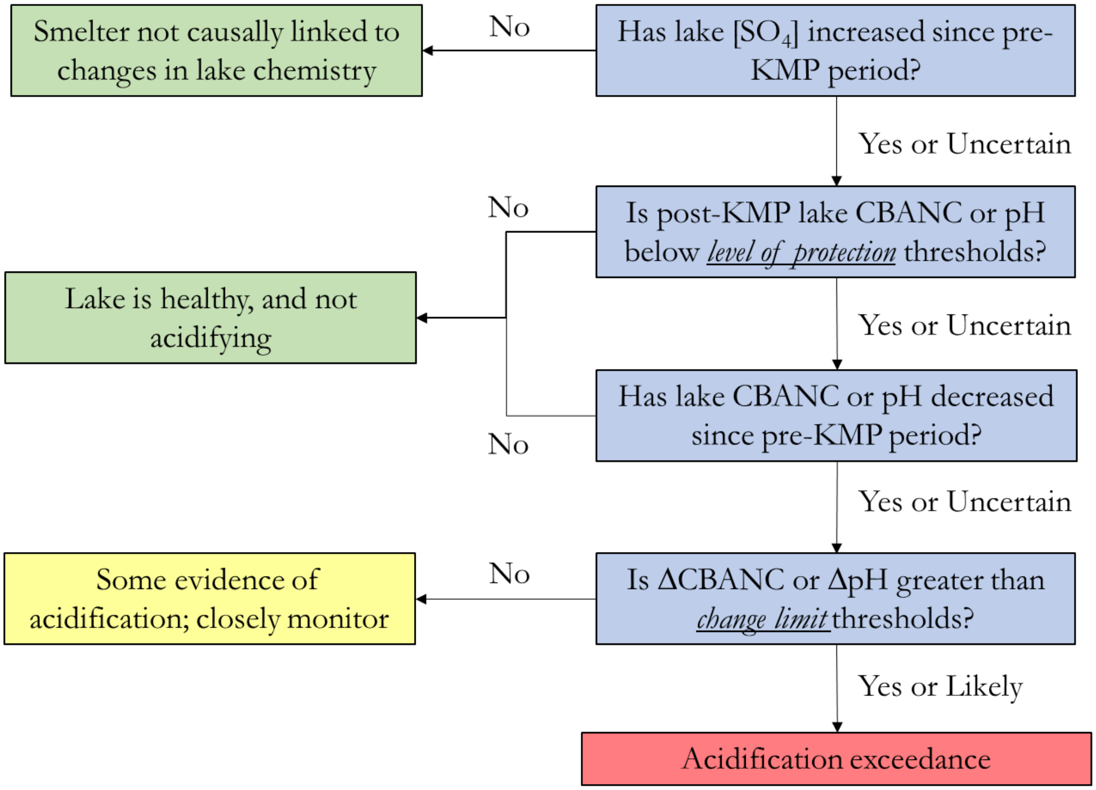


Figure 2-3. The Evidentiary Framework. The framework developed in the 2019 Comprehensive Review was revised in the SO_2 EEM Program 2020 Annual Report order to align with the two-threshold structure for the KPI and informative indicators in the SO_2 EEM Program Phase III Plan.

3 Results

3.1 Empirical Changes in Water Chemistry

Empirical changes in CBANC, Gran ANC, BCS, pH, [SO_4^{2-}], DOC, sum of base cations, chloride, and calcium are shown in Table 3-1. A map of the observed changes in [SO_4^{2-}], CBANC, and pH at the EEM lakes is shown in Figure 3-1. Changes are reported in terms of the difference between the post-KMP average (2020-2022) and the pre-KMP baseline (2012 for the sensitive and less sensitive lakes; 2013 for the control lakes). The sensitive EEM lakes and less sensitive EEM lakes are presented separately within each of the tables. The inter-annual changes presented in this report use the mean annual values whenever multiple within-season samples were acquired from a given lake in a given year.

Unlike the annual reports prior to the 2019 Comprehensive Review, the annual changes between individual years are no longer reported and analyzed. As already stated in previous years (e.g., ESSA 2018, Technical Memo W07), year-to-year changes should be interpreted cautiously:

> *"... 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… multiple years of observations are required to reliably detect changes in mean pH, Gran ANC and SO4; it is risky to draw conclusions based only on annual changes”.*

Furthermore, in the December 2018 workshop on the terms of reference for the SO_2 EEM Program Comprehensive Review, the ENV external acidification expert recommended that we stop reporting annual changes because inter-annual variability in lake chemistry is too variable to make any meaningful interpretation of the changes between two years.

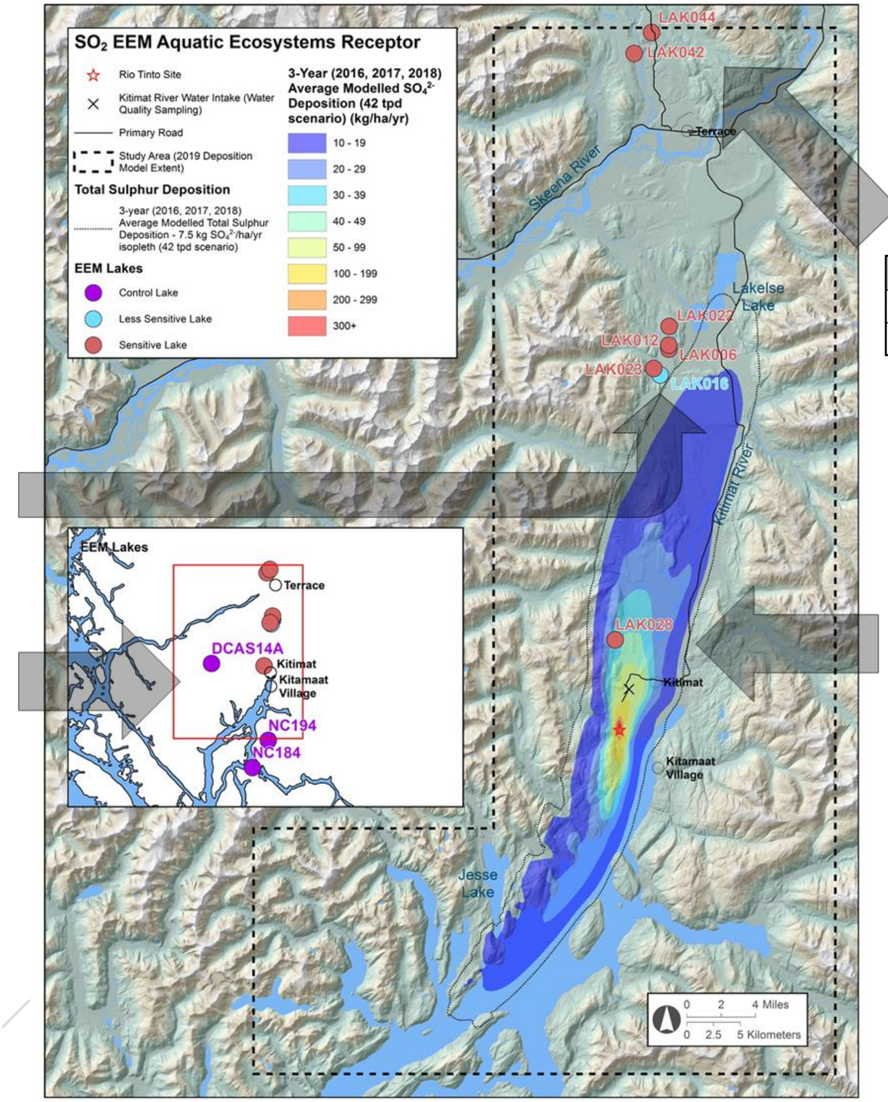
Table 3-1. Empirical changes in CBANC, Gran ANC, BCS, pH, SO_4^{2-}, DOC, base cations, chloride, calcium, and NO_3 for EEM lakes. These values represent the difference between the average of the post-KMP period (2020-2022) and the 2012 baseline. Numbers shown are the value in the later period minus the value in the earlier year. Increases are shaded in green; decreases are shaded in red. The Gran ANC and pH values are based on the “integrated” time series (i.e., values from the Trent University laboratory from 2012 to 2019 with the 2020, 2021, and 2022 values imputed from the values measured by the BASL laboratory (“integ”); see details in Section 2.1). Signs after each number show the direction of change in the reported values since the SO_2 EEM Program 2021 Annual Report (i.e., [+] = increase; [-] = decrease; [ ] = identical value).

SITE	CBANC (µeq/L)	Gran ANC (integ) (µeq/L)	BCS (µeq/L)	pH (integ)	SO4* (µeq/L)	DOC (mg/L)	∑ BC* (µeq/L)	Cl (µeq/L)	Ca* (µeq/L)
LAK006	20.2 [+]	11.6 [+]	14.2 [+]	0.2 [ ]	3.5 [-]	1.2 [+]	23.9 [+]	0.6 [-]	13.6 [+]
LAK012	4.1 [+]	11.3 [+]	-7.9 [+]	0.3 [ ]	9.0 [-]	2.4 [ ]	13.4 [+]	3.0 [-]	6.9 [+]
LAK022	4.1 [+]	-1.6 [-]	1.5 [ ]	-0.2 [-]	6.5 [-]	0.5 [ ]	10.8 [+]	0.3 [-]	5.7 [-]
LAK023	12.0 [-]	3.8 [+]	3.8 [+]	0.1 [ ]	-2.0 [-]	1.6 [-]	10.5 [+]	0.3 [-]	7.3 [-]
LAK028	-2.9 [+]	5.4 [+]	-17.9 [+]	0.0 [ ]	58.5 [-]	3.0 [+]	56.6 [+]	2.9 [-]	41.7 [-]
LAK042	17.7 [+]	18.5 [+]	10.6 [+]	0.2 [ ]	2.0 [-]	1.4 [-]	19.8 [+]	-0.5 [-]	11.2 [-]
LAK044	8.1 [+]	3.0 [ ]	7.0 [-]	0.2 [ ]	-2.1 [-]	0.2 [-]	6.2 [+]	0.5 [-]	1.9 [-]
Total ↑	**6**	**6**	**5**	**5**	**5**	**7**	**7**	**6**	**7**
Total ↓	**1**	**1**	**2**	**2**	**2**	**0**	**0**	**1**	**0**

LAK016	12.5 [+]	23.0 [+]	-1.5 [+]	0.0 [ ]	11.6 [ ]	2.8 [-]	25.0 [-]	1.4 [-]	16.3 [+]
Total ↑	**1**	**1**	**0**	**0**	**1**	**1**	**1**	**1**	**1**
Total ↓	**0**	**0**	**1**	**1**	**0**	**0**	**0**	**0**	**0**

DCAS14A	13.8 [-]	1.3 [-]	11.6 [-]	-0.3 [ ]	-3.8 [-]	0.5 [ ]	7.8 [-]	-2.6 [-]	3.5 [-]
NC184	-7.2 [-]	-1.2 [-]	-4.7 [-]	-0.3 [ ]	-1.7 [-]	-0.5 [+]	-9.0 [-]	-6.9 [-]	-4.7 [-]
NC194	0.3 [-]	-3.6 [-]	-1.2 [-]	-0.5 [-]	-1.6 [-]	0.3 [-]	-1.2 [-]	-2.1 [-]	-0.6 [-]
Total ↑	**2**	**1**	**1**	**0**	**0**	**2**	**1**	**0**	**1**
Total ↓	**1**	**2**	**2**	**3**	**3**	**1**	**2**	**3**	**2**

SO4*, BC* and Ca* mean that concentrations of sulfate, base cations and calcium were each reduced using the ratio of each to chloride in seawater, to account for marine sources.



	2012 to 2020-22		
LAKE	ΔSO_4^{2-}	Δ CBANC	ΔpH
Lak006	3.5	20.2	0.2
LAK012	9.0	4.1	0.3
LAK022	6.5	4.1	-0.2
LAK023	-2.0	12.0	0.1
LAK016	11.6	12.5	0.0

	2012 to 2020-22		
LAKE	ΔSO_4^{2-}	Δ CBANC	ΔpH
DCAS14A	-3.8	13.8	-0.3
NC184	-1.7	-7.2	-0.3
NC194	-1.6	0.3	-0.5

	2012 to 2020-22		
LAKE	ΔSO_4^{2-}	Δ CBANC	ΔpH
LAK042	2.0	17.7	0.2
LAK044	-2.1	8.1	0.2

	2012 to 2020-22		
LAKE	ΔSO_4^{2-}	Δ CBANC	ΔpH
LAK028	58.5	-2.9	0.0

Figure 3-1. Observed changes in SO_4^{2-}, CBANC and pH from the baseline period (2012) to the post-KMP period (2020-2022). Green cells indicate increases and red cells indicate decreases.

Exceptional Annual Context for 2022

The year 2022 was exceptional in the 11-year history of the SO_2 EEM Program. Notwithstanding the above-stated limitations on interpreting annual changes in lake chemistry, it is important to acknowledge the exceptional situation in 2022. Emissions from the smelter were dramatically less than in any previous year of the SO_2 EEM Program, due to a reduction in smelter operations associated with a labour dispute. In August 2021, emissions dropped by approximately 83%, from 27.1 tpd during January to June 2021, to 4.6 tpd during August to December 2021. This change was discussed in the SO_2 EEM Program 2021 Annual Report. We did not expect to see much influence of the reductions in emissions on lake chemistry in 2021 because: a) the drop in emissions happened only 1-2 months before the lakes were sampled in October 2021; and b) any small response to that change in emissions would have been swamped by the dominant influence of exceptionally wet hydrologic conditions in September and October 2021 (discussed last year).

Smelter emissions remained low into 2022 and started to increase very gradually only starting in the summer of 2022. As a result, the average emissions from September 2021 to August 2022 (i.e., the 12 months prior to the fall sampling period in 2022) were 5.1 tpd. Emissions during the 12 months prior to 2022 fall sampling were 21% of the levels in 2020 and 17% of the 2016-2018 period applied in the 2019 Comprehensive Review.

The prolonged reduction in emissions after August 2021 could alter lake chemistry, especially since the estimated water residence time is less than a year for most of the sensitive EEM lakes (less than nine months for 5 out of 7 sensitive EEM lakes, 1.4 years for LAK006, and 2.1 years for LAK044 (see 2019 Comprehensive Review, Technical Appendix 7, Table 7.19; ESSA et al. 2020b)). We expected that the decline in SO_2 emissions would cause a decline in lake [SO_4], and possibly an increase in CBANC, Gran ANC and pH, in at least the 5 sensitive EEM lakes with short water residence times. Increases in lake [SO_4] are generally associated with increases in lake base cations, due to cation exchange processes in the watershed. The converse also holds: decreases in lake [SO_4] would be expected to result in lower base cation concentrations.

The dominant responses in the 2022 data were generally consistent with our expectations:

- [SO_4] declined in all sensitive lakes except LAK028 (+3.5 μeq/L); some of the decreases were quite substantial
- Gran ANC went up in ALL lakes
- CBANC showed an increase in 4 of the sensitive EEM lakes, a limited decrease in 2 of them, and LAK042 (far north of the study area) decreased by 9.7 μeq/L
- pH increased by 0.2-0.8 pH units in all 11 lakes, with the same range across the sensitive EEM lakes alone)
- base cations dropped in all sensitive EEM lakes except LAK028 (+9.9 μeq/L)

The changes observed in 2022 *generally* countered the changes of the previous year:

- Across all lakes ~80% of the annual changes observed over 2021-2022 for CBANC, Gran ANC, BCS, pH, and SO_4 were in the opposite direction of the changes observed over 2020-2021
- For CBANC, this general pattern was less consistent - two lakes showed decreases for two years in a row (LAK023, LAK042) and two lakes showed increases for two years in a row (LAK016, LAK028)

- For pH, this general pattern was universally observed - all 11 lakes decreased in pH over 2020-2021 and increased in pH over 2021-2022
- The combined result from the two annual changes (i.e., the net change from 2020 to 2022) was more variable – that is, in some cases the changes in 2022 only partially offset the significant changes in 2021 and in other cases they more than offset the previous year's changes

An important net result is that these "reversals" of the previous year's anomalous changes tended on the whole to reduce the magnitude of changes based on the 3-year averaging period relative to the results reported last year.

Analyses of change based on the recent 3-year average

To protect aquatic ecosystems in the sensitive lakes, we want to avoid declines in recent measurements of CBANC, Gran ANC, BCS, and pH (i.e., the KPI and other acidification informative indicators) compared to the pre-KMP 2012 baseline. We use the average of the last 3 years to dampen the effects of an unusual year. Results of our analyses indicate a general recovery of lake chemistry in most of the sensitive lakes from the changes observed in 2021. The estimated changes since 2012 for CBANC, Gran ANC and BCS became more positive in 5 to 6 of the 7 sensitive lakes, as compared to the SO_2 EEM Program 2021 Annual Report (i.e., + signs next to these values in Table 3-1). Relative to the SO_2 EEM Program 2021 Annual Report, all seven sensitive lakes showed reductions in the estimated change in $[SO_4]$ since 2012, consistent with the reductions in SO_2 emissions since August 2021. In addition, all seven lakes showed an increase in the estimated long-term change in base cations since 2012. The only exception to this general pattern of recovery is that the estimated change in pH since 2012 remained the same for 6 of the 7 sensitive lakes (i.e., no + or – sign next to these values in Table 3-1).

Of the two lakes showing a long-term decline in CBANC in last year's report, only LAK028 continues to show a long-term decline, albeit a smaller magnitude (-2.9 μeq/L now vs. -7.9 μeq/L last year). Two lakes still show long-term declines in BCS compared to 2012 (LAK012 and LAK028), though the magnitudes of these declines are smaller than in last year's report. LAK022 continues to be the only lake with a decline in Gran ANC relative to the 2012 baseline, though the magnitude is small and only slightly greater than previously reported (-1.6 μeq/L now vs. -0.9 μeq/L last year). LAK022 also continues to be the only lake with a decline in pH relative to pre-KMP conditions, which looks to have increased in magnitude but closer inspection reveals that the apparent increase is predominantly due to rounding (i.e., last year the calculated change was -0.149 and this year it increased to −0.16, a negligible difference). LAK022 is the only sensitive lake which is sampled just once per year; the other 6 lakes are sampled 4 times during the fall index period.

In LAK028 (the lake closest to the smelter with the highest deposition) mean $[SO_4^{2-}]$ is estimated to have increased by 58.5 μeq/L since 2012, and total base cations (ΣBC^*) increased by 56.6 μeq/L (both lower magnitudes than shown in last year's Annual Report). The changes in ΣBC^* and SO_4^{2-} largely explain the observed change in CBANC, a decline of 2.9 μeq/L. CBANC equals the sum of base cations minus the sum of strong acid anions, and $\Delta\Sigma BC^* - \Delta[SO_4^{2-}] = 56.6 - 58.5 = -1.9$, close to the 2.9 μeq/L decline in CBANC. Gran ANC shows a long-term increase (5.4 μeq/L) in LAK028 and there continues to be no change in mean pH, similar to last year.

LAK028 showed a decline in Base Cation Surplus (BCS) since the pre-KMP period, though BCS has shown considerable variation in LAK028, with its lowest value in 2013 (Table 3-2).

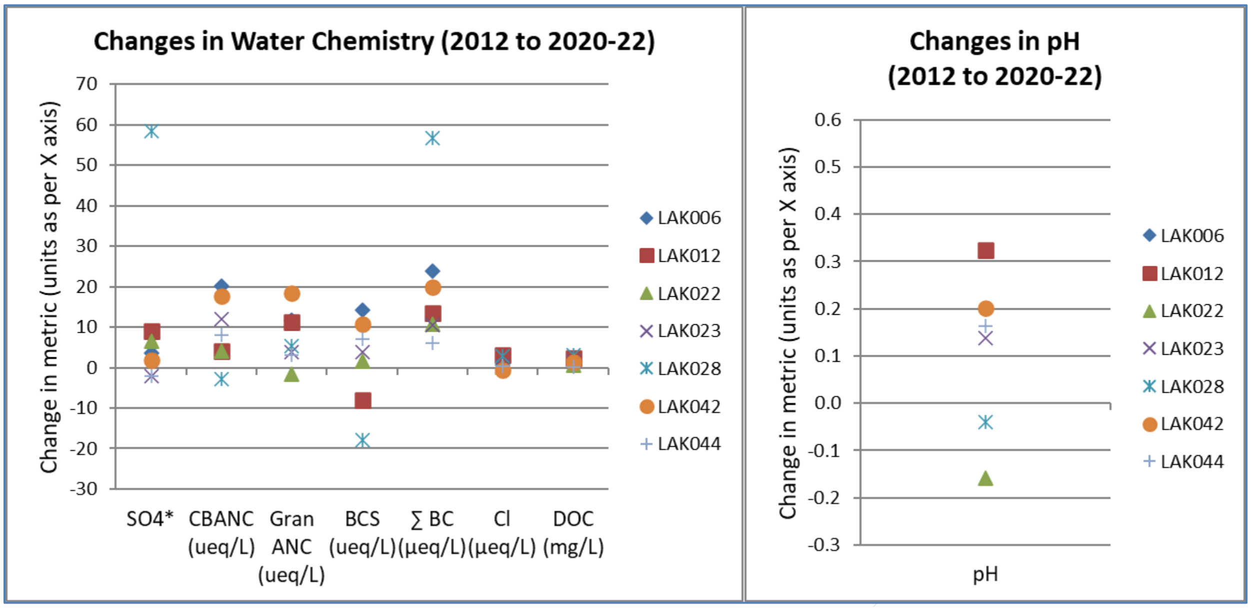
Table 3-2. Mean values of BCS in LAK028 by year. Units are µeq/L. Data from Appendix 1.

Year	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
BCS (µeq/L)	-5.1	-40.2	4.8	1.5	-24.9	-32.5	-8.4	-18.1	-26.7	-20.5	-10.6

Figure 3-2 and Figure 3-3 show the changes in the same water chemistry parameters graphically. These figures allow an alternate visualization of the distribution and variability in the observed changes between 2012 and 2020-2022.

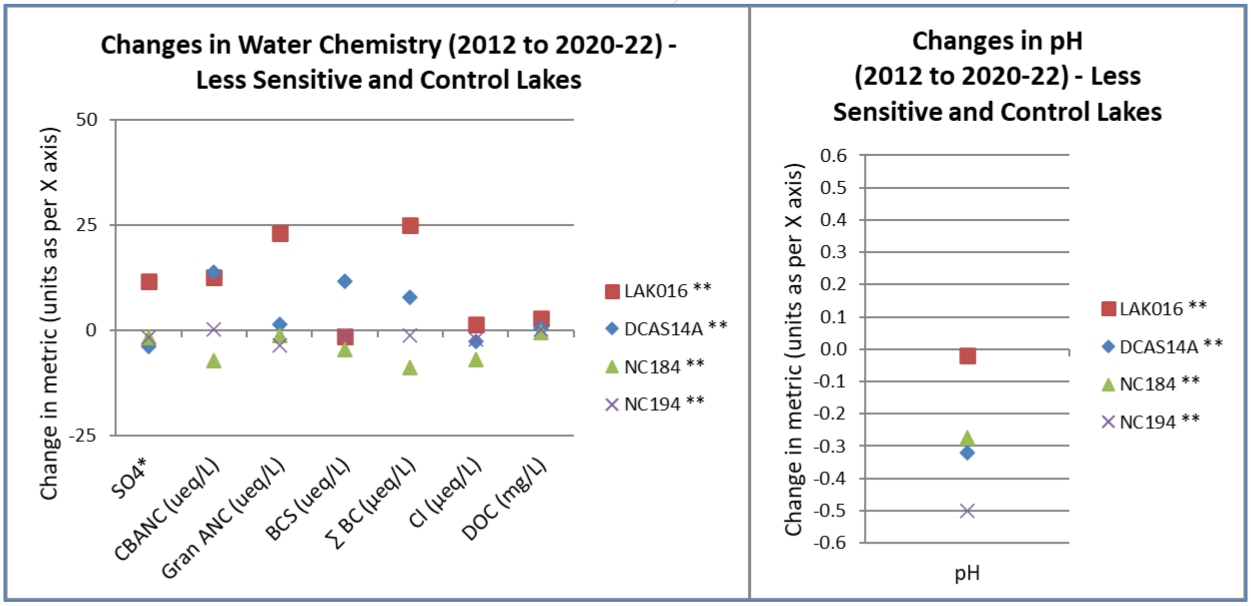
For additional reference, Table 3-3 and Table 3-4 show the CBANC and pH values, respectively, over the period of record for EEM lakes, average values for the post-KMP period (2020-2022) and the differences between the post-KMP period and both the pre-KMP baseline (2012) and the transition period baseline (2012-2014). The changes in CBANC are generally similar using both the pre-KMP and the transition period as a baseline (Table 3-3), except for LAK012 which shows a much larger increase in CBANC from the transition period baseline. The changes in pH were consistently more negative using the 2012-2014 transition period as a baseline instead of the pre-KMP 2012 measurement (Table 3-4).

Appendix 2 provides a detailed set of figures showing the inter-annual changes in major water chemistry metrics (CBANC, Gran ANC, BCS, pH, SO_4^{2-}, base cations, calcium, chloride, and DOC) for each of the EEM lakes across the eleven years of annual monitoring (2012-2022). Similar figures are also included for the three control lakes based on their eight years of monitoring (2013, 2015-2019, and 2021-2022).


Changes in Water Chemistry (2012 to 2020-22)

Changes in pH (2012 to 2020-22)

Figure 3-2. Changes in water chemistry metrics (left panel) and pH (right panel) across all of the sensitive EEM lakes, from 2012 to 2020-2022. Values shown are the mean 2020-2022 value minus the mean 2012 value. The large increase in lake SO_4^{2-} in LAK028 has been buffered by a large increase in base cations, due to cation exchange in watershed soils.


Changes in Water Chemistry (2012 to 2020-22) - Less Sensitive and Control Lakes

Changes in pH (2012 to 2020-22) - Less Sensitive and Control Lakes

Figure 3-3. Changes in water chemistry metrics (left panel) and pH (right panel) across all of the less sensitive and control lakes, from 2012 to 2020-2022. Values shown are the mean 2020-2022 value minus the mean 2012 value. All three control lakes have shown no increase in SO_4* (left panel); the pH decrease (right panel) reflects very high precipitation in September 2021.

Table 3-3. CBANC values over period of record for EEM lakes, average CBANC values for the post-KMP period and the relative change from the pre-KMP baseline and the transition period baseline. The post-KMP averaging period applied in the 2019 comprehensive review (CR) is also shown for reference. Green represents an increase and red represents a decrease. Bolded purple values are below the 20 µeq/L *level of protection* threshold for CBANC.

	Mean CBANC values (µeq/L)											Post-KMP averaging period		Change from baseline to current post-KMP average (2020-22)	
	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2016-18 (CR)	2020-22 (current)	From pre-KMP baseline (2012)†	From transition period baseline (2012-14)†
LAK006	49.2	43.1	52.9	55.1	56.9	58.0	59.3	63.8	70.3	67.8	70.1	58.0	69.4	20.2	21.0
LAK012	114.5	97.5	99.8	106.1	103.2	101.1	90.4	96.5	142.1	101.2	112.4	98.2	118.6	4.1	14.7
LAK022	67.9	62.0	76.1	75.2	80.3	70.4	76.6	74.8		68.8	75.4	75.8	72.1	4.1	3.4
LAK023	46.9	37.7	59.4	58.0	59.5	59.9	61.3	59.4	66.6	56.2	54.0	60.2	58.9	12.0	10.9
LAK028	**16.0**	**-8.1**	31.2	38.6	**12.3**	**0.7**	**8.4**	**4.5**	**8.0**	**11.7**	**19.3**	7.1	13.0	-2.9	0.0
LAK042	47.2	55.1	51.6	55.4	64.0	63.1	50.4	52.1	79.5	62.4	52.8	59.2	64.9	17.7	13.6
LAK044	**8.0**	**8.9**	**12.6**	**16.4**	**13.9**	**13.8**	**13.2**	**14.8**	**14.5**	**17.1**	**16.8**	13.6	16.1	8.1	6.3
LAK016	127.2	108.7	132.5	147.1	140.8	125.3	138.1	129.8		138.1	141.4	134.7	139.8	12.5	17.0
DCAS14A†		53.5		74.9	72.7	67.8	79.0	81.1		63.8	70.9	73.2	67.4	13.8	13.8
NC184†		80.4		73.0	94.6	76.3	95.0	86.1		61.2	85.3	88.6	73.2	-7.2	-7.2
NC194†		35.6		40.9	40.0	46.5	43.1	46.7		35.6	36.3	43.2	35.9	0.3	0.3

†The pre-KMP for the control lakes is 2013. The transition period baseline for the control lakes is also only 2013 because the lakes were not sampled in 2014. Therefore, the results for the two baselines are identical.

Table 3-4. pH values over period of record for EEM lakes, average pH values for the post-KMP period and the relative change from the pre-KMP baseline and the transition period baseline. The post-KMP averaging period applied in the 2019 comprehensive review (CR) is also shown for reference. Green represents an increase and red represents a decrease. Bolded purple values are below the *level of protection* threshold for pH (6.0). As explained in the STAR, the 2012 chemistry of most of the sensitive lakes was influenced by organic acids contributed by DOC. Mean DOC has not changed much in the sensitive lakes since 2012 (Figure 3-2).

	Mean pH values											Post-KMP averaging period		Change from baseline to current post-KMP average (2020-22)	
	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2016-18 (CR)	2020-22 (current)	From pre-KMP baseline (2012)†	From transition period baseline (2012-14)†
LAK006	**5.8**	6.2	6.1	6.0	6.0	6.0	6.1	6.1	6.0	**5.8**	6.2	6.0	6.0	0.2	0.0
LAK012	**5.6**	6.3	6.0	6.0	6.2	6.1	6.2	6.1	6.0	**5.7**	6.2	6.2	6.0	0.3	0.0
LAK022	**5.9**	6.2	6.3	6.1	6.1	6.1	6.1	6.1		**5.4**	6.1	6.1	**5.8**	-0.2	-0.3
LAK023	**5.7**	6.0	**5.9**	**5.9**	**5.9**	**5.9**	6.0	**5.8**	**5.9**	**5.7**	6.0	**5.9**	**5.8**	0.1	0.0
LAK028	**5.0**	**5.2**	**5.3**	**5.1**	**5.0**	**4.8**	**5.3**	**5.2**	**4.9**	**4.7**	**5.2**	**5.0**	**4.9**	0.0	-0.2
LAK042	**4.7**	**5.5**	**5.1**	**5.4**	**5.4**	**5.2**	**5.1**	**5.4**	**4.6**	**4.6**	**5.4**	**5.2**	**4.9**	0.2	-0.2
LAK044	**5.4**	**5.7**	**5.8**	**5.8**	**5.5**	**5.6**	**5.5**	**5.5**	**5.6**	**5.5**	**5.7**	**5.6**	**5.6**	0.2	0.0
LAK016	6.3	6.7	6.7	6.8	6.6	6.7	6.7	6.6		6.1	6.5	6.7	6.3	0.0	-0.3
DCAS14A†		6.5		6.6	6.6	6.6	6.8	6.6		**5.9**	6.4	6.6	6.2	-0.3	-0.3
NC184†		**5.7**		**5.5**	**5.8**	**5.4**	6.2	**5.7**		**5.1**	**5.8**	**5.8**	**5.5**	-0.3	-0.3
NC194†		6.6		6.5	6.4	6.4	6.5	6.4		**5.9**	6.3	6.4	6.1	-0.5	-0.5

†The pre-KMP for the control lakes is 2013. The transition period baseline for the control lakes is also only 2013 because the lakes were not sampled in 2014. Therefore, the results for the two baselines are identical.

Resampling of LAK027

Table 3-5 shows the results for LAK027 for ANC, pH, SO_4^{2-}, DOC, sum of base cations, chloride, and calcium, including the results from the 2012 STAR sampling and the difference between the two sampling years. As explained earlier (and in the recommendations of the SO_2 EEM Program 2021 Annual Report), LAK027 was resampled for a second year in 2022 due to the influence of anomalous hydrologic conditions in fall 2021 across all of the lakes. Therefore we are primarily focused on comparing 2022 to 2012 to achieve the original intent of resampling this lake. CBANC, Gran ANC, and BCS all increased substantially, whereas pH declined by 0.1 pH units. There were also substantial increases in both ΣBC* (123.9 μeq/L) and SO_4^{2-} (63.9 μeq/L) and the relative difference between those increases explains the increase in CBANC (i.e., 123.9 – 63.9 = 60.0 μeq/L).

Table 3-5. CBANC, Gran ANC, BCS, pH, SO42-, DOC, base cations, chloride, and calcium values for LAK027, from the 2012 STAR sampling and the resampling in 2021 and 2022. The change from 2012 to 2022 is shown. Increases are shaded in green; decreases are shaded in red. The Gran ANC and pH values are based on the "integrated" time series (i.e., values from the Trent University laboratory from 2012 with the 2022 values imputed from the values measured by the BASL laboratory ("integ"); see details in Section 2.1). Note that the imputation uses the regression based on the 2019 data for the EEM Lakes (i.e., LAK027 did not contribute to the regression).

	CBANC (μeq/L)	Gran ANC (integ) (μeq/L)	BCS (μeq/L)	pH (integ)	SO4* (μeq/L)	DOC (mg/L)	∑ BC* (μeq/L)	Cl (μeq/L)	Ca* (μeq/L)
2012	101.3	69.8	98.8	6.6	110.4	1.1	211.6	3.2	189.3
2021	94.8	56.9	65.9	5.9	90.3	6.4	185.2	8.2	157.9
2022	160.8	124.3	142.5	6.5	174.3	4.3	335.5	5.6	295.2
Change (2012 to 2022)	59.6	54.5	43.6	-0.1	63.9	3.2	123.9	2.5	105.9

3.2 Water Chemistry Sampling Results

Appendix 1 reports the results of the water chemistry sampling for the EEM lakes and control lakes from the sampling conducted in 2022 (with the data from 2012-2022 included for reference), for major water chemistry metrics (ANC, pH, DOC, base cations, and major anions).

Sulphate Levels Relative to B.C. Water Quality Guidelines

The B.C. water quality guideline for sulphate concentration in very soft waters is 128 mg/L. The sulphate concentration of the EEM lakes is shown in Figure 3-4 for all water chemistry samples taken in 2022. All of the samples are less than 4% of the guideline. Other than LAK028, all other samples for all other lakes are less than 2% of the guideline.

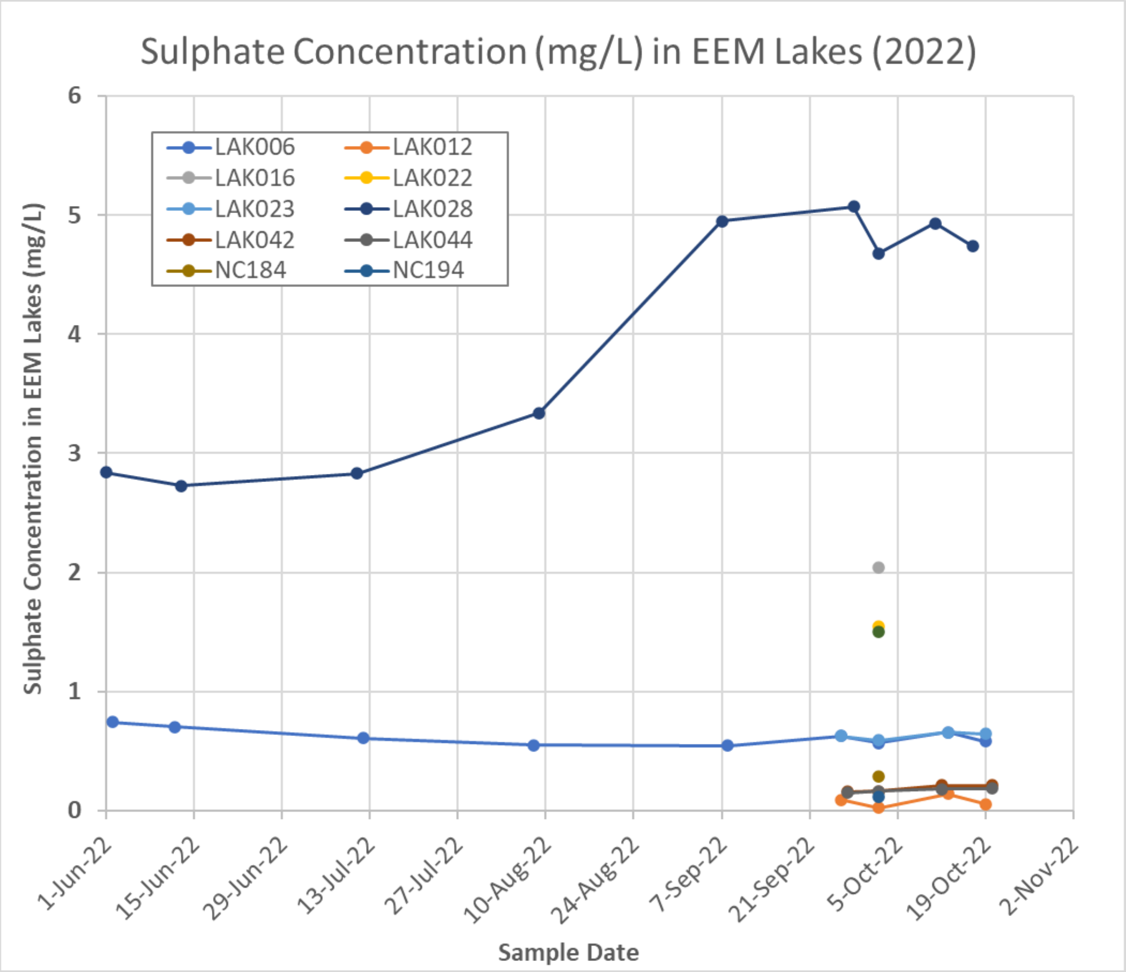


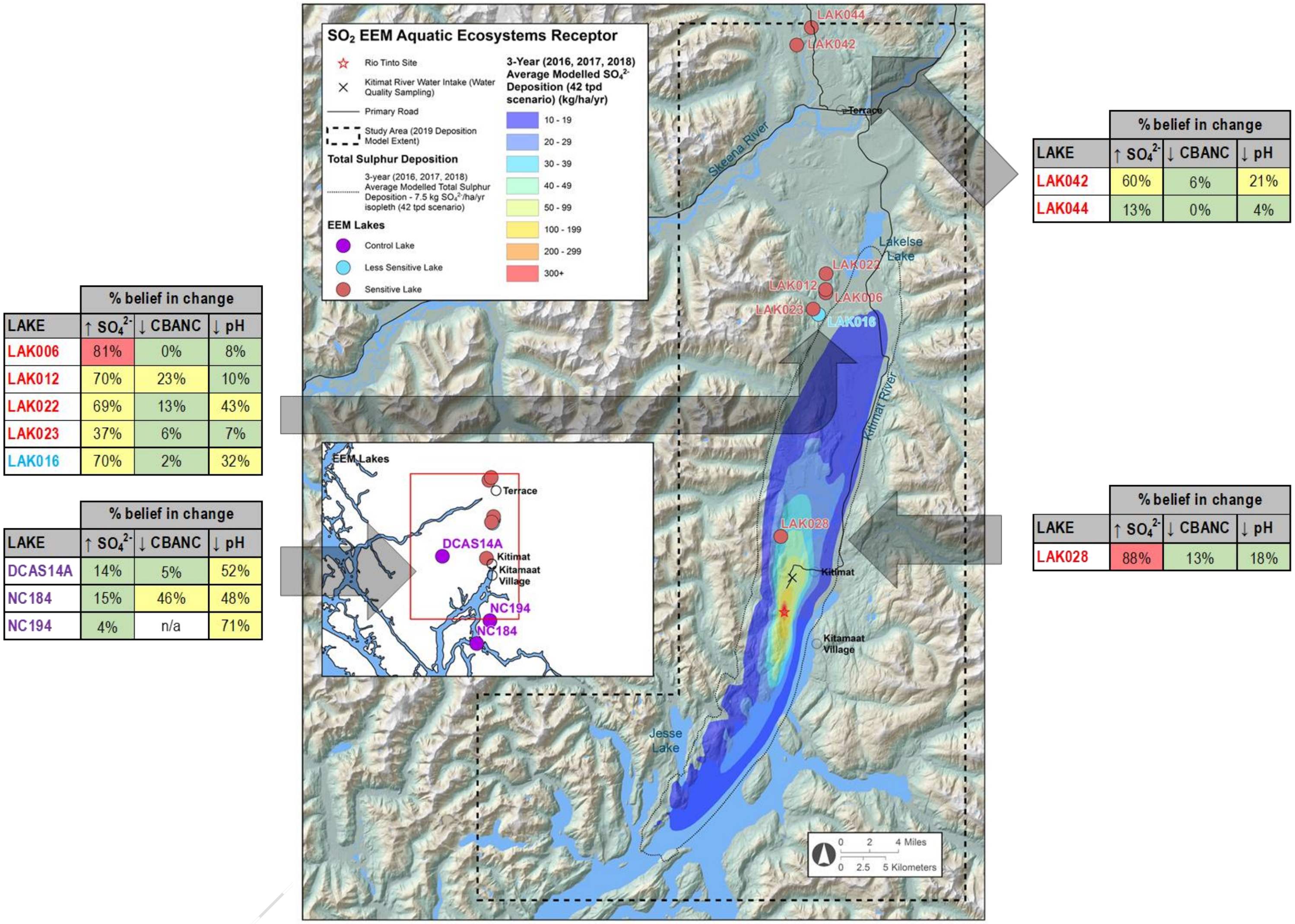
Figure 3-4. Sulphate concentration (mg/L) in EEM lakes during 2022. The applicable B.C. water quality guideline for sulphate concentration (i.e., for very soft waters) is 128 mg/L. All samples in 2022, across all EEM lakes, were <4% of the guideline.

3.3 Statistical Analysis of Changes in Water Chemistry

We have summarized the key results of the statistical analyses of changes in lake chemistry across all the lakes in the SO₂ EEM Program in Table 3-6 and Figure 3-5. These results applied Bayesian Method 1, described in Appendix F of the 2019 Comprehensive Review (ESSA et al. 2020b).

Table 3-6. Summary of findings across all lakes monitored in the SO_2 EEM Program. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review(ESSA et al. 2020b). Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red. Both the Gran ANC and pH results are based on the integrated ("integ") time series (as per Section 2.1). Note: because NC194 does not have a lake-specific *change limit* threshold for CBANC / Gran ANC, it is not possible to evaluate these indicators).

	Changes in SO_4	**Exceedance of *CHANGE LIMIT***				**Exceedance of *LEVEL OF PROTECTION***			
	(% belief that threshold exceeded; from Bayesian analysis method 1)	(% belief that metric value has decreased by more than the threshold; from Bayesian analysis method 1)				(% belief that metric value is below threshold; from Bayesian analysis method 1)			
Metric	**SO_4**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**
Threshold	Increase > 0	Lake-spec.	Lake-spec.	Δ 13 ueq/L	Δ 0.3 pH units	20 ueq/L	30.7 ueq/L	0 ueq/L	6.0 pH units
LAK006	81%	0%	0%	1%	8%	0%	0%	0%	70%
LAK012	70%	23%	14%	42%	10%	0%	0%	0%	77%
LAK022	69%	13%	30%	9%	43%	0%	80%	0%	84%
LAK023	37%	6%	2%	3%	7%	0%	100%	0%	100%
LAK028	88%	13%	8%	62%	18%	100%	100%	100%	100%
LAK042	60%	6%	6%	20%	21%	0%	100%	80%	100%
LAK044	13%	0%	4%	1%	4%	100%	100%	0%	100%
LAK016	70%	2%	7%	33%	32%	0%	0%	0%	1%
DCAS14A	14%	5%	7%	13%	52%	0%	0%	0%	10%
NC184	15%	46%	30%	43%	48%	0%	100%	1%	97%
NC194	4%	▨	▨	4%	71%	0%	100%	0%	33%



LAKE	% belief in change		
	↑ SO$_4^{2-}$	↓ CBANC	↓ pH
LAK006	81%	0%	8%
LAK012	70%	23%	10%
LAK022	69%	13%	43%
LAK023	37%	6%	7%
LAK016	70%	2%	32%

LAKE	% belief in change		
	↑ SO$_4^{2-}$	↓ CBANC	↓ pH
DCAS14A	14%	5%	52%
NC184	15%	46%	48%
NC194	4%	n/a	71%

LAKE	% belief in change		
	↑ SO$_4^{2-}$	↓ CBANC	↓ pH
LAK042	60%	6%	21%
LAK044	13%	0%	4%

LAKE	% belief in change		
	↑ SO$_4^{2-}$	↓ CBANC	↓ pH
LAK028	88%	13%	18%

Figure 3-5. Spatial distribution of percent belief in chemical change. Numbers show % belief in: a) SO_4 increase (no threshold), b) CBANC decrease below lake-specific threshold, and c) pH decrease below 0.3 threshold. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review(ESSA et al. 2020b). NC194 does not have an estimated ANC threshold because it did not have appropriate titration data available.

Before-After Control-Impact (BACI) Analyses

The results of the BACI analyses for CBANC, pH, Gran ANC, and BCS are shown in Table 3-7, Table 3-8, Table 3-9, and Table 3-10). None of the seven lakes showed statistically significant differences in Δ CBANC, Δ Gran ANC, or Δ BCS relative to the control lakes. One lake showed significantly more positive Δ pH over time than was observed in the control lakes, which is evidence against acidification.

Table 3-7. BACI analyses of mean CBANC for 7 sensitive and 3 control lakes. "BACI estimate" is a bit counter-intuitive: it is the Δ mean CBANC in the controls (i.e., CBANC $_{\text{post-KMP}}$ minus CBANC $_{\text{pre-KMP}}$), averaged over the 3 control lakes, minus the Δ mean CBANC in the sensitive lake. If BACI value is <0, then the Δ CBANC was lower in the controls than in the sensitive lake (and, equivalently, the Δ CBANC was greater (more positive) in the sensitive lake than in the controls), evidence against acidification (if statistically significant). If BACI value is >0, then Δ CBANC in the controls was greater than that in the sensitive lake (and, equivalently, the Δ CBANC was lower (less positive) in the sensitive lake than in the controls), evidence for acidification (if statistically significant). SE is the standard error of the BACI estimate. The p-value is the statistical significance of the test.

Site	BACI estimate	SE	p-value	Interpretation of BACI estimate	Change in interpretation from 2021
LAK006	-17.81	10.63	0.15	Change in CBANC was **more positive** in LAK006 than in the control lakes *(but not statistically significant)*	None
LAK012	8.31	11.13	0.49	Change in CBANC was **more negative** in LAK012 than in the control lakes *(but not statistically significant)*	None
LAK022	-1.82	11.03	0.88	Change in CBANC was **similar** in LAK022 to changes in the control lakes *(but not statistically significant)*	None
LAK023	-9.23	11.84	0.47	Change in CBANC was **more positive** in LAK023 than in the control lakes *(but not statistically significant)*	None
LAK028	4.50	10.68	0.69	Change in CBANC was **more negative** in LAK028 to changes in the control lakes *(but not statistically significant)*	None
LAK042	-15.38	14.98	0.35	Change in CBANC was **more positive** in LAK042 than in the control lakes *(but not statistically significant)*	None
LAK044	-5.90	10.85	0.61	Change in CBANC was **more positive** in LAK044 to changes in the control lakes *(but not statistically significant)*	From similar to more positive

Table 3-8. BACI analyses of mean pH (integrated) for 7 sensitive and 3 control lakes. "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. If BACI value is <0, then the Δ pH was lower in the controls than in the sensitive lake (and, equivalently, the Δ pH was greater (more positive) in the sensitive lake than in the controls), evidence against acidification (if statistically significant). If BACI value is >0, then Δ pH in the controls was greater than that in the sensitive lake (and, equivalently, the Δ pH was lower (less positive) in the sensitive lake than in the controls), evidence for acidification (if statistically significant). SE is the standard error of the BACI estimate. The p-value is the statistical significance of the test.

Site	BACI estimate	SE	p-value	Interpretation of BACI estimate	Change in interpretation from 2021
LAK006	-0.55	0.17	0.02	Change in pH was **more positive** in LAK006 than in the control lakes *(but not statistically significant)*	None
LAK012	-0.67	0.16	0.01	Change in pH was **significantly more positive** in LAK012 than in the control lakes; *evidence against acidification*	None
LAK022	-0.20	0.16	0.26	Change in pH was **more positive** in LAK0022 than in the control lakes *(but not statistically significant)*	None
LAK023	-0.49	0.18	0.04	Change in pH was **more positive** in LAK023 than in the control lakes *(but not statistically significant)*	None
LAK028	-0.33	0.17	0.10	Change in pH was **more positive** in LAK028 than in the control lakes *(but not statistically significant)*	None
LAK042	-0.67	0.19	0.02	Change in pH was **more positive** in LAK042 than in the control lakes *(but not statistically significant)*	No longer significant
LAK044	-0.53	0.20	0.04	Change in pH was **more positive** in LAK044 than in the control lakes *(but not statistically significant)*	None

Table 3-9. BACI analyses of mean Gran ANC (integrated) for 7 sensitive and 3 control lakes. "BACI estimate" is a bit counter-intuitive: it is the Δ mean Gran ANC in the controls (i.e., Gran $ANC_{post\text{-}KMP}$ minus Gran $ANC_{pre\text{-}KMP}$), averaged over the 3 control lakes, minus the Δ mean Gran ANC in the sensitive lake. If BACI value is <0, then the Δ Gran ANC was lower in the controls than in the sensitive lake (and, equivalently, the Δ Gran ANC was greater (more positive) in the sensitive lake than in the controls), evidence against acidification (if statistically significant). If BACI value is >0, then Δ Gran ANC in the controls was greater than that in the sensitive lake (and, equivalently, the Δ Gran ANC was lower (less positive) in the sensitive lake than in the controls), evidence for acidification (if statistically significant). SE is the standard error of the BACI estimate. The p-value is the statistical significance of the test.

Site	BACI estimate	SE	p-value	Interpretation of BACI estimate	Change in interpretation from 2021
LAK006	-12.35	4.55	0.04	Change in Gran ANC was **more positive** in LAK006 than in the control lakes *(but not statistically significant)*	None
LAK012	-6.79	6.93	0.37	Change in Gran ANC was **more positive** in LAK012 than in the control lakes *(but not statistically significant)*	From more negative to more positive
LAK022	0.46	5.77	0.94	Change in Gran ANC was **similar** in LAK0022 than in the control lakes *(but not statistically significant)*	None
LAK023	-4.43	4.96	0.41	Change in Gran ANC was **more positive** in LAK023 than in the control lakes *(but not statistically significant)*	From similar to more positive
LAK028	-6.89	5.18	0.24	Change in Gran ANC was **more positive** in LAK028 than in the control lakes *(but not statistically significant)*	From similar to more positive
LAK042	-21.79	7.96	0.04	Change in Gran ANC was **more positive** in LAK042 than in the control lakes *(but not statistically significant)*	None
LAK044	-4.74	4.88	0.37	Change in Gran ANC was **more positive** in LAK044 than in the control lakes *(but not statistically significant)*	From similar to more positive

Table 3-10. BACI analyses of mean BCS (base cation surplus) for 7 sensitive and 3 control lakes. “BACI estimate” is a bit counter-intuitive: it is the Δ mean BCS in the controls (i.e., $BCS_{post\text{-}KMP}$ minus $BCS_{pre\text{-}KMP}$), averaged over the 3 control lakes, minus the Δ mean BCS in the sensitive lake. If BACI value is <0, then the Δ BCS was lower in the controls than in the sensitive lake (and, equivalently, the Δ BCS was greater (more positive) in the sensitive lake than in the controls), evidence against acidification (if statistically significant). If BACI value is >0, then Δ BCS in the controls was greater than that in the sensitive lake (and, equivalently, the Δ BCS was lower (less positive) in the sensitive lake than in the controls), evidence for acidification (if statistically significant). SE is the standard error of the BACI estimate. The p-value is the statistical significance of the test.

Site	BACI estimate	SE	p-value	Interpretation of BACI estimate	Change in interpretation from 2021
LAK006	-12.39	10.75	0.30	Change in BCS was **more positive** in LAK006 than in the control lakes *(but not statistically significant)*	None
LAK012	15.36	11.25	0.23	Change in BCS was **more negative** in LAK012 than in the control lakes *(but not statistically significant)*	None
LAK022	0.38	11.49	0.98	Change in BCS was **similar** in LAK0022 than in the control lakes *(but not statistically significant)*	From more negative to similar
LAK023	-1.42	12.09	0.91	Change in BCS was **similar** in LAK023 than in the control lakes *(but not statistically significant)*	None
LAK028	18.82	10.80	0.14	Change in BCS was **more negative** in LAK028 than in the control lakes *(but not statistically significant)*	None
LAK042	-11.33	12.62	0.41	Change in BCS was **more positive** in LAK042 than in the control lakes *(but not statistically significant)*	None
LAK044	-5.32	11.28	0.66	Change in BCS was **more positive** in LAK044 than in the control lakes *(but not statistically significant)*	From similar to more positive

Table 3-11. BACI analysis of Δ CBANC, Δ pH (integrated), Δ Gran ANC, and Δ BCS, respectively, with all lakes combined. BACI estimate is the Δ mean in the 3 control lakes (i.e., post-KMP minus pre-KMP, averaged over the 3 control lakes), minus the Δ mean in the 7 sensitive lakes (i.e., post-KMP minus pre-KMP, averaged over the 7 sensitive lakes). SE is the standard error of the BACI estimate. The p-value is the statistical significance of the test.

Metric	BACI estimate	SE	p-value	Interpretation of BACI estimate	Change in interpretation from 2021
CBANC	-7.66	9.74	0.44	Change in CBANC was **more positive** in the sensitive lakes than in the control lakes *(but not statistically significant)*	From more negative to more positive
pH (integ)	-0.42	0.12	0.00	Change in pH was **significantly more positive** in the sensitive lakes than in the control lakes; *evidence against acidification.*	None
Gran ANC (integ)	-11.45	8.14	0.17	Change in Gran ANC was **more positive** in the sensitive lakes than in the control lakes *(but not statistically significant)*	None
BCS	0.47	9.79	0.96	Change in BCS was **more negative** in the sensitive lakes than in the control lakes *(but not statistically significant)*	None

For the BACI analyses of changes in CBANC:

- 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 (all lakes have p-values >0.01)
- Four of the seven sensitive lakes (one more than last year) showed a ΔCBANC that was more positive than the ΔCBANC observed in the group of control lakes (negative effect in the BACI analysis), but none of these differences were statistically significant at $p<0.01$
- Two of the seven sensitive lakes showed a ΔCBANC that was more negative than the ΔCBANC observed in the group of control lakes (positive effect in the BACI analysis), but none of these differences were statistically significant at $p<0.01$
- When analyzed as a combined group, the sensitive lakes showed ΔCBANC that was more positive than the ΔCBANC observed in the group of control lakes, which was a reversal of the results from last year (though the results were not statistically significant in either year)
- No support for an effect across any of the lakes individually or an effect for all lakes combined.

For the BACI analyses of changes in pH:

- One of the lakes (decreased from two lakes last year) showed a statistically significant effect ($p < 0.01$) – i.e., before-after differences that were significantly different than the before-after changes in the control lake group (LAK012 and LAK042)
    - The change in pH for LAK012 was more positive than in the control lakes, a statistically significant difference which is evidence against acidification
    - LAK042 (which showed a significant effect last year) and LAK006 had p-values than only marginally exceeded the criterion for significance (i.e., 0.02 for both lakes), for changes in pH that were more positive than in the control lakes
    - None of the other lakes showed a statistically significant effect

- When analyzed as a combined group, the sensitive lakes showed a statistically significant effect (at $p < 0.01$) of a change that was more positive than in the control lakes, which is evidence against acidification.

For the BACI analyses of changes in Gran ANC:

- 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 (all lakes have p-values >0.01)
- Six of the seven sensitive lakes (up from two lakes last year) showed a Δ Gran ANC that was more positive than the Δ Gran ANC observed in the group of control lakes (negative effect in the BACI analysis), but none of these differences were statistically significant at $p<0.01$ (LAK006 and LAK042 have p-values of <0.05)
- No support for an effect across any of the lakes individually or an effect for all lakes combined.

For the BACI analyses of changes in BCS:

- 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 (all lakes have p-values >0.01)
- Three of the seven sensitive lakes (up from two lakes last year) showed a ΔBCS that was more positive than the ΔBCS observed in the group of control lakes (negative effect in the BACI analysis), but none of these differences were statistically significant at $p<0.01$
- Two of the seven sensitive lakes showed a ΔBCS that was more negative than the ΔBCS observed in the group of control lakes (positive effect in the BACI analysis), but none of these differences were statistically significant at $p<0.01$
- No support for an effect across any of the lakes individually or an effect for all lakes combined.

3.4 Episodic Acidification

We reviewed the data from the continuous pH monitors installed in LAK006 and LAK028 to identify any acidic episodes (Figure 3-6, Figure 3-7). The lake-level monitoring data are shown in Figure 3-8.

LAK006 shows three periods with notable declines - late August, early September, and the very end of October – albeit the magnitude of these declines are quite small (i.e., declines of ~0.2 pH units over a period of less than one week). These periods align with notable increases in lake levels as the result of precipitation events. The decline at the end of October is also consistent with the pattern observed in previous years of pH decreasing during the end of the monitoring season as precipitation events increase in frequency and magnitude.

LAK028 showed only one pronounced drop (~0.4 pH units) in late October, corresponding with increased precipitation at the end of October. The late August and early September events observed in LAK006 are evident in the lake levels for LAK028 (i.e., significant local peaks in lake level) but do not show up as any notable declines in pH. Other than the decline at the end of October, which is consistent with the pattern observed in many previous years, the continuous pH data for LAK028 stayed within an range of ~0.2 pH units for the entire year.

Because this decline is at the very end of the field season, there are not any samples with full lake chemistry after this time with which to examine changes in lake chemistry during this period.

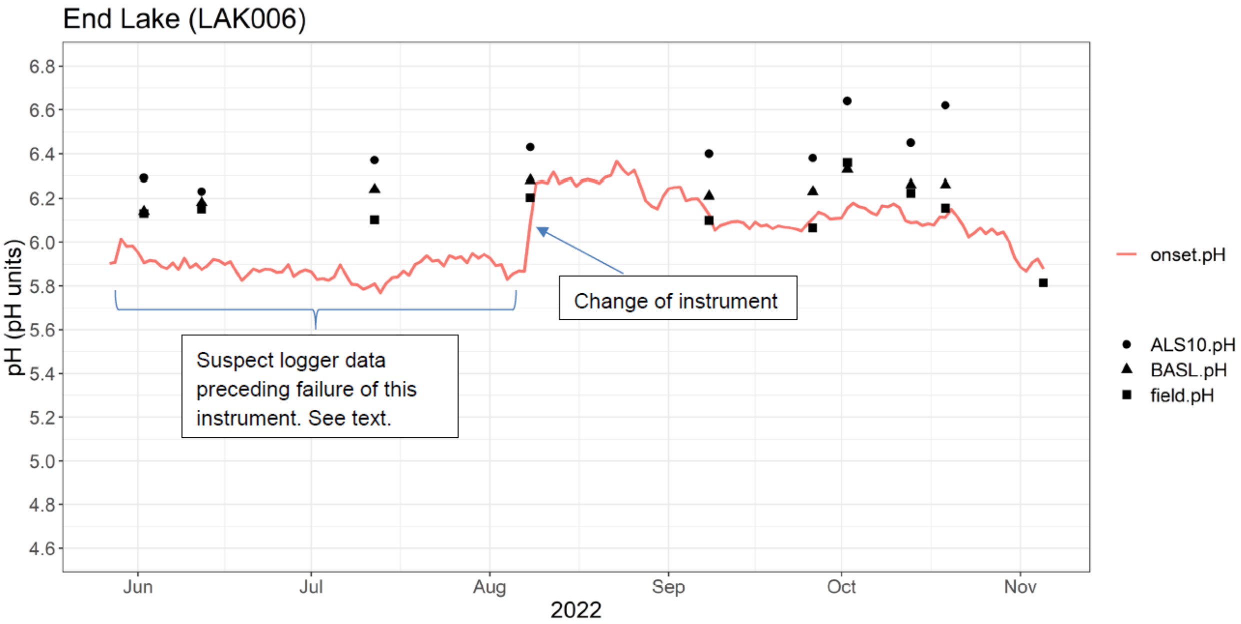


Figure 3-6. LAK006 pH measurements during the 2022 monitoring season, including continuous monitoring as well as field and laboratory measurements. See Limnotek 2023 for details on instrument failure referenced in the figure. Source: Limnotek 2023

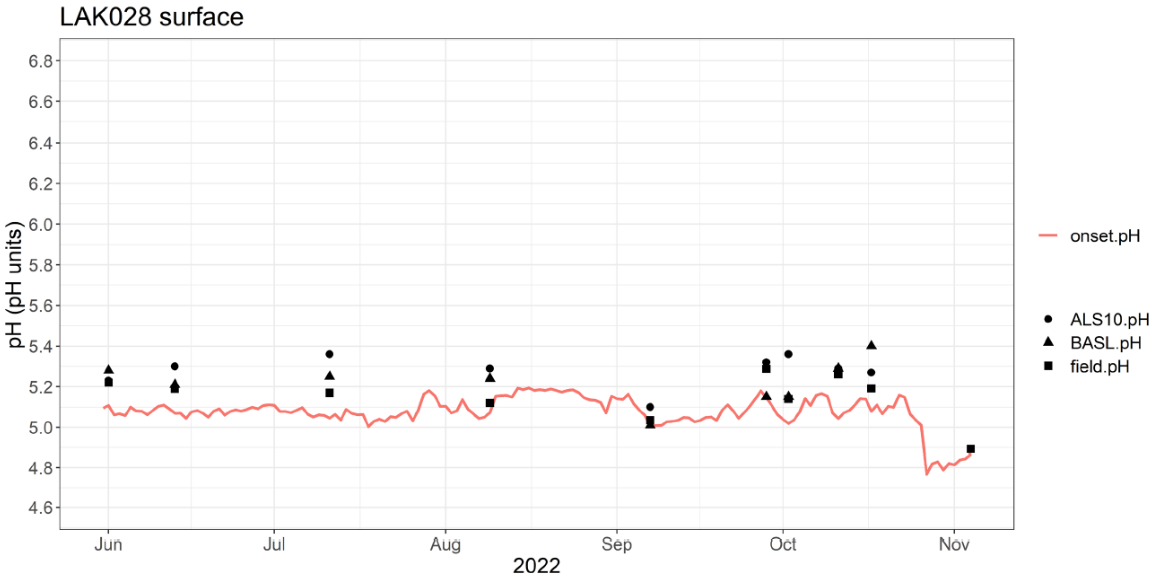


Figure 3-7. LAK028 pH measurements during the 2022 monitoring season, including continuous monitoring as well as field and laboratory measurements. Source: Limnotek 2023

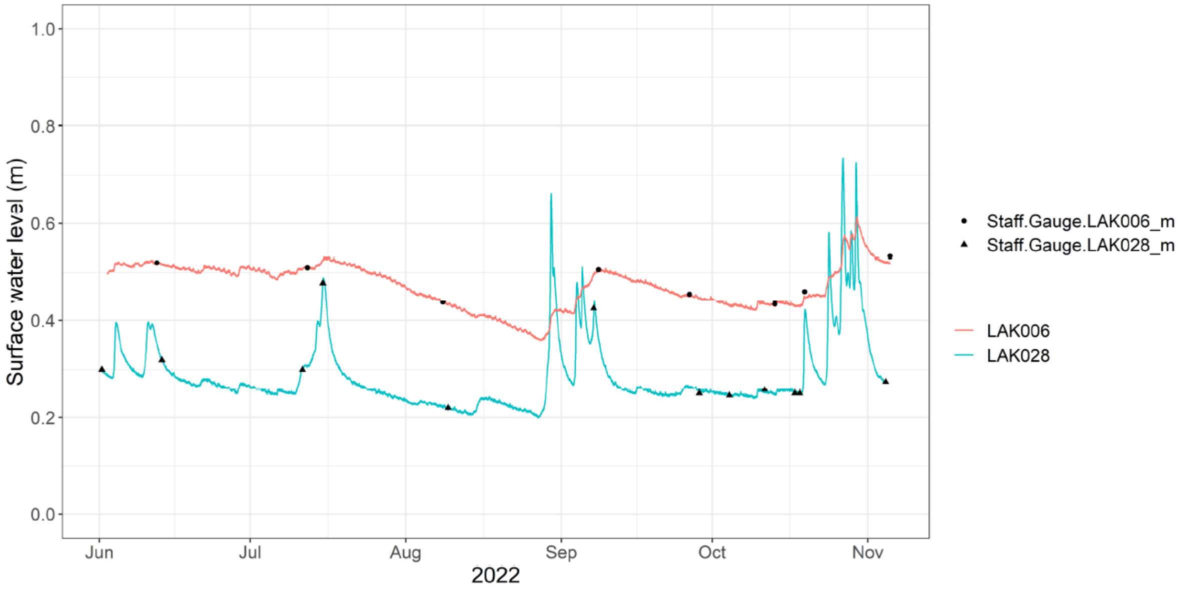


Figure 3-8. Water level during the 2022 monitoring season for LAK006 and LAK028. Source: Limnotek 2023

4 Discussion

4.1 Separating Natural and Anthropogenic Factors: the Environmental Context

The SO_2 EEM Program has moved away from reporting and analyzing the annual changes between individual years (due to challenges in interpretability associated with the high degree of variability). However, it is still useful to look at the year-to-year changes to assess whether there are any widespread patterns of significance that may influence our analyses and interpretation of long-term changes in water chemistry.

The graphs in Appendix 2 enable comparisons of the 2022 monitoring data to 2021. These graphs show (as also described in Section 3.1) that the patterns of annual change in the primary metrics had a high level of consistency across the entire region – i.e., pH and Gran ANC increased in all 11 lakes, BCS increased in 10 lakes, and CBANC increased in 8 lakes. These changes are consistent with significant reductions in emissions, and presumably also in deposition (deposition data still to be analyzed). The changes in the ANC metrics and pH are also consistent with the particularly dry hydrologic conditions in 2022. as well, since the three control lakes also showed increases in ANC metrics and pH, but showed either no change or slight increases in sulphate (see graphs in Appendix 2). The control lakes are serving their purpose of removing the effects of variation in emissions and deposition.

On the other hand, the changes in SO_4 and BC both appear to reflect the net balance between two opposing processes. The dry conditions alone could contribute to increasing concentrations of SO_4 but the consistent declines in SO_4 (as observed in 8 of 11 lakes, including

6 of 7 sensitive lakes) suggest that any such response to dryer conditions this year has been swamped by the effects of reduced emissions. Similarly, dry conditions could contribute to increasing concentrations of BC , through a concentration effect, but reduced deposition could reduce the inputs of BC into lakes both through changes in direct deposition of BC in the watershed (likely minor) and by reducing the amount of hydrogen-driven cation-exchange in the watershed (likely more significant). The consistent declines observed for BC (in 7 of 11 lakes, including 6 of 7 sensitive lakes) suggest that effects of the reduced emissions were much stronger than the influence of the hydrological conditions.

Although it is difficult to completely disentangle the relative contributions of these two major drivers in 2022 – dry hydrologic conditions and reduced emissions – it does appear that reduced emissions have been the more dominant influence on the lake chemistry observed in the sensitive lakes, and that dry conditions were the more dominant influence in the control lakes.

Environmentally mediated decrease in pH in LAK042 in 2020 – two years later

As described in detail in the SO_2 EEM Program 2020 Annual Report, LAK042 had a notable 1-year decrease in pH between 2019 and 2020 that was attributed to anomalous environmental conditions – i.e., high water levels flooding the shoreline and leading to a large increase in DOC and a concurrent drop in pH.

In the SO_2 EEM Program 2021 Annual Report, we reported:

> *"If it were not for the significant precipitation events in 2021, as described above, we may have expected to see some recovery of the pH in LAK042. However, the pH in LAK042 remained at a very similar level in the fall of 2020 and 2021. Since LAK042 was not sampled in 2021 prior to September, it is not possible to determine whether its pH remained at a similar level since the fall of 2020, or increased in the spring/summer of 2021 and then declined again during the fall of 2021. "*

In 2022, the pH in LAK042 increased by 0.8 pH units (the largest increase observed), effectively reversing the significant decrease from two years ago and returning to the 2019 levels (actually 0.1 pH units higher). However, given the context of emissions and precipitation conditions in 2022, it is not possible to disentangle how much of this increase is due to the contrast in environmental conditions in the months preceding sampling in the different years or the marked reduction in SO_2 emissions over the entire year. LAK042 and LAK044 both showed declines in $[SO_4^{2}]$ consistent with reduced levels of S deposition.

4.2 Empirical Changes in Lake Chemistry with respect to the Aquatic Key Performance Indicator

This section only addresses the CBANC KPI and the pH informative indicator (of specific interest as the prior KPI) as the statistical analyses represent the primary assessment of the KPI and informative indicators.

The mean values of CBANC indicate that there have been no exceedances of the KPI.

For the CBANC KPI, only 2 of the 7 sensitive lakes (LAK028 and LAK044) have post-KMP values below the *level of protection* threshold. Both of those lakes were already below that threshold in 2012 (and the alternate, transition period baseline) and neither of those lakes have exceeded the *change limit* threshold (LAK028 shows a decrease of -2.9 µeq/L; LAK044 shows an increase of +8.1 µeq/L . None of the 7 sensitive lakes exceeded the *change limit* threshold and only one lake (LAK028) shows any long-term decrease in CBANC. In the sensitivity analyses with the alternate, transition period baseline (2012-2014), there are no lakes with an estimated long-term decrease in CBANC. The empirical data therefore indicate that none of the lakes exceeded the KPI.

For the pH informative indicator, 5 of the 7 sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028, LAK042, and LAK044) have post-KMP values below the *level of protection* threshold (a pH of 6.0). All 7 lakes were already below that threshold in 2012, and four of the lakes have been at or below that threshold throughout the entire period of record. None of the sensitive lakes have exceeded the *change limit* threshold. Only one lake (LAK022) shows any decrease in pH relative to 2012. The empirical data therefore indicate that none of the lakes have exceeded the pH informative indicator.

In the sensitivity analyses with the alternate, transition period baseline (2012-2014), 2 sensitive lakes show decreases of <0.1 pH units, 2 lakes (LAK028, LAK042) show decreases of ~0.2 pH units (LAK028 and LAK042), and 1 lake (LAK022) shows a decrease of ~0.3 pH units. The empirical data therefore indicate that one of the lakes exceeds the change limit for the pH informative indicator when evaluated against the alternate, transition period baseline.

The following section (Section 4.3) applies the statistical analyses to the same data to assess the percent belief that CBANC KPI and the pH, Gran ANC and BCS informative indicators could have been exceeded.

LAK027 – Comparison with STAR Results

As discussed earlier, LAK027 was resampled again in 2022 because of how the anomalous precipitation levels influenced lake chemistry across the region, thus confounding the original rationale for sampling LAK027 in 2021. As such, we currently focus on examining the changes between the values measured in the STAR in 2022.

The results for 2022 showed substantial increases in all of the main lake chemistry metrics (i.e., CBANC, Gran ANC, BCS, SO_4, DOC, BC, Cl, Ca) since 2012, with a small decrease in pH of 0.1 units. However, as discussed earlier 2022 was also subject to anomalous conditions (i.e., significantly reduced emissions), which tended to drive changes in the opposite direction than the previous year. Similar to the other EEM lakes, LAK027 shows very substantial changes between 2021 and 2022 that reflect the transition in influence between these sequential precipitation and emissions anomalies. It is therefore impossible to disentangle the potential long-term change in lake chemistry from the STAR from the short-term effects experienced by all the other EEM lakes. To obtain a more reliable assessment of the chemical status of LAK027, relative to the status observed in the STAR, it would be prudent to again resample this lake in 2023.

4.3 Statistical Analysis of Changes in Lake Chemistry

We evaluated the KPI and the informative indicators using the two-threshold structure (Table 4-1). None of the 11 EEM lakes have a high % belief in exceedance of either the KPI or any of the informative indicators. None of the 11 EEM lakes have even a moderate % belief in exceedance of the KPI - all lakes show a low % belief in exceedance of the CBANC KPI. However, three sensitive EEM lakes and two control lakes show moderate % belief of one or two of the informative indicators:

- LAK022 shows moderate % belief in exceedance of Gran ANC and pH
- LAK028 shows moderate % belief in exceedance of BCS
- LAK042 shows moderate % belief in exceedance of BCS and pH
- NC184 shows moderate % belief in exceedance of Gran ANC and pH
- NC194 shows moderate % belief in exceedance of pH

The only two changes in classification (across all lakes and metrics) from last year are the changes from low to moderate for LAK042 BCS and NC194 pH. All other results are the same as last year in terms of final classification.

Table 4-2 shows the results from 2022 compared to the results reported in the previous three annual reports and the 2019 comprehensive review, specifically for the evaluation of the *change limit*.

All 11 lakes have similar results to 2021 for CBANC, Gran ANC and pH – i.e., same classification and very similar percent belief values. All of the lakes were within 5% of their previous results for these metrics, which is very minor, except for LAK012 for CBANC (-12%) and NC194 for pH (+9%), which are still only small changes. For SO_4, there were a number of larger differences due to the significant reduction in emissions in 2022. The percent belief in an increase in SO_4 decreased in all 11 EEM lakes except LAK044, which still remained in the low category. LAK023 and LAK028 only decreased by ≤5% and LAK006, LAK012, LAK022, and LAK044 all decreased by 16-18%. The less sensitive lake (LAK016) and two of the control lakes had even larger decreases (-29% to -42%). Two sensitive lakes (LAK012 and LAK022) and the one less sensitive lake (LAK016) shifted from “high” to “moderate”. These changes are not at all surprising given the dramatic reduction in emissions compared to all prior years.

Two of the control lakes (DCAS14A and NC184) shifted from a “moderate” to “low” percent belief in an increase in SO_4 (Table 4-2). This is because this year’s report used a multi-year average for 2021 and 2022, which excluded higher concentrations of SO_4 in 2019 that were used in last year’s report. The graphs of changes in SO_4 between 2021 and 2022 (Appendix 2) show that SO_4 actually increased slightly in two of the control lakes (DCAS14A and NC184) and remained the same in the third control lake (NC194). The fact that the control lakes showed different trends in SO_4 from the other lakes is encouraging. The control lakes were deliberately located outside of the plume, and were not affected by the large decrease in smelter emissions of SO_2 since August 2021.

This is only the third year that the Bayesian analyses were performed on CBANC. Despite the widespread changes in numerous water chemistry metrics observed in both 2021 and 2022, the CBANC results remain remarkably similar to the 2020 results for almost all of the lakes, possibly providing an indication of the robustness of the CBANC metric to anomalous conditions.

This is the fifth year that the Bayesian analyses were performed for Gran ANC and pH. That length of time provides an opportunity to see how the results have changed since these analyses were first implemented in the 2019 Comprehensive Review. For Gran ANC, there are only two lakes that have showed a change in category over the five years of repeating the analyses – LAK022 and NC194 increases from low to moderate, albeit still at the low end of the moderate range (~30% belief). For pH, 2 sensitive lakes, 1 less sensitive lake, and all 3 control lakes have showed a change in category – from low to moderate in all cases. In all cases, the shift occurred with the 2021 results (driven by high precipitation in September 2021) and the 2022 results remained quite similar[4]. LAK042 and LAK016 have been only in the low end of the moderate category. LAK022, DCAS14A and NC184 have been in the mid-range of the moderate category and only NC194 has been at the top end. However, decreases in pH in the control lakes must be driven by factors other than the smelter because they are well outside the deposition plume, and all three control lakes have a low percent belief in any sulphate increase (Table 4-2).

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[4] Note: 4 out of these 5 lakes were not sampled in 2020, meaning the 2020 results were based only on 2018-2019, and therefore it is not actually possible to determine whether the shifts that show up in the 2021 results reflect changes in lake chemistry in 2020, 2021 or both

Table 4-1. Evaluation of the KPI and informative indicators based on the results for both the *change limit* and the *level of protection* thresholds. The first three sets of columns are the same as Table 3-6. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review (ESSA et al. 2020b). Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red. Both the Gran ANC and pH results are based on the integrated ("integ") time series (as per Section 2.1). Note: because NC194 does not have a lake-specific *change limit* threshold for CBANC / Gran ANC, it is not possible to evaluate these indicators).

	Changes in SO4	**Exceedance of *CHANGE LIMIT***				**Exceedance of *LEVEL OF PROTECTION***				**KPI and Informative Indicator Evaluation**			
	(% belief that threshold exceeded; from Bayesian analysis method 1)	(% belief that metric value has decreased by more than the threshold; from Bayesian analysis method 1)				(% belief that metric value is below threshold; from Bayesian analysis method 1)				(Classification of % belief that both the change limit and level of protections thresholds are exceeded)			
Metric	**SO_4**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**	**CBANC**	**Gran ANC (integ)**	**BCS**	**pH (integ)**
Threshold	Increase > 0	Lake-spec.	Lake-spec.	Δ 13 ueq/L	Δ 0.3 pH units	20 ueq/L	30.7 ueq/L	0 ueq/L	6.0 pH units	KPI	Inform. Indic.	Inform. Indic.	Inform. Indic.
LAK006	81%	0%	0%	1%	8%	0%	0%	0%	70%	LOW	LOW	LOW	LOW
LAK012	70%	23%	14%	42%	10%	0%	0%	0%	77%	LOW	LOW	LOW	LOW
LAK022	69%	13%	30%	9%	43%	0%	80%	0%	84%	LOW	MOD	LOW	MOD
LAK023	37%	6%	2%	3%	7%	0%	100%	0%	100%	LOW	LOW	LOW	LOW
LAK028	88%	13%	8%	62%	18%	100%	100%	100%	100%	LOW	LOW	MOD	LOW
LAK042	60%	6%	6%	20%	21%	0%	100%	80%	100%	LOW	LOW	MOD	MOD
LAK044	13%	0%	4%	1%	4%	100%	100%	0%	100%	LOW	LOW	LOW	LOW
LAK016	70%	2%	7%	33%	32%	0%	0%	0%	1%	LOW	LOW	LOW	LOW
DCAS14A	14%	5%	7%	13%	52%	0%	0%	0%	10%	LOW	LOW	LOW	LOW
NC184	15%	46%	30%	43%	48%	0%	100%	1%	97%	LOW	MOD	LOW	MOD
NC194	4%	▨	▨	4%	71%	0%	100%	0%	33%	▨	▨	LOW	MOD

Table 4-2. Comparison of the results of the updated statistical analyses of the changes relative to the *change limit* to the results in the previous two reporting periods (i.e., 2019 Annual Report and the 2019 comprehensive review (CR)). The 2021 results are the same as Table 3-6. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review (ESSA et al. 2020b). Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red.

LAKE	**Changes in CBANC** (% belief that CBANC *change limit* threshold exceeded)			**Changes in SO_4** (% belief in SO_4 increase > 0 µeq/L)					**Changes in Gran ANC** (% belief that Gran ANC *change limit* threshold exceeded)					**Changes in pH** (% belief that pH *change limit* threshold exceeded)				
Results from:	**2020**	**2021**	**2022**	**CR**	**2019[1]**	**2020**	**2021**	**2022**	**CR**	**2019[1]**	**2020**	**2021**	**2022**	**CR**	**2019[1]**	**2020**	**2021**	**2022**
Sensitive Lakes																		
LAK006	2%	1%	0%	83%	85%	98%	97%	81%	0%	0%	5%	2%	0%	1%	0%	1%	5%	8%
LAK012	40%	35%	23%	91%	95%	99%	86%	70%	1%	0%	19%	18%	14%	1%	0%	1%	8%	10%
LAK022 [2]	2%	11%	13%	88%	89%	89%	87%	69%	0%	0%	10%	31%	30%	0%	0%	0%	39%	43%
LAK023	2%	3%	6%	5%	2%	0%	42%	37%	0%	0%	3%	2%	2%	1%	0%	3%	4%	7%
LAK028	13%	15%	13%	96%	97%	94%	92%	88%	2%	1%	0%	4%	8%	18%	6%	9%	18%	18%
LAK042	9%	6%	6%	36%	44%	81%	76%	60%	0%	0%	2%	4%	6%	2%	0%	13%	23%	21%
LAK044	0%	1%	0%	1%	0%	4%	6%	13%	0%	0%	3%	3%	4%	0%	0%	0%	1%	4%
Less Sensitive Lakes																		
LAK016 [2]	7%	7%	2%	97%	81%	81%	99%	70%	0%	0%	1%	4%	7%	1%	0%	6%	28%	32%
Control Lakes																		
DCAS14A [2]	1%	10%	5%	68%	75%	99%	56%	14%	0%	0%	1%	11%	7%	6%	0%	12%	50%	52%
NC184 [2]	10%	43%	46%	58% (in negligible increase)	69% (in negligible increase)	86%	50%	15%	5%	4%	17%	28%	30%	28%	14%	19%	48%	48%
NC194 [2]	n/a	n/a	n/a	1%	1%	2%	12%	4%	n/a	n/a	n/a	n/a	n/a	12%	4%	17%	62%	71%

[1] The 2019 Annual Report applied a 4-year post-KMP averaging period (i.e., 2016-2019; adding the new year of observations to the post-KMP period used in the CR), whereas the subsequent Annual Reports apply a 3-year post-KMP averaging period.

[2] For lakes not sampled in 2020, the post-KMP averaging periods applied in 2020 to 2022 are based on only two years of data.

4.4 Application of the Evidentiary Framework

We applied the evidentiary framework, as described in Section 2.6, using the updated results of the statistical analyses. The results are shown in Figure 4-1 and the underlying values are compiled in Table 4-3. Results show that: a) 1 sensitive lake and 3 control lakes[5] land within the first box, “smelter not causally linked to changes in lake chemistry”; b) 1 less sensitive lake lands within the second box, “lake is healthy, and not acidifying”; and c) 6 sensitive lakes (LAK006, LAK012, LAK022, LAK023, LAK028 and LAK042) land within the third box, “some evidence of acidification; closely monitor”.

For LAK028, this classification is based on: a) average post-KMP values below the *level of protection* for both CBANC and pH, and b) moderate support for a decline in CBANC (66% belief) and pH (57% belief), but with low support for exceedance of either *change limit* threshold (13% belief for CBANC and 18% belief for pH). The overall result is similar to last year, but the level of support for declines in CBANC has decreased from strong to moderate.

For LAK006, LAK012, LAK022, LAK023, and LAK042, this classification is based on pH only. All five lakes have 0% belief in CBANC being below the *level of protection.*

LAK022 and LAK042 show: a) average post-KMP values below the *level of protection* for pH only, and b) moderate support for declines in pH (60% and 36% belief, respectively), with moderate support for exceedance of the *change limit* threshold (43% and 21% belief, respectively).

LAK023 shows: a) average post-KMP values below the *level of protection* for pH only, and b) moderate support for declines in pH (28% belief), but with low support for exceedance of the *change limit* threshold for pH (7%).

LAK006 and LAK012 show: a) a moderate belief in exceeding the *level of protection* for pH (70% and 77% belief, respectively), and b) moderate to low support for declines in pH (25% and 20% belief, respectively), with low support for exceedance of the *change limit* threshold (8% and 10% belief, respectively).

There are no lakes that have acidification exceedances.

The only change in lake classification from last year’s Annual Report is LAK012, due to the percent belief in a decrease in pH changing from 18% to 20% and thus being identified as a moderate level of support for such a change. This small change is within the range of variability from repeat runs of the Bayesian analyses. It is a negligible difference between years but happens to span the defined boundary between low and moderate classifications.

All of the other lakes have the same classification and generally very similar underlying results as last year.

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[5] All of the control lakes are classified in the first box regardless of increases in sulphate because any such increases cannot be causally linked to the smelter due to their location well outside the smelter plume.

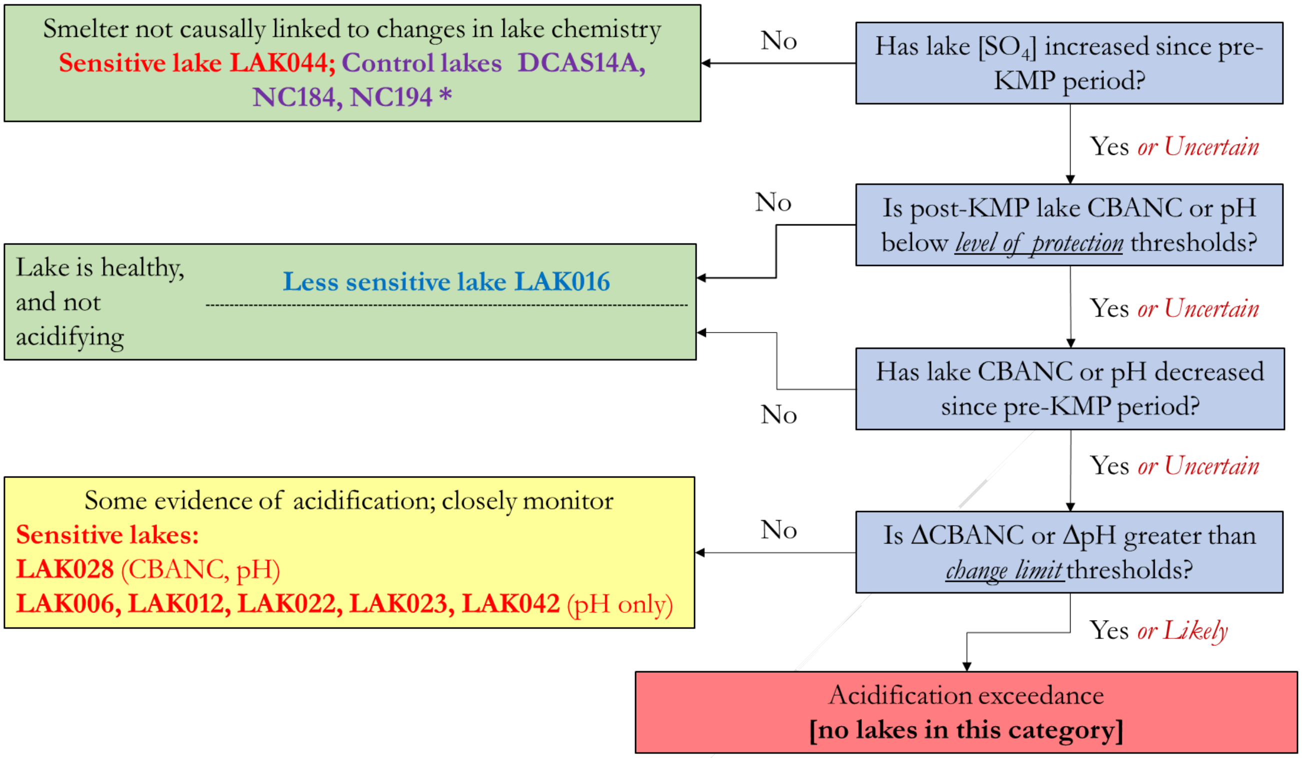

Figure 4-1. Classification of EEM lakes according to the simplified evidentiary framework. LAK028 has moderate support for declines in CBANC and pH but low support for exceeding either *change limit* threshold. LAK006, LAK012, LAK022, LAK023, and LAK042 have moderate support for declines pH with low to moderate support for exceeding the *change limit* thresholds; however, they are all still above the CBANC *level of protection*. The control lakes (*) all show low support for increases in SO_4; however, they are classified in the first box regardless of potential increase in sulphate (as observed in some past years) because any such increases cannot be causally linked to the smelter due to their location well outside the smelter plume.

Table 4-3. Results used in the application of the simple evidentiary framework. The first four columns are identical to Table 3-6 but the last two show the results for the % belief of *any* change in Gran ANC and pH. The % belief values are derived from the Bayesian version of Method 1, as described in Aquatic Appendix F of the 2019 Comprehensive Review (ESSA et al. 2020b). Values of % belief < 20% are coloured green, 20-80% yellow, and >80% red.

LAKE	**Changes in SO_4** (% belief in SO_4 increase / decrease)	**State of post-KMP CBANC** (% belief that CBANC *level of protection* threshold exceeded)	**State of post-KMP pH** (% belief that pH *level of protection* threshold exceeded)	**Changes in CBANC** (% belief that CBANC *change limit* threshold exceeded)	**Changes in pH** (% belief that pH *change limit* threshold exceeded)	**Change in CBANC (no threshold)** (% belief that CBANC decreased)	**Change in pH (no threshold)** (% belief that pH decreased)
Threshold type	**Any change (increase)**	**Level of Protection**	**Level of Protection**	**Change Limit**	**Change Limit**	**Any change (decrease)**	**Any change (decrease)**
Sensitive Lakes							
LAK006	81%	0%	70%	0%	8%	0%	25%
LAK012	70%	0%	77%	23%	10%	45%	20%
LAK022	69%	0%	84%	13%	43%	31%	60%
LAK023	37%	0%	100%	6%	7%	14%	28%
LAK028	88%	100%	100%	13%	18%	66%	57%
LAK042	60%	0%	100%	6%	21%	18%	36%
LAK044	13%	100%	100%	0%	4%	2%	16%
Less Sensitive Lakes							
LAK016	70%	0%	1%	2%	32%	8%	49%
Control Lakes							
DCAS14A	14%	0%	10%	5%	52%	15%	71%
NC184	15%	0%	97%	46%	48%	54%	63%
NC194	4%	0%	33%	n/a	71%	33%	82%

5 Recommendations

We recommend sampling LAK027 again in 2023. In 2021, the widely-observed storm-driven dilution event negated the ability of the sampling data to provide a meaningful comparison against the initial STAR data as intended. In 2022, the combination of exceptionally low deposition and particularly dry hydrologic conditions again negate the ability to provide the intended comparison.

We do not recommend any other changes or adjustments to next year's program.

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Appendix 1: Water Chemistry Data from Annual Sampling, 2012-2022

The two tables below show the sample results for each of the EEM lakes and control lakes from annual monitoring conducted from 2012 to 2022, including charge balance ANC (CBANC), Gran ANC, base cation surplus (BCS), pH, dissolved organic carbon (DOC), and the concentration of major anions and cations, as well as the sum of all base cations (BC). The pH of the water samples has been measured by three different laboratories with (Trent University, 2012-2019; ALS, 2013-2022; BASL, 2019-2022). Gran ANC also transitioned from Trent University to BASL, overlapping in 2019.

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. Lakes with only a single annual sample will show the same value in both tables and no measure of variability. 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.

Mean Annual Values

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

Lake	Year	CBANC (μeq/L)	SE	Gran ANC (μeq/L) (Trent)	SE	Gran ANC (μeq/L) (BASL)	SE	BCS (μeq/L)	SE	pH (Trent)	SE	pH (ALS)	SE	pH (BASL)	SE	DOC (mg/L)	SE	SO4 * (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)	∑ Anions (μeq/L)
Lak006	2012	49.2		25.7				34.6		5.8						3.6		11.4		5.8		4.5		30.3		12.5		2.9		14.9		60.6	66.2
LAK007	2012	1452.4		1437.6				1452.5		8.0						0.6		51.4		24.6		2.8		1272.2		157.0		19.3		55.4		1503.9	1552.5
LAK012	2012	114.5		57.0				94.5		5.6						4.6		6.1		4.2		5.0		74.5		20.8		5.2		20.0		120.6	115.9
LAK016	2012	127.2		68.7				112.0		6.3						3.7		39.0		6.3		7.8		117.7		20.5		7.3		20.8		166.3	166.4
LAK022	2012	67.9		27.8				44.5		5.9						5.3		30.2		6.9		6.1		58.1		16.0		3.2		20.8		98.1	99.4
LAK023	2012	46.9		19.8				29.3		5.7						4.2		19.0		4.5		5.6		39.4		12.0		3.7		10.8		65.9	72.2
LAK024	2012	315.4		299.5				311.7		7.1						1.4		24.8		27.3		1.6		273.2		33.0		4.2		29.6		340.0	376.5
LAK028	2012	16.0		-4.0				-5.1		5.0						4.9		56.9		6.1		20.7		47.5		9.5		3.1		12.8		72.9	95.7
LAK034	2012	177.6		99.4				158.1		6.7						4.5		24.1		5.8		5.8		119.3		31.6		5.8		44.9		201.7	221.4
LAK042	2012	47.2		-20.4				-15.4		4.7						13.2		6.2		6.1		3.2		7.4		22.7		3.1		20.3		53.4	73.4
LAK044	2012	8.0		1.3				2.5		5.4						1.7		6.2		5.6		2.9		6.8		3.2		4.1		0.0		14.2	27.7
Lak006	2013	43.1		29.0				30.3		6.2		6.1				3.2		14.4		8.7		5.6		27.1		13.0		5.3		12.2		57.6	80.1
LAK007	2013	1385.6		1462.1				1388.3		7.9		8.1				0.1		66.5		36.3		3.7		1226.0		156.5		21.9		47.6		1452.0	1598.9
LAK012	2013	97.5		63.5				79.5		6.3		6.1				4.2		11.3		14.7		8.2		64.8		20.3		9.2		14.6		108.9	168.1
LAK016	2013	108.7		96.9				90.9		6.7		7.2				4.2		56.9		12.3		11.5		114.4		23.9		11.2		17.6		167.1	206.6
LAK022	2013	62.0		36.4				33.9		6.2		6.1				6.2		47.1		12.4		8.7		65.1		19.2		6.0		18.8		109.1	145.9
LAK023	2013	37.7		23.8				20.7		6.0		6.0				4.0		24.1		7.5		7.4		37.1		13.3		5.1		8.3		63.9	89.7
LAK024	2013																																
LAK028	2013	-8.1		4.8				-40.2		5.2		5.5				7.1		128.1		17.7		32.0		85.1		18.3		5.0		13.0		121.3	184.0
LAK034	2013	219.5		210.4				199.4		6.9		7.4				4.7		38.1		8.2		10.0		152.7		41.7		9.2		54.1		257.7	287.0
LAK042	2013	55.1		21.0				10.0		5.5		5.4				9.7		5.7		7.7		3.2		16.0		22.3		3.4		19.3		61.0	87.4
LAK044	2013	8.9		8.6				4.5		5.7		6.0				1.5		6.2		8.9		3.8		7.8		3.6		5.9		-2.0		15.3	35.0
Lak006	2014	52.9	*2.0*	38.8	*0.6*			37.2	*2.6*	6.1	*0.1*	6.6	*0.2*			3.8	*0.3*	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	84.2
LAK007	2014	1484.8		1445.7				1484.5		8.1		8.0				0.7		30.7		19.2		1.9		1276.8		156.7		20.2		61.8		1515.5	1527.8
LAK012	2014	99.8	*3.1*	68.8	*6.8*			71.8	*7.9*	6.0	*0.1*	6.7	*0.2*			6.3	*1.0*	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	135.7
LAK016	2014	132.5		105.7				115.6		6.7		6.7				4.0		48.2		9.3		9.5		122.4		25.0		10.1		23.3		180.8	194.2
LAK022	2014	76.1		46.9				51.0		6.3		6.4				5.7		37.8		9.0		6.9		68.5		18.9		5.2		21.4		114.0	133.0
LAK023	2014	59.4	*3.3*	32.1	*1.1*			34.3	*2.1*	5.9	*0.1*	6.7	*0.3*			5.7	*0.4*	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	93.0
LAK024	2014	473.4		472.1				468.1		7.6		7.5				1.7		37.2		65.7		2.3		402.3		50.1		7.8		50.2		510.4	617.9

Lake	Year	CBANC (μeq/L)	SE	Gran ANC (μeq/L) (Trent)	SE	Gran ANC (μeq/L) (BASL)	SE	BCS (μeq/L)	SE	pH (Trent)	SE	pH (ALS)	SE	pH (BASL)	SE	DOC (mg/L)	SE	SO4 * (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)	∑ Anions (μeq/L)
LAK028	2014	31.2		22.6				4.8		5.3		5.7				5.9		94.4		11.0		23.3		85.9		17.7		4.4		17.6		125.7	156.6
LAK034	2014	249.1		205.0				217.2		6.7		7.0				7.0		17.0		6.5		7.7		161.4		43.6		9.4		51.9		266.3	270.9
LAK042	2014	51.6		12.5				1.8		5.1		5.4				10.6		4.0		11.8		2.6		10.5		23.6		3.7		17.9		55.7	89.4
LAK044	2014	12.6		5.9				6.8		5.8		5.6				1.8		4.6		5.9		2.8		7.8		3.9		5.3		0.4		17.3	28.5
Lak006	2015	55.1	*0.8*	32.4	*0.4*			38.7	*1.5*	6.0	*0.1*	6.4	*0.3*			3.9	*0.2*	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	77.0
LAK007	2015	1461.9		1565.6				1463.9		8.0		7.9				0.3		45.6		24.0		2.6		1266.6		161.5		21.0		58.6		1507.7	1666.8
LAK012	2015	106.1	*2.0*	65.9	*2.1*			71.8	*3.9*	6.0	*0.1*	6.3	*0.2*			7.5	*1.0*	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	140.3
LAK016	2015	147.1		113.1				128.8		6.8		6.9				4.3		40.9		8.7		8.6		130.9		25.0		9.8		22.9		188.6	192.1
LAK022	2015	75.2		35.6				47.0		6.1		6.2				6.3		32.5		7.9		5.9		64.1		18.1		4.4		21.2		107.8	117.3
LAK023	2015	58.0	*1.0*	30.0	*1.0*			34.4	*0.9*	5.9	*0.1*	6.2	*0.1*			5.4	*0.4*	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	83.0
LAK024	2015	472.8		443.0				465.0		7.4		7.5				2.2		34.7		59.0		2.1		400.5		49.3		8.7		49.0		507.6	580.6
LAK028	2015	38.6		10.8				1.5		5.1		5.3				8.1		71.1		9.0		20.5		76.5		15.7		3.2		14.4		109.8	122.1
LAK034	2015	233.0		177.8				198.5		6.6		6.7				7.6		0.9		6.2		4.7		146.5		37.1		5.3		45.1		234.0	231.8
LAK042	2015	55.4		13.8				16.9		5.4		5.5				8.3		3.8		6.5		2.3		10.7		23.1		2.5		23.0		59.3	70.7
LAK044	2015	16.4		6.2				11.6		5.8		5.8				1.6		3.7		5.9		2.7		9.8		4.4		5.5		0.5		20.3	28.0
Lak006	2016	56.9	*2.4*	26.9	*1.0*			38.9	*2.4*	6.0	*0.0*	6.3	*0.1*			4.2	*0.1*	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	74.0
LAK007	2016	1495.8		1368.6				1495.2		8.0		8.1				0.8		46.7		25.4		2.6		1301.5		162.8		20.2		58.3		1542.8	1474.0
LAK012	2016	103.2	*1.6*	65.8	*1.2*			81.0	*2.1*	6.2	*0.0*	6.5	*0.1*			5.1	*0.3*	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	115.7
LAK016	2016	140.8		93.9				118.3		6.6		6.9				5.2		44.9		8.5		8.2		127.4		26.4		8.9		23.7		186.5	189.4
LAK022	2016	80.3		34.4				50.1		6.1		6.4				6.7		34.2		7.9		5.8		68.1		19.2		4.2		23.1		114.6	119.0
LAK023	2016	59.5	*1.4*	27.9	*1.9*			33.6	*1.0*	5.9	*0.0*	6.2	*0.1*			5.8	*0.1*	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	80.8
LAK024	2016	525.1		463.1				514.8		7.5		7.6				2.7		39.2		70.0		2.3		446.5		55.3		9.5		53.9		565.3	619.2
LAK028	2016	12.3	*3.8*	-4.9	*6.2*			-24.9	*5.2*	5.0	*0.1*	5.1	*0.1*			8.1	*0.3*	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	179.1
LAK034	2016	212.2		151.6				177.6		6.5		7.1				7.6		0.0		5.4		4.4		130.0		34.3		3.8		44.1		212.3	215.4
LAK042	2016	64.0	*1.7*	14.0	*1.5*			18.0	*1.1*	5.4	*0.0*	5.7	*0.0*			9.8	*0.2*	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	78.8
LAK044	2016	13.9	*0.6*	4.1	*1.3*			7.0	*0.6*	5.5	*0.0*	6.0	*0.1*			2.0	*0.1*	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	27.7
Lak006	2017	58.0	*0.6*	27.9	*2.7*			42.1	*1.0*	6.0	*0.1*	6.4	*0.1*			3.8	*0.1*	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	71.4
LAK007	2017	1402.3		1381.6				1404.3		8.0		8.0				0.3		47.1		25.9		2.4		1201.7		165.2		19.9		62.6		1449.4	1492.4
LAK012	2017	101.1	*3.7*	58.2	*3.2*			78.2	*1.9*	6.1	*0.1*	6.5	*0.1*			5.2	*0.5*	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	117.5
LAK016	2017	125.3		82.7				107.8		6.7		6.8				4.1		43.2		7.3		7.7		114.0		24.7		6.9		22.9		168.6	167.5
LAK022	2017	70.4		34.2				44.2		6.1		6.3				5.9		39.0		7.1		5.4		64.1		19.5		3.8		22.2		109.6	112.4
LAK023	2017	59.9	*1.5*	28.5	*2.4*			36.0	*1.3*	5.9	*0.0*	6.2	*0.0*			5.4	*0.1*	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	71.3
LAK024	2017	479.2		416.6				472.3		7.4		7.6				2.0		34.9		57.5		2.0		399.6		52.2		8.5		54.2		514.4	557.5
LAK028	2017	0.7	*5.3*	-9.9	*4.5*			-32.5	*7.8*	4.8	*0.1*	5.1	*0.1*			7.3	*0.6*	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	199.2
LAK034	2017	177.6		136.5				150.7		6.4		6.8				6.0		0.1		4.5		3.4		105.6		30.3		2.7		39.1		177.8	179.1
LAK042	2017	63.1	*3.0*	2.3	*2.1*			8.4	*2.7*	5.2	*0.1*	5.4	*0.1*			11.6	*1.1*	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	80.8
LAK044	2017	13.8	*0.3*	7.0	*2.2*			9.1	*0.3*	5.6	*0.1*	6.0	*0.1*			1.6	*0.0*	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	26.2
Lak006	2018	59.3	*1.2*	28.3	*1.2*			43.6	*1.5*	6.1	*0.0*	6.4	*0.0*			3.8	*0.1*	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	82.1
LAK007	2018	1443.8		1407.6				1445.7		8.1		8.1				0.3		47.1		27.9		2.6		1251.5		157.4		20.6		61.3		1490.8	1518.7
LAK012	2018	90.4	*1.2*	50.9	*4.3*			70.5	*0.9*	6.2	*0.1*	6.6	*0.1*			4.6	*0.1*	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	112.3
LAK016	2018	138.1		92.8				118.4		6.7		6.9				4.6		45.3		7.3		8.1		128.5		23.3		7.3		24.3		183.5	195.3

Lake	Year	CBANC (µeq/L)	SE	Gran ANC (µeq/L) (Trent)	SE	Gran ANC (µeq/L) (BASL)	SE	BCS (µeq/L)	SE	pH (Trent)	SE	pH (ALS)	SE	pH (BASL)	SE	DOC (mg/L)	SE	SO4 * (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)	∑ Anions (µeq/L)
LAK022	2018	76.6		30.3				51.8		6.1		6.3				5.6		43.2		7.3		5.8		72.1		19.3		4.2		24.4		119.9	120.1
LAK023	2018	61.3	0.7	23.0	0.7			36.3	1.6	6.0	0.1	6.4	0.1			5.6	0.2	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	78.6
LAK024	2018	553.5		509.9				548.8		7.6		7.6				1.6		42.6		77.3		2.4		472.7		56.4		9.4		57.2		595.7	680.2
LAK028	2018	8.4	1.8	4.2	1.6			-10.2	1.9	5.3	0.0	5.5	0.0			4.4	0.1	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	147.4
LAK034	2018	183.4		130.6				161.0		6.5		6.6				5.1		0.1		3.7		3.7		113.1		27.7		2.1		40.8		183.7	176.3
LAK042	2018	50.4	1.0	0.6	1.9			0.7	1.3	5.1	0.0	5.3	0.0			10.6	0.4	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	74.4
LAK044	2018	13.2	0.3	3.9	0.9			7.0	0.2	5.5	0.0	5.9	0.0			1.9	0.1	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	27.5
Lak006	2019	63.8	2.2	31.6	2.7	40.0	1.1	49.7	1.8	6.1	0.0	6.5	0.1	6.2	0.0	3.5	0.2	16.8	0.6	6.7	0.6	4.0	0.2	38.0	0.6	17.8	0.4	5.1	0.2	19.9	0.9	80.8	74.1
LAK007	2019	1443.5		1374.5		1496.3		1445.4		8.1		8.1		8.0		0.3		43.0		27.1		2.4		1246.6		158.4		20.4		61.2		1486.5	1469.6
LAK012	2019	96.5	0.4	55.3	0.9	64.1	2.6	74.8	1.6	6.1	0.0	6.6	0.1	6.2	0.0	5.0	0.3	13.5	0.9	7.1	0.2	4.4	0.2	59.7	0.5	21.3	0.2	6.5	0.2	22.6	0.6	110.1	121.4
LAK016	2019	129.8		90.8		100.9		111.2		6.6		7.1		6.6		4.4		58.6		9.0		7.9		127.9		26.5		9.7		24.4		188.6	219.5
LAK022	2019	74.8		35.9		44.4		47.8		6.1		6.4		6.2		6.0		49.3		8.7		5.6		71.5		22.4		5.0		25.3		124.2	123.4
LAK023	2019	59.4	1.6	20.7	2.4	26.8	1.5	33.4	1.3	5.8	0.0	6.3	0.1	6.0	0.0	5.9	0.2	13.5	0.8	5.4	0.2	4.8	0.2	42.2	0.4	15.4	0.6	3.3	0.2	12.1	1.1	73.1	79.4
LAK024	2019	570.7		496.9		548.7		566.0		7.7		7.7		7.3		1.6		40.8		75.3		2.1		478.3		58.1		8.7		66.3		611.4	652.5
LAK028	2019	4.5	4.4	3.3	0.7	4.0	3.1	-18.1	6.0	5.2	0.0	5.4	0.0	5.1	0.0	5.2	0.3	148.5	4.0	11.3	0.6	25.8	1.1	103.5	1.2	26.6	0.5	3.7	0.2	20.0	0.9	153.7	200.1
LAK034	2019	196.8		148.9		166.9		173.8		6.4		7.0		6.6		5.3		0.9		4.5		4.1		122.1		30.4		1.8		43.5		197.8	195.9
LAK042	2019	52.1	2.1	10.1	0.6	16.5	1.0	9.1	1.4	5.4	0.0	5.6	0.1	5.4	0.0	9.2	0.5	7.6	0.6	6.2	0.3	2.3	0.1	12.6	1.8	23.1	0.6	2.2	0.3	22.0	0.3	59.9	77.1
LAK044	2019	14.8	0.6	6.1	0.4	6.6	0.3	5.7	1.2	5.5	0.0	5.9	0.1	5.7	0.0	2.5	0.3	4.7	0.3	6.5	0.3	2.3	0.1	8.9	0.2	4.5	0.2	6.0	0.2	0.3	0.2	19.6	32.0
Lak006	2020	70.3	1.5			44.7	1.3	48.1	3.8			6.3	0.0	6.1	0.0	5.1	0.5	15.3	0.5	6.5	0.6	4.0	0.1	44.9	1.3	17.6	0.7	4.7	0.4	18.6	0.4	85.7	91.4
LAK012	2020	142.1	6.4			93.1	9.0	101.4	4.9			6.4		6.1	0.0	8.8		15.6		9.3		5.0		97.5		28.1		7.8		24.5		157.9	165.7
LAK016	2020																																
LAK022	2020																																
LAK023	2020	66.6	0.5			29.6	1.6	37.6	2.8			6.1		6.0	0.0	6.4		13.9		5.1		4.8		49.0		15.7		3.7		12.2		80.6	80.5
LAK028	2020	8.0	1.4			0.5	0.6	-26.7	1.5			5.0	0.0	5.0	0.0	7.6	0.2	149.1	4.2	9.8	0.2	24.3	0.9	110.6	3.2	24.5	0.6	3.4	0.2	20.3	0.9	158.8	193.3
LAK042	2020	79.5	0.4			-10.0	3.6	-13.2	0.9			4.8		4.7	0.1	19.2		7.6		6.5		2.5		23.6		33.2		2.9		27.5		87.2	102.9
LAK044	2020	14.5	0.9			2.4	1.6	8.1	1.1			5.7	0.1	5.6	0.0	1.9	0.0	5.2	0.2	6.9	0.1	2.1	0.1	8.4	0.2	4.6	0.1	6.6	0.0	0.3	0.5	19.9	21.8
Lak006	2021	67.8	3.6			39.1	0.8	46.0	3.8			6.3	0.1	5.9	0.0	5.0	0.5	17.5	0.5	6.8	0.5	4.0	0.2	45.0	1.8	17.2	0.7	4.9	0.2	18.3	0.8	85.4	91.3
LAK012	2021	101.2	2.6			58.7	6.9	68.1	4.1			6.3	0.0	5.8	0.0	7.3	0.7	28.7	2.6	6.5	0.9	4.2	0.2	79.4	2.7	23.9	0.6	6.0	0.2	21.6	0.8	130.8	133.3
LAK016	2021	138.1				95.9		97.9				6.7		6.2		8.7		59.5		8.2		8.7		139.4		28.0		8.2		23.3		198.8	213.4
LAK022	2021	68.8				20.6		44.2				5.4		5.5		5.6		41.9		7.6		5.6		65.1		20.1		3.9		21.8		110.8	104.5
LAK023	2021	56.2	3.9			24.9	1.0	32.4	3.9			6.1	0.1	5.7	0.0	5.4	0.3	24.5	1.1	4.7	0.3	4.6	0.3	51.9	2.8	15.1	0.6	3.5	0.2	11.5	0.5	81.9	82.0
LAK028	2021	11.7	1.9			-5.7	0.9	-31.9	2.5			4.9	0.1	4.8	0.0	9.4	0.3	96.9	6.8	10.2	0.5	19.4	0.3	76.5	3.7	17.9	1.4	2.7	0.1	12.9	1.2	110.0	141.1
LAK042	2021	62.4	4.3			-11.8	3.8	-16.5	4.3			4.7	0.1	4.7	0.1	16.5	0.6	13.5	1.1	5.6	0.3	2.3	0.2	20.9	1.8	28.2	0.6	2.7	0.1	24.3	0.8	76.1	100.5
LAK044	2021	17.1	1.4			5.4	1.9	9.5	1.6			5.5	0.1	5.5	0.0	2.2	0.2	4.2	0.3	5.6	0.1	1.8	0.1	9.4	1.4	4.4	0.3	6.5	0.2	1.1	0.3	21.5	25.6
Lak006	2022	70.1	1.3			44.1	1.7	52.2	1.7			6.5	0.0	6.3	0.0	4.2	0.3	12.1	0.4	5.9	0.3	3.7	0.0	42.0	0.7	17.2	0.2	4.2	0.1	18.9	0.5	82.3	84.7
LAK012	2022	112.4	1.1			81.9	1.6	90.2	2.2			6.7	0.0	6.3	0.0	5.1	0.2	1.0	0.5	5.8	0.1	4.1	0.0	67.7	1.1	22.0	0.2	3.2	0.1	20.7	0.5	113.6	115.9
LAK016	2022	141.4				113.1		123.2				7.0		6.6		4.3		41.7		7.3		7.3		128.5		24.8		8.6		21.8		183.6	188.4
LAK022	2022	75.4				39.4		47.8				6.3		6.2		6.2		31.6		6.8		5.1		62.6		18.7		4.0		21.7		107.1	107.0
LAK023	2022	54.0	0.5			26.3	5.8	29.6	1.3			6.2	0.0	6.1	0.0	5.5	0.2	12.7	0.3	4.6	0.1	4.2	0.0	39.4	0.4	13.3	0.1	3.9	0.1	10.2	0.3	66.8	72.0
LAK028	2022	19.3	4.0			10.4	1.9	-10.6	3.6			5.3	0.1	5.2	0.1	6.6	0.4	100.4	1.8	7.1	0.1	16.4	0.8	80.7	2.2	18.7	0.3	3.2	0.1	17.3	0.5	119.9	139.4
LAK042	2022	52.8	1.3			15.4	1.7	15.6	2.2			5.6	0.0	5.5	0.0	8.1	0.3	3.4	0.3	4.8	0.4	1.7	0.1	11.0	0.3	20.6	0.3	2.2	0.2	22.5	0.7	56.3	65.7

Lake	Year	CBANC (µeq/L)	SE	Gran ANC (µeq/L) (Trent)	SE	Gran ANC (µeq/L) (BASL)	SE	BCS (µeq/L)	SE	pH (Trent)	SE	pH (ALS)	SE	pH (BASL)	SE	DOC (mg/L)	SE	SO4 * (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)	∑ Anions (µeq/L)
LAK044	2022	16.8	0.4			7.3	0.5	10.9	1.6			5.8	0.1	5.8	0.0	1.8	0.3	3.0	0.1	5.7	0.2	1.7	0.1	8.2	0.2	4.2	0.1	6.7	0.3	0.8	0.2	19.9	22.1
NC184	2012																																
NC194	2012																																
DCAS14A	2012																																
NC184	2013	80.4		16.2				25.6		5.7						11.6		5.7		24.0		0.3		50.5		17.5		4.4		13.8		86.2	132.0
NC194	2013	35.6		28.0				35.3		6.6						0.7		3.6		7.6		0.3		23.2		3.4		5.2		7.4		39.2	59.3
DCAS14A	2013	53.5		50.6				49.9		6.5						1.4		33.4		9.2		0.6		63.9		10.3		10.3		6.1		90.6	115.6
NC184	2014																																
NC194	2014																																
DCAS14A	2014																																
NC184	2015	73.0		18.4				27.2		5.5		5.6				9.8		5.7		21.7		0.5		48.8		16.1		2.9		10.8		78.7	104.6
NC194	2015	40.9		33.0				40.2		6.5		6.5				0.8		2.3		7.3		0.5		26.9		4.4		4.3		7.9		43.4	56.3
DCAS14A	2015	74.9						73.6		6.6		6.7				0.9		35.7		7.3		0.5		77.6		12.4		11.2		9.9		111.0	49.0
NC184	2016	94.6		27.3				44.9		5.8		6.2				10.6		5.5		21.2		0.5		62.6		19.3		2.7		15.5		100.1	120.5
NC194	2016	40.0		28.7				35.1		6.4		6.6				1.6		2.3		7.9		0.5		26.4		4.3		3.8		7.9		42.4	55.4
DCAS14A	2016	72.7		57.5				68.3		6.6		6.8				1.5		36.8		8.5		0.5		77.5		11.8		10.5		9.7		109.6	116.1
NC184	2017	76.3		9.8				13.0		5.4		6.0				13.3		4.7		14.7		0.5		45.2		17.4		2.5		15.9		81.0	104.6
NC194	2017	46.5		12.4				44.8		6.4		6.4				1.0		2.5		4.8		0.5		29.9		5.7		3.6		9.9		49.1	39.4
DCAS14A	2017	67.8		51.0				63.3		6.6		6.7				1.5		31.1		5.6		0.5		68.2		11.8		9.1		9.9		99.0	99.0
NC184	2018	95.0		44.0				63.1		6.2		6.4				7.0		8.3		16.6		0.5		67.8		17.3		3.1		15.3		103.4	113.3
NC194	2018	43.1		26.1				45.0		6.5		6.7				0.3		2.6		5.1		0.5		28.3		4.3		4.1		9.1		45.8	45.6
DCAS14A	2018	79.0		59.3				77.3		6.8		6.8				1.0		41.3		7.3		0.5		85.6		12.6		11.5		10.7		120.4	124.2
NC184	2019	86.1	*1.7*	24.9	*1.5*	47.3	*14.2*	42.9	*2.2*	5.7	*0.0*	6.1	*0.1*	5.9	*0.0*	9.3	*0.3*	7.1	*0.2*	23.2	*1.0*	0.5	*0.0*	58.3	*0.3*	19.0	*0.6*	2.6	*0.1*	13.5	*1.1*	93.3	114.5
NC194	2019	46.7	*0.6*	30.4	*5.3*	41.4	*0.2*	44.7	*0.4*	6.4	*0.0*	6.6	*0.1*	6.5	*0.0*	1.0	*0.2*	2.7	*0.3*	9.2	*0.4*	0.5	*0.0*	31.4	*0.6*	4.8	*0.1*	4.7	*0.2*	8.5	*0.3*	49.4	50.0
DCAS14A	2019	81.1	*1.5*	58.6	*5.9*	73.0	*0.3*	78.3	*1.4*	6.6	*0.1*	6.8	*0.0*	6.6	*0.0*	1.2	*0.0*	41.0	*0.9*	8.8	*1.0*	0.5	*0.0*	85.3	*1.2*	13.7	*0.2*	11.9	*0.3*	11.9	*0.3*	122.8	138.6
NC184	2020																																
NC194	2020																																
DCAS14A	2020																																
NC184	2021	61.2				9.2		6.4				5.1		5.2		11.6		3.5		18.9		0.3		37.3		13.5		2.0		11.8		64.7	100.8
NC194	2021	35.6				27.4		33.1				6.2		6.0		1.1		2.1		5.9		0.3		22.4		3.9		3.8		7.7		37.8	54.9
DCAS14A	2021	63.8				55.6		55.0				6.6		6.0		2.4		28.5		7.9		0.6		63.6		11.9		10.2		9.4		95.1	101.0
NC184	2022	85.3				25.2		35.5				6.1		5.9		10.6		4.5		15.2		0.3		54.3		18.0		2.8		14.7		89.8	110.1
NC194	2022	36.3				28.6		35.1				6.5		6.4		0.9		1.9		5.1		0.3		22.7		4.0		3.8		7.7		38.3	40.8
DCAS14A	2022	70.9				62.7		68.1				6.8		6.5		1.2		30.7		5.4		0.3		71.2		11.4		10.1		9.1		101.7	98.5

[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	Gran Alkalinity (mg/L) (Trent)	Gran Alkalinity (mg/L) (BASL)	pH (Trent)	pH (ALS)	pH (BASL)	DOC (mg/L)	Conductivity (µS/s)	SO4 (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	1.3		5.8			3.6	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	71.9		8.0			0.6	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	2.9		5.6			4.6	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	3.4		6.3			3.7	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	1.4		5.9			5.3	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	1.0		5.7			4.2	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	15.0		7.1			1.4	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	-0.2		5.0			4.9	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	5.0		6.7			4.5	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	-1.0		4.7			13.2	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	0.1		5.4			1.7	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	1.5		6.2	6.1		3.2	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	73.2		7.9	8.1		0.1	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	3.2		6.3	6.1		4.2	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	4.9		6.7	7.2		4.2	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	1.8		6.2	6.1		6.2	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	1.2		6.0	6.0		4.0	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	0.2		5.2	5.5		7.1	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	10.5		6.9	7.4		4.7	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	1.1		5.5	5.4		9.7	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	0.4		5.7	6.0		1.5	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	1.9		6.1	6.6		3.8	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	72.4		8.1	8.0		0.7	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	3.4		6.0	6.7		6.3	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	5.3		6.7	6.7		4.0	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	2.3		6.3	6.4		5.7	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	1.6		5.9	6.7		5.7	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	23.6		7.6	7.5		1.7	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	1.1		5.3	5.7		5.9	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	10.3		6.7	7.0		7.0	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	0.6		5.1	5.4		10.6	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
LAK044	2014	0.3		5.8	5.6		1.8	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	1.6		6.0	6.4		3.9	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	78.4		8.0	7.9		0.3	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	3.3		6.0	6.3		7.5	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	5.7		6.8	6.9		4.3	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	1.8		6.1	6.2		6.3	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	1.5		5.9	6.2		5.4	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

Lake	Year	Gran Alkalinity (mg/L) (Trent)	Gran Alkalinity (mg/L) (BASL)	pH (Trent)	pH (ALS)	pH (BASL)	DOC (mg/L)	Conductivity (µS/s)	SO4 (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)
LAK024	2015	22.2		7.4	7.5		2.2	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	0.5		5.1	5.3		8.1	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	8.9		6.6	6.7		7.6	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	0.7		5.4	5.5		8.3	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	0.3		5.8	5.8		1.6	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	1.3		6.0	6.3		4.2	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	68.5		8.0	8.1		0.8	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	3.3		6.2	6.5		5.1	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	4.7		6.6	6.9		5.2	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	1.7		6.1	6.4		6.7	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	1.4		5.9	6.2		5.8	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	23.2		7.5	7.6		2.7	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	-0.2		5.0	5.1		8.1	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	7.6		6.5	7.1		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	0.7		5.4	5.7		9.8	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	0.2		5.5	6.0		2.0	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	1.4		6.0	6.4		3.8	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	69.1		8.0	8.0		0.3	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	2.9		6.1	6.5		5.2	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	4.1		6.7	6.8		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	1.7		6.1	6.3		5.9	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	1.4		5.9	6.2		5.4	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	20.9		7.4	7.6		2.0	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	-0.5		4.8	5.1		7.3	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	6.8		6.4	6.8		6.0	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	0.1		5.2	5.4		11.6	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	0.4		5.6	6.0		1.6	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
Lak006	2018	1.4		6.1	6.4		3.8	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	70.4		8.1	8.1		0.3	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	2.5		6.2	6.6		4.6	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	4.6		6.7	6.9		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	1.5		6.1	6.3		5.6	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	1.1		6.0	6.4		5.6	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	25.5		7.6	7.6		1.6	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	0.2		5.3	5.5		4.4	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		6.5	6.6		5.1	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	0.0		5.1	5.3		10.6	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	0.2		5.5	5.9		1.9	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
Lak006	2019	1.6	2.0	6.1	6.5	6.2	1.1	8.3	0.8	0.2	0.1	2.5	2.5	0.8	0.2	0.2	0.6	0.0	0.0	0.0
Lak007	2019	68.8	74.9	8.1	8.1	8.0	0.3	147.2	2.2	1.0	0.0	2.5	2.5	25.0	2.0	0.8	1.9	0.0	0.0	0.0
LAK012	2019	2.8	3.2	6.1	6.6	6.2	1.8	11.0	0.7	0.3	0.1	3.2	2.5	1.2	0.3	0.3	0.7	0.2	0.0	0.0

Lake	Year	Gran Alkalinity (mg/L) (Trent)	Gran Alkalinity (mg/L) (BASL)	pH (Trent)	pH (ALS)	pH (BASL)	DOC (mg/L)	Conductivity (µS/s)	SO4 (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)
LAK016	2019	4.5	5.1	6.6	7.1	6.6	2.5	19.8	2.9	0.3	0.2	2.5	6.2	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2019	1.8	2.2	6.1	6.4	6.2	1.3	13.6	2.4	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.8	0.1	0.1	0.0
LAK023	2019	1.0	1.3	5.8	6.3	6.0	1.0	7.1	0.7	0.2	0.1	2.5	3.6	0.9	0.2	0.1	0.4	0.0	0.1	0.0
LAK024	2019	24.9	27.5	7.7	7.7	7.3	6.9	66.8	2.3	2.7	0.0	8.0	2.5	9.6	0.9	0.4	3.0	0.0	0.0	0.0
LAK028	2019	0.2	0.2	5.2	5.4	5.1	5.4	24.0	7.2	0.4	0.5	11.9	5.2	2.1	0.4	0.2	0.7	0.1	0.6	0.0
LAK034	2019	7.5	8.4	6.4	7.0	6.6	3.0	17.8	0.1	0.2	0.1	2.5	2.5	2.5	0.4	0.1	1.1	0.0	0.0	0.0
LAK042	2019	0.5	0.8	5.4	5.6	5.4	1.5	6.6	0.4	0.2	0.0	4.3	2.5	0.3	0.3	0.1	0.6	0.2	0.3	0.0
LAK044	2019	0.3	0.3	5.5	5.9	5.7	1.5	2.4	0.3	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2020		2.2		6.3	6.1	5.1	8.5	0.8	0.2	0.1	2.5	2.5	0.9	0.2	0.2	0.6	0.1	0.1	0.0
LAK012	2020		4.7		6.4	6.1	8.8	15.1	0.8	0.3	0.1	2.5	2.5	2.0	0.4	0.3	0.7	0.5	0.1	0.1
LAK016	2020																			
LAK022	2020																			
LAK023	2020		1.5		6.1	6.0	6.4	7.3	0.7	0.2	0.1	2.5	2.5	1.0	0.2	0.1	0.4	0.0	0.1	0.0
LAK028	2020		0.0		5.0	5.0	7.6	25.0	7.2	0.3	0.5	25.4	3.8	2.2	0.3	0.1	0.7	0.1	0.7	0.0
LAK042	2020		-0.5		4.8	4.7	19.2	14.2	0.4	0.2	0.0	2.5	2.5	0.5	0.4	0.1	0.8	0.6	0.6	0.0
LAK044	2020		0.2		5.6	5.6	1.9	2.5	0.1	0.1	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2021		2.0		6.3	5.9	5.0	8.3	0.9	0.2	0.1	2.5	5.3	0.9	0.2	0.2	0.6	0.1	0.1	0.0
LAK012	2021		2.9		6.3	5.8	7.3	13.1	1.4	0.2	0.1	12.9	4.8	1.6	0.3	0.2	0.6	0.4	0.1	0.0
LAK016	2021		4.8		6.7	6.2	8.7	20.5	2.9	0.3	0.2	18.1	2.5	2.8	0.4	0.3	0.7	0.1	0.2	0.0
LAK022	2021		1.0		5.4	5.5	5.6	12.6	2.1	0.3	0.1	2.5	2.5	1.3	0.3	0.2	0.7	0.1	0.2	0.0
LAK023	2021		1.2		6.1	5.7	5.4	8.3	1.2	0.2	0.1	18.7	3.3	1.0	0.2	0.1	0.4	0.0	0.1	0.0
LAK028	2021		-0.3		4.9	4.8	9.4	20.4	4.7	0.4	0.4	20.5	3.2	1.5	0.2	0.1	0.5	0.2	0.7	0.0
LAK042	2021		-0.6		4.7	4.7	16.5	14.5	0.7	0.2	0.0	2.5	4.1	0.4	0.4	0.1	0.7	0.5	0.5	0.0
LAK044	2021		0.3		5.5	5.5	2.2	2.7	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.3	0.1	0.0	0.0	0.0
Lak006	2022		1.8		5.2	5.0	3.4	9.4	0.5	0.2	0.1	2.0	2.5	0.7	0.2	0.1	0.4	0.1	0.0	0.0
LAK012	2022		4.1		6.7	6.3	5.1	11.9	0.1	0.2	0.1	2.5	2.5	1.4	0.3	0.1	0.6	0.2	0.0	0.0
LAK016	2022		5.7		7.0	6.6	4.3	20.7	2.0	0.3	0.1	7.2	6.0	2.6	0.3	0.3	0.6	0.0	0.1	0.0
LAK022	2022		2.0		6.3	6.2	6.2	12.1	1.6	0.2	0.1	2.5	2.5	1.3	0.2	0.2	0.6	0.1	0.1	0.0
LAK023	2022		1.3		6.2	6.1	5.5	7.6	0.6	0.2	0.1	2.5	2.5	0.8	0.2	0.2	0.3	0.0	0.1	0.0
LAK028	2022		0.4		4.3	4.2	5.3	18.6	3.9	0.2	0.2	2.6	2.0	1.3	0.2	0.1	0.4	0.1	0.4	0.0
LAK042	2022		0.8		5.6	5.5	8.1	7.0	0.2	0.2	0.0	2.5	3.1	0.2	0.3	0.1	0.6	0.2	0.2	0.0
LAK044	2022		0.4		5.8	5.8	1.8	3.4	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.3	0.1	0.0	0.0	0.0
NC184	2012																			
NC194	2012																			
DCAS14A	2012																			
NC184	2013	0.8		5.7			11.6	10.0	0.4	0.9	0.0	5.0	1.0	1.0	0.3	0.2	0.8			
NC194	2013	1.4		6.6			0.7	3.9	0.2	0.3	0.0	1.0	1.0	0.5	0.1	0.2	0.3			
DCAS14A	2013	2.5		6.5			1.4	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																			

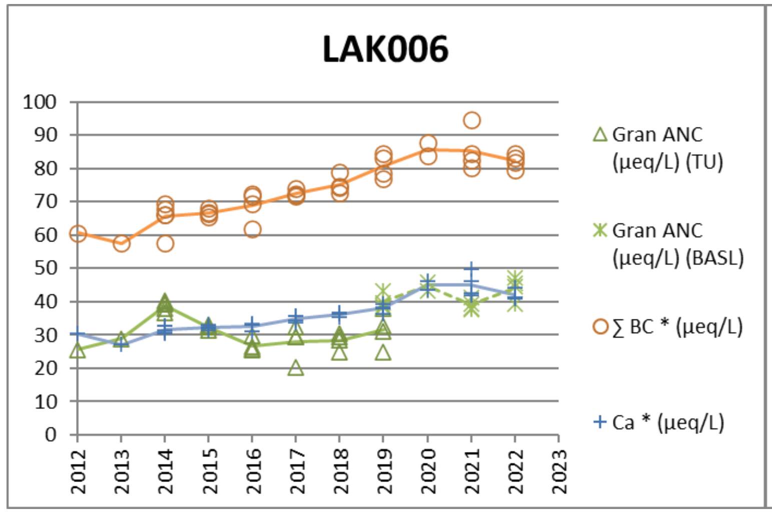
Lake	Year	Gran Alkalinity (mg/L) (Trent)	Gran Alkalinity (mg/L) (BASL)	pH (Trent)	pH (ALS)	pH (BASL)	DOC (mg/L)	Conductivity (µS/s)	SO4 (mg/L)	Cl (mg/L)	F (mg/L)	NO3 (µg/L)	NH4 (µg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
NC184	2015	0.9		5.5	5.6		9.8	11.6	0.4	0.8	0.0	2.5	2.5	1.0	0.2	0.1	0.7	0.2	0.3	0.0
NC194	2015	1.7		6.5	6.5		0.8	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	1.4		5.8	6.2		10.6	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	1.4		6.4	6.6		1.6	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	2.9		6.6	6.8		1.5	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	0.5		5.4	6.0		13.3	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	0.6		6.4	6.4		1.0	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	2.6		6.6	6.7		1.5	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	2.2		6.2	6.4		7.0	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	1.3		6.5	6.7		0.3	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	3.0		6.8	6.8		1.0	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
NC184	2019	1.2	2.4	5.7	6.1	5.9	1.1	11.1	0.5	0.8	0.0	3.7	2.5	1.2	0.3	0.1	0.8	0.1	0.3	0.0
NC194	2019	1.5	2.1	6.4	6.6	6.5	0.9	5.3	0.2	0.3	0.0	2.5	2.5	0.6	0.1	0.2	0.4	0.0	0.0	0.0
DCAS14A	2019	2.9	3.7	6.6	6.8	6.6	1.4	13.7	2.0	0.3	0.0	10.3	2.5	1.7	0.2	0.5	0.4	0.0	0.0	0.0
NC184	2020																			
NC194	2020																			
DCAS14A	2020																			
NC184	2021		0.5		5.1	5.2	11.6	9.5	0.3	0.7	0.0	2.5	2.5	0.8	0.2	0.1	0.6	0.2	0.3	0.0
NC194	2021		1.4		6.2	6.0	1.1	3.3	0.1	0.2	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	2021		2.8		6.6	6.0	2.4	10.8	1.4	0.3	0.0	39.8	2.5	1.3	0.2	0.4	0.4	0.0	0.0	0.0
NC184	2022		1.3		6.1	5.9	10.6	10.9	0.3	0.5	0.0	2.5	2.5	1.1	0.3	0.1	0.6	0.1	0.3	0.0
NC194	2022		1.4		6.5	6.4	0.9	4.6	0.1	0.2	0.0	2.5	2.5	0.5	0.1	0.2	0.3		0.0	0.0
DCAS14A	2022		3.1		6.8	6.5	1.2	12.1	1.5	0.2	0.0	2.5	2.5	1.4	0.2	0.4	0.3	0.0	0.0	0.0

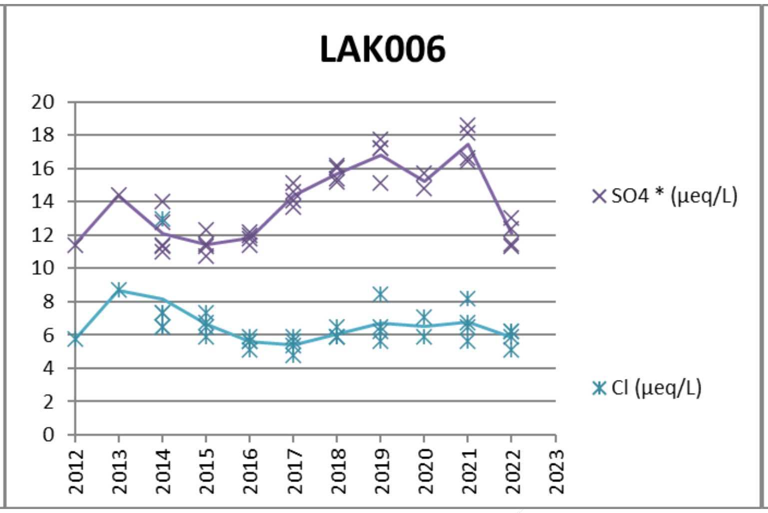
Appendix 2: Changes in Ion Concentrations from 2012 to 2022

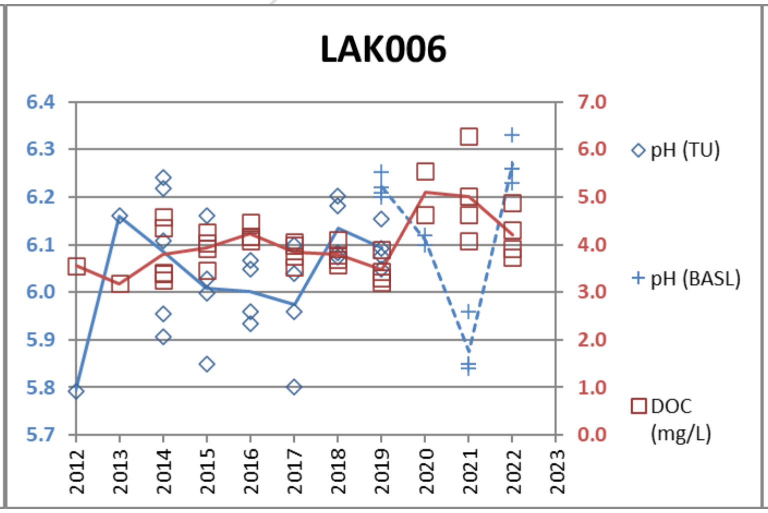
For each of the EEM lakes, the figures in this appendix show the inter-annual changes in six major water chemistry metrics from 2012 to 2022: Gran ANC, base cations and calcium (left panel), sulfate and chloride (centre-left panel), pH and dissolved organic carbon (centre-right panel), and CBANC, Gran ANC, and BCS (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 center-right panel has two Y-axes. The axis for pH does not 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 for individual lakes across the sampling record and determining whether similar patterns are observed across lakes and/or metrics.

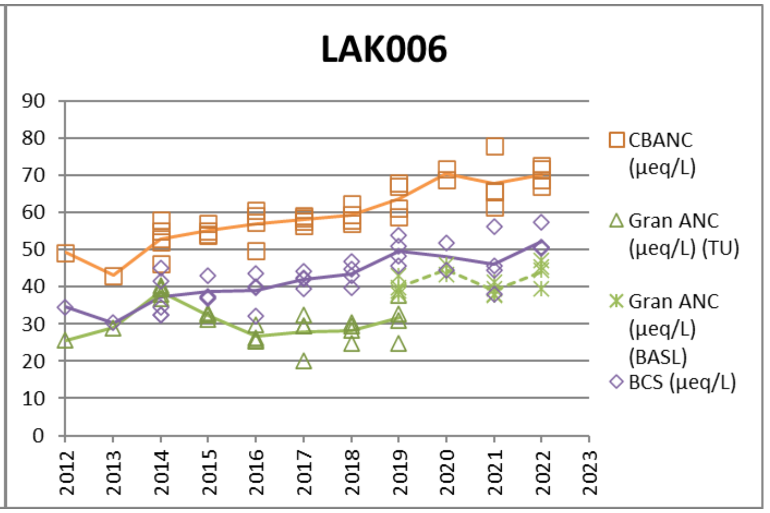
These figures show the results for all of the sampling events for each lake in each year, whether that included multiple within-season samples or only a single annual sample. The points represent the values for individual sampling events. The solid lines represent the annual trend, based on either the single annual sample or the average of all the within-season samples, as appropriate for the lake and year. For the sensitive lakes (the only lakes where intensive, within-season sampling was conducted), the point markers have been made hollow so that it is possible to see if there were multiple within-season samples with similar values.

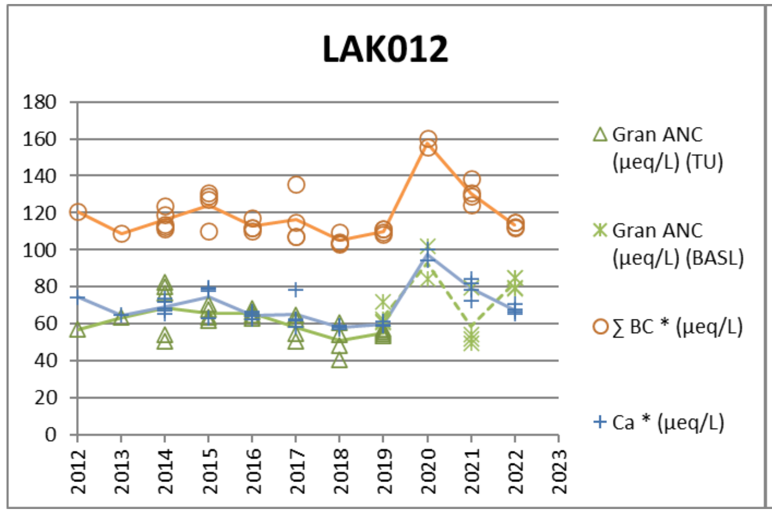
Sensitive Lakes

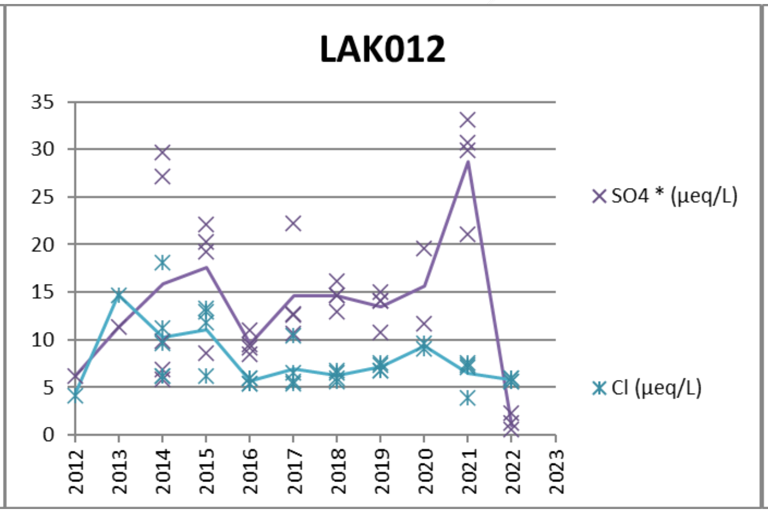


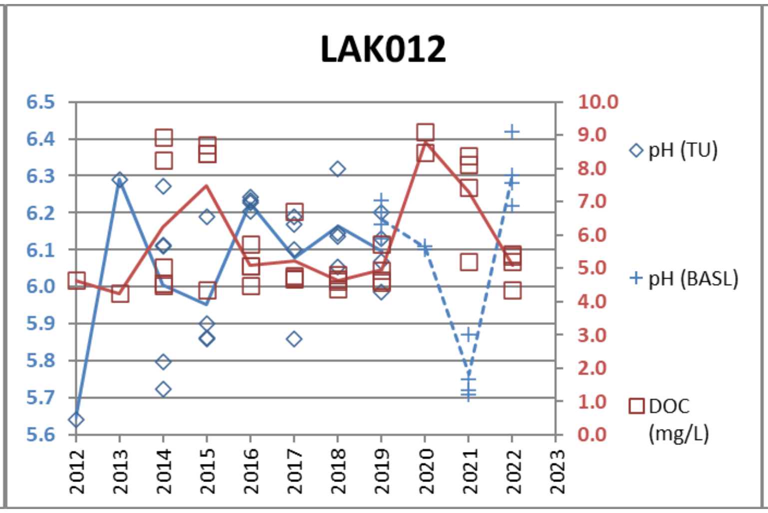


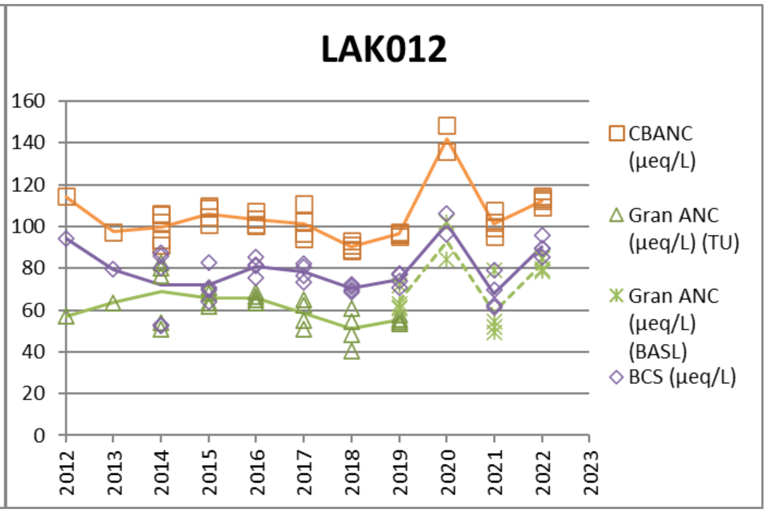


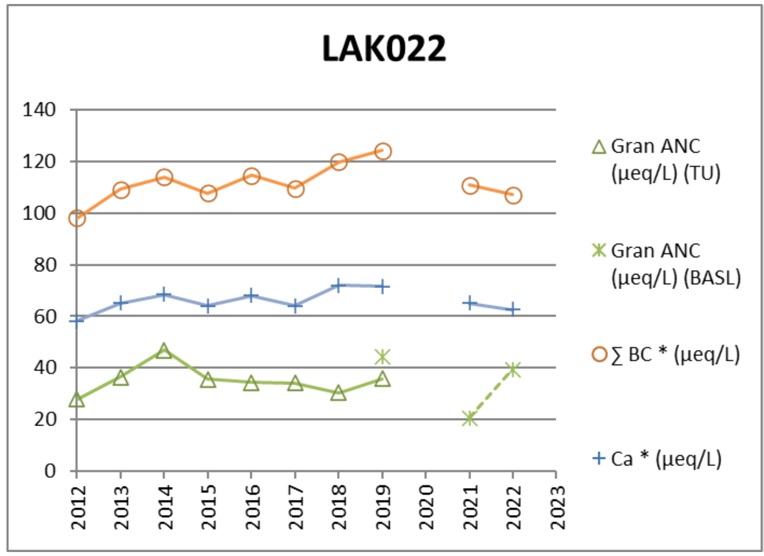


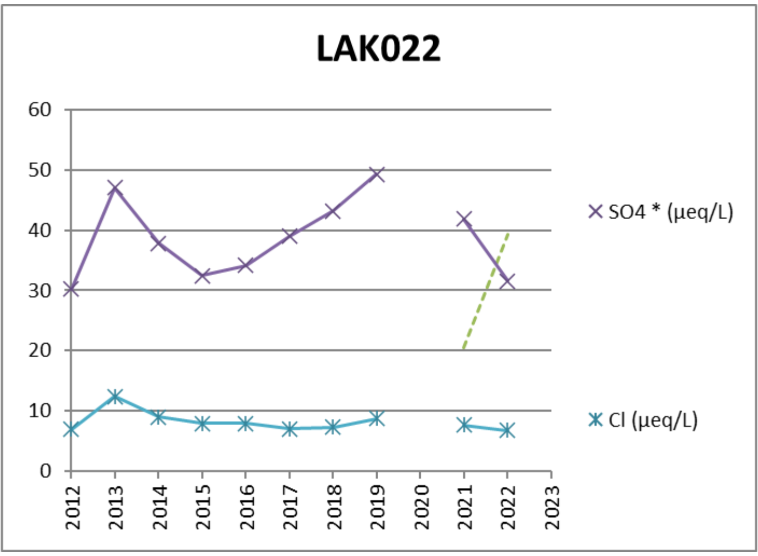


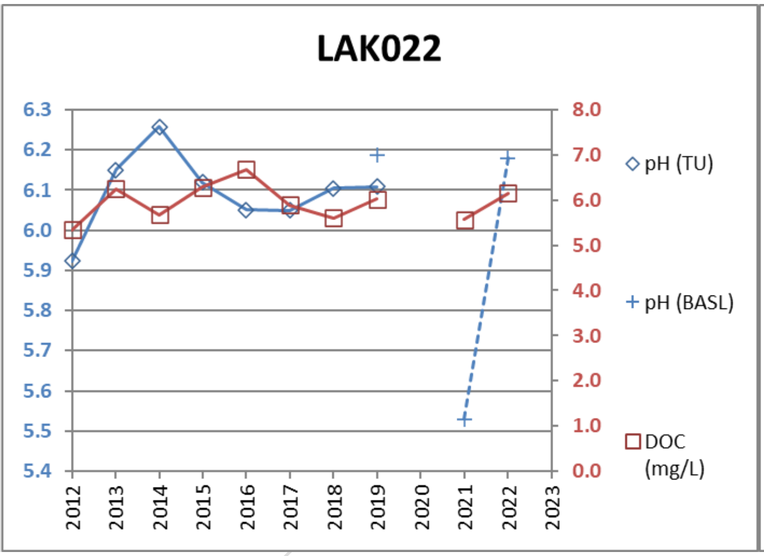


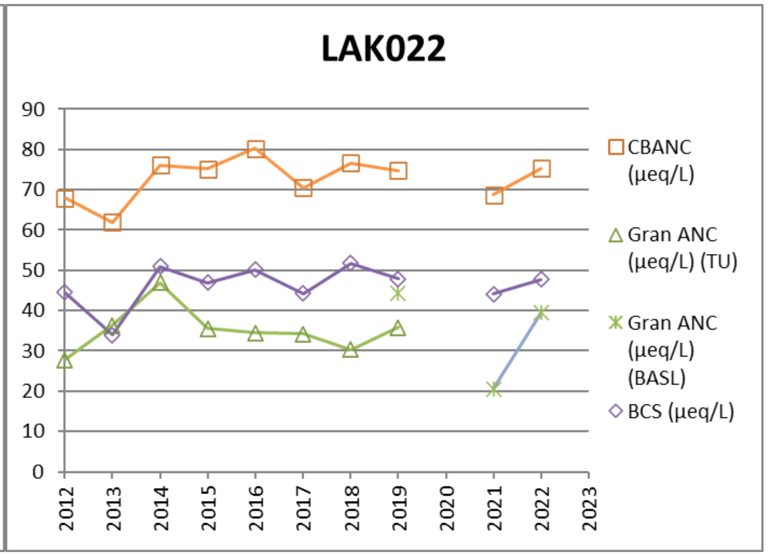


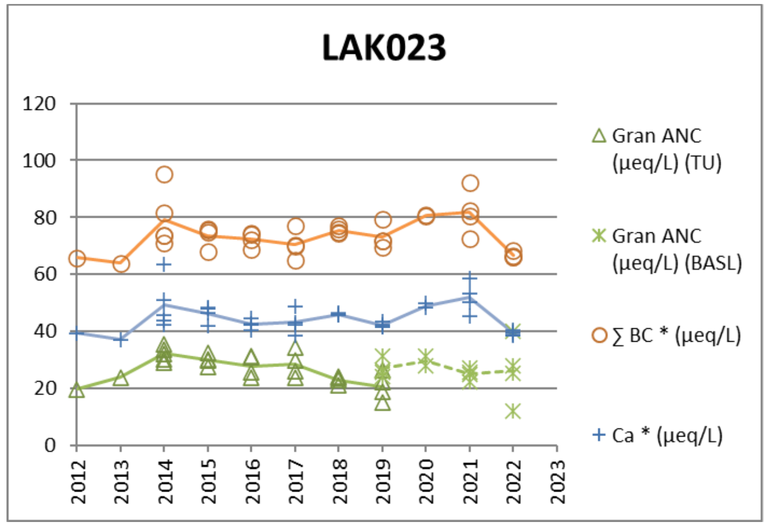


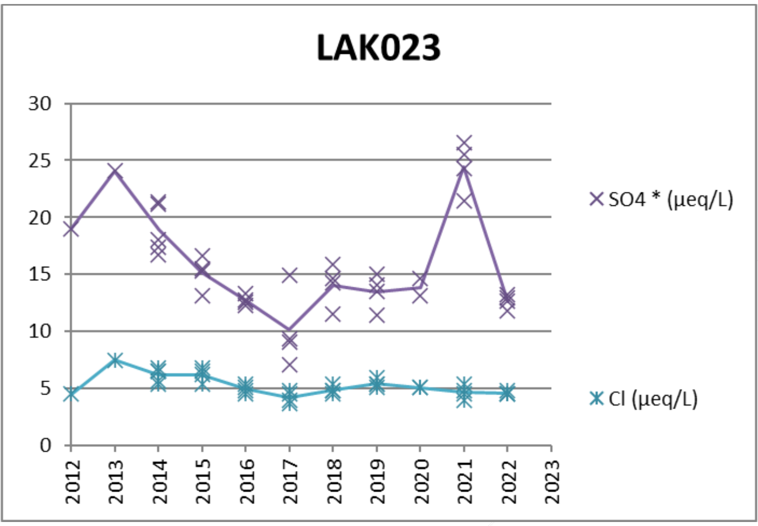

LAK022
0 20 40 60 80 100 120 140
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

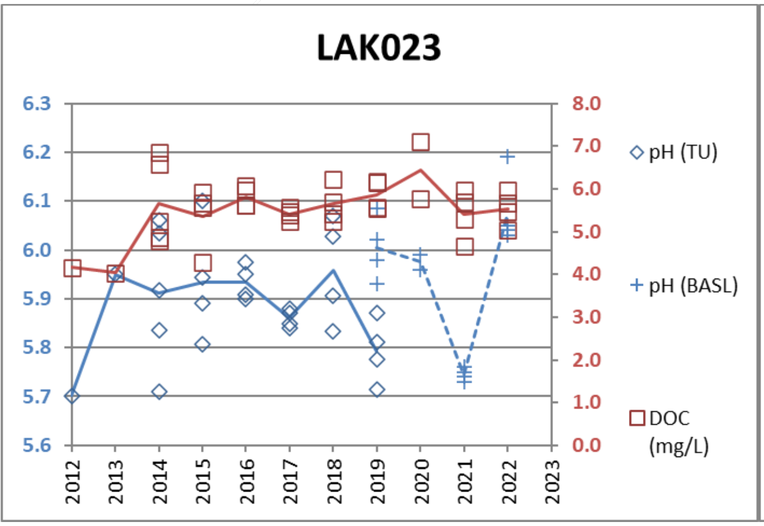

LAK022
0 10 20 30 40 50 60
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
× SO4 * (µeq/L)
✳ Cl (µeq/L)

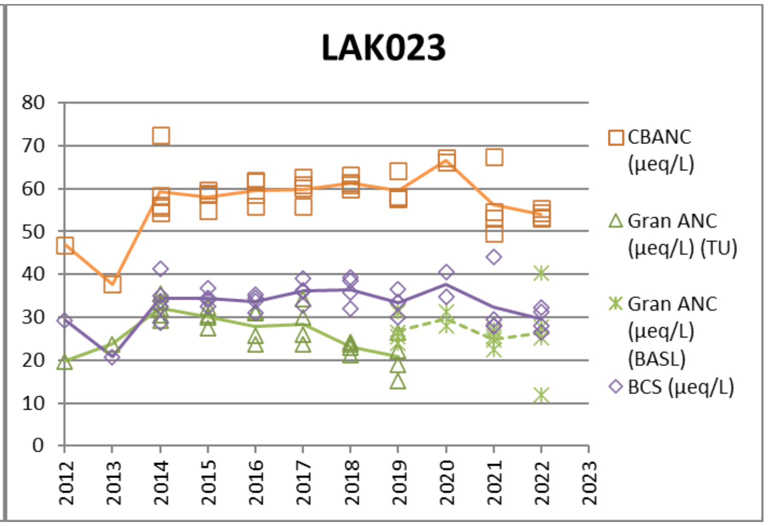

LAK022
5.4 5.5 5.6 5.7 5.8 5.9 6.0 6.1 6.2 6.3
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)

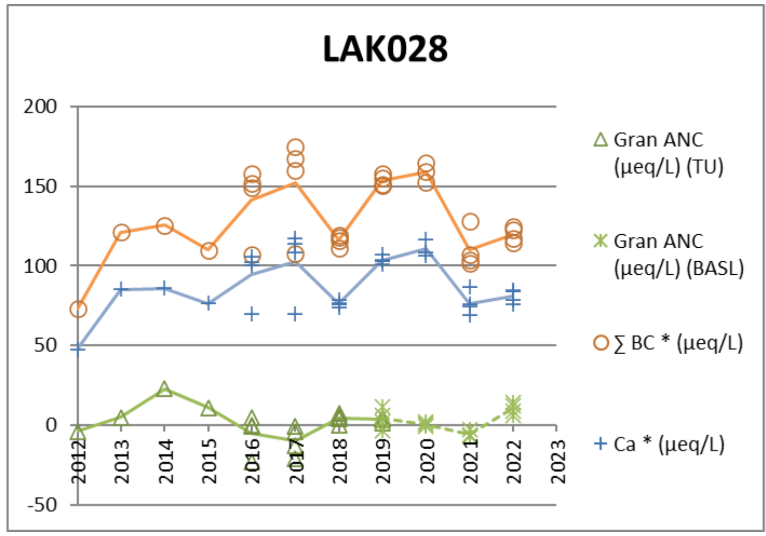

LAK022
0 10 20 30 40 50 60 70 80 90
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
□ CBANC (µeq/L)
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
◇ BCS (µeq/L)

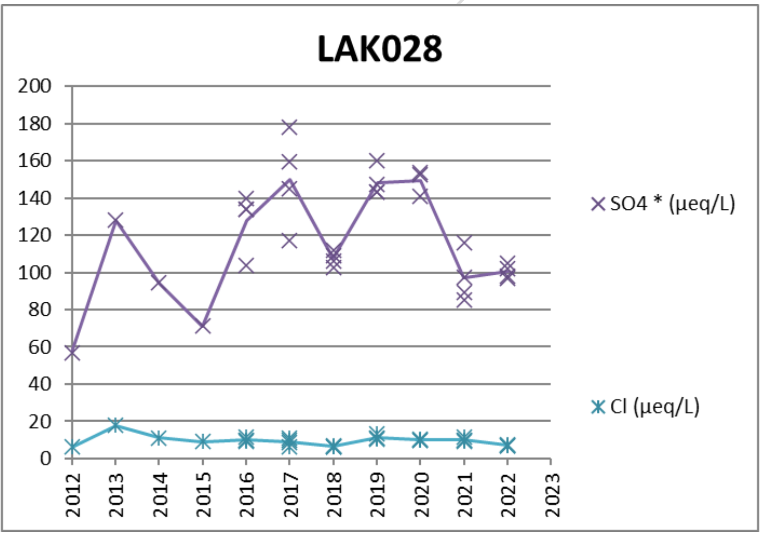

LAK023
0 20 40 60 80 100 120
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

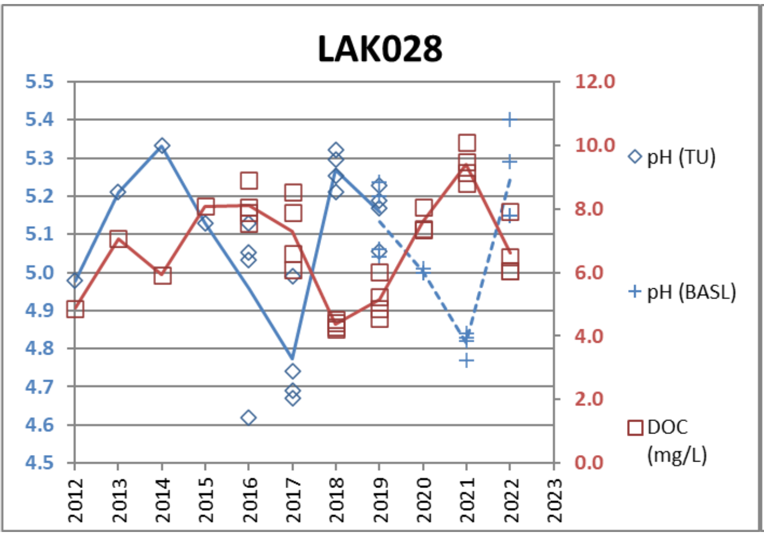

LAK023
0 5 10 15 20 25 30
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
× SO4 * (µeq/L)
✳ Cl (µeq/L)

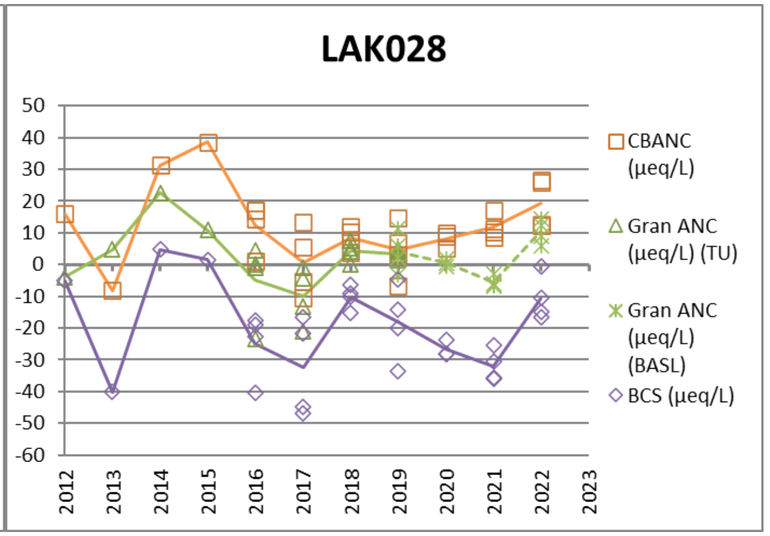

LAK023
5.6 5.7 5.8 5.9 6.0 6.1 6.2 6.3
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)

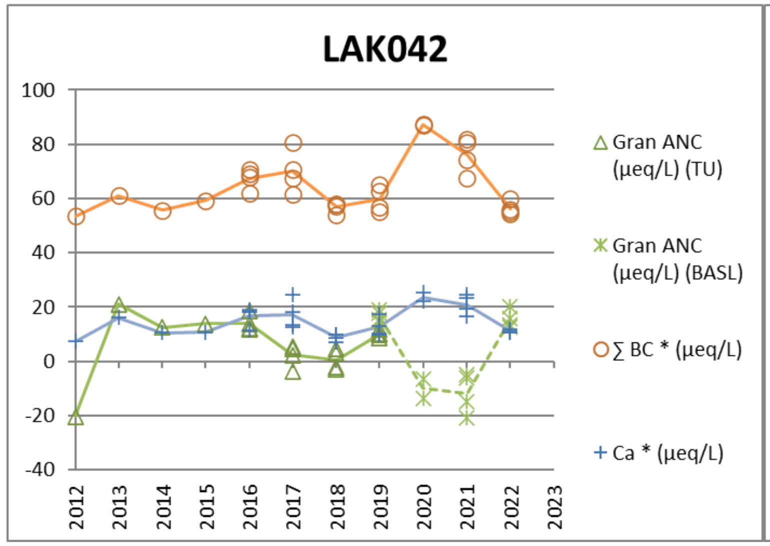

LAK023
0 10 20 30 40 50 60 70 80
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
□ CBANC (µeq/L)
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
◇ BCS (µeq/L)

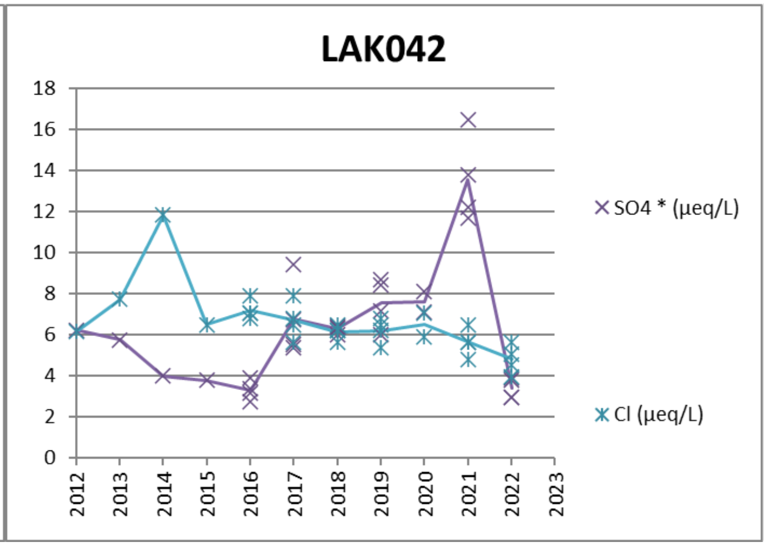

LAK028
-50 0 50 100 150 200
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

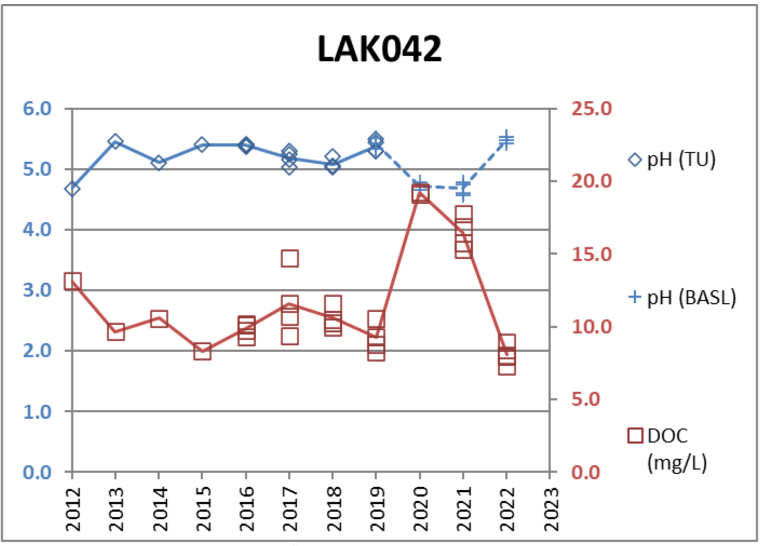

LAK028
0 20 40 60 80 100 120 140 160 180 200
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
× SO4 * (µeq/L)
✳ Cl (µeq/L)

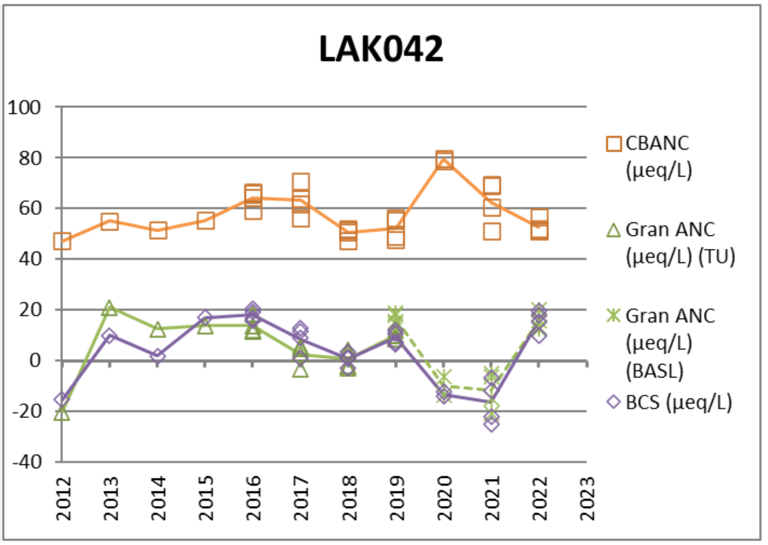

LAK028
4.5 4.6 4.7 4.8 4.9 5.0 5.1 5.2 5.3 5.4 5.5
0.0 2.0 4.0 6.0 8.0 10.0 12.0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)

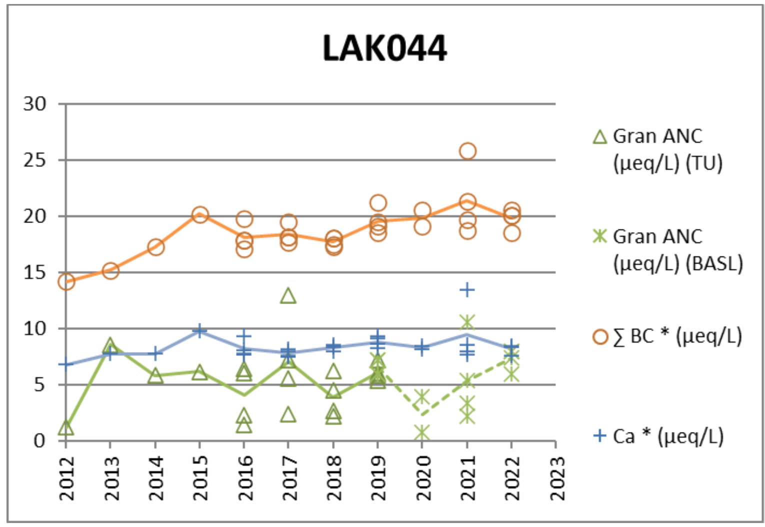

LAK028
-60 -50 -40 -30 -20 -10 0 10 20 30 40 50
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
□ CBANC (µeq/L)
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
◇ BCS (µeq/L)

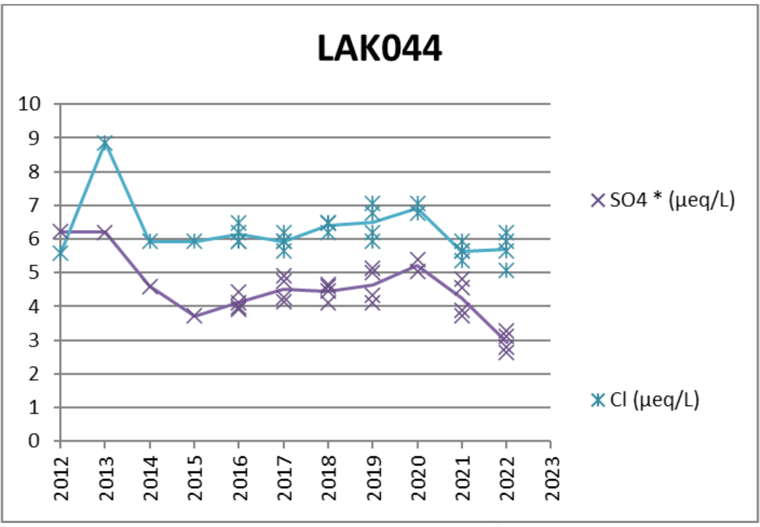

LAK042
100
80
60
40
20
0
-20
-40
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

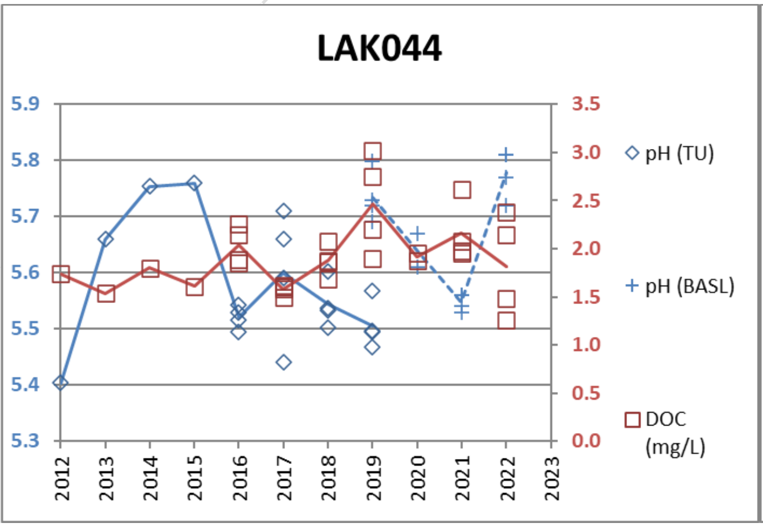

LAK042
18
16
14
12
10
8
6
4
2
0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
× SO4 * (µeq/L)
✳ Cl (µeq/L)

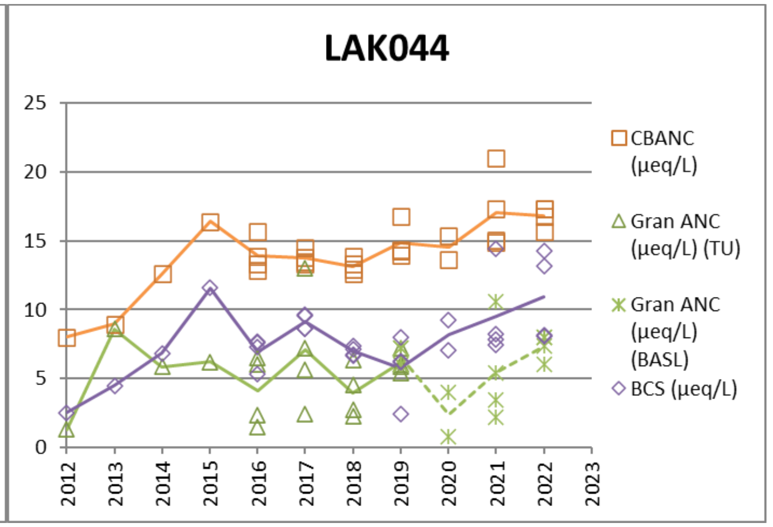

LAK042
6.0
5.0
4.0
3.0
2.0
1.0
0.0
25.0
20.0
15.0
10.0
5.0
0.0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)


LAK042
100
80
60
40
20
0
-20
-40
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
□ CBANC (µeq/L)
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
◇ BCS (µeq/L)

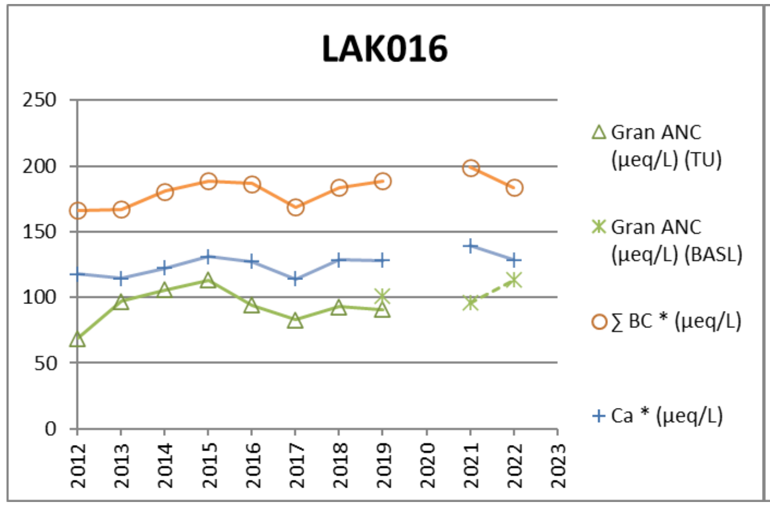

LAK044
30
25
20
15
10
5
0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

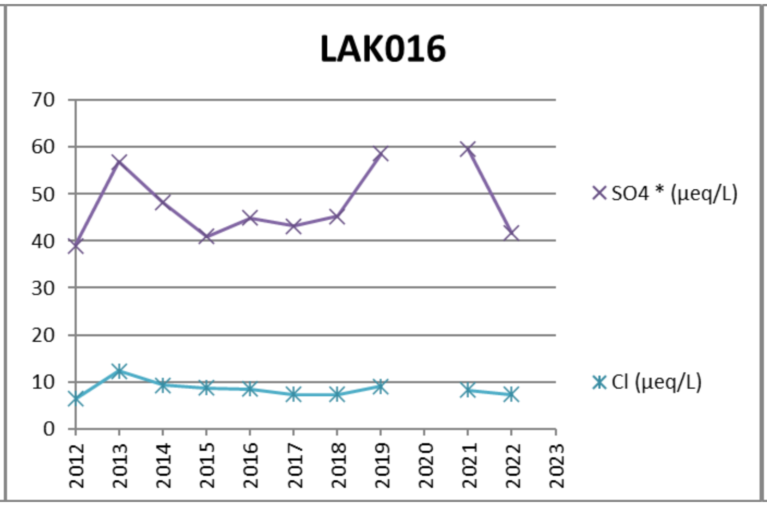

LAK044
10
9
8
7
6
5
4
3
2
1
0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
× SO4 * (µeq/L)
✳ Cl (µeq/L)

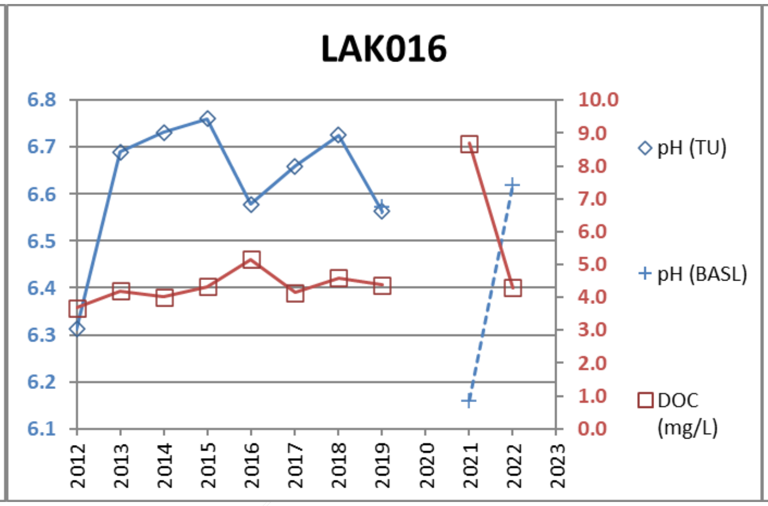

LAK044
5.9
5.8
5.7
5.6
5.5
5.4
5.3
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)

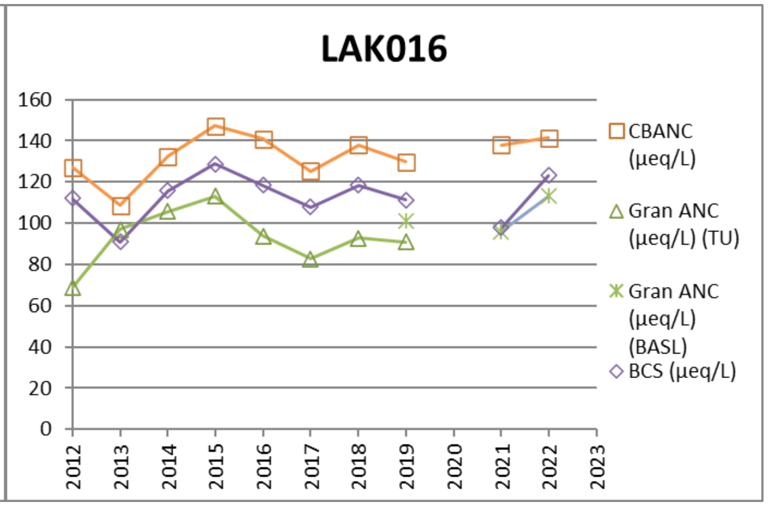

LAK044
25
20
15
10
5
0
2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023
□ CBANC (µeq/L)
△ Gran ANC (µeq/L) (TU)
✳ Gran ANC (µeq/L) (BASL)
◇ BCS (µeq/L)

Less Sensitive Lakes

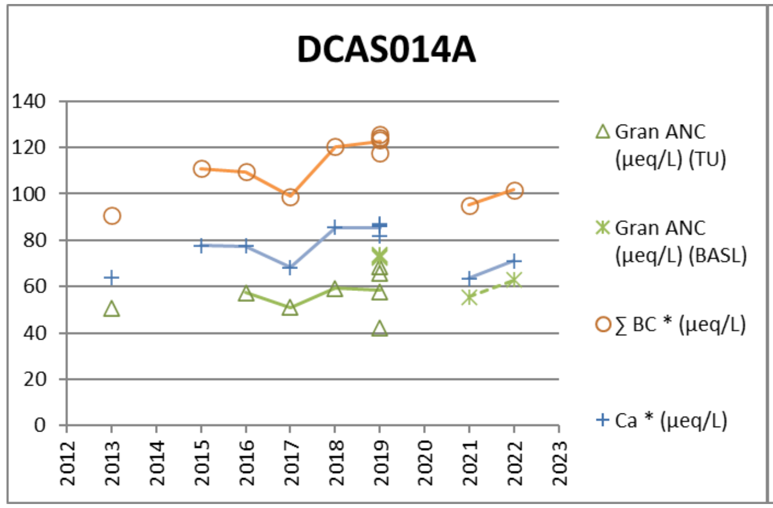


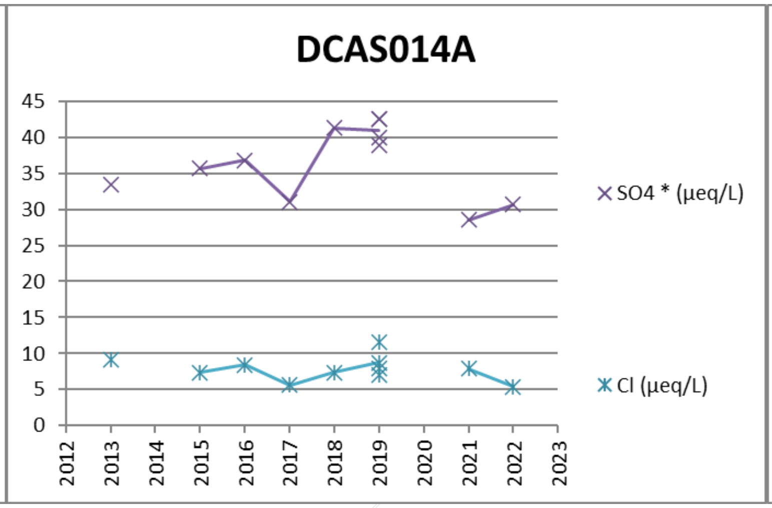


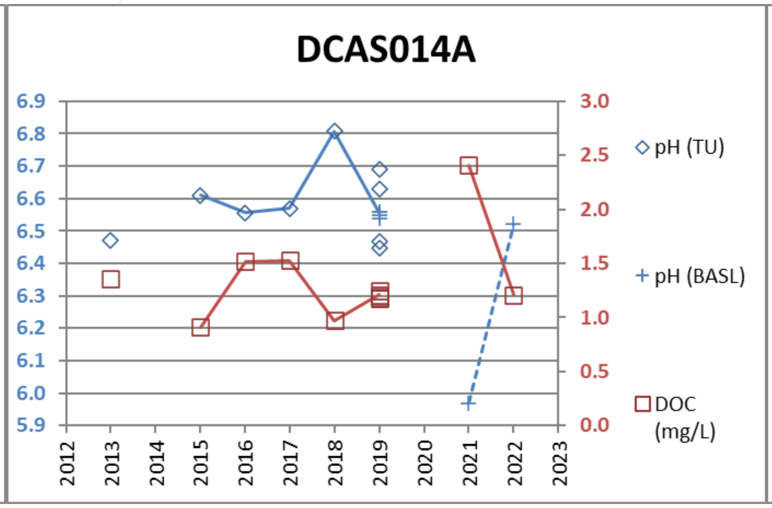


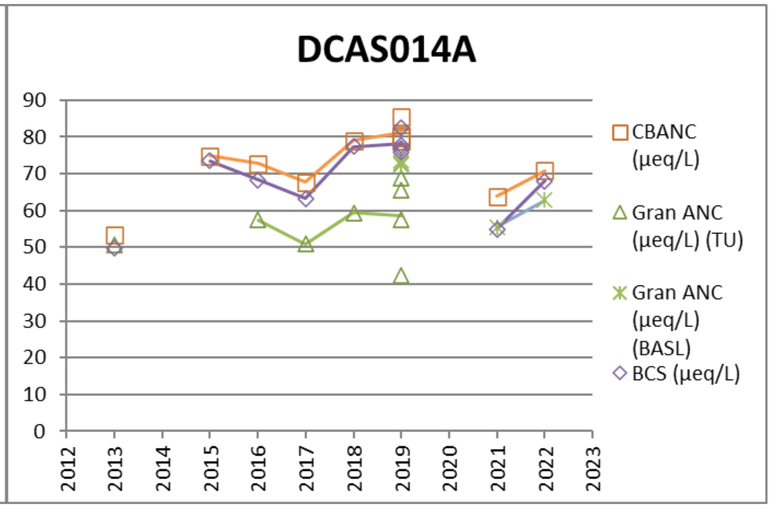


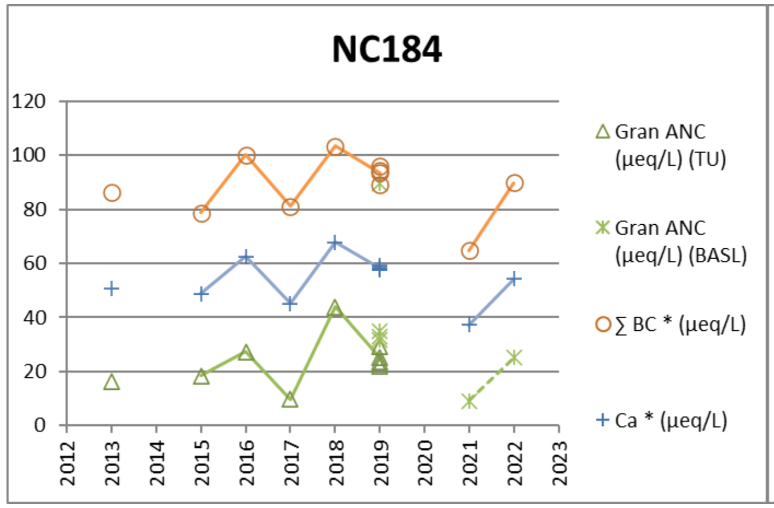
Control Lakes

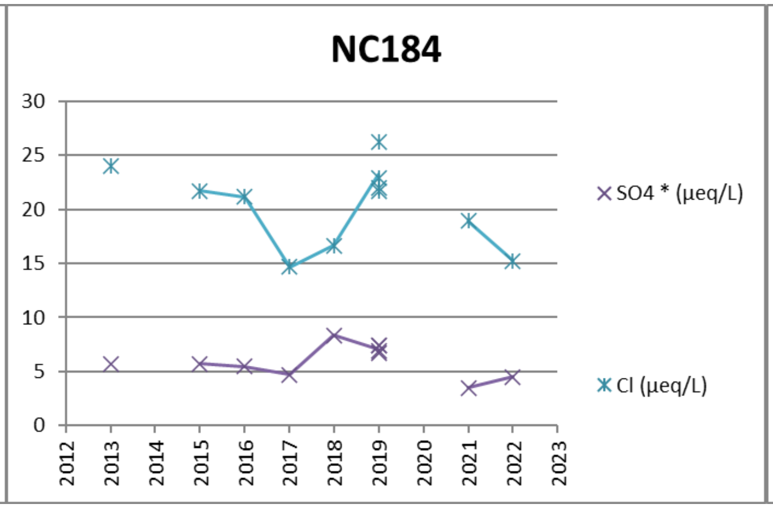


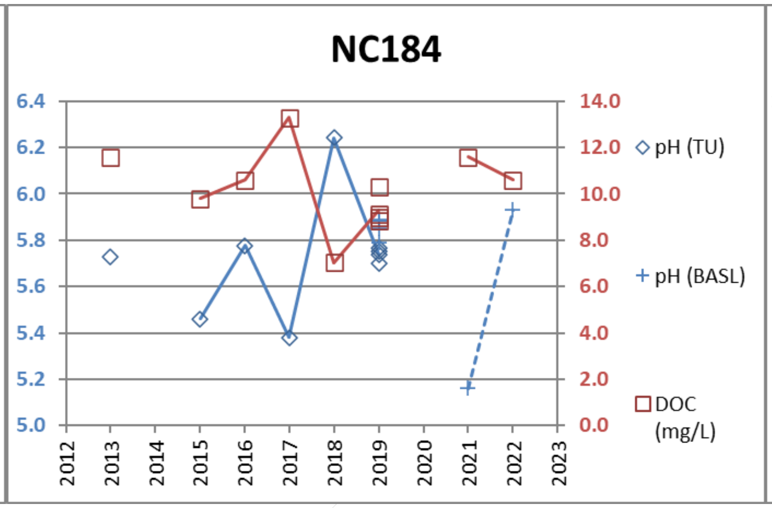


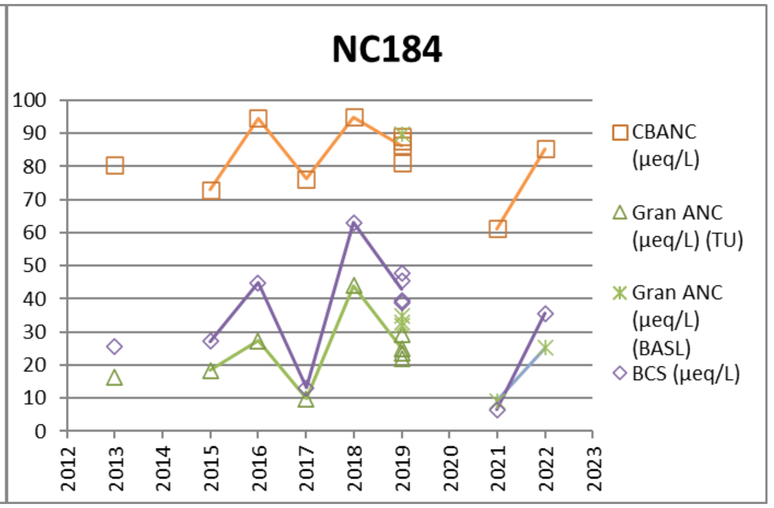


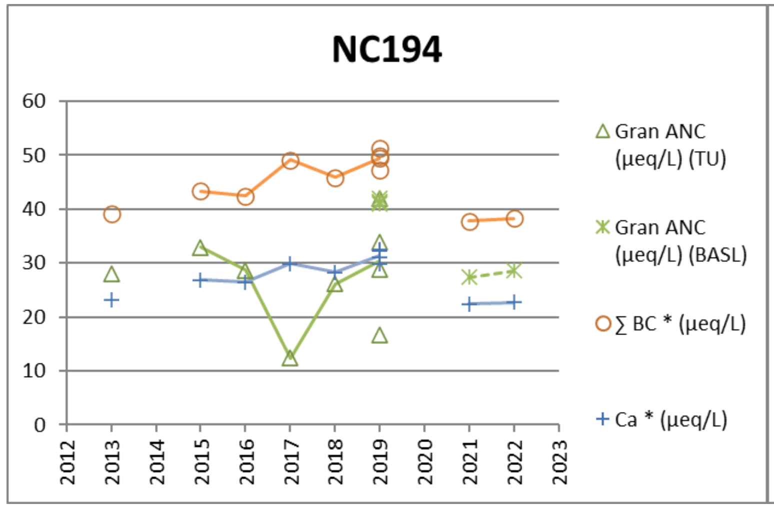


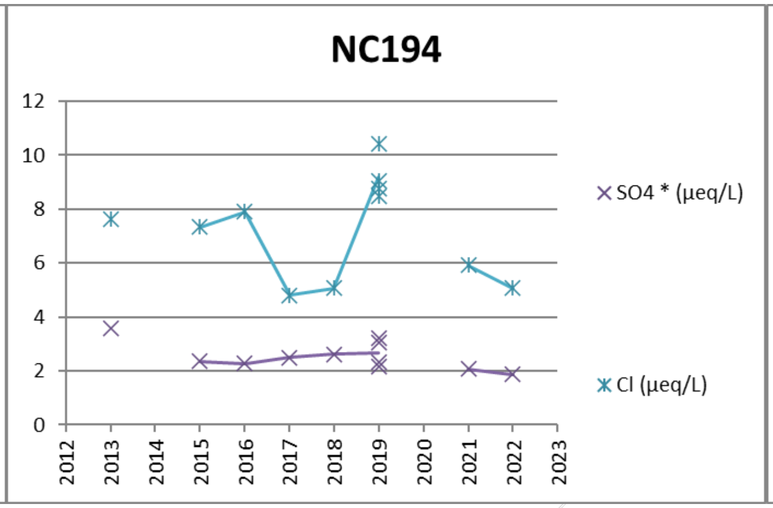

NC184
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
△ Gran ANC (μeq/L) (TU)
⁎ Gran ANC (μeq/L) (BASL)
○ ∑ BC * (μeq/L)
+ Ca * (μeq/L)

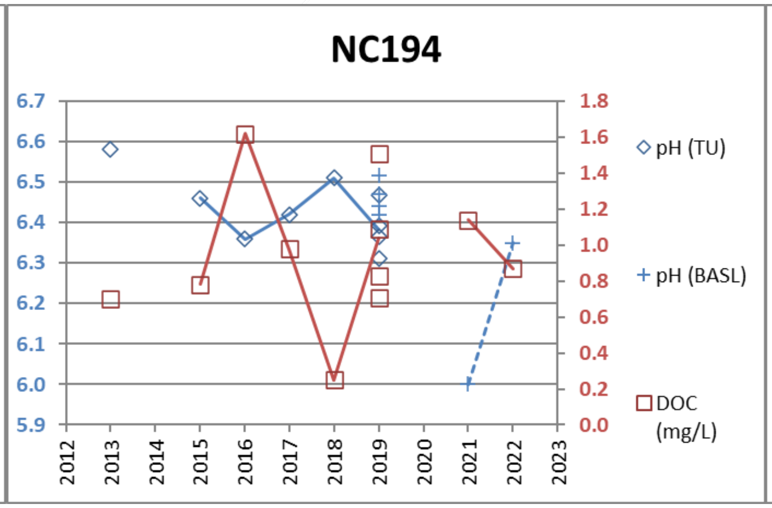

NC184
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
× SO4 * (μeq/L)
⁎ Cl (μeq/L)

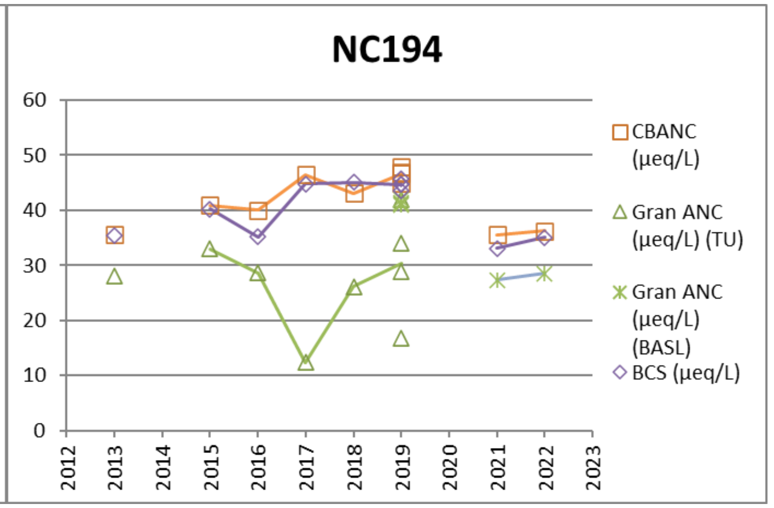

NC184
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)


NC184
100
90
80
70
60
50
40
30
20
10
0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
□ CBANC (μeq/L)
△ Gran ANC (μeq/L) (TU)
⁎ Gran ANC (μeq/L) (BASL)
◇ BCS (μeq/L)


NC194
60
50
40
30
20
10
0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
△ Gran ANC (μeq/L) (TU)
⁎ Gran ANC (μeq/L) (BASL)
○ ∑ BC * (μeq/L)
+ Ca * (μeq/L)


NC194
12
10
8
6
4
2
0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
× SO4 * (μeq/L)
⁎ Cl (μeq/L)


NC194
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
◇ pH (TU)
+ pH (BASL)
□ DOC (mg/L)

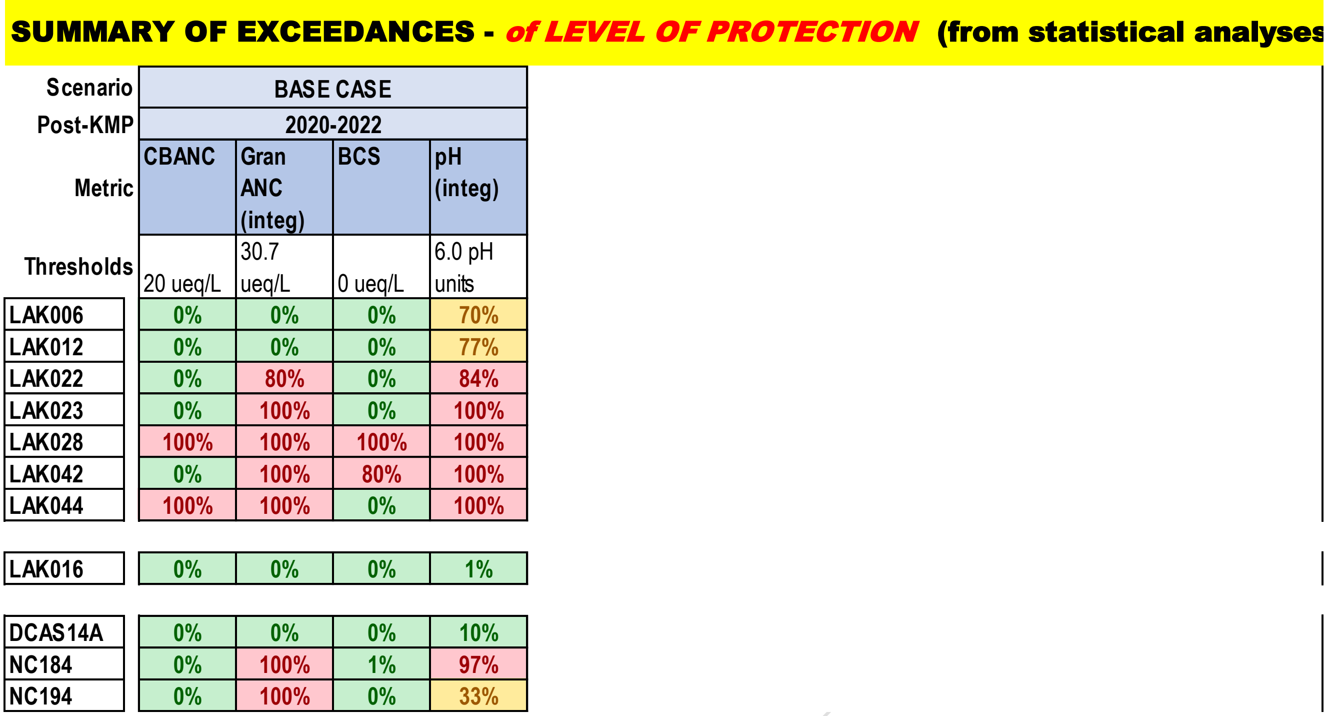

NC194
60
50
40
30
20
10
0
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
□ CBANC (μeq/L)
△ Gran ANC (μeq/L) (TU)
⁎ Gran ANC (μeq/L) (BASL)
◇ BCS (μeq/L)

Appendix 3: Sensitivity Analyses for Statistical Analyses of Post-KMP Changes in Lake Chemistry

This appendix includes the results of the primary statistical analyses presented in Section 3.3 alongside the results of the sensitivity analyses performed using the alternate transition period baseline (2012-2014, as compared to the 2012 pre-KMP baseline applied in the base case). The upper panel shows the % belief in an exceedance of the *change limit*, the middle panel shows the % belief in an exceedance of the *level of protection*, and the bottom panel indicates the level of support for an overall exceedance of each indicator (based on the approach described in the main text).

SUMMARY OF EXCEEDANCES - *of CHANGE LIMIT* (from statistical analyses)

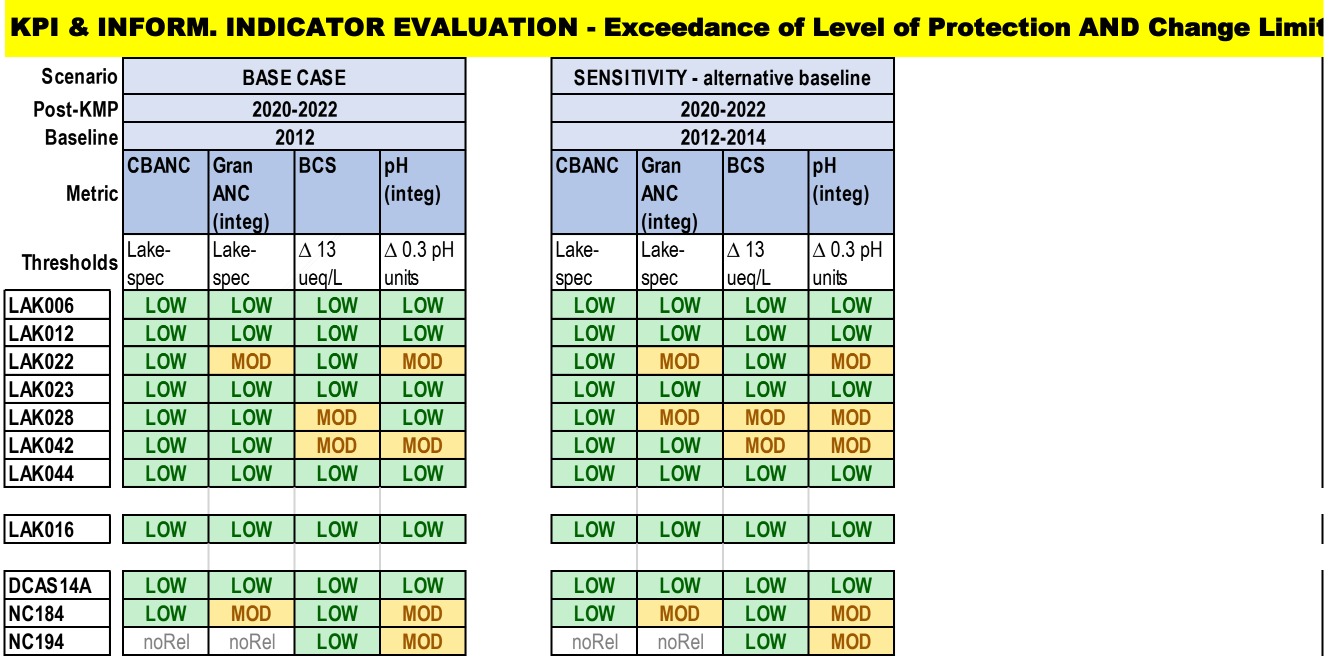
Scenario	BASE CASE				SENSITIVITY - alternative baseline			
Post-KMP	2020-2022				2020-2022			
Baseline	2012				2012-2014			
Metric	CBANC	Gran ANC (integ)	BCS	pH (integ)	CBANC	Gran ANC (integ)	BCS	pH (integ)
Thresholds	Lake-spec	Lake-spec	Δ 13 ueq/L	Δ 0.3 pH units	Lake-spec	Lake-spec	Δ 13 ueq/L	Δ 0.3 pH units
LAK006	0%	0%	1%	8%	0%	0%	0%	9%
LAK012	23%	14%	42%	10%	4%	4%	11%	16%
LAK022	13%	30%	9%	43%	5%	47%	4%	55%
LAK023	6%	2%	3%	7%	2%	4%	1%	5%
LAK028	13%	8%	62%	18%	16%	23%	43%	35%
LAK042	6%	6%	20%	21%	0%	16%	26%	39%
LAK044	0%	4%	1%	4%	0%	5%	0%	5%
LAK016	2%	7%	33%	32%	1%	9%	14%	46%
DCAS14A	5%	7%	13%	52%	4%	7%	15%	52%
NC184	46%	30%	43%	48%	45%	30%	39%	48%
NC194	▨	▨	4%	71%	▨	▨	5%	70%



SUMMARY OF EXCEEDANCES - *of LEVEL OF PROTECTION* (from statistical analyses

Scenario	BASE CASE			
Post-KMP	2020-2022			
Metric	CBANC	Gran ANC (integ)	BCS	pH (integ)
Thresholds	20 ueq/L	30.7 ueq/L	0 ueq/L	6.0 pH units
LAK006	0%	0%	0%	70%
LAK012	0%	0%	0%	77%
LAK022	0%	80%	0%	84%
LAK023	0%	100%	0%	100%
LAK028	100%	100%	100%	100%
LAK042	0%	100%	80%	100%
LAK044	100%	100%	0%	100%
LAK016	0%	0%	0%	1%
DCAS14A	0%	0%	0%	10%
NC184	0%	100%	1%	97%
NC194	0%	100%	0%	33%

Note: This row of tables (i.e., *level of protection*) is not missing a table – there is no "alternative baseline" scenario because the *level of protection* is solely based on the post-KMP status. Therefore, the overall assessment under the alternative baseline scenario (i.e., middle table in last row of tables) is based on the alternative baseline scenario the *change limit* assessment and the base case scenario for the *level of protection* assessment.



KPI & INFORM. INDICATOR EVALUATION - Exceedance of Level of Protection AND Change Limit

Scenario	BASE CASE				SENSITIVITY - alternative baseline			
Post-KMP	2020-2022				2020-2022			
Baseline	2012				2012-2014			
Metric	CBANC	Gran ANC (integ)	BCS	pH (integ)	CBANC	Gran ANC (integ)	BCS	pH (integ)
Thresholds	Lake-spec	Lake-spec	Δ 13 ueq/L	Δ 0.3 pH units	Lake-spec	Lake-spec	Δ 13 ueq/L	Δ 0.3 pH units
LAK006	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
LAK012	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
LAK022	LOW	MOD	LOW	MOD	LOW	MOD	LOW	MOD
LAK023	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
LAK028	LOW	LOW	MOD	LOW	LOW	MOD	MOD	MOD
LAK042	LOW	LOW	MOD	MOD	LOW	LOW	MOD	MOD
LAK044	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
LAK016	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
DCAS14A	LOW	LOW	LOW	LOW	LOW	LOW	LOW	LOW
NC184	LOW	MOD	LOW	MOD	LOW	MOD	LOW	MOD
NC194	noRel	noRel	LOW	MOD	noRel	noRel	LOW	MOD

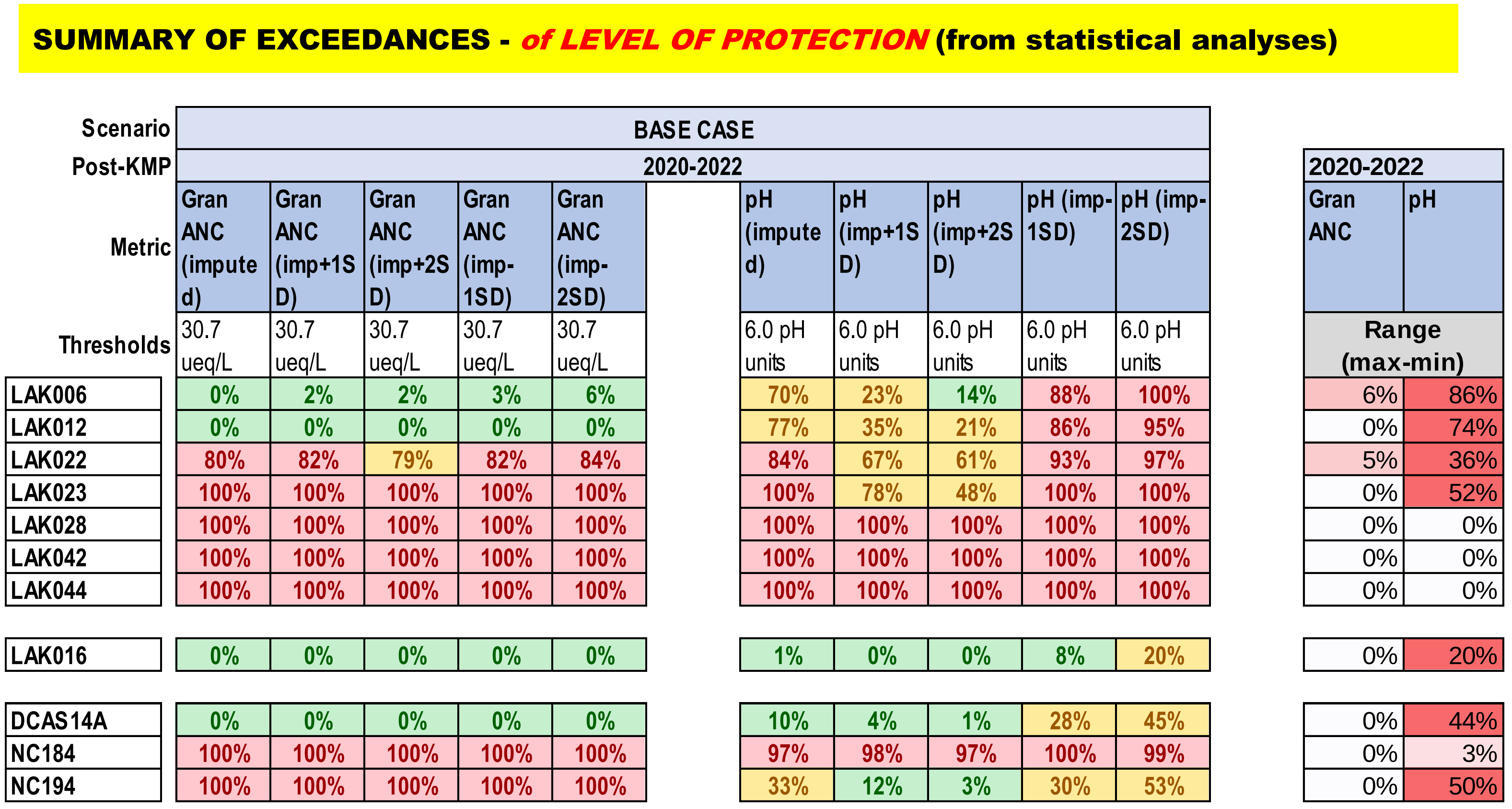
Appendix 4: Sensitivity Analyses on Imputation of Gran ANC and pH Values for Integrated Time Series

This appendix includes the results of the Bayesian statistical analyses for Gran ANC and pH using alternate values for the imputed 2020, 2021, and 2022 values in order to explore the sensitivity of the results to the uncertainty in the imputation process (see description in Section 2.1 of the SO_2 EEM Program 2020 Aquatic Technical Memo W09 for full details). Results are shown for the range of data series for Gran ANC and pH across the base case scenario, the alternative baseline scenario, and the alternative post-KMP period scenario. For each scenario, the tables below show the results across all lakes for each data series and the range of results across all of the permutations of a particular metric for each lake. *Note: "Gran ANC (imputed)" is the same metric that is referenced as "Gran ANC (integ)" in the main text; same for pH as well.*

SUMMARY OF EXCEEDANCES - *of CHANGE LIMIT* (from statistical analyses)

Scenario	BASE CASE											
Post-KMP	2020-2022										2020-2022	
Baseline	2012										2012	
Metric	Gran ANC (imputed)	Gran ANC (imp+1SD)	Gran ANC (imp+2SD)	Gran ANC (imp-1SD)	Gran ANC (imp-2SD)	pH (imputed)	pH (imp+1SD)	pH (imp+2SD)	pH (imp-1SD)	pH (imp-2SD)	Gran ANC	pH
Thresholds	Lake-spec	Lake-spec	Lake-spec	Lake-spec	Lake-spec	Δ 0.3 pH units	Δ 0.3 pH units	Δ 0.3 pH units	Δ 0.3 pH units	Δ 0.3 pH units	Range (max-min)	
LAK006	0%	1%	1%	1%	1%	8%	6%	4%	11%	16%	1%	12%
LAK012	14%	11%	12%	14%	11%	10%	9%	7%	11%	16%	3%	9%
LAK022	30%	32%	31%	30%	31%	43%	37%	33%	47%	54%	2%	21%
LAK023	2%	1%	1%	1%	1%	7%	5%	3%	11%	14%	1%	11%
LAK028	8%	8%	7%	8%	6%	18%	13%	12%	28%	40%	2%	28%
LAK042	6%	5%	5%	6%	4%	21%	20%	16%	26%	32%	2%	16%
LAK044	4%	2%	4%	4%	4%	4%	3%	2%	6%	8%	2%	6%
LAK016	7%	7%	7%	10%	8%	32%	26%	21%	40%	42%	3%	21%
DCAS14A	7%	8%	7%	8%	7%	52%	48%	40%	57%	65%	1%	25%
NC184	30%	25%	27%	31%	29%	48%	42%	38%	52%	58%	6%	20%
NC194	▨	▨	▨	▨	▨	71%	60%	52%	73%	79%	0%	27%

Scenario	SENSITIVITY - alternative baseline											
Post-KMP	2020-2022										2020-2022	
Baseline	2012-2014										2012-2014	
Metric	Gran ANC (imputed)	Gran ANC (imp+1SD)	Gran ANC (imp+2SD)	Gran ANC (imp-1SD)	Gran ANC (imp-2SD)	pH (imputed)	pH (imp+1SD)	pH (imp+2SD)	pH (imp-1SD)	pH (imp-2SD)	Gran ANC	pH
Thresholds	Lake-spec	Lake-spec	Lake-spec	Lake-spec	Lake-spec	Δ 0.3 pH units	Δ 0.3 pH units	Δ 0.3 pH units	Δ 0.3 pH units	Δ 0.3 pH units	Range (max-min)	
LAK006	0%	1%	1%	1%	2%	9%	3%	2%	13%	29%	2%	27%
LAK012	4%	3%	3%	5%	5%	16%	10%	6%	23%	36%	2%	30%
LAK022	47%	46%	46%	49%	50%	55%	44%	32%	68%	78%	4%	46%
LAK023	4%	4%	3%	5%	5%	5%	2%	1%	10%	21%	2%	20%
LAK028	23%	24%	23%	23%	25%	35%	20%	10%	55%	74%	2%	64%
LAK042	16%	15%	15%	16%	17%	39%	31%	20%	52%	60%	2%	40%
LAK044	5%	5%	4%	6%	6%	5%	2%	1%	12%	30%	2%	29%
LAK016	9%	9%	8%	10%	11%	46%	35%	24%	61%	76%	3%	52%
DCAS14A	7%	7%	8%	8%	8%	52%	46%	41%	57%	63%	1%	22%
NC184	30%	30%	27%	29%	32%	48%	40%	40%	54%	62%	5%	22%
NC194	▨	▨	▨	▨	▨	70%	61%	50%	74%	78%	0%	28%



SUMMARY OF EXCEEDANCES - *of LEVEL OF PROTECTION* (from statistical analyses)

Scenario	BASE CASE													
Post-KMP	2020-2022												2020-2022	
Metric	Gran ANC (imputed)	Gran ANC (imp+1SD)	Gran ANC (imp+2SD)	Gran ANC (imp-1SD)	Gran ANC (imp-2SD)		pH (imputed)	pH (imp+1SD)	pH (imp+2SD)	pH (imp-1SD)	pH (imp-2SD)		Gran ANC	pH
Thresholds	30.7 ueq/L	30.7 ueq/L	30.7 ueq/L	30.7 ueq/L	30.7 ueq/L		6.0 pH units	6.0 pH units	6.0 pH units	6.0 pH units	6.0 pH units		Range (max-min)	
LAK006	0%	2%	2%	3%	6%		70%	23%	14%	88%	100%		6%	86%
LAK012	0%	0%	0%	0%	0%		77%	35%	21%	86%	95%		0%	74%
LAK022	80%	82%	79%	82%	84%		84%	67%	61%	93%	97%		5%	36%
LAK023	100%	100%	100%	100%	100%		100%	78%	48%	100%	100%		0%	52%
LAK028	100%	100%	100%	100%	100%		100%	100%	100%	100%	100%		0%	0%
LAK042	100%	100%	100%	100%	100%		100%	100%	100%	100%	100%		0%	0%
LAK044	100%	100%	100%	100%	100%		100%	100%	100%	100%	100%		0%	0%
LAK016	0%	0%	0%	0%	0%		1%	0%	0%	8%	20%		0%	20%
DCAS14A	0%	0%	0%	0%	0%		10%	4%	1%	28%	45%		0%	44%
NC184	100%	100%	100%	100%	100%		97%	98%	97%	100%	99%		0%	3%
NC194	100%	100%	100%	100%	100%		33%	12%	3%	30%	53%		0%	50%

Appendix 5: Lake-specific thresholds for change limits for CBANC

The lake-specific CBANC thresholds for the *change limit* are shown in the table below. The table and caption below are directly copied from Table 14 of the SO_2 EEM Program Phase III Plan.

Lake-specific thresholds for change limits in CBANC. Values calculated from analyses of the titration data, showing the change in CBANC associated with a pH decline of 0.3 pH units from the 2012 (or 2013 for control lakes) pH value for each lake. A lake-specific threshold cannot be estimated for control lake NC194 given limited data.

	EEM Group	Lake-specific CBANC threshold (μeq/L)
LAK006	Sensitive Lake	-10.8
LAK012	Sensitive Lake	-16.3
LAK022	Sensitive Lake	-11.5
LAK023	Sensitive Lake	-10.5
LAK028	Sensitive Lake	-13.4
LAK042	Sensitive Lake	-24.4
LAK044	Sensitive Lake	-6.2
LAK016	Less Sensitive Lake	-25.6
DCAS14A	Control Lake	-21.7
NC184	Control Lake	-10.8
NC194	Control Lake	n.a.

Appendix D: Technical Report of Lake Monitoring in 2022

The following pages contain the full **Rio Tinto BC Works SO_2 Environmental Effects Program: Monitoring of Lakes in 2022, Final Report**, in PDF format.

Citation: Limnotek. 2023. Rio Tinto BC Works SO_2 Environmental Effects Program: Monitoring of Lakes in 2022. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Ltd. 73 pp.

Rio Tinto BC Works SO_2 Environmental Effects Program: Monitoring of Lakes in 2022

Final Report

March 31, 2023

LIMNOTEK

Rio Tinto BC Works SO_2 Environmental Effects Program: Monitoring of Lakes in 2022

Final Report

Submitted to

Rio Tinto BC Works Ltd.
Kitimat, B.C.

Prepared by

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March 31, 2023

Citation: Limnotek. 2023. Rio Tinto SO_2 Environmental Effects Program: Monitoring of lakes in 2022. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Ltd. 73pp.

Cover photo: Lake NC194 (one of the control lakes) during the annual EEM sampling on October 2, 2022. Photo credit, Chris Perrin.

EXECUTIVE SUMMARY

Chemical measurements among selected lakes between Kitimat and Terrace were completed in 2022 as part of ongoing environmental effects monitoring (EEM) of SO_2 emissions from the Rio Tinto smelter in Kitimat, British Columbia. The lake sampling and analysis is the aquatic component of the larger EEM that also includes atmospheric SO_2 and acidic deposition, human health, vegetation, and soils. Activities in 2022 included the following nine tasks, determined collaboratively by Rio Tinto, ESSA Technologies (prime contractor on SO_2 emissions EEM), and Provincial regulatory authorities:

1. Annual water sampling and analytical chemistry from 12 lakes completed on October 2, 2022, using helicopter sampling techniques that were developed in early years of the EEM by Limnotek. The lakes included seven *acid-sensitive* lakes (LAK006 (End Lake), LAK012 (Little End Lake), LAK022, LAK023 (West Lake), LAK028, LAK042, and LAK044), one *less acid-sensitive* lake (LAK016), three *control* lakes (DCAS14A, NC184, NC194) and one non-EEM lake (LAK027 Bowbyes Lake, added at the request of BC Environment).

2. Two sampling episodes in June followed by monthly sampling in July through September 2022 to provide data for later analysis of spring and summer variability among chemical analytes in LAK028 and LAK006 (End Lake) and to describe their basic limnology. These two selected lakes were representative of acid – sensitive lakes in the study area.

3. Addition of three sampling episodes in late September through late October for later analysis of variability among chemical analytes during the fall sampling period in LAK012, LAK023, LAK028, LAK006, LAK042, and LAK044. This sampling supplemented the annual EEM sampling in Task 1.

4. Quality assurance testing of the 2022 water chemistry results.

5. Time course monitoring of pH and water level using data loggers in LAK006 and LAK028 in June through October 2022 to supplement Task 2.

6. Full year temperature monitoring at several depths in LAK028 from Nov 1, 2021 through to the end of October 2022. This sampling started in 2018 to examine physical differences between surface and bottom layers in LAK028 that are associated with meromixis that was detected in 2017.

7. Operation of a pH logger at the surface and bottom of LAK028 and a pH logger near the surface in LAK006 to examine seasonal variation in pH and provide insight into meromixis in LAK028.

8. Begin operation of a conductivity mooring on LAK028 for use in interpreting long term stability of the chemocline.

9. Maintenance of an instrument raft on LAK028. The raft supported temperature and pH moorings. Tripods that were secured to the raft deck hosted air samplers that were part of the SO_2 sampler network in the Terrace-Kitimat valley (ESSA et al. 2022).

Quality assurance testing showed high accuracy and precision among analytes, indicating excellent repeatability of sample handling and analysis procedures in 2022.

Field contamination of DOC blanks that was found in 2020 and less so in 2021 was eliminated in 2022 by changing to hydrophilic Teflon filters.

Positive blanks were found for total and dissolved aluminum and barium but mostly after September 28, 2022. Review of contamination sources showed that lab gloves purchased on that date and used for handling water samples and running sample filtrations were the most likely source. Due to supply chain issues, lab gloves from normal sources were not available after September 28, 2022, resulting in purchase of nitrile gloves from a local supplier in Terrace. The positive blanks coincided with use of those gloves. We subsequently found from glove testing at ALS Environmental that nitrile gloves may have metals contamination. Other possible contamination sources were found less likely. In all cases of positive blanks, the contaminant concentrations were 15 – 300 times lower than found in the lake water samples. This relatively minor contamination is negligible for the later analyses to be run by ESSA but needs to be corrected in future sampling activities.

Using a method of paired comparisons, pH measured at ALS Environmental was significantly greater than pH from a field instrument, field pH loggers, and mostly greater than pH measured at the Biogeochemical Analytical Service Laboratory (BASL) at the University of Alberta. This finding was similar to that in previous years. Electrode immersion time was found to be a significant factor influencing pH in 2020, but not in 2021 and 2022. These inconsistencies of effects of electrode immersion times on pH between years imply that other factors were important in affecting differences in pH measurements between instruments and labs.

A survey of labs in January 2023 showed that the duration that a water sample was exposed to air before pH measurement was directly correlated with an “instrument effect” on pH. Longest exposure time was at ALS, which reported highest pH among controlled sample pairings. Shortest exposure time occurred with field instruments, which reported lowest pH among those same pairings. The amount of CO_2 lost from degassing upon exposure of a water sample to air may increase with duration of exposure. That loss of CO_2 will raise pH. These findings point to time of exposure to air as being a possible cause of differences among paired sample measurements of pH between instruments and labs.

Water sampling in LAK028 in 2022 provided further insight into meromixis that was initially detected in 2017. Lines of evidence included presence of a strong and stable chemocline, no weakening of the chemocline during isothermal conditions, relatively high pH in the chemocline (mean of 6.1) compared to lower pH in surface water (mean of 5.0), and anoxia and chemical reducing conditions in the chemocline. Sulfate found in surface waters was reduced to sulfide in the chemocline, which produced a strong hydrogen sulfide odor when samples from that depth were retrieved. Sulfate concentrations in the surface water of LAK028 were 32 times below Provincial water quality guidelines for protection of aquatic life. The sample odour inferred presence of sulfur bacteria at depth. High stability of the chemocline presents low risk of episodic entrainment of water from bottom water into surface water of LAK028. This conclusion means that surface water chemistry that is sampled for the EEM is not expected to be confounded by mixing of chemically different water associated with meromixis in LAK028.

Ten recommendations emerged from the 2022 field season, some of which were also mentioned in 2021:

1. Use hydrophilic Teflon filters, not cellulose ester filters for all water filtrations in the field to minimize the incidence of minor DOC contamination.
2. All sample handling and filtrations in the field should be performed using vinyl lab gloves, not nitrile gloves that may incidentally carry metals contamination.
3. Start each field season with new pH loggers to minimize risk of both logger and electrode failure during the spring to fall field season. Five new pH loggers with new electrodes and six other replacement electrodes should be purchased to start sampling each year. Three of the loggers should be installed to start in the spring (2 in LAK028, 1 in End Lake). The other two loggers should be available for swapping out the installed loggers as needed during the field season. One of those loggers should be part of the field gear, ready to swap with any logger showing evidence of failure during a site visit. Replace the electrode on a given pH logger once every two months (not longer) to avoid electrode error on long term deployments.
4. When requesting pH measurement at ALS, we recommend selection of the method that provides an electrode immersion period of 10 minutes, not the standard method in which the instrument times out after 3 minutes of electrode immersion. The longer immersion period allows for adequate stabilization of voltage in the low conductivity waters of the BC north coast. Water samples assigned to 10-minute immersion times are handled manually, resulting in a benefit of a shorter time of sample exposure to air before analysis compared to automated handling that incorporates 3-minute electrode immersion times and relatively long periods during which a sample is uncapped before electrode immersion. This shorter time of sample exposure to air will minimize CO_2 degassing that can raise pH.
5. pH data from BASL should continue to be used for statistical analyses of long term trends, building on the time series of prior pH measurements from Trent University. For comparative purposes, field pH measurements could also be used for tracking long term changes, since the field data have the smallest error associated with sample exposure to air that may affect pH and have the longest record of continuous measurement since the RIO Tinto SO_2 EEM program started. In 2022, the pH data from BASL were not statistically different from the field data, and previous reports showed no statistically significant differences between pH measurements from Trent University and BASL.
6. Run an experiment to test the “exposure time effect” on sample pH. These data are needed to unequivocally answer the question as to how the duration of sample exposure to air affects sample pH. An example experiment is provided.
7. Sample bacteria from LAK028 to confirm the presence of phototrophic sulfur bacteria and sulfate-reducing bacteria or point to other species that may play different roles. These data would provide insight into what processes of the sulfur cycle are active in LAK028 (e.g. uptake and settlement of sulfur by phototrophic

bacteria and/or production of sulfide by sulfate reducing bacteria in bottom waters.

8. Measure profiles of photosynthetically active radiation (PAR) during regular monthly sampling visits to LAK028 to examine depths where phototrophic bacteria, if present, may be active in taking up sulfur that is loaded at the lake surface. These data would also show the euphotic zone depth that is the depth where photosynthesis is active. PAR is basic limnological information in most studies of lake functioning.
9. Monitoring of the complete LAK028 water column is required during EEM sampling to ensure that surface chemistry is not confounded by possible mixing that could affect pH, Gran ANC, base cations, etc. Any future anomaly from LAK028 can then be investigated with respect to potential influence from change in stability of the chemocline.
10. Continue operation of a conductivity mooring year-round in LAK028. Conductivity and temperature data will show if perennial meromixis is present.

ACKNOWLEDGEMENTS

Several people contributed to this project. Work was managed by Chris Perrin. Field operations were run by Shauna Bennett with site logistics and safety organization provided by Fred Seiler. Chris Perrin and Shauna Bennett were authors of this report. Rio Tinto safety planning and oversight was managed by Shawn Zettler (Rio Tinto). Personnel who assisted in the field were Jared Sanders, Calder Azak, Dalace Bennett, Nathan McMillan, and Gavin Friend all with Wai Wah Environmental GP Ltd. that was on contract with Rio Tinto. Chemical analysis of water samples was provided by the Biogeochemical Analytical Service Laboratory (BASL) at the University of Alberta (managed by Dr. Mingsheng Ma) and ALS Environmental in Burnaby, B.C. with account management from Carla Fuginski. Safety check-in was provided by Jason Bennett for ground-based sampling and by Shawn Zettler (Rio Tinto) for sampling by helicopter. Special thanks go to David Marmorek (ESSA Technologies Ltd.), Shawn Zettler (Rio Tinto), and Alex Hall (ESSA Technologies Ltd.) for their ongoing communications with the authors during the project.

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1 INTRODUCTION

At the end of March 2016, Rio Tinto completed modernization of its Kitimat smelter to increase production of aluminum. The modernization, hereafter called the Kitimat Modernization Project or KMP, increased emissions of SO_2 , which could potentially change the acidity of precipitation affecting downwind watersheds, particularly near the communities of Terrace and Kitimat. ESSA et al. (2013a) estimated that the acidic deposition may exceed the critical load of acidity for some lakes. Critical load (CL) is defined as “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” (Nilsson and Grennfelt, 1988). An environmental effects monitoring program (EEM) was developed by ESSA et al. (2013b) in consultation with representatives of Rio Tinto, the Haisla First Nation, and the BC Ministry of Environment. The monitoring plan included indicators of atmospheric SO_2 and acidic deposition, SO_2 thresholds for human health, vegetation, soils, water chemistry, and aquatic biota. In the water and aquatic biota component, indicators include a Key Performance Indicator (charge balance ANC (CBANC)), and a set of informative indicators (Gran ANC, base cation surplus (BCS), pH). Additional indicators (dissolved organic carbon (DOC), and the concentration of major anions and cations) are used to perform QA/QC checks and evaluate year on year changes (ESSA 2022). Measurement of these indicators has been completed as part of the annual EEM among lakes within the local airshed affected by emissions from the smelter. Chemical measurements in streams downstream of a lake closest to the smelter have also been conducted, but less frequently than the lake sampling. In 2015, the annual water sampling expanded to include three control lakes (called DCAS14A, NC184 and NC194) that are not within the smelter-influenced airshed. A comprehensive review of the EEM data collected during 2013 – 2018 showed no evidence of exceedances of pH or ANC thresholds (ESSA et al. 2019). This outcome showed that ambient base cation supply was sufficient to offset acid loading among lakes and streams of local drainages affected by smelter emissions, thus limiting change in ANC and pH.

This report presents measurements collected from lakes that were sampled in 2022 in support of the continued EEM program. Nine tasks were as follows:

1. Annual water sampling and analytical chemistry from 12 lakes completed on October 2, 2022, using helicopter sampling techniques that were developed in early years of the EEM by Limnotek. The lakes included seven *acid-sensitive* lakes (LAK006 (End Lake), LAK012 (Little End Lake), LAK022, LAK023 (West Lake), LAK028, LAK042, and LAK044), one *less acid-sensitive* lake (LAK016), three *control* lakes (DCAS14A, NC184, NC194) and one non-EEM lake (LAK027 Bowbyes Lake, added at the request of BC Environment).

2. Two sampling episodes in June followed by monthly sampling in July through September 2022 to provide data for later analysis of spring and summer variability among chemical analytes in LAK028 and LAK006 (End Lake) and to

describe their basic limnology. These two selected lakes were representative of acid – sensitive lakes in the study area.

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4. Quality assurance testing of the 2022 water chemistry results.
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7. Operation of a pH logger at the surface and bottom of LAK028 and a pH logger near the surface in LAK006 to examine seasonal variation in pH and provide insight into meromixis in LAK028.
8. Begin operation of a conductivity mooring on LAK028 for use in interpreting long term stability of the chemocline.
9. Maintenance of an instrument raft on LAK028 (Figure 1). The raft supported temperature and pH moorings. Tripods that were secured to the raft deck hosted air samplers that were part of the SO_2 sampler network in the Terrace-Kitimat valley (ESSA et al. 2022).

All data were supplied to ESSA Technologies Ltd. to update analyses needed for the EEM program.

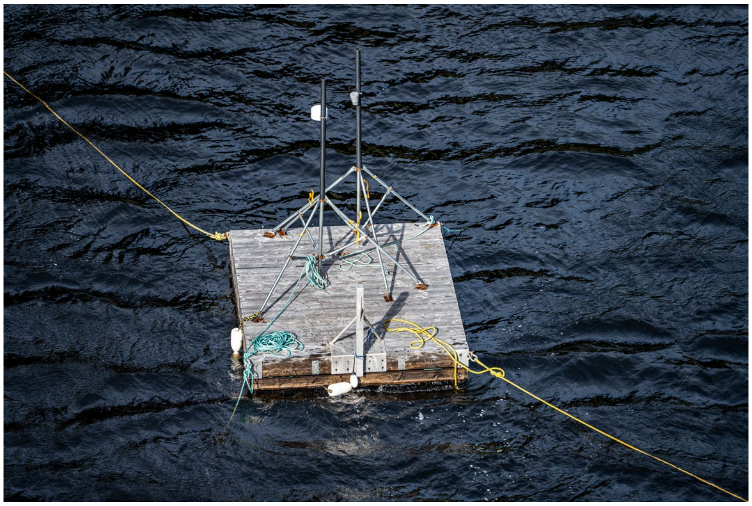

Figure 1. Image of the instrument raft on LAK028 in 2022. The temperature and conductivity moorings and pH loggers (surface and bottom) were suspended from the raft. The tripods supported air sampling equipment that is reported by ESSA et al. (2022).

2 METHODS

2.1 Sampling sites

The 2022 EEM lake water sampling was done in 12 lakes following recommendations in a 2019 program review (ESSA et al. 2020) (Table 1). The lakes included seven *acid-sensitive* lakes (LAK006 (End Lake), LAK012 (Little End Lake), LAK022, LAK023 (West Lake), LAK028, LAK042, and LAK044), one *less acid-sensitive* lake (LAK016), three *control* lakes (DCAS14A, NC184, NC194) and one non-EEM lake (LAK027 Bowbyes Lake) (Figure 2). Bowbyes Lake (LAK027) was added in 2021 following a request from BC Environment to sample another lake in the high SO_2 deposition zone.

Table 1. List of 11 EEM lakes and one non-EEM lake sampled in 2022.

Number of water body	Lake or stream name	Lake area (ha)	Lake designation[a]	UTM zone	Easting	Northing	Sampling activity in the EEM program[b]
LAK006	End Lake	10.25	Sensitive	9U	524155	6020661	SWC, F
LAK012	Little End Lake	2.30	Sensitive	9U	524145	6021028	SWC, F
LAK022		5.74	Sensitive	9U	524185	6022796	SWC
LAK023	West Lake	6.77	Sensitive	9U	522750	6018850	SWC, F
LAK028		1.02	Sensitive	9U	519139	5993425	SWC[c]
LAK042		1.46	Sensitive	9U	520911	6048362	SWC
LAK044		2.01	Sensitive	9U	522541	6050321	SWC, F
LAK016		2.58	Less sensitive	9U	523347	6018243	SWC, F
DCAS14A	Allistair Lake	717.2	Control	9U	488170	5994898	SWC
NC184		6.8	Control	9U	512321	5933333	SWC
NC194		35.6	Control	9U	522119	5949616	SWC
LAK027	Bowbyes Lake	19.5	Non-EEM lake	9U	518232	5995394	N/A

a. There are three sets of lakes in ESSA et al (2020) defined as: ***"Less sensitive lakes"****. These lakes were expected to show changes in lake SO_4^{2-} if exposed to increased deposition of S, but no biologically significant changes in pH of Gran ANC due to their greater ability to neutralize acidic deposition,* ***Sensitive lakes:*** *seven lakes that were predicted in the STAR to decrease in pH >0.1 units under maximum future emission levels, and* ***Control lakes****: three sensitive lakes located well outside of the deposition plume from Rio Tinto. The control lakes were added in 2015 but had sampling data from 2013 KAEEA program[1]."*

b. EEM sampling activities have included surface water chemistry (SWC) and fish (F)

c. Fish sampling was conducted in LAK028 in 2017 but it was not part of the original EEM program.

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[1] ESSA et al 2014

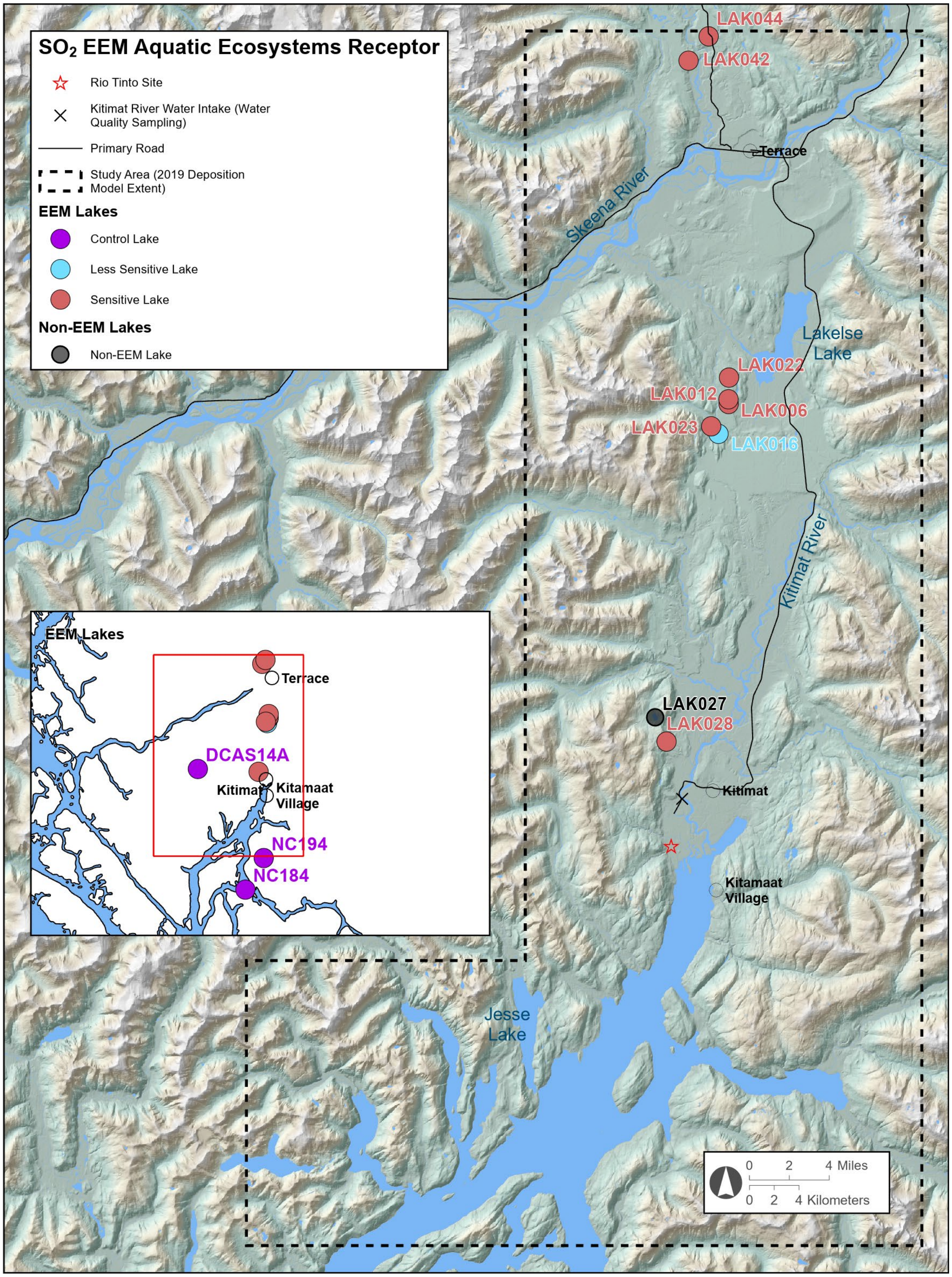

Figure 2. Layout of 12 lakes sampled in 2022.

2.2 Annual lake water sampling, 2022

The one – day annual sampling of the EEM lakes was completed on October 2, 2022. At each lake, instruments were deployed and water was collected from a Twinstar helicopter in a hover position approximately 4 m above the water surface using a crew of three people plus the pilot. The crew leader in the front seat recorded data on a standard field sheet (Appendix A), took site photos, double-checked the global positioning system (GPS) waypoint location, and provided overall direction of sampling activities. The other two crew members worked together in the back seat to take instrument readings and collect the water samples. The pilot made all decisions related to safety. Crew members and the pilot were always in communication via headsets. Lab gloves were worn by crew members handling the instruments and water bottles.

The following sampling procedure was followed at each lake. As the helicopter approached a lake, the crew leader (front seat) provided the pilot with general guidelines about where the sampling station should be located, which was usually at an expected deep point, based on lake morphometry. The pilot decided on the actual location. Station coordinates from the helicopter GPS were logged on the field form. Once on station in a stable hover, the sliding back door of the helicopter was opened, a weighted transducer was lowered into the lake just under the water surface and the water depth and temperature was measured using a Lowrance Mark-5X portable depth sounder. The sounder transducer was retrieved. The data were recorded on a field sheet (Table 2, Appendix A). A 5 L VanDorn water bottle (Wildlife Supply Co. Yulee, FL) was lowered to a depth of 1 m, triggered with a messenger to collect a water sample and retrieved.

At LAK028, a second water sample from a depth of 13 m was also collected by helicopter in three steps. A 13m depth mark was placed on the haul line. The Van Dorn water bottle was lowered to the point where the 13m mark on the haul line was at the water surface. The messenger for the Van Dorn was then released to trigger the closing mechanism on the Van Dorn, which was then hauled back into the helicopter. This method resulted in the collection of a sample from a depth of approximately 13 m based on the haul line mark. Due to movement of the helicopter in a hover position, that sampling depth may have been plus or minus 1m.

Samples at all lakes were dispensed from the VanDorn bottle into the following bottles on board the helicopter:

- two 250 mL pre-cleaned polyethylene bottles,
- one 125 mL precleaned amber glass bottle,
- two precleaned 125 mL polyethylene bottles,
- one 1 L precleaned polyethylene bottle,

- At LAK028 only, an additional 145 mL polyethylene bottle precharged with preservative (sodium hydroxide and zinc acetate) was filled.

After filling all bottles at a given lake, the sample bottles were placed in a plastic bag labelled with the lake number and packed on ice in a cooler that was carried in the helicopter skid basket. At the end of the day of sample collections, water samples from each site were handled as follows:

- Sample in the 125 mL amber glass bottle was preserved with H_2SO_4, packed on ice, and shipped to ALS Environmental in Burnaby, B.C. for fluorometric analysis of NH_4-N concentration, total phosphorus (TP), and total nitrogen (TN) by standard methods (APHA 2011).

- Sample in one of the 125 mL polyethylene bottles was preserved with HNO_3, packed on ice, and shipped to ALS for analysis of total base cation (Ca, K, Mg, Na, Sr, Al, Mn, Fe) concentrations using inductively coupled plasma – mass spectrometry (ICPMS).

- From the second 125 mL polyethylene bottle, ALS analyzed pH using a revised method for low ionic strength waters, as requested by Limnotek in 2020. This method was identical to the standard pH method (see below) with the exception that the instrument did not time out after 3-minutes but was allowed to stabilize for up to 10-minutes before a pH value was recorded. Field tests in 2019 showed that immersion of the electrode for 10-minutes provided stable pH readings (Limnotek 2020).

- Sample in the 145 mL polyethylene bottle precharged with preservative (collected at LAK028 only) was packed on ice and shipped to ALS for analysis of total sulfide (as H_2S and S) by colourimetry (APHA 2011).

- The first 250 mL polyethylene bottle was packed on ice and shipped to Biogeochemical Analytical Service Laboratory (BASL) at the University of Alberta in Edmonton, Alberta, for analysis of pH and Gran ANC by titration on a PC-titration Plus system (https://mantech-inc.com/analysis-systems/automated-titration-analysis/). Detailed methods for this procedure are provided in Appendix B). Note that prior to 2020, these samples were shipped to Trent University in Ontario. After a cross-lab comparison using paired samples collected in October 2019 (Limnotek 2020), this transition from Trent to BASL was implemented in 2020. The change in labs was due to Trent not having the capacity to provide lab services beyond 2019.

- The second 250 mL poly bottle was packed on ice and shipped to ALS for analysis of anion (HCO_3, Cl, SO_4, F, NO_3-N) concentrations by ion chromatography, total dissolved solids by gravimetric analyses, specific conductivity using an automated bench top conductivity meter, soluble reactive phosphorus (SRP) by standard methods (APHA 2011), and pH using a Skalar Sp2000 auto-titrator system (https://www.skalar.com/analyzers/sp2000-robotic-analyzers-turnkey-or-custom-made-automation-solutions/) or a Metrohm 848 Titrino Plus system (https://www.metrohm.com/en/products/titration/titrino-plus/28480010). The Metrohm system included stirring of the sample during pH measurement. These instruments recorded a stable signal if the pH changed less than 0.05 pH units in five consecutive readings that were five seconds apart. The instruments timed out after 3-minutes, which means that even if a stable signal was not found before 3-minutes of electrode immersion, a pH value was recorded.

- Aliquots from the 1 L polyethylene bottle were handled as follows:
  - At the field lab in Terrace, B.C. a 40 mL aliquot was dispensed in smooth flow without bubbles to a 50 mL polyethylene flask pre-rinsed with sample water for immediate pH measurement using a WTW ProfiLine 3210 Portable pH meter equipped with a Sentix 41 pH combination electrode (Xylem Analytics, Weilheim, Germany) prior to any other aliquots being dispensed to avoid degassing of CO_2 from the sample prior to pH measurement. This field pH measurement followed procedures in EPA method 150.3 (EPA 2017) that is followed by the Canadian federal agencies (e.g. https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-ph.html#a42 , CCME 2011). No stirring of the sample was done during electrode stabilization to avoid degassing of CO_2 from the samples as recommended by Busenberg and Plummer (1987) for measurement of pH in very low conductivity waters. The field pH meter was equipped with a new electrode on May 27, 2022.
  - A 125 mL aliquot was filtered (0.45 µm) and preserved with HNO_3, packed on ice, and shipped to ALS for analysis of dissolved base cation (Ca, K, Mg, Na, Sr, Al, Mn, Fe) concentrations using ICPMS.
  - A 125 mL aliquot was filtered (0.45 µm) and shipped to ALS for analysis of dissolved inorganic carbon (DIC) by combustion (APHA 2011).
  - A 125 mL aliquot was filtered into a glass amber bottle, preserved with H_2SO_4, packed on ice, and shipped to ALS for analysis of total dissolved phosphorus (TDP) and dissolved organic carbon (DOC) concentration by standard methods (APHA 2011).

Measurements of descriptive variables were compiled on a field data form (Appendix A) at each lake. The listing of these variables and how they were measured is provided in Table 2. These data provided supportive evidence of lake conditions that could later assist with interpretation of lake water chemistry.

Table 2. List of descriptive variables and associated methods of calculation that were recorded on the field data sheet (Appendix A).

Habitat or other descriptive variable	**Units**	**Description and method**
Lake name	No units	Station label
Site ID	No units	Preassigned site identification number
Date	No units	Date of sampling
Time on station	24-hour clock	Time of arrival at station
Time off station	24-hour clock	Time of departure from station
Field Crew	No units	Names of field crew
Northing	UTM	UTM northing recorded with a Garmin GPSmap 76CSx GPS receiver
Easting	UTM	UTM easting recorded with a Garmin GPSmap 76CSx GPS receiver
Weather	No units	Coding for present conditions and conditions in past 24 hours and past week
Riparian Vegetation	%	Estimate (%) of each type, totaling 100% including: unvegetated, grasses/ferns/herbs, shrubs, deciduous forest, coniferous forest, and wetland
Water depth at sampling station	m	Water depth at the sampling station measured using the Lowrance Mark-5XDSI portable depth sounder.
Water sample depth	m	Depth of sample collection recorded from the calibrated line used to deploy the VanDorn water bottle.
Temperature	ºC	Instantaneous surface temperature in all lakes measured with the Lowrance Marck 5XSDI portable depth sounder.
pH	Relative units	Measurement taken with the WTW ProfiLine 3210 Portable pH meter in a field lab on the day of sample collection from each lake. The WTW meter was calibrated with fresh pH buffers on the day of measurement.

2.3 Frequent lake water sampling, 2022

2.3.1 Overview

Frequent sampling of selected lakes (specified in following sections) was done during spring through fall, 2022 to provide data for later analysis by ESSA Technologies. The lakes included LAK006, LAK012, LAK023 LAK028, LAK042, and LAK044. All lakes were sampled at the surface except LAK028 where samples were collected from both surface and 2m off bottom. The added sampling at LAK028 was to capture meromixis that was not present in the other lakes.

An Onset (Bourne, MA) MX2501 pH and temperature logger (hereafter referred to as an “Onset”) was installed at a water depth of 2 m in LAK006 and at depths of 2 m and 13 m in LAK028 during 2022 to continuously record pH. Data from the deep Onset in LAK028 assisted with continued interpretation of meromixis that was detected in 2017. Prior to 2021, electrodes were changed every 2-3 months in the field. However, field replacements of electrodes during rainy or damp weather may allow moisture into electronics of the instrument. In 2021 and 2022, new electrodes were installed on spare instruments during the evening before the field day, and the whole instrument was replaced on the field day. All loggers had an anti-biofouling ring on the pH electrode, which prevented growth of a biofilm on the electrodes. Methods for the water sampling at all lakes and lab procedures are described in the following sub-sections.

2.3.2 LAK028

The frequent water samples from LAK028 were collected on June 1, June 13, July 11, Aug. 9, Sept. 7, Sept. 28, Oct. 4, Oct. 11 and Oct. 17, 2022. Access was by truck off the Wedeene forest service road (FSR) for 2 km until the Mt. Claque trailhead. From there, the field crew hiked 750 m up the steep Mt. Claque trail and then another 550 m from the Mt. Claque trail to the edge of LAK028. Once at the lake, the crew unlocked and launched a 12 foot aluminum Marlon jon boat from the lake edge (which had been slung into LAK028 via helicopter and received by the Limnotek field crew in October 2016) and paddled to the centre of the lake where the raft was anchored. The boat was tied to the raft for water sampling and servicing of instruments. Water samples were collected from the surface and 2 m off bottom using a Van Dorn sampler. Sampling depth was exact using this method. On all dates, the water samples were analyzed for all parameters described in Section 2.2.

On each sampling date, profiling of temperature, specific conductivity, turbidity and concentration of dissolved oxygen was completed using a YSI ProDSS handheld multiparameter water quality meter that was calibrated on the day of use. After a 10-minute electrode stabilization period at the surface, the instrument was lowered at a rate of 20 $cm \cdot s^{-1}$ from the raft until it reached the bottom of the lake, while logging readings once every 2 seconds to instrument memory. Logged data were uploaded a computer on the day of sampling.

Scripts in R ([www.**r**-project.org](http://www.r-project.org)) were used to produce colour filled three dimensional plots of the temperature, conductivity, dissolved oxygen and turbidity profiles over time from those profiling data. Depth of the thermocline during stratification and chemocline was captured from these images as the range of depths where water temperature or other physical attributes changed more rapidly with depth than it did in stable layers above and below.

After each day of water sampling, the boat was pulled out of the water and locked to a tree. The crew hiked out with the water samples, which were packed on ice in a soft cooler nested in a backpack. The total return trip time from the parking area on the Wedeene FSR was 5 hours. After the final sampling event in 2022, the boat was chained and locked to a tree in an upright, inverted position to shed snowfall.

A temperature mooring was installed in LAK028 in 2019 to examine mixing patterns needed to interpret potential interaction between meromixis and surface water chemistry that was used for interpretation of time course change in pH and Gran ANC. Ten Onset TidBit temperature loggers were distributed from surface to bottom on a vertical line that was attached to the raft and weighted with a 10 lb dumbbell. Logger depths (m) were 1, 3, 6, 8, 9, 10, 11, 12, 13, and 14 m. The mooring and loggers were installed on June 13, 2019. Data were recorded in 30-minute intervals. In 2022, the logger data were uploaded on May 31. New temperature loggers were installed on July 11, 2022. A second data upload was done on August 9, 2022 and a third upload was done at the end of field work on November 4, 2022. Each winter since 2019, the temperature mooring has been set up independent from the raft using a weighted line and floats to overwinter in the centre of the lake.

On June 1, 2022 an Onset pH logger was clipped onto the mooring at a depth of 2 m and another at 13 m. Pre-and post-calibration checks were performed and calibrations were conducted on each sampling date using a two point calibration with standard buffers of pH 4 and 7 via a bluetooth application on a cell phone. The loggers were removed at the end of sampling on October 17, 2022, and data were uploaded to computer. The logger electrodes were cleaned using a Q-tip at the time of calibration if needed. Battery replacement on the Onsets was not required.

A conductivity mooring consisting of one logger situated at each of 1m, 8m, 10m, 12m, and 14m on a vertical line was installed on July 11, 2022. The loggers at 1m and 12m recorded conductivity once every 30 minutes. The loggers at 8m, 10m and 14m had a scheduling error and recorded data once every 5 minutes. These loggers ran out of memory on September 7, 2022, resulting in data only for 1m and 12m after September 7. All the conductivity loggers were removed on October 16, data were uploaded at the field lab, and loggers were reinstalled on October 17 with logging interval corrected to once every 30 minutes on all loggers. The loggers will remain in LAK028 over winter along with the temperature mooring. The 30-minute measurement frequency is expected to be sufficient to not fill logger memory before spring 2023.

2.3.3 LAK006 (End Lake)

Frequent water sampling at End Lake (Figure 3) occurred on June 2, June 12, July 12, Aug. 8, Sep. 8, Sep. 26, Oct. 13, and Oct. 19. Access was by truck and sampling was done from a 10 foot long inflatable boat equipped with 2.2hp outboard engine. Water samples were collected using a Van Dorn bottle and were analyzed for all parameters described in Section 2.2.

An Onset pH logger was installed on a submerged mooring line in LAK006. Weights anchored the mooring. The line length was 1 m less than water depth at the chosen site. The line was held vertical through the water column with submerged floats. The Onset was attached to the line 1 m beneath the floats using a locking carribiner. During instrument calibrations that occurred on each of the water sampling dates, the submerged floats were captured using a boat hook, pulled to the surface, and another float was clipped onto the vertical mooring using a tag line. This arrangement allowed easy access to the mooring for redeployment of the instruments after calibration on the boat.

For servicing on each visit, the Onset logger was clipped off the mooring line, pre- and post-calibration checks were run using solutions of known pH, data were downloaded, and a two point calibration was run using standard buffers of pH 4 and 7 via a bluetooth application on a cell phone as was done in LAK028 (2.3.2). All this was done on the boat.

On each sampling day, temperature, specific conductivity, turbidity and concentration of dissolved oxygen was measured over the water profile using a YSI ProDSS handheld multiparameter water quality meter, as was done in LAK028 (section 2.3.2). Again, scripts in R (www.**r**-project.org) were used to produce colour filled three dimensional plots of the temperature, conductivity, dissolved oxygen and turbidity profiles over time from those profiling data. Depth of the thermocline during stratification was captured from these images as the range of depths where water temperature or other physical attributes changed more rapidly with depth than it did in stable layers above and below.

2.3.4 LAK012, LAK023, LAK042, and LAK044

Frequent water sampling at LAK012 and LAK023 occurred on Sept 26, Oct 13 and Oct 19 and at LAK042 and LAK044 it occurred on Sept. 27, Oct 12 and Oct 20, 2022 (Figure 3). Access to LAK042 was via a spur road to a wood waste dump off the Kalum West FSR approximately 7 kilometers north of Hwy 16. A small inflatable boat, paddles and PFD's were carried down to the lake along with the water sample bottles and sampling equipment (roughly 300m). The boat was launched from the edge of the lake and paddled out to the centre, where water samples were collected. Following collection of the samples, the gear and boat were packed back to the truck. Access to

LAK044 was by truck and then by hiking 40 meters with the inflatable boat. The crew paddled the boat to the centre of the lake, where water samples were collected. Access to LAK012 and LAK023 was by truck to close to the lake shore. Sampling was done from a depth of 1m using the VanDorn water bottle and all water samples were analyzed of the full suite of analytes described in Section 2.2.

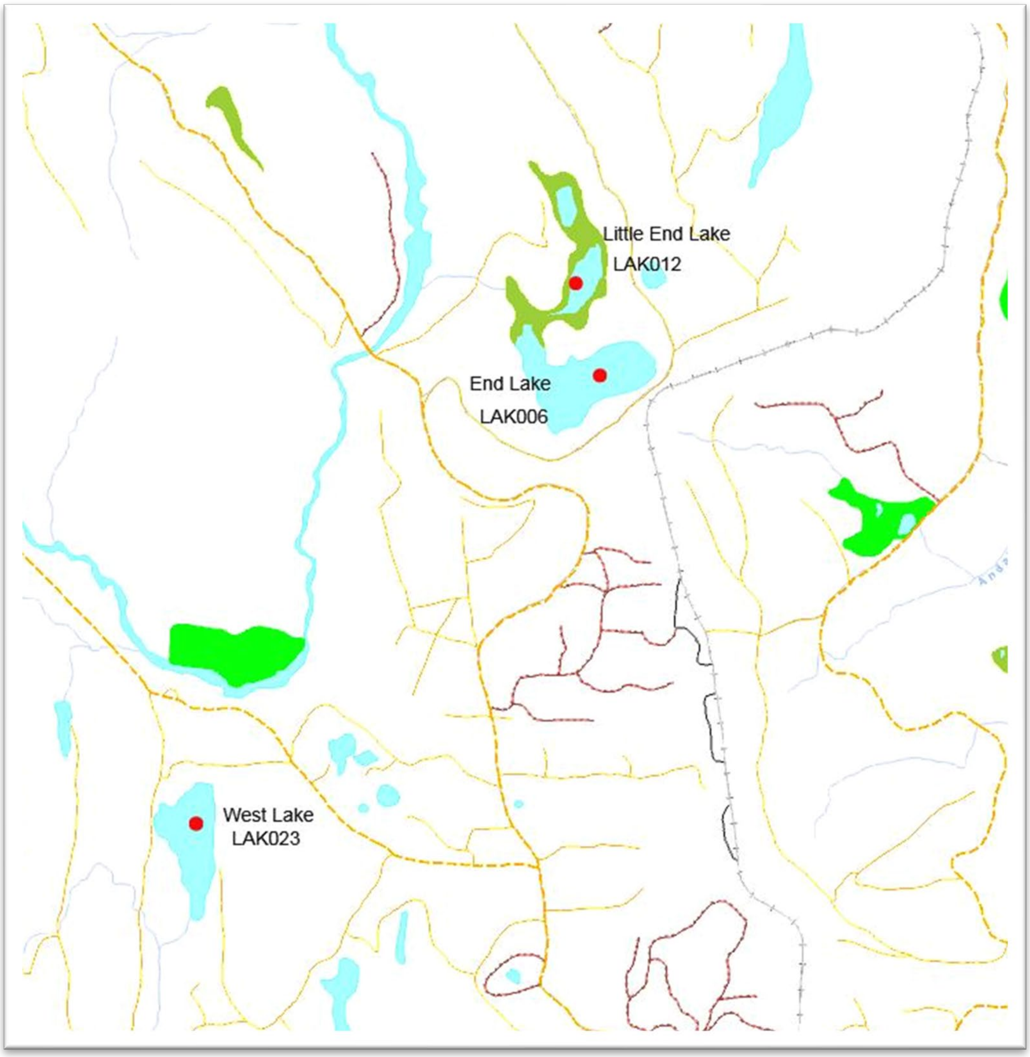

Figure 3. Location of End Lake (LAK006), Little End Lake (LAK012) and West lake (LAK023) with water sampling locations shown as red solid circles. General location of the lakes is shown in Figure 2. The yellow dotted lines represent roads or ATV trails.

2.4 Quality of chemical data

2.4.1 Blanks and duplicates

A blank and blind duplicate water sample were collected on each sampling date for calculation of precision and accuracy. Blanks were deionized water provided by ALS

Environmental and handled the same way as all test samples including water transfers to sample bottles, filtrations, storage, and shipping. Duplicates were water samples collected from a randomly selected station and again handled the same way as test samples. The presence of cations and anions in the blank samples indicated contamination during sample processing and the chemical concentration showed the amount of contamination.

2.4.2 Precision

Precision (D_f) was calculated as relative percent difference of an analyte concentration between a sample and its corresponding duplicate using the following equation recommended by the BC Field Sampling Manual (2013):

$$D_f = \left(\frac{A-B}{(A+B)/2}\right) * 100 \qquad \text{Equation 1}$$

where A is the concentration of an analyte in sample A and B is the concentration of the same analyte in the duplicate sample. The measurement of precision was associated with field and lab processes because it integrated sample collection, processing in the field, transport to the lab, and processing of samples in the labs.

2.4.3 Accuracy

Lab accuracy was tested by calculating percent recovery on solutions of known concentrations. Accuracy was determined as percent recovery (R_p) according to the following equation:

$$R_p = \left(\frac{B}{A}\right) * 100 \qquad \text{Equation 2}$$

where B is the recovered concentration and A is the known concentration of a given analyte in a solution. A solution containing the known analyte concentration was prepared in each lab using inorganic standards. The average value from up to 9 separate spiked samples was used to show average percent recovery from known standards of each cation and anion. Tests of percent recovery were limited to analytical values that were more than five times greater than the method detection limit, where the method detection limit was the concentration above which there was a high probability that a substance could be detected, following procedures reported by the BC Field Sampling Manual (2013).

2.5 Handling effects on pH measurement

2.5.1 Effect of electrode immersion time on pH at the ALS lab

Paired water samples were collected from all sites and dates to continue analysis of the effect of electrode immersion time on pH at ALS. Each sample pair was dispensed from the same water sample collected with the VanDorn into two separate bottles. Both bottles were shipped to ALS, where each of two methods were used to measure pH. First was the standard automated method in which the instrument timed out after 3 minutes whether a stable pH reading was attained or not. The second method forced a 10-minute electrode stabilization period. The 10-minute period was based on results by Limnotek (2020) with the field pH meter that showed that up to 9 minutes was needed for electrode stabilization in low ionic strength sample waters. The Shapiro-Wilk test was run to test for normality of the sample distribution. If significant ($p<0.05$), the non-parametric Wilcoxon test was used to test for significance of paired differences. If the Shapiro-Wilk test was not significant, a paired t-test was run to test for significance of paired differences. There was no control for this test (no known values of pH for each pair). Therefore, if the test showed a method effect on pH, the assumption was that the pH values using the new method allowing a longer time for electrode stabilization would be more accurate than the standard method. If the test for paired differences was not significant ($p<0.05$), there would be no evidence to support use of the longer electrode immersion times for measurement of pH at ALS. If the P value for a paired t-test or Wilcoxin test was less than 0.05, the mean difference between paired values reported by the two methods that were contrasted was considered significantly different from zero. The statistical analyses were run in R (R Core Team 2022).

2.5.2 Onset pH electrode drift

Output drift of a pH electrode was examined on each of the Onsets. Drift was the difference between observed and expected pH values following a period of operation. The expected value was the pH in a standard buffer solution of pH 4.0 and 7.0. The observed value was the pH in that buffer solution before calibration to the buffer value. Electrode drift is caused by the slow passage of hydrogen ions across the glass bulb which leads to dilution of the reference solution.

2.5.3 Test of instrument effects on pH during sampling of lakes on Oct 2, 2022

Following sampling of the 12 lakes (Table 1) on Oct 2, 2022, the following instruments and sample handling procedures were used to measure pH:

- The WTW ProfilLine 3210 portable pH meter (described in Section 2.2). There was no air space in the sample bottle used for measurement of pH using this meter, thus minimizing effects of CO_2 degassing on pH. The instrument was set up and calibrated before opening a sample bottle. A sample bottle was then opened, an aliquot was gently poured to a measurement vial that was rinsed with sample water. The sample bottle was recapped and pH measurment was made, in that order. A measurement was recorded following pH stabilization shown on the instrument.

- Bench top automated pH meter at ALS Environmental located in Burnaby within four days after sampling. There was no air space in the sample bottle thus minimizing effects of CO_2 degassing on pH. Two measurements were made: one using a standard 3-minute electrode immersion period and another using a 10-minute electrode immersion period for methods testing that is described in Section 2.5.1.

- Mantech PC automatic titrator (Mantech Inc. Guelph, Ontario) at the BASL located in Edmonton, Alberta within 16 days after sampling. The difference in time between sampling and measurement at BASL and ALS was due to shipping and not time for processing in each lab. There was no air space in the sample bottle thus minimizing effects of CO_2 degassing on pH.

Resulting data supported a test of an instrument effect on pH. A series of paired t-tests were run as a batch analysis wherein the pairs were WTW versus ALS, WTW versus BASL, and BASL versus ALS. The null hypothesis was that pH measurement in a lake sample by a given instrument was more similar to its corresponding measurement by one of the other instruments than to samples from the other lakes. The significance level for a single contrast of $p=0.05$ was adjusted using the Bonferroni correction to account for random effects, resulting in conservative control over Type I error (probability of rejecting the null hypothesis of no difference in pH between a pair of instruments when the null hypothesis is actually true). The Bonferroni correction was α/c where α was the nominal significance level (e.g., 0.05) and c was the number of paired contrasts, which in this case was three, resulting in the corrected significance level of 0.017.

The equation for calculating the t value for each paired test was as follows:

$$t = \frac{Mean\ differences}{SE\ of\ differences} \qquad \text{Equation 3}$$

If the P value for a paired t-test was less than 0.017, the mean difference between paired values reported by the two instruments that were contrasted was considered significantly different from zero.

The statistical analyses were run in R (R Core Team 2022).

2.5.4 Time course pH in LAK006 (End Lake) and LAK028

During the frequent sampling of End Lake (2.3.3) and LAK028 (2.3.2), the following instruments and sample handling procedures were used to measure pH:

- Onset pH logger installed at a depth of 2 m in each lake and another one installed at a depth of 2 m off bottom (13 m from the surface) in LAK028 with a new pH electrode in each Onset at the start of the season. A new electrode was installed in a spare instrument that replaced the existing instrument at the lake station every two to three months. The purpose of replacing the entire instrument was to avoid electrode replacements in the field which may result in moisture entering the instrument electronics during inclement weather. The two to three months period for electrode replacement was based on monitoring the electrode offset value during calibrations to avoid logging and calibration errors associated with the end of electrode life. In the low conductivity waters of LAK006 and surface water of LAK028, the electrode life is less than the manufacturer's recommendation.

- The WTW ProfilLine 3210 portable pH meter (described in Section 2.2). Measurements were made in the field laboratory within 5 hours of water sample collection. There was no air space in sample bottles thus minimizing effects of CO_2 degassing on pH between the time of sample collection and pH measurement.

- Two samples were shipped to the lab at ALS Environmental located in Burnaby for analyses using a bench top automated pH meter in the lab. On average, there were 3 days between sampling and analyses. The pH in one sample was measured using a 3-minute electrode stabilization period and the other was measured with up to 10-minute electrode stabilization (See Section 2.5.1). There was no air space in the sample bottle thus minimizing effects of CO_2 degassing on pH. If tests showed that the effect of electrode immersion time on pH was statistically significant, the pH value from the longer immersion period was used in describing pH over time in End Lake and LAK028.

- Bench top automated pH meter in the lab at BASL in Edmonton within 16 days after sampling. Measurement was done on a Mantech PC automatic titrator (Mantech Inc. Guelph, Ontario).

For both LAK006 and LAK028 there were 9 dates of measurement for each instrument corresponding with the 9 sampling dates during June 1 – October 19, 2022 (see dates in Section 2.3.2 for LAK028 and Section 2.3.3 for End Lake).

A repeated measures design was used to test the hypothesis that a pH measurement by a given instrument at a lake was more similar to its corresponding measurement by one of the other instruments than to samples from other dates. Measurements from the four instruments were compared using a repeated measures one-way ANOVA run on data from each lake. There were four levels (Onset, WTW, ALS lab, BASL) followed by post hoc tests between the instrument pairs. The significance level for the overall test of instrument effect was 0.05 adjusted using the Bonferroni correction for multiple comparisons to avoid the influence of random effects on those comparisons. The statistical analyses were run in R (R Core Team 2022).

2.6 Water surface elevation in End Lake and LAK028

Water surface elevation was monitored during June 2 through November 5, 2022 in End Lake and during June 1 through November 4, 2022 in LAK028. The measurement interval was 30 minutes at both lakes. Instrumentation included a standard staff gauge for manual water level readings and a Onset Hobo water level logger. The logger in End Lake was model MX2001-04 equiped with automatic compensation for atmospheric pressure (new in 2022). The model in LAK028 was U20-001-04 coupled with a Hobo barometric logger used for atmospheric barometric pressure compensation that was suspended from the top of the angle iron directly above the water level logger at the shoreline. Each logger was suspended using a 1 m length of aircraft cable inside a 2 inch PVC stand-pipe. The pipe was fitted with a grated cover on the lower end, and had holes drilled in it to allow free water movement. The staff gauge and logger assembly was secured to a 2.7m length of angle iron that was bolted into a shoreline tree (Figure 4, Figure 5), thus providing a fixed station for readings of water level at each lake. A simple 3-point survey with a rod and level was completed on the day of logger installation and day of removal to fix the monitoring location and determine if position of the staff gauge and logger housing shifted or was moved during the period of data logging. In 2022, there was no shift in position between June and November.

During water sampling visits to each lake, water depth on the staff gauge was recorded on the field notes and the logger installations were checked for signs of tampering or vandalism. There were no signs of tampering or vandalism of the staff gauges or water level loggers during 2022.

Figure 4. Photo showing the installed water level staff gauge and 2-inch PVC pipe that housed the water level logger in End Lake.

Figure 5. Photo showing the installed water level staff gauge and 2-inch PVC pipe that housed the Hobo water level logger in LAK028.

3 RESULTS

3.1 Overview

All water sampling and measurements were completed as planned. There were no safety incidents, and all work was completed on time within the planned schedule. All field and laboratory data were compiled into csv files ready for import into R data analysis software (R Core Team 2022). Those files have been sent to ESSA Technologies for further data analysis. A standard field sheet supporting the water sampling is shown in Appendix A. The lab method used for measurement of Gran ANC is shown in Appendix B.

3.2 Quality of chemical data

3.2.1 Blanks and duplicates

A total of 20 blanks and 20 duplicate samples were collected in 2022. Positive blanks were found for Al (total and dissolved), Ba (total and dissolved) and TP (Table 3). Positive blanks were not found for the other analytes. Mean concentrations of the Al and Ba analytes in the positive blanks were 181 - 15 times lower than those in corresponding lake water samples. The total phosphorus concentration in the positive blank was 6 times lower than the average concentration in lake samples. With the exception of one positive blank for dissolved Al, all incidents of positive blanks occurred on or after September 26, 2022. A new shipment of supplies were opened and used during that time window, which points to a supplies contamination issue contributing to the positive blanks. The absence of blank contamination (with the exception of one dissolved Al analysis) before September 26, 2022, and consistency of field methods on all sampling dates shows that water handling procedures did not contribute to the positive blanks.

3.2.2 Precision

The average relative percent difference (the measure of precision) between replicate pairs of samples in 2022 ranged between 1% and 13% (Table 4). Precision is considered high among field duplicates when relative percent difference is less than 20% (Ministry of Environment Lands and Parks 2013). It was high among all tests.

Table 3. Incidence of positive blanks (deionized water having an analyte concentration above the method detection limit) and comparison of analyte concentrations in positive blanks with analyte concentrations in lake water samples, 2022.

Analyte	Method detection limit (mg·L^{-1})	Number of positive blanks (maximum possible is 20)	Average concentration in positive blanks (mg·L^{-1}) (range in brackets)	Average concentration in lake samples in 2022 (mg·L^{-1})
Aluminum, dissolved	0.0010	11**	0.0017 (0.0011 – 0.0023)	0.308
Aluminum, total	0.0030	2*	0.0059 (0.0039 – 0.0078)	0.332
Barium, dissolved	0.0001	10*	0.00025 (0.0002 – 0.0003)	0.0038
Barium, total	0.0001	9*	0.00026 (0.0002 – 0.0004)	0.0042
Phosphorus, Total	0.0020	1	0.0024 (0.0024 – 0.0024)	0.014

*all occurred on or after September 27, 2022

**all occurred on or after September 26, 2022 except for one on July 11, 2022

Table 4. Relative percent difference of analyte concentration between surface replicates in 2022. Data are shown only for sample pairs having analyte concentrations greater than five times the method detection limit (except pH), following protocols reported by the Ministry of Environment Lands and Parks (2013).

Analyte	Average value of relative percent differences between replicate pairs of samples in 2022 (%)
Aluminum, dissolved	4 (n=20)
Aluminum, total	4 (n=20)
Ammonium-N	9 (n=4)
Calcium	3 (n=17)
Chloride	5 (n=4)
Conductivity	3 (n=10)
Conductivity (BASL)	1 (n=20)
Dissolved Inorganic Carbon	6 (n=4)
Dissolved Organic Carbon	13 (n=17)
Fluoride	3 (n=17)
Gran ANC (BASL)	4 (n=20)
Iron, dissolved	8 (n=16)
Iron, total	6 (n=17)
Magnesium, dissolved	3 (n=20)
Magnesium, total	3 (n=20)
Manganese, dissolved	5 (n=20)

Analyte	Average value of relative percent differences between replicate pairs of samples in 2022 (%)
Manganese, total	5 (n=20)
Nitrate-N	no values >5X MDL
Nitrogen, total	8 (n=11)
Orthophosphate, dissolved	no values >5X MDL
pH (ALS)	0.01[a] pH units (n=20)
pH (ALS new 2020 method)	0.01[a] pH units (n=20)
pH (BASL)	0.005[a] pH units (n=20)
pH Field (WTW)	0.003[a] pH units (n=20)
Phosphorus, total	9 (n=8)
Phosphorus, total dissolved	8 (n=4)
Potassium	7 (n=7)
Sodium	2 (n=17)
Solids, total dissolved	9 (n=4)
Strontium, dissolved	3 (n=20)
Strontium, total	4 (n=15)
Sulfide (as S)	10 (n=4)
Sulfide (as H_2S)	10 (n=4)
Sulfate	11 (n=16)

3.2.3 Accuracy

Average percent recovery in spiked and certified reference samples tested at the ALS lab ranged from 94% to 108% among all analytes, with an overall average percent recovery of 100% among all analytes (Table 5). These results show high accuracy.

Table 5. Percent recovery of analyte concentrations in lab control and spiked samples for the test of lab accuracy in 2022.

Analyte	Known concentration ($mg{\cdot}L^{-1}$ unless otherwise noted)	Average recovered concentration ($mg{\cdot}L^{-1}$ unless otherwise noted)	Sample size	Average percent recovery
Aluminum, dissolved	0.20 – 2.0	0.19 – 1.94	20	97
Aluminum, dissolved	2.00	2.02	24	101
Aluminum, total	0.20 - 0.40	0.18 – 0.40	16	97
Aluminum, total	2.00	2.05	21	103
Ammonium-N	0.2	0.2	21	99
Ammonium-N	0.100	0.101	13	101
Calcium, dissolved	50.0	49.9	24	100
Calcium, dissolved	4.0	3.9	6	98
Calcium, total	4.0 - 8.0	3.8	4	95
Calcium, total	50.0	50.1	21	100

Analyte	**Known concentration (mg·L^{-1} unless otherwise noted)**	**Average recovered concentration (mg·L^{-1} unless otherwise noted)**	**Sample size**	**Average percent recovery**
Chloride	100	101.3	20	101
Chloride	100 - 500	98.6 - 503.0	20	104
Conductivity (uS/cm)	146.9	145.6	20	99
Dissolved Inorganic Carbon	5 - 25	4.8 - 29.4	17	108
Dissolved Inorganic Carbon	8.0	8.3	25	104
Dissolved Organic Carbon	5	5.1	12	103
Dissolved Organic Carbon	8.57	8.571	21	100
Fluoride	1.00	0.99	20	99
Fluoride	1 - 5	0.86 - 5.15	20	101
Iron, dissolved	1.00	1.03	24	103
Iron, dissolved	2.0 - 20.0	1.8 - 18.4	19	94
Iron, total	1.00	1.04	21	104
Iron, total	2 - 4	1.8 - 3.9	21	95
Magnesium, dissolved	1 - 2	0.95 - 1.02	6	98
Magnesium, dissolved	50	50.6	24	101
Magnesium, total	1 - 2	0.90 - 0.99	6	96
Magnesium, total	50	51.3	21	103
Manganese, dissolved	0.02 - 0.2	0.04	14	95
Manganese, dissolved	0.25	0.248	24	99
Manganese, total	0.02 - 0.04	0.019	14	98
Manganese, total	0.25	0.251	21	100
Nitrate-N	2.50	2.56	20	102
Nitrate-N	2.5 - 50.0	2.5 - 50.5	19	103
Nitrogen, total	0.40	0.35 - 0.42	8	96
Nitrogen, total	0.500	0.499	21	100
Orthophosphate, dissolved	0.030	0.030	20	99
Orthophosphate, dissolved	0.030	0.030	19	101
pH	7.00	7.00	40	100
Phosphorus, dissolved	10	10.4	24	104
Phosphorus, dissolved	10 - 100	9.3 - 105	20	102
Phosphorus, total	0.05 - 10	0.04 - 11.7	42	98
Phosphorus, total	0.05 - 20	0.04 - 21.6	41	99

Analyte	Known concentration ($mg \cdot L^{-1}$ unless otherwise noted)	Average recovered concentration ($mg \cdot L^{-1}$ unless otherwise noted)	Sample size	Average percent recovery
Phosphorus, total dissolved	0.050	0.044	20	94
Phosphorus, total dissolved	0.05 - 0.0676	0.038 - 0.070	21	96
Potassium, dissolved	4.0 - 8.0	3.7 - 7.9	13	99
Potassium, dissolved	50.0	51.4	24	103
Potassium, total	4.00	4.00	14	99
Potassium, total	50	51.6	21	103
Sodium, dissolved	2.00	2.03	9	101
Sodium, dissolved	50.0	51.9	24	104
Sodium, total	2.00	1.97	7	98
Sodium, total	50.0	52.3	21	105
Strontium, dissolved	0.02	0.021	6	103
Strontium, dissolved	0.25	0.254	24	102
Strontium, total	0.02	0.021	6	103
Strontium, total	0.25	0.255	21	102
Sulfate	100.0	103.5	20	103
Sulfate	100 - 500	126.1	20	105
Sulfide (as S)	0.08 - 0.085	0.08	18	97
Sulfide (as S)	0.1 - 1.0	0.089 - 1.070	9	95
Total Dissolved Solids	1000	1019	26	102

3.3 Handling effects on pH measurement

3.3.1 Effect of electrode immersion time on pH at the ALS lab

The distribution of paired differences of pH between methods did not meet the assumption of normality (Shapiro-Wilk p value <0.001), so the non-parametric Wilcoxin test was used to test for an effect of electrode immersion time on pH. Differences in pH between the methods was not significantly different from zero (p value = 0.08). There was no consistent pattern: 38 ALS-3 pH values were greater than ALS-10 values and 28 ALS-3 pH values were less than the ALS-10 values. Overall, a finding of no significant difference in pH with a change in immersion time in 2022 was the same as in 2021 but different from findings in 2020, where longer immersion time was found to produce lower pH values (Limnotek 2021). To be conservative, all tests using ALS pH data from this point forward in the report were based on values using the 10-minute electrode immersion method.

3.3.2 Onset pH electrode drift

Mean drift in pH logged by each of the LAK006 and LAK028 Onsets (the difference between observed and expected values in pH readings taken in solutions of a known pH) was 0.01 – 0.02 pH units immediately after calibration (a measure of calibration accuracy), increasing to 0.01 - 0.05 pH units up to a month of operation in LAK006 and LAK028 (Figure 6) without time course trend or pattern (Figure 7). This magnitude of electrode drift was among the lowest of all years of continuous pH monitoring in LAK006 and LAK028 (Limnotek 2022).

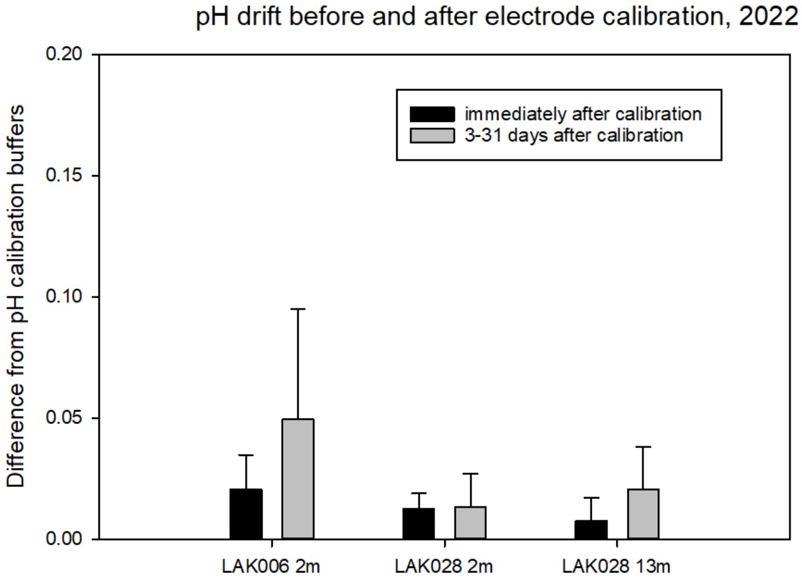

Figure 6. Onset pH electrode drift, shown as the mean difference (± standard deviation) between observed pH (field measured value of a buffer solution) and expected pH (certified pH value of a buffer solution) measured immediately after calibration and after a period up to 31 days in End Lake and LAK028 in 2022.

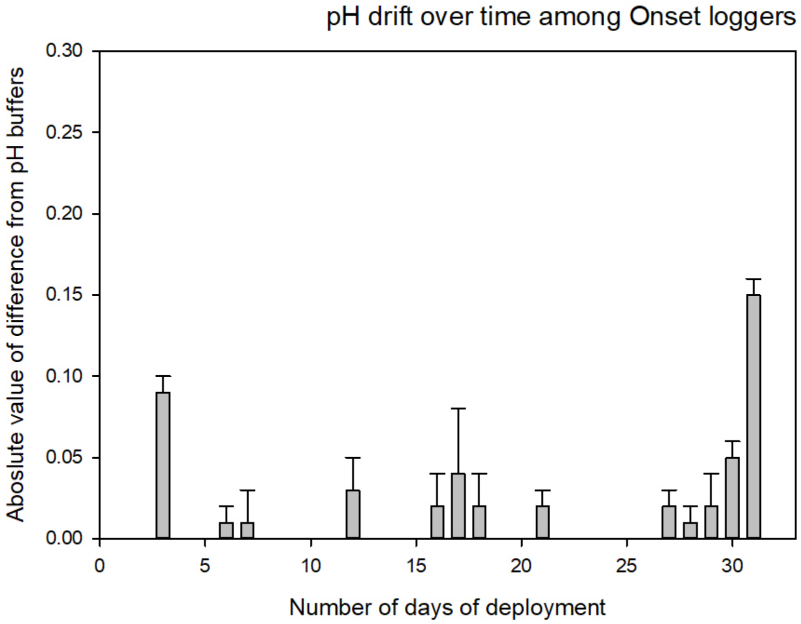

Figure 7. Onset pH electrode drift (the difference between observed pH (field measured value) and expected pH (certified pH value of a solution) after varying times of deployment following calibrations in 2022. Data are pooled for all Onset instruments in End Lake and LAK028.

3.3.3 12 lakes sampled on October 2, 2022

The batch of paired t-tests run on pH among water samples from the 12 lakes sampled on October 2, 2022 showed that the ALS_{10} values were significantly higher than those among all other instruments ($p<0.017$; Bonferroni corrected from 0.05) (Table 6). The mean difference was 0.31 pH units for the ALS-BASL comparison and 0.28 pH units for the ALS-WTW comparison. There was no significant difference in pH between BASL and field pH (WTW).

Table 6 Mean difference in pH between all combinations of instrument pairs among lakes that were sampled on October 2, 2022 (n=14 includes field duplicates). WTW was the field pH meter used to measure pH in each sample at the end of the sampling day, ALS_{10} was the method at the ALS lab in Burnaby, and BASL was the Mantech PC-titration Plus system used at BASL. The * indicates a significant mean difference ($p< 0.017$; Bonferroni corrected from 0.05) and “ns” indicates no significant difference in pH between paired instruments.

	Difference in pH between instrument pairs in 2022		
	WTW	**BASL**	**ALS_{10}**
WTW			
BASL	0.03 (ns)		
ALS_{10}	0.28 (*)	0.31(*)	

*shows a significant mean difference ($p< 0.017$; Bonferroni corrected from 0.05).
“ns” indicates no significant difference in pH between paired instruments ($p>0.017$).

3.3.4 Time course pH in End Lake and LAK028

The Onset pH loggers were installed and retrieved in End Lake and LAK028 according to the schedule shown in Table 7. Two loggers failed in 2022, both occurring at the 13m depth in LAK028. One occurred immediately after deployment on August 9 to replace the first logger that was installed on June 1. The second occurred five days after deployment on September 7. Electrodes on both instruments calibrated within acceptable ranges at the time of installation but when recovered on the following calibration date, either no data were recorded or pH values were clearly out of range and of no use. These errors pointed to internal electronics failure. Once the errors were discovered, the loggers were decommissioned and sent to recycling.

The logger failures resulted in two periods of missing pH logger data at the 13m depth in LAK028. One was August 9 – September 7. The other was September 7 – 28.

Table 7. Schedule of Onset pH instruments deployment and removal from End Lake (LAK006) and LAK028 in 2022.

pH logger location	Onset pH logger serial number	Instrument commissioning date	2022 installation Date	2022 retrieval date	Number of continuous days of monitoring in 2022
End Lake (LAK006), 2m depth	21025206	September 6, 2021	2022-05-27	2022-08-08	73
	20573567	May 21, 2019	2022-08-08	2022-11-05	89
LAK028 2m depth	21025205	September 7, 2021	2022-06-01	2022-08-09	69
	20573569	June 13, 2019	2022-08-09	2022-11-04	87
LAK028 13m depth (lake bottom was 15m)	20468200	October 11, 2018	2022-06-01	2022-08-09	69
	20984023	June 8, 2021	2022-08-09	2022-09-07	logger failed on deployment
	21025206	June 6, 2021	2022-09-07	2022-09-28	logger failed after 5 days of deployment
	21025205	September 7, 2021	2022-09-28	2022-11-04	37

Mean daily pH from each Onset pH logger was plotted with discrete pH values from the other instruments (WTW, ALS lab, and BASL) for each of End Lake and LAK028 surface and LAK028 deep (Figure 8 and Figure 9 and Figure 10 respectively).

In End Lake there was an upwards shift of close to 4 pH units when the initially installed logger was replaced on August 8. The removed logger was the same one that failed 5 days after installation at 13m in LAK028 on September 7, 2022. Although there was no evidence of imminent failure based on calibration output in End Lake, this coincidence shows that pH from that instrument during May 27 through August 8 in End Lake may be suspect due to the logger being near end of life. Those May 27 through August 8 pH logger date from End Lake were discarded from further use as a precaution to avoid possible error in tests of instrument effects on pH during time course monitoring in End Lake. No shift in pH at the 2m depth in LAK028 exceeding background variability was found by swapping out instruments. No data were available to show pH shift from swapping out the pH electrode at the 13m depth in LAK028 because of the logger failures shown in Table 7.

Repeated measures ANOVA showed differences between lab and field measurement of pH (Figure 11, Figure 12, and Figure 13). In LAK006, pH measured at ALS (ALS_{10}) was significantly greater than pH measured in the field (WTW and Onset) and at BASL. In the deep water at LAK028, smaller differences were found but again ALS_{10} pH was significantly greater than pH from the field instruments. BASL pH was in between. The same significantly higher pH at ALS_{10} compared to the field instruments was found in water from the 2m depth in LAK028. Unique to this water was significantly lower pH recorded by the Onset loggers compared to the WTW. The general pattern of instrument effects was pH being highest using ALS10, next highest was BASL, followed by similar results between the Onset loggers and the field WTW. The one exception was at the 2m depth in LAK028 where Onset pH was lower than the WTW.

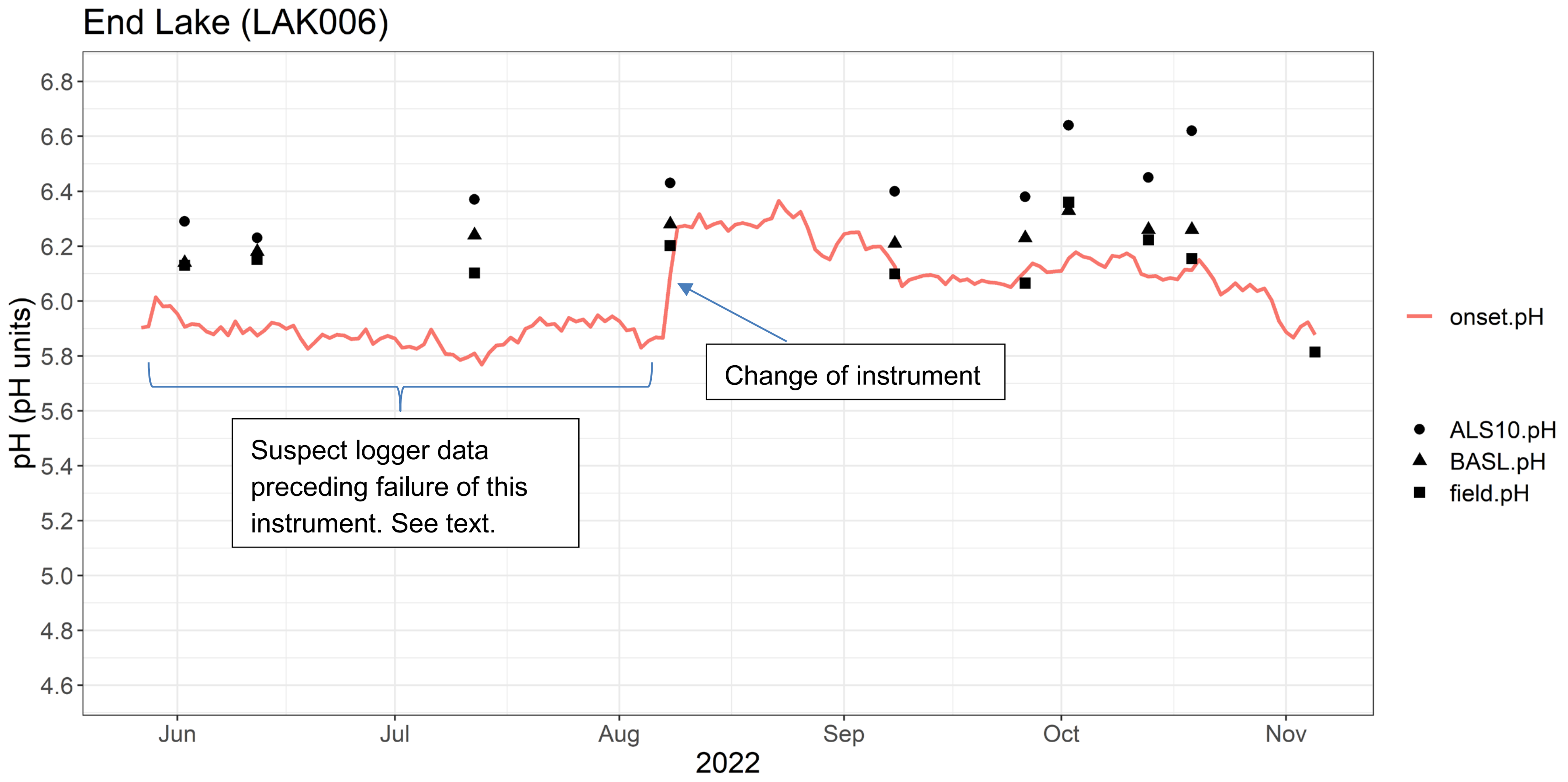

Figure 8. Mean daily pH for Onset pH logger in End Lake (continuous red line) shown with discrete pH measurements using other instruments in 2022. Field.pH is WTW meter, ALS10.pH is a bench top meter used at ALS labs in Burnaby using a 10-minute electrode immersion time, and BASL.pH is the Mantech PC-titration Plus system used at BASL. Discrete sampling dates correspond to dates when the Onset logger was calibrated except for on Oct 2nd when the lake was sampled from a helicopter.

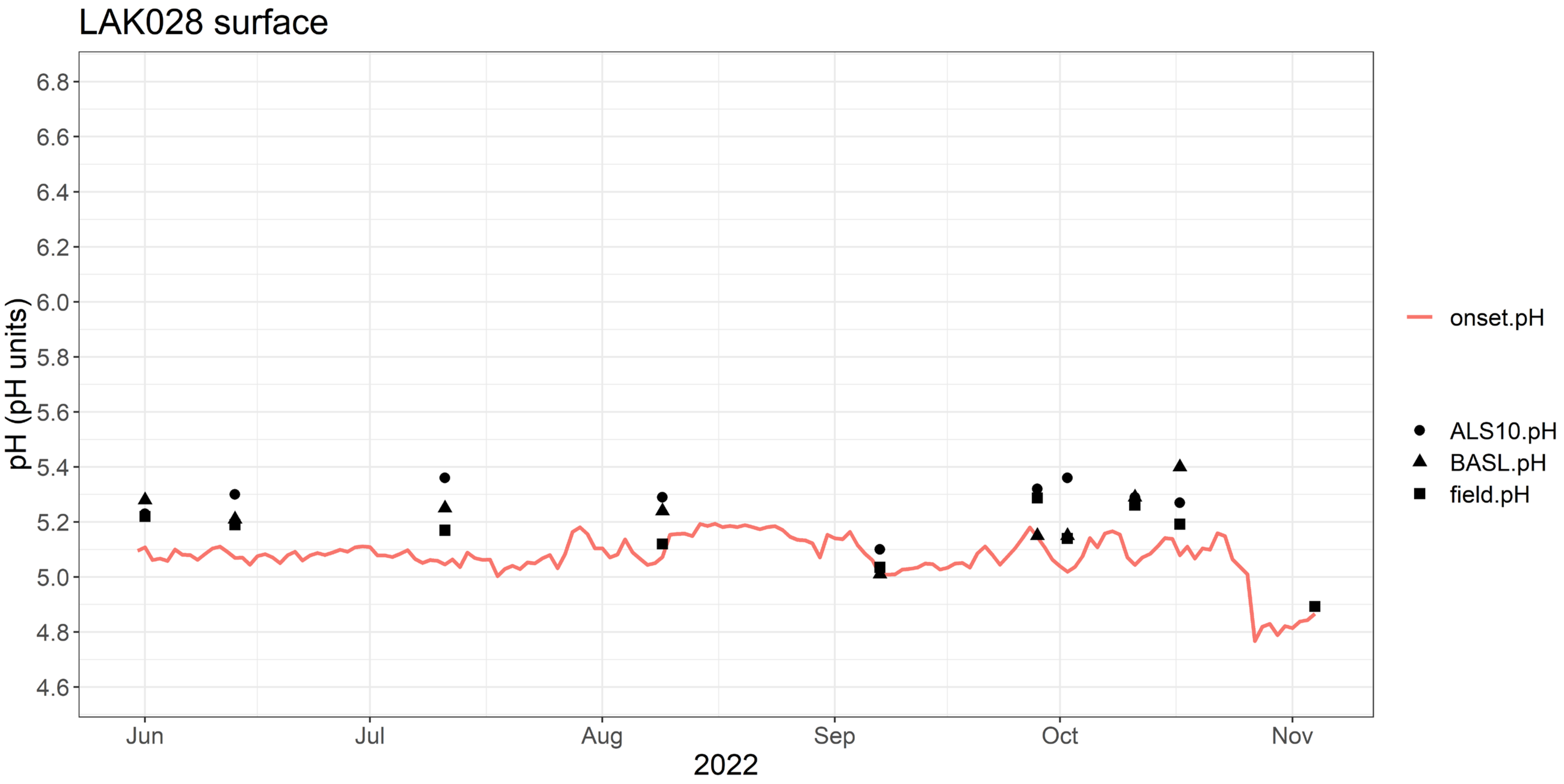

Figure 9. Mean daily pH for Onset pH logger in LAK028 deployed at a depth of 2 m (continuous red line) shown with discrete pH measurements in samples from the same depth using other instruments in 2022. Field.pH is WTW meter, ALS10.pH is a bench top meter used at ALS labs in Burnaby using a 10-minute electrode immersion time, and BASL.pH is the Mantech PC-titration Plus system used at BASL. Discrete sampling dates correspond to dates when the Onset logger was calibrated except for on Oct 2nd when the lake was sampled from a helicopter.

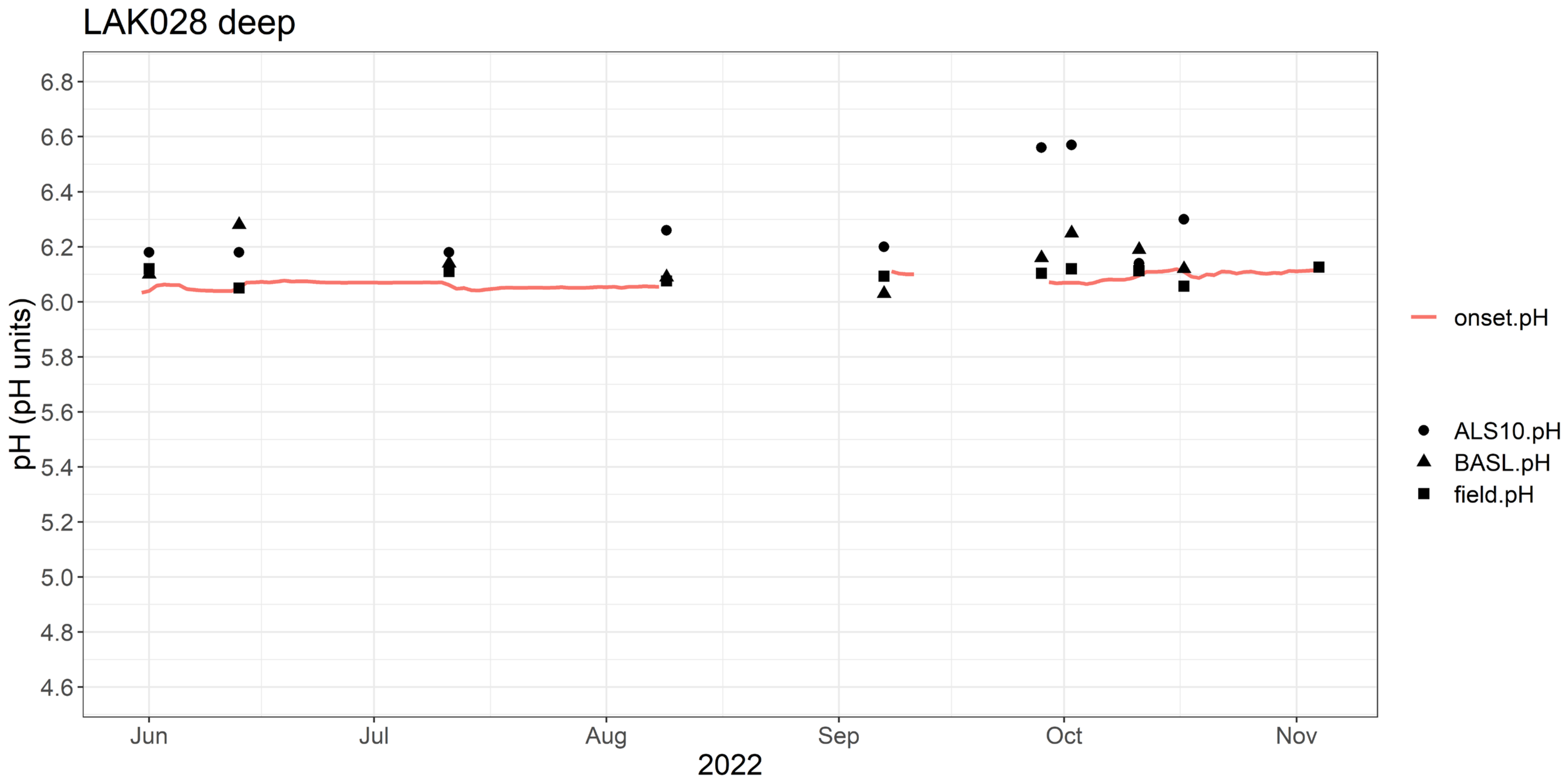

Figure 10. Mean daily pH for Onset pH logger in LAK028 deployed at a depth of 13 m (continuous red line) shown with discrete pH measurements in samples from the same depth using other instruments in 2022. Gaps in the time series show when a logger was not operating due to failure found on a calibration date. A failed logger was replaced on the following calibration date. Field.pH is WTW meter, ALS10.pH is a bench top meter used at ALS labs in Burnaby using a 10-minute electrode immersion time, and BASL.pH is the Mantech PC-titration Plus system used at BASL. Discrete sampling dates correspond to dates when the Onset logger was calibrated except for on Oct 2nd when the lake was sampled from a helicopter.

End Lake at 2m depth

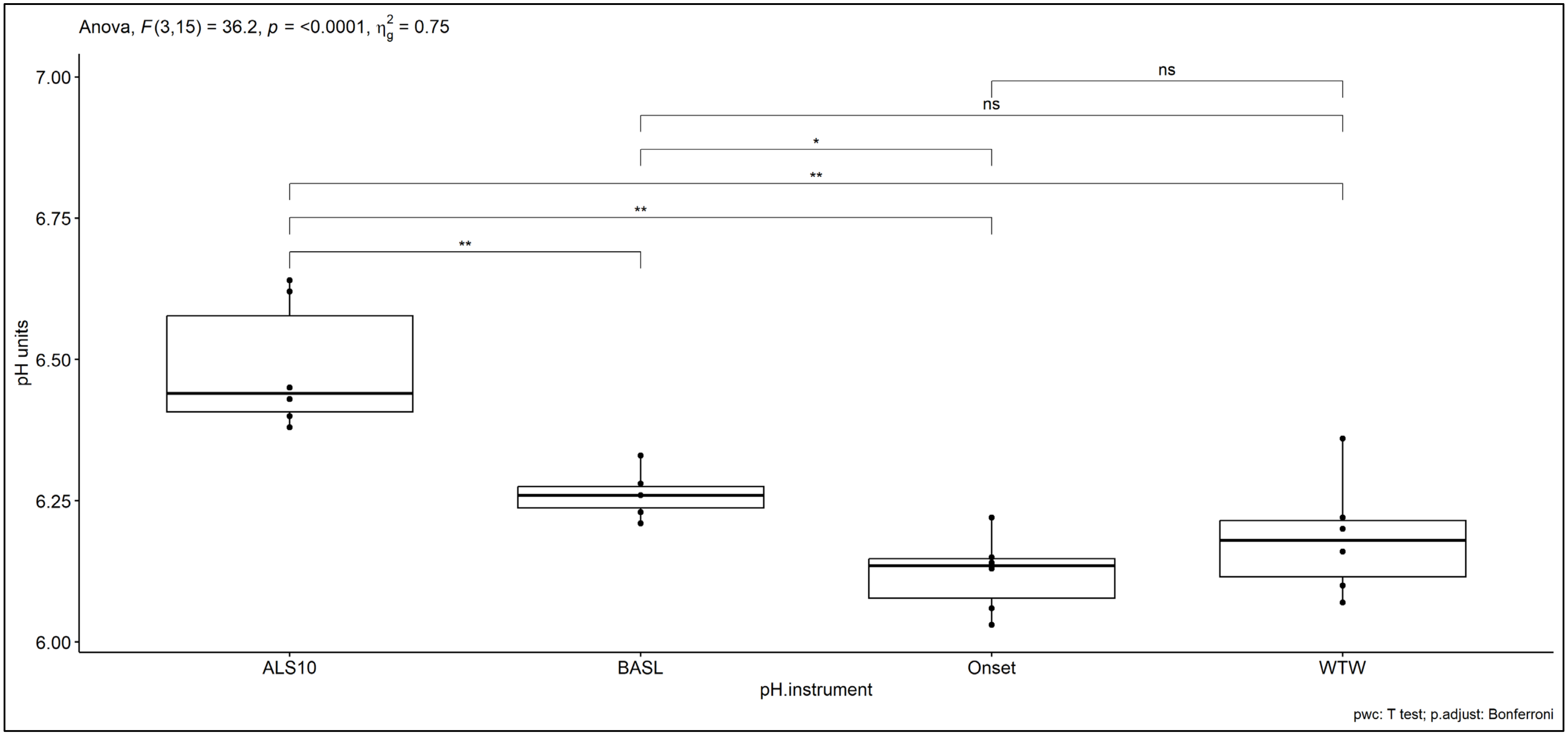

Figure 11.Box plot showing difference in pH in End Lake between all combinations of instrument pairs during sampling in August through October 2022 (n=6). Three sampling dates in June and July were omitted because data from the Onset were suspect (see Figure 8). Instrument names are ALS10 (instrument at the ALS lab using 10-minute electrode immersion time), BASL (instrument at the BASL lab), Onset (in situ pH logger), and WTW (field pH meter). Horizontal bars at the top of the box plot span instrument pairs being tested along with symbols indicating significance of a difference in pH using repeated measures ANOVA. The * or ** indicates a significant mean difference and “ns” indicates no significant difference in pH between the paired instruments.

LAK028 at 2m depth

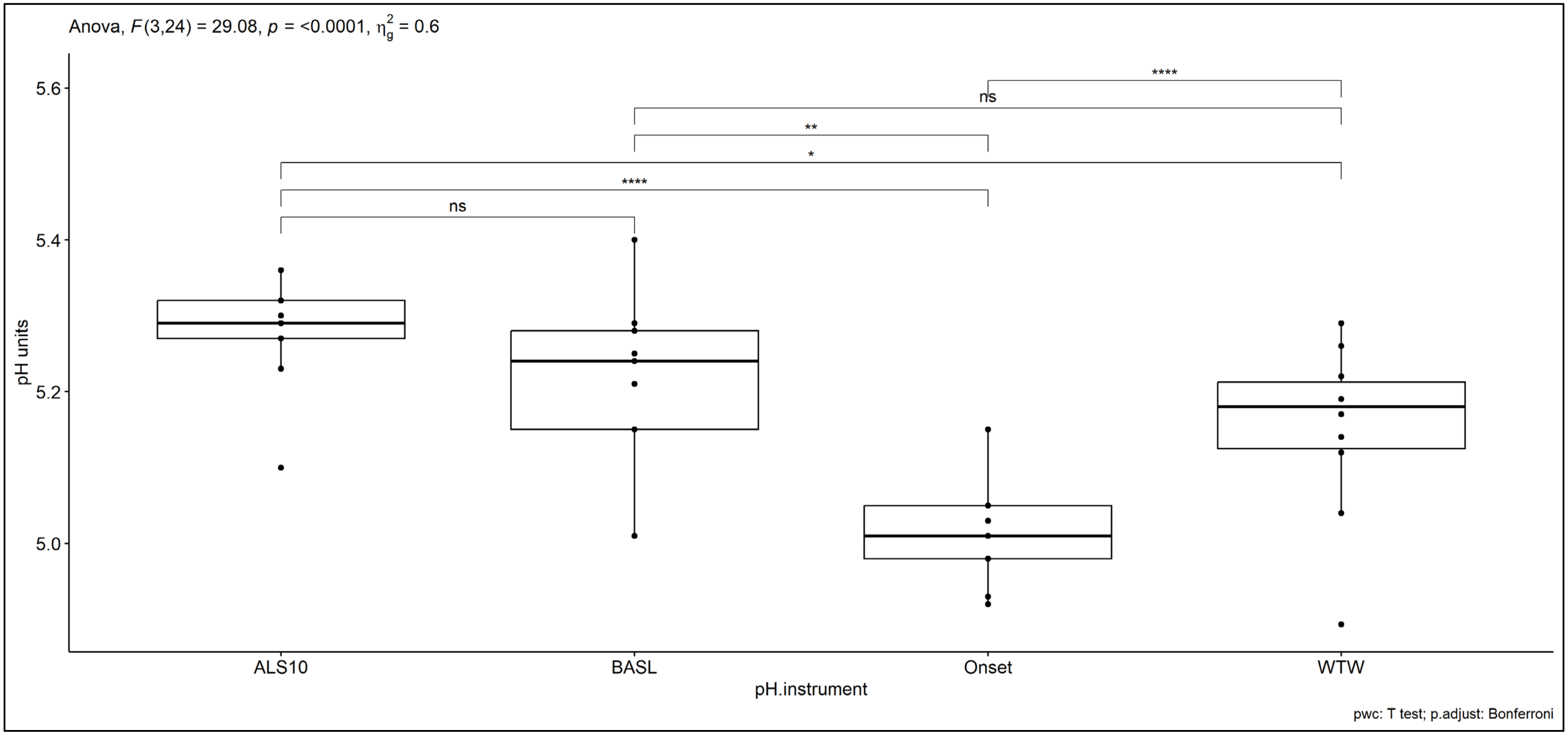

Figure 12. Box plot showing difference in pH in LAK028 (2m depth) between all combinations of instrument pairs during sampling in June through October 2022 (n=9). Instrument names are ALS10 (instrument at the ALS lab using 10-minute electrode immersion time), BASL (instrument at the BASL lab), Onset (in situ pH logger), and WTW (field pH meter). Horizontal bars at the top of the box plot span instrument pairs being tested along with symbols indicating significance of a difference in pH using repeated measures ANOVA. The * or ** or *** or **** indicate a significant mean difference and “ns” indicates no significant difference in pH between the paired instruments.

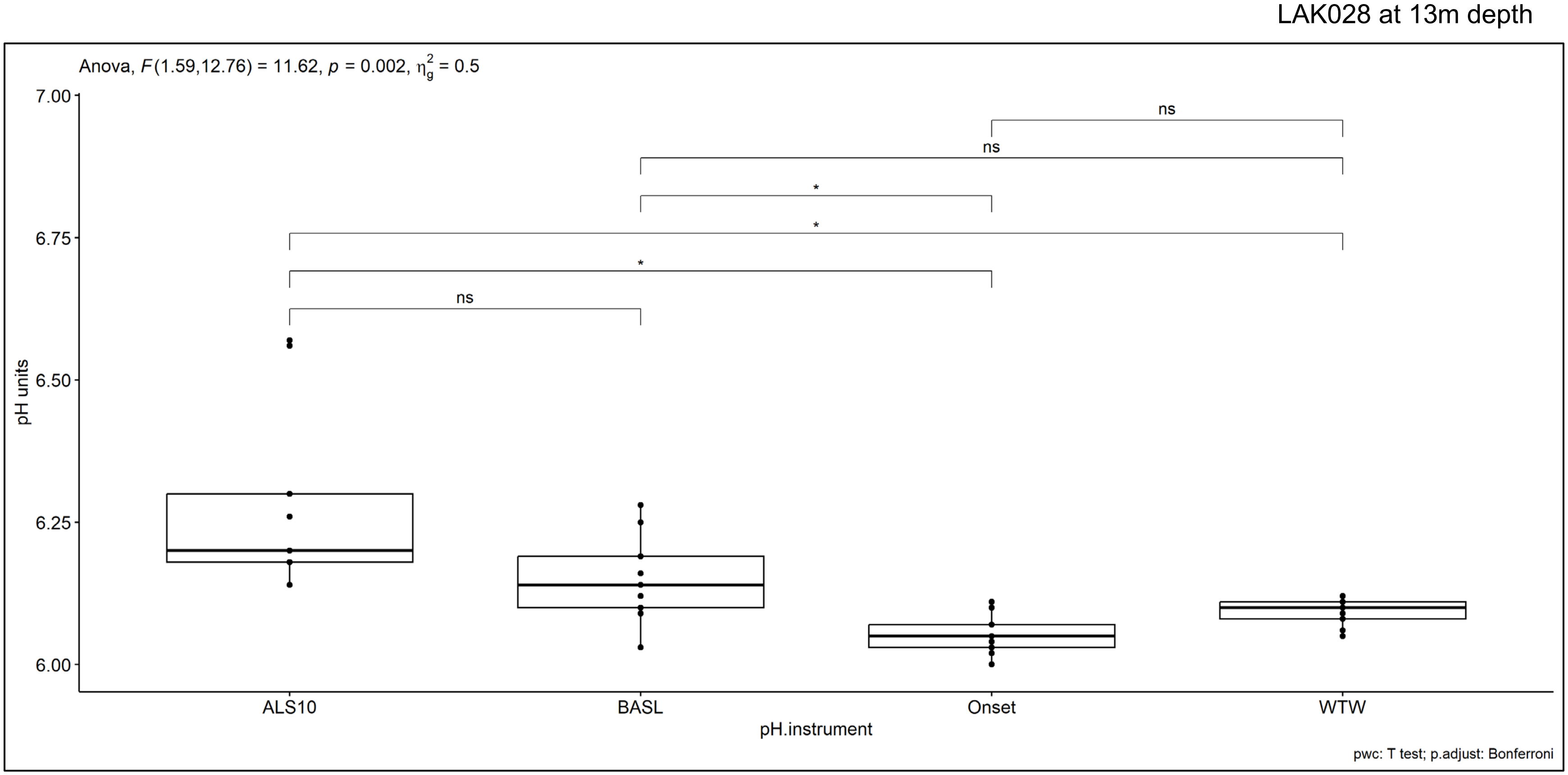

Figure 13. Box plot showing difference in pH in LAK028 (13m depth) between all combinations of instrument pairs during sampling in June through October 2022 (n=9). Instrument names are ALS10 (instrument at the ALS lab using 10-minute electrode immersion time), BASL (instrument at the BASL lab), Onset (in situ pH logger), and WTW (field pH meter). Horizontal bars at the top of the box plot span instrument pairs being tested along with symbols indicating significance of a difference in pH using repeated measures ANOVA. The * indicates a significant mean difference and "ns" indicates no significant difference in pH between the paired instruments.

3.4 Water surface elevation in End Lake and LAK028.

Water surface elevation varied by 25.5 cm in LAK006 and 53.5 cm in LAK028 in 2022 (Figure 15) in response to rainfall events (compare Figure 14 and Figure 15). In 2022, May, June, July, and October were relatively wet and August and September had about average precipitation compared to earlier years of the EEM (Table 8). Differences in change of surface elevation between the two lakes are attributed to spatial variation in rainfall, lake morphometry, and basin hydrology.

Table 8. Total rainfall by month reported by Environment Canada at the Terrace Airport (Terrace A) for May to October 2017, 2018, 2019 and 2020 except data marked with an * that is from a nearby Terrace Braun's Island station (Terrace PCC).

Month	**Total rainfall at Terrace airport (mm)**					
	2017	**2018**	**2019**	**2020**	**2021**	**2022**
May	95	58	19	31*	63	67
June	90	37	58	24*	73	107
July	36	22	75	51*	39	75
Aug	79	9	74	160	83	66
Sept	104	24	99	143	231	71
Oct	310	94	139	135	152	190

*from Terrace Braun's Island Station.

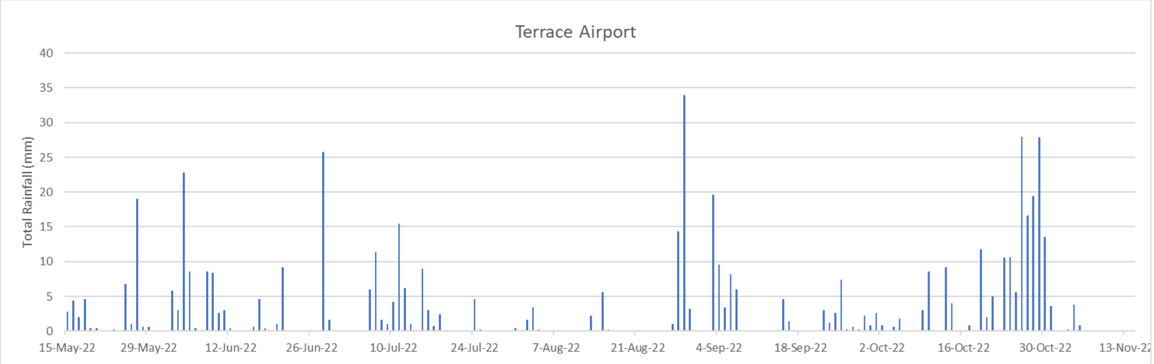

Figure 14 Total daily rainfall reported by Environment Canada at the Terrace Airport (Terrace A) for May through October 2022.

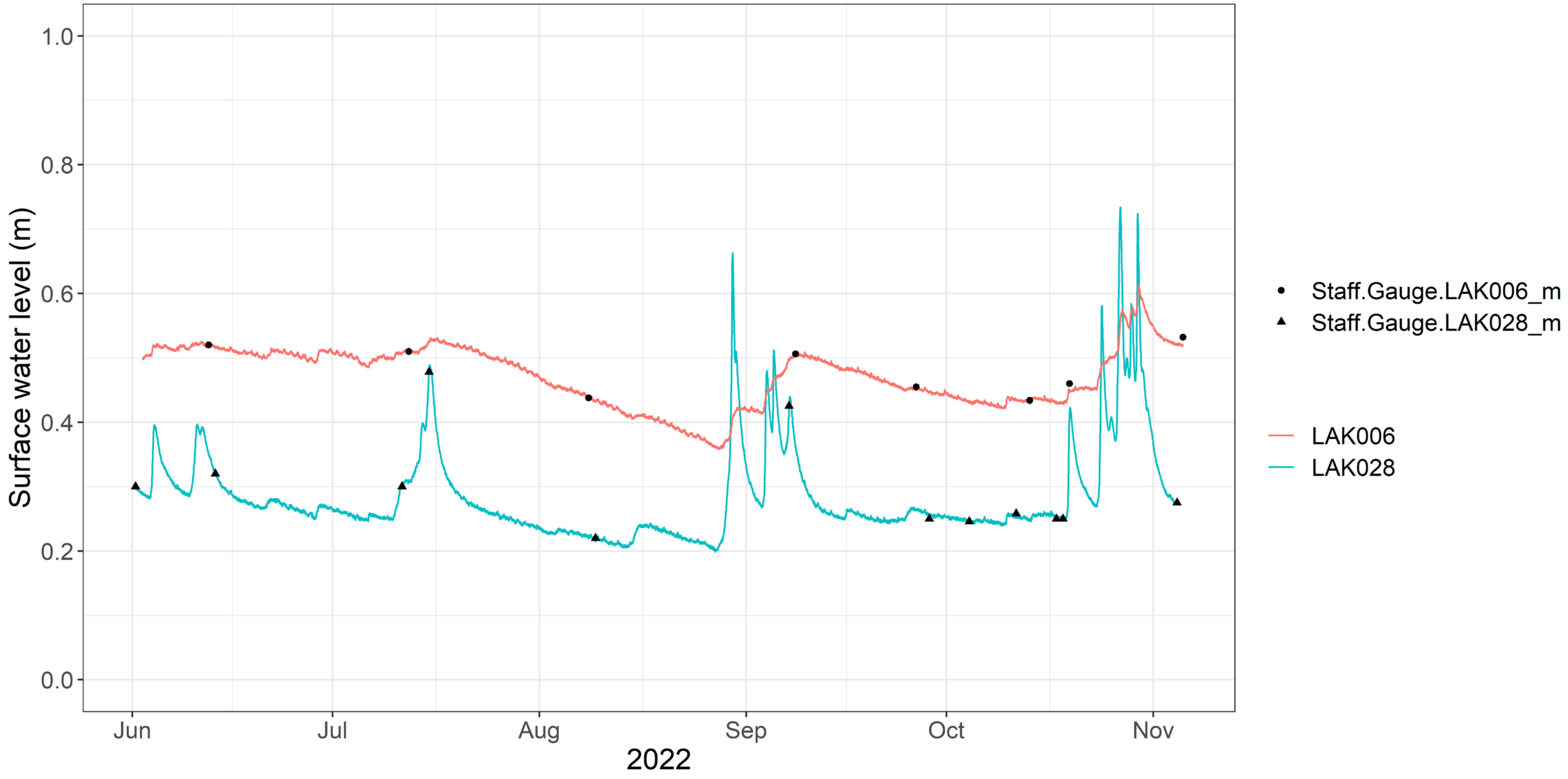

Figure 15. Mean daily surface water level (cm) in End Lake and LAK028 in 2022. Note that water level is relative to a benchmark at each lake, not to a common benchmark.

3.5 Limnology of LAK006

Temperature stratification was present in LAK006 throughout the monitoring period in 2022 (Figure 16). At the time of the first measurement in June, a surface warm layer (epilimnion) was developing above 2m which deepened to 3m in mid-summer and then 4m in September. By mid-October, the epilimnion cooled and resistance to mixing weakened. The hypolimnion (bottom layer) was 4-5º C for the entire monitoring period. The peak surface temperature of 20.9ºC occurred on August 8, 2022, one month later and 2ºC cooler than in 2021.

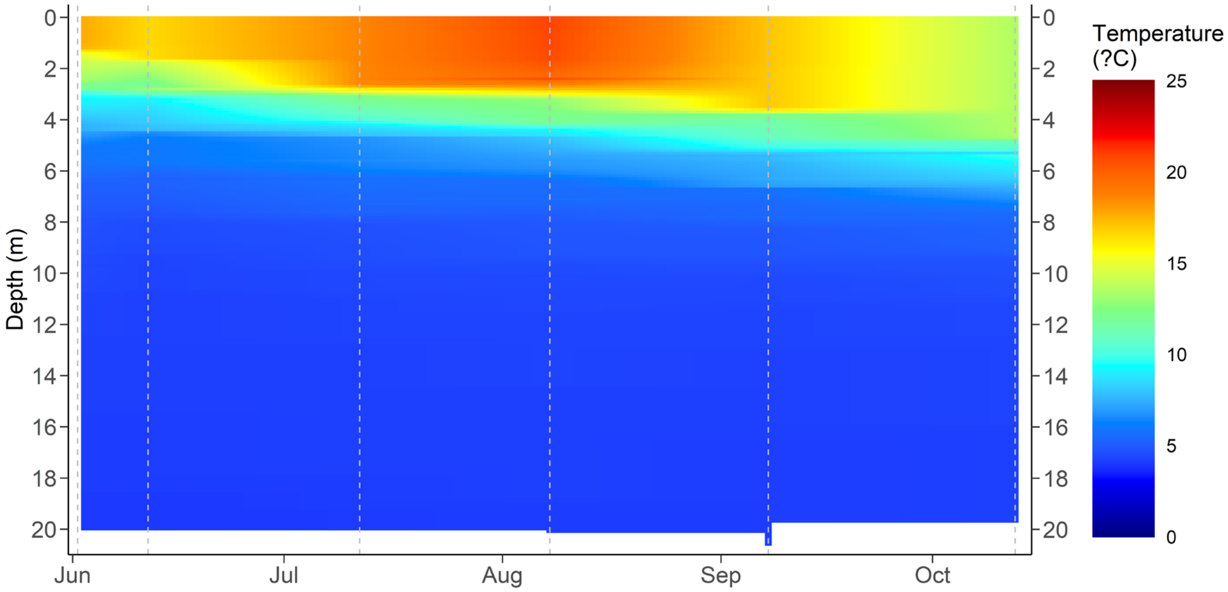

Figure 16 LAK006 water temperature from CTD casts in 2022. The vertical dotted lines indicate dates of measurement. Data between those were linearly interpolated.

Dissolved oxygen (DO) concentrations were highest in surface waters and lowest near the sediment - water interface in 2022 (Figure 17). Highest DO concentrations near 10 mg·L^{-1} were found in June at a water depth of 3 – 4m, likely associated with an algal bloom. Equally high concentrations occurred near the surface in October, potentially driven by wind from storm events. DO concentrations close to or less than 5 mg·L^{-1} were found in close proximity to the sediment – water interface in June but expanded to water depths halfway up the water column by late summer.

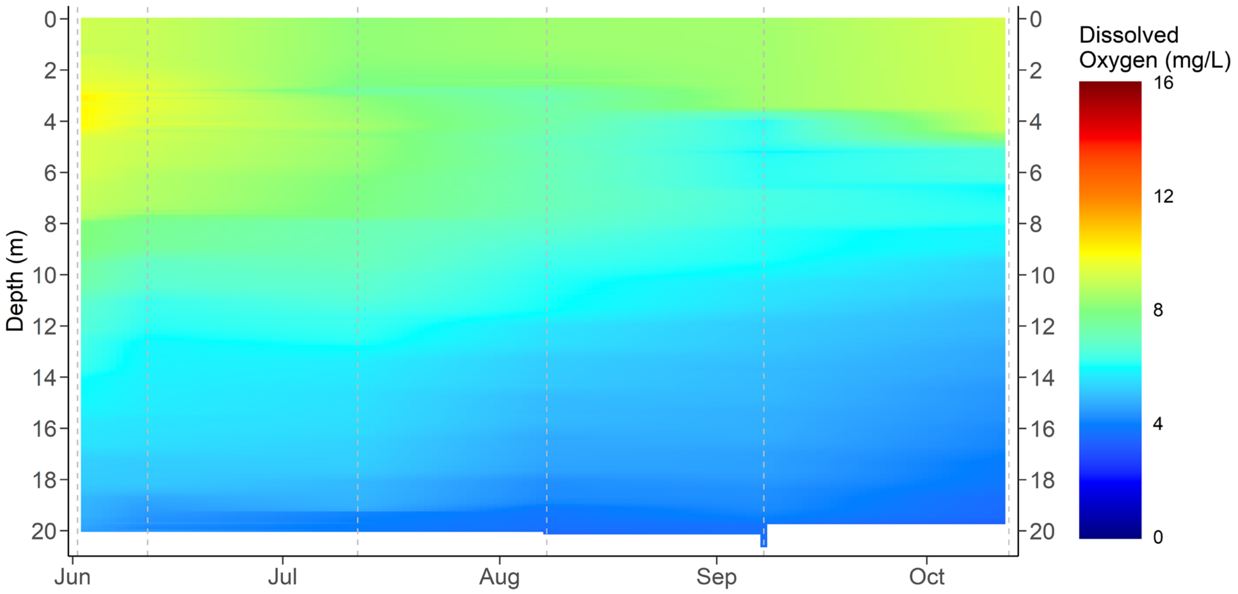

Figure 17 LAK006 dissolved oxygen concentrations from CTD casts in 2022. The vertical dotted lines indicate dates of measurement. Data between those were linearly interpolated.

The CTD casts showed no time or depth variation in specific conductivity or turbidity in 2022 (Figure 18 and Figure 19). Specific conductance was <12 uS/cm (mean of 9.9 uS/cm) and turbidity was <2.2 NTU (mean of 0.4 NTU) among all casts.

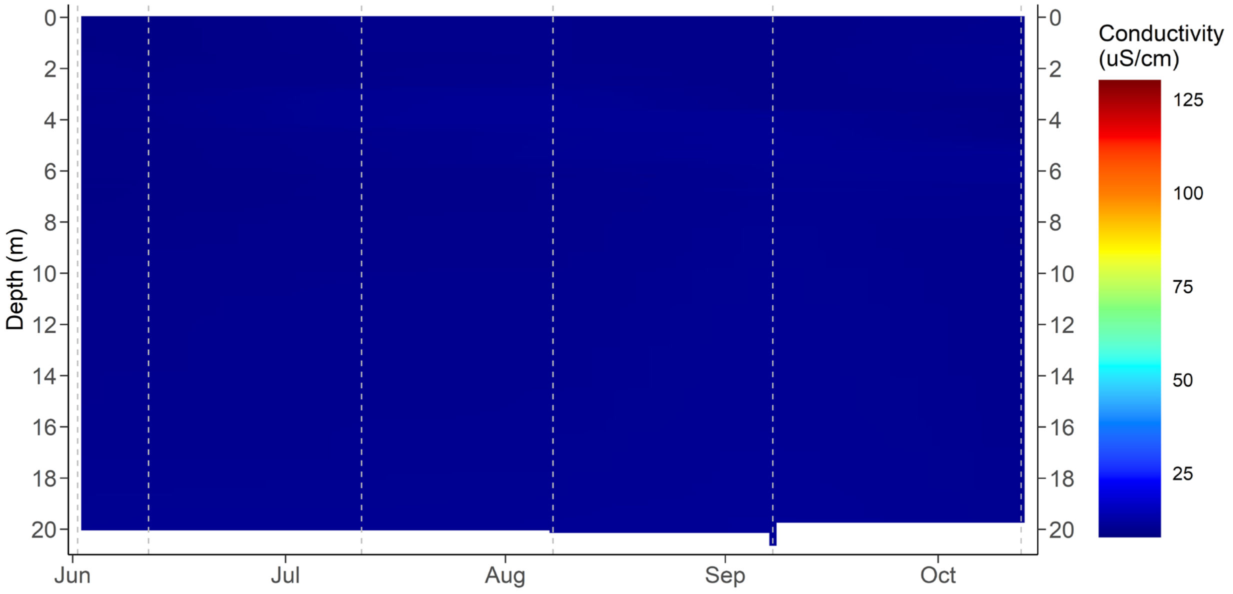

Figure 18 LAK006 specific conductivity from CTD casts in 2022. The vertical dotted lines indicate dates of measurement. Data between those were linearly interpolated. Note that the conductivity is relatively uniform at all depths in the lake, resulting in a solid-colored plot.

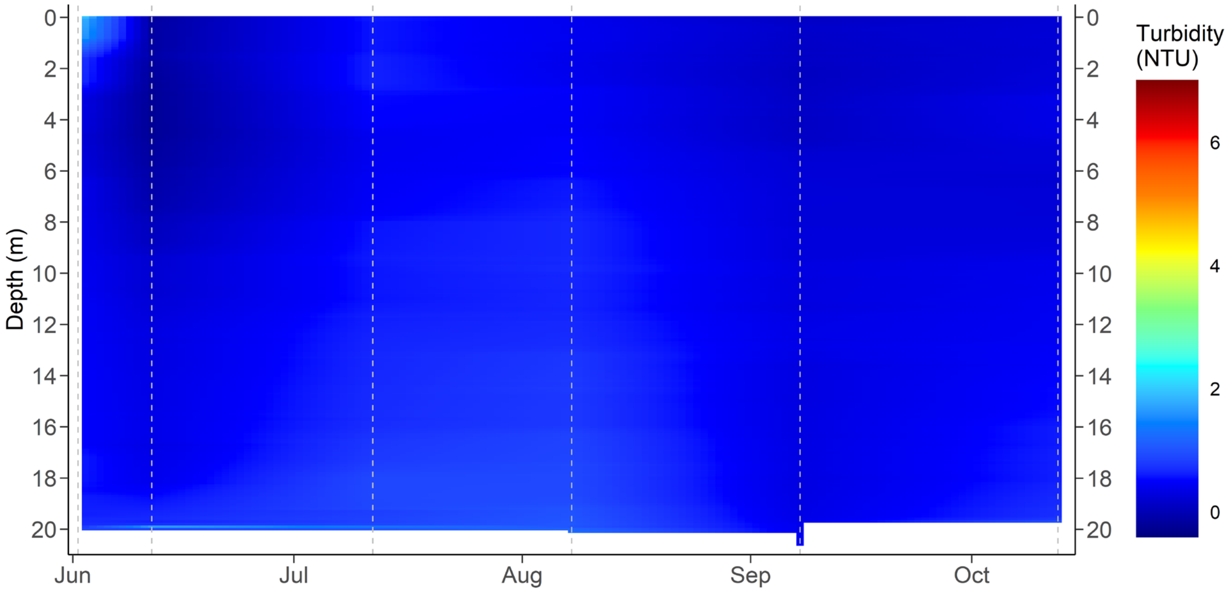

Figure 19 LAK006 turbidity from CTD casts in 2022. The vertical dotted lines indicate dates of measurement. Data between those were linearly interpolated. Note that the turbidity is relatively uniform at all depths in the lake, resulting in a solid-colored plot.

3.6 Limnology of LAK028

Data from the LAK028 mooring showed temperature stratification was present in LAK028 in July and August with an intervening period of surface mixing in mid-July (Figure 20 and Figure 21). That temporary mixing was likely due to a storm event and associated rise in water level from rainfall (Figure 14, Figure 15). The lake was not thermally stratified from November through June. Surface waters were colder than bottom waters in February through April (Figure 20). The summertime thermocline was established at a depth of about 2m. Isothermal conditions were not re-established by the end of the data record in October. The peak surface temperature in 2022 was 21.7°C. Under the thermocline, water temperature was consistently near 4°C, the temperature at which water has highest density.

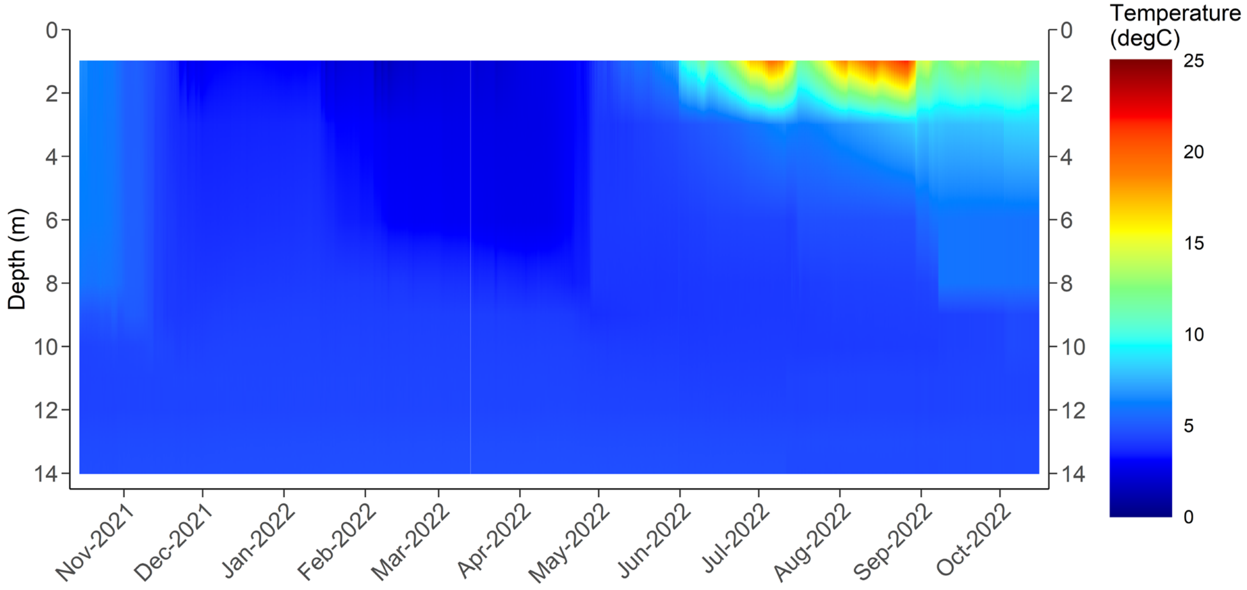

Figure 20 Temperature over time and depth from the mooring in Lak028 during Nov 2021 through October 2022. Measurements were taken at 10 depths every 30 minutes and data between those depths and times were linearly interpolated.

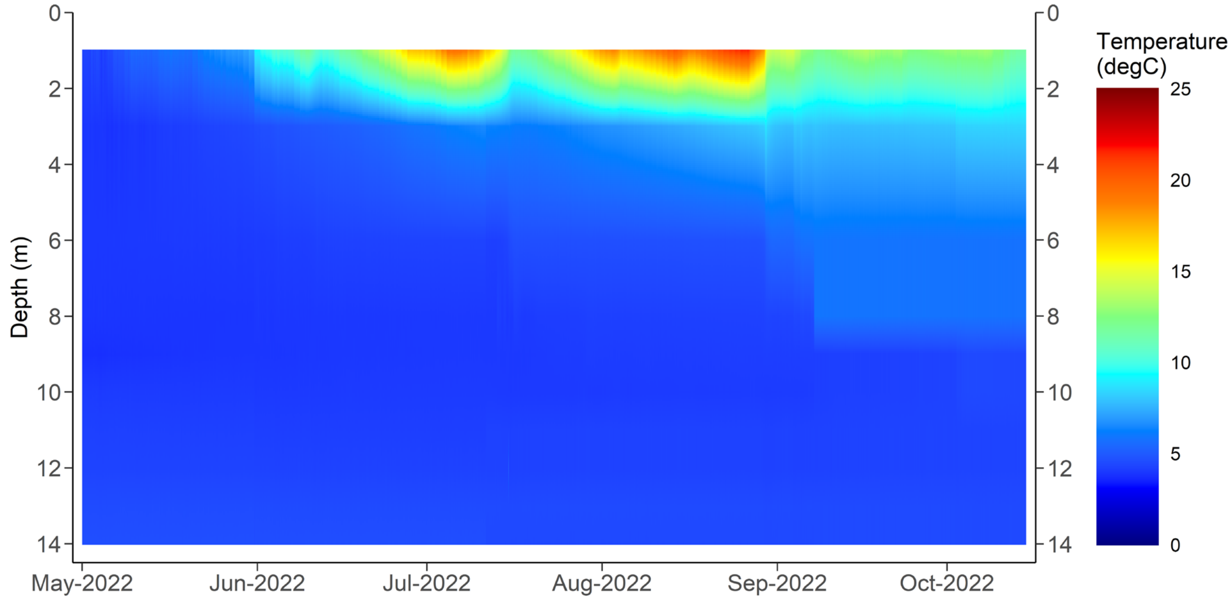

Figure 21 Same temperature mooring data as in Figure 20, but only showing May through October.

A strong oxycline was present at 9-11 m in LAK028 from June through October 2022 (Figure 22). DO concentrations were >8 mg·L^{-1} above the oxycline, and the lake was mostly anoxic below the oxycline (Figure 22). DO concentrations >8 mg·L^{-1} were present in June through September at depths <8m, and in October at depths <7m. DO concentrations >11 mg·L^{-1} were only found in early June near the lake surface. There was a band of dissolved oxygen concentrations >10 mg·L^{-1} at the 0 – 5m depth in June and July, possibly associated with photosynthetic production of oxygen. In September and October, the dissolved oxygen concentrations declined in surface water, showing less influence from photosynthetic production of oxygen. Although depths and concentrations of dissolved oxygen concentrations varied slightly, the patterns were similar to those found in 2021 (Limnotek 2022).

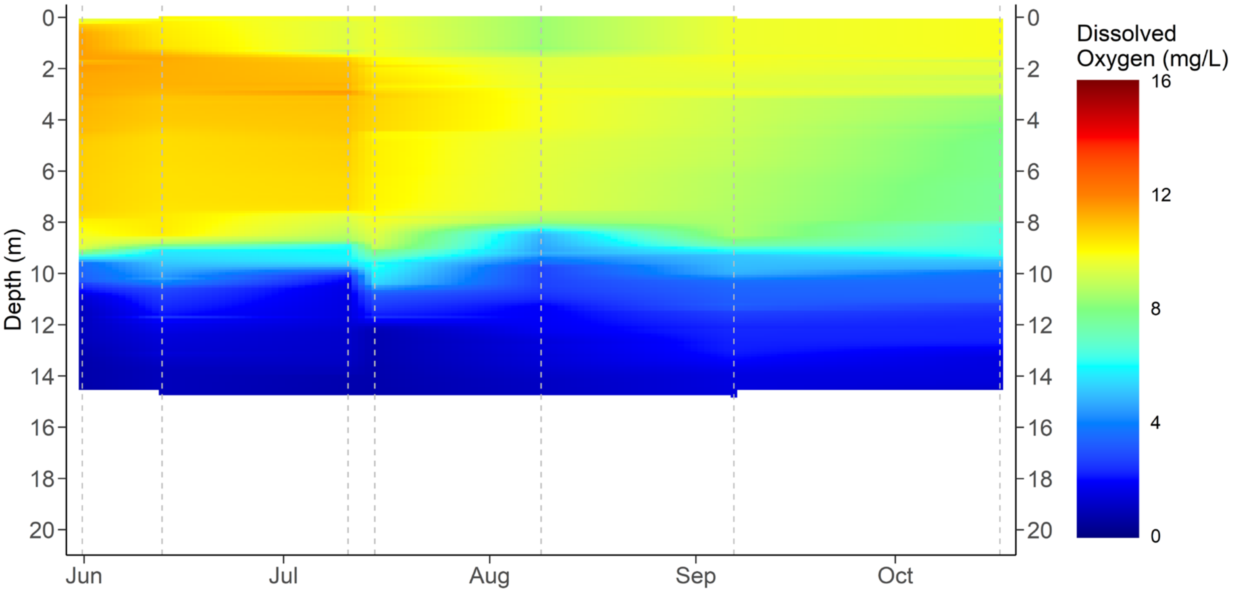

Figure 22 Dissolved oxygen concentrations from CTD casts among dates and depths in LAK028 at the raft station in 2022. The vertical dotted lines indicate dates of measurement. Data between those dates were linearly interpolated.

A stable chemocline was observed in June to October 2022 (Figure 23). This pattern was the same as found in 2020 and 2021 (Limnotek 2022) The chemocline separated water with low conductivity (< 22 uS/cm) and low turbidity (< 1.6 NTU) at depths < 9m from high conductivity (up to 119 uS/cm) and higher turbidity (up to 4.9 NTU) at the bottom (>11 m) (Figure 23 and Figure 24). Turbidity within the chemocline may have been associated with bacterial assemblages (e.g. Tonolla et al 2014). Permanence of the chemocline in June through October (Figure 23) showed lack of chemical mixing. A monimolimnion, a dense layer under a chemocline that has stable chemical conditions in meromictic lakes was not present in LAK028. Only the chemocline was well defined.

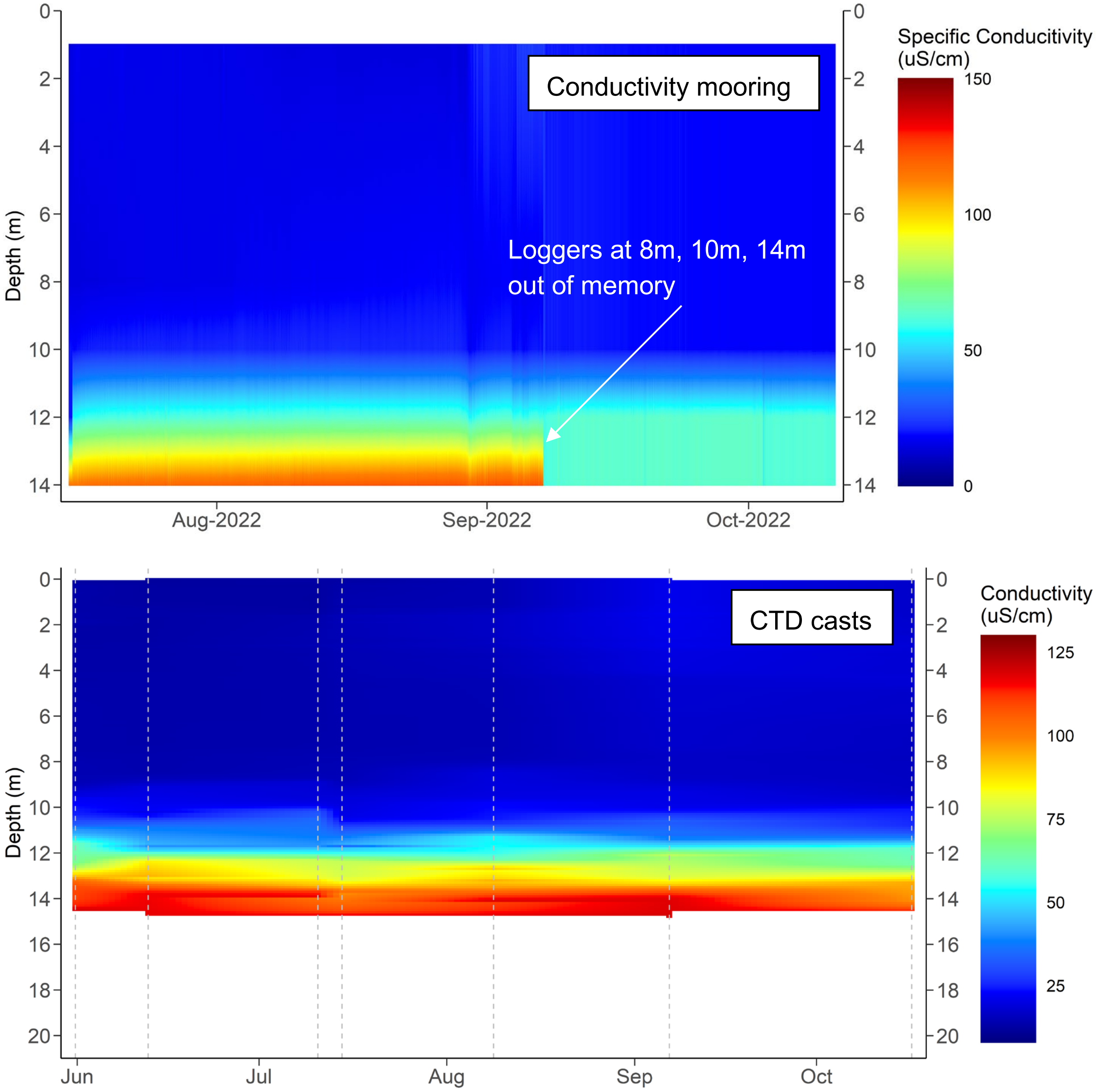

Figure 23 Specific conductivity from the conductivity mooring (top) and CTD casts (bottom) across dates and depths in LAK028 at the raft station in 2022. The vertical dotted lines in the bottom figure show dates of measurement. Data between those dates were linearly interpolated. The top image shows truncated bottom data on September 7 when loggers at 8m, 10m and 14m ran out of memory due to too frequent a logging interval (5 minutes versus 30 minutes for the other loggers).

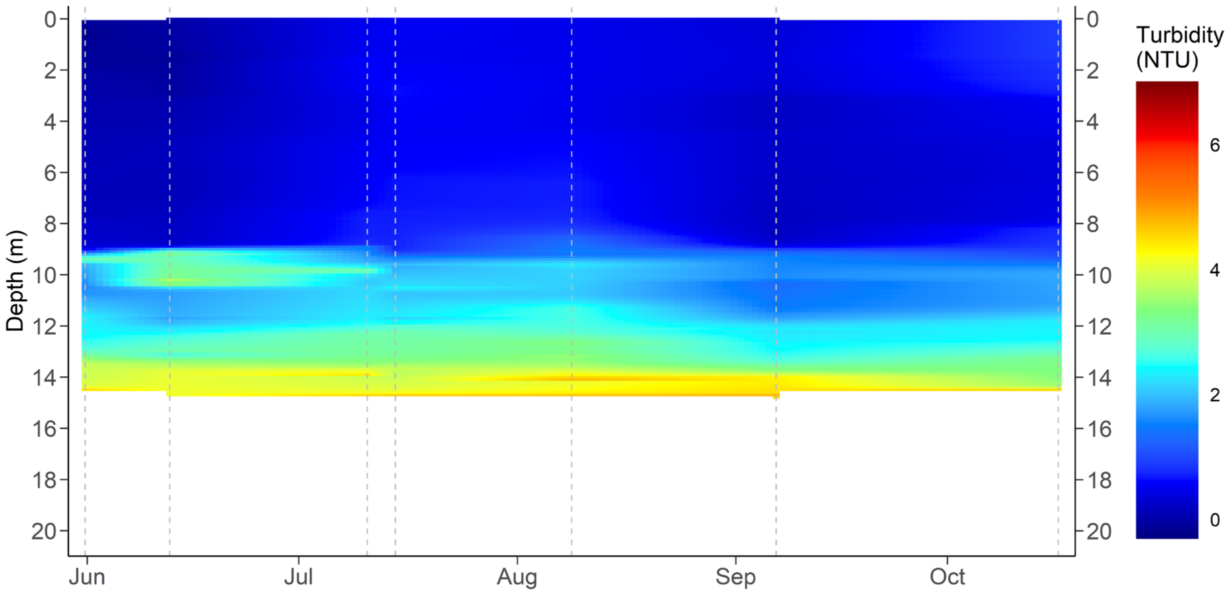

Figure 24 Turbidity from CTD casts across dates and depths in LAK028 at the raft station in 2022. The vertical dotted lines indicate dates of measurement. Data between those dates were linearly interpolated.

Chemical differences between the surface and chemocline in LAK028 that were present in 2017 through 2021 (Limnotek 2022) were again found in 2022 (Table 9). The mean concentration of SO_4, an anion that only occurs in the presence of oxygen, was more than 10 times greater at the surface (4.0 mg·L-1) than near the bottom (0.2 mg·L-1). The surface SO_4 concentrations were 32 times lower than BC guidelines for protection of aquatic life (128 mg·L^{-1} at assumed soft water conditions: Meays and Nordin 2013). Mean sulfide concentration (as H_2S) of <0.011 mg·L-1 in surface water and 0.68 mg·L-1 near the bottom showed sulfate reduction was favoured in the chemocline, as expected given the anoxia. Combined SO_4 and SO_2 concentrations expressed as S increased by almost 80% in surface water between June and October but there was little change in the chemocline (Table 10).

This difference may show time course sulfur loading at the surface with potential uptake by phototrophic sulfur bacteria exceeding sulfur production by sulfate-reducing bacteria (if both types are present) and anaerobic respiration of internal storage compounds of the phototrophic bacteria (Tonolla et al. 2014). Emissions from the smelter are a likely source of the sulfur loading, given no other known S source in the drainage pocket of LAK028 and LAK028 is in the direct path of emissions. There may be subsequent settlement of the bacterial assemblage, explaining removal of sulfur from solution, leading to no net change in S concentration in the chemocline over time. Alternatively, there may be volatilization loss of H_2S that keeps S concentrations stable in the chemocline and offsets surface loading to some extent. Quantitative aspects of these S fluxes are unknown for LAK028 and would require measurements beyond the scope of the present workplan.

There were numerous other chemical differences between the mixolimnion (surface mixed layer) and chemocline. Mean pH measured by either of the methods was approximately 6.2 in the chemocline and 5.2 at the surface. Average Gran ANC was about 30 times greater in the chemocline (28.7 mg·L-1 CaCO3) than at the surface (0.9 mg·L-1 CaCO3). This difference was much less than the 400 times difference in 2021. Mean ammonium (NH_4-N) concentration was undetectable at the surface (<5 µg·L-1) compared with 3528 µg·L-1 in reducing conditions of the chemocline. NO_3-N was present near the surface but absent in the chemocline. This inverse association between NO_3-N and NH_4-N is expected: NO_3-N occurs in the presence of oxygen, NH_4-N is a reduced form of nitrogen. The very high concentration of NH_4-N near the bottom can be attributed to release of reduced N from sediments in the absence of dissolved oxygen. It is also possible that NO_3-N may be removed from the chemocline by denitrification resulting in volatilization loss of N_2. Similarly, concentrations of soluble reactive phosphorus (SRP), total phosphorus (TP), and total dissolved phosphorus (TDP) were greater near the bottom than in surface water, inferring release of P from sediments in the absence of oxygen. Released P would have been isolated from surface water at the chemocline due to no mixing making it unavailable for biological production near the surface. Release of other solutes at the sediment – water interface can also explain relatively high concentration of total nitrogen (TN) and dissolved inorganic carbon (DIC) in bottom water compared to surface water. Higher dissolved organic carbon (DOC) near the bottom compared to the top may be related to bacterial assemblages (phototrophic and sulfur reducing species) at depth that would be absent in the presence of oxygen near the surface.

Table 9 Average values of chemical attributes at water depths of 2 m and 13 m in LAK028 in June through October, 2022.

Analyte	**Units**	**Mean value or concentration ± standard deviation in LAK028, 2022**	
		Surface (n=9)	**Deep (2 m off bottom) (n=9)**
SO_4 (sulfate)	$mg \cdot L^{-1}$	4.0 ± 1.0	0.2 ± 0.1
Sulfide (as H_2S)	$mg \cdot L^{-1}$	<0.01	0.68 ± 0.1
Specific conductivity	$\mu S \cdot cm^{-1}$	16 ± 3	59 ± 8
Total dissolved solids	$mg \cdot L^{-1}$	34 ± 32	71 ± 13
pH- WTW field meter	pH units	5.2 ± 0.1	6.1 ± 0.0
pH - BASL	pH units	5.2 ± 0.1	6.2 ± 0.1
pH - ALS (low ionic strength method)	pH units	5.3 ± 0.1	6.3 ± 0.2

Analyte	Units	Mean value or concentration ± standard deviation in LAK028, 2022	
		Surface (n=9)	Deep (2 m off bottom) (n=9)
Gran Alkalinity – BASL	$mg \cdot L^{-1}$ as $CaCO_3$	0.9 ± 1.4	28.7 ± 4.0
NH_4-N (total ammonia as N)	$\mu g \cdot L^{-1}$	<5	3528 ± 577
NO_3-N (nitrate as N)	$\mu g \cdot L^{-1}$	7 ± 7	<5
TN (total nitrogen)	$\mu g \cdot L^{-1}$	146 ± 36	3873 ± 599
SRP (soluble reactive phosphorus)	$\mu g \cdot L^{-1}$	1.1 ± 0.3	1.9 ± 0.8
TDP (total dissolved phosphorus)	$\mu g \cdot L^{-1}$	3.9 ± 1.8	21.3 ± 2.7
TP (total phosphorus)	$\mu g \cdot L^{-1}$	6 ± 3	35 ± 6
DOC (dissolved organic carbon)	$mg \cdot L^{-1}$	6.4 ± 1.0	14.3 ± 1.7
DIC (dissolved inorganic carbon)	$mg \cdot L^{-1}$	1.2 ± 0.7	14.7 ± 3.9

Table 10. Mean concentration of SO_4 -S plus SO_2 -S in surface and chemocline water of LAK028, by month in 2022.

Sampling date in 2022	Mean SO_4 plus SO_2 concentration as S ($mg \cdot L^{-1}$)	
	2m water depth	13m water depth (in chemocline)
June 1 and 13	1.410	0.745
July 11	1.410	0.673
August 9	1.675	0.608
September 7 and 28	2.515	0.810
October 2, 11, 17	2.410	0.685

4 DISCUSSION AND RECOMMENDATIONS

4.1 Data compilation

Data from 2022 were appended to those from previous years (2012 to 2021) to provide an up-to-date compilation of chemical and other descriptive information for further analysis by ESSA Technologies. This process of continuous updates provides a single source of data for review, analysis, and reporting over time. Formatting is structured as a long data frame for reading in R (R Core Team 2022) or other software.

4.2 Quality of chemical data

High precision and excellent percent recovery among analytes provided confidence that the ALS lab was providing sufficient repeatability and accuracy of sample data in 2022.

Incidence of positive field blanks for dissolved organic carbon (DOC) in 2021 was resolved in 2022 with use of disposable Sartorius Minisart® syringe filter (28mm, 0.45um Hydrophilic Teflon DIGIFilter) cartridges instead of the previously used Swinnex filter system with GN-6 Metricel® 0.45 µm, 47mm membrane disc filter made of mixed cellulose esters. No DOC contamination was found in blanks in 2022.

Recommendation 1. Use Sartorius Minisart® syringe filter (28mm, 0.45um Hydrophilic Teflon DIGIFilter) or similar product for all sample filtrations to avoid DOC contamination caused by filters composed of cellulose esters. A larger diameter Teflon filter may also be used in the Swinnex filter apparatus to avoid DOC contamination.

Among the positive blanks described in Section 3.2.1, the greater number of filtered positive blanks than unfiltered for Al shows mostly a filtering effect on incidences of positive blanks. It is noteworthy that all positive blanks occurred after September 26, 2022, when a new shipment of supplies was received. Given that field procedures did not change before and after this date, supplies may be the source of contamination. Many supplies after September 26 came from the ALS warehouse in Terrace. Some contamination may have occurred at that location given exposure to rock grinding there although that’s unlikely given that lab supplies are always in sealed plastic bags. At all other times the bottle, syringe, and filter supplies came from the Burnaby ALS lab that has a dedicated area for supplies logistics. The shipping change resulted from supply chain issues that prevented shipments from Burnaby. Those supply chain issues also resulted in filters being changed from Sartorius to Phenex CA Membran 0.45 micron 28mm syringe filters manufactured by Phenomenex, which were the only ones available. These shipping and filter changes may have introduced contamination but an actual source among these supplies is unknown.

A more likely source of contamination was a new source of lab gloves after September 26. Normally gloves were purchased from a lab supplier but again due to supply chain issues, those gloves were not available and nitrile gloves were purchased locally in Terrace. We have since found from testing at ALS that nitrile gloves may carry metals contamination. As a result, ALS recommends use of vinyl gloves, which avoids this potential contamination.

Recommendation 2. It is recommended that all sample handling and filtrations in the field be performed using vinyl gloves, not nitrile gloves that may incidentally carry metals contamination. It is also recommended that a filtration stand be used to minimize repeated user contact with the syringe that is purged and filled several times during swapping out of several filter cartridges needed for completing the filtration of a single sample. An example filtration stand is shown in Figure 25.

Figure 25. Example of a filtration stand for use in minimizing user contact with the syringe plunger during water filtrations in the field. Image source: “ALS EnviroMail 06 December 2017. Best practices to prevent false positives and negatives for dissolved metals”. Note that vinyl gloves are preferred over nitrile gloves that may host metals contamination.

The Al and Ba concentrations in positive blanks in 2022 were 15 to 181 times lower than corresponding concentrations in the lake samples and all were close to the method detection limits. This large difference means that the Al and Ba contamination is not expected to interfere with later base cation calculations.

Notwithstanding this finding, any blank contamination is not to be taken lightly. Close attention should be paid to positive blanks in future sampling. Potential sources of contamination should be investigated through a review of field procedures with the lab throughout the 2023 field season.

4.3 Instrument effects on pH measurement

Frequent replacement of the Onset pH logger electrode as recommended following the 2021 water monitoring worked well but different failures beyond electrodes were found in 2022. Instrument age may be a factor but the two loggers having general failure were only one year old and were younger than others still in operation. This inconsistent reliability suggests that Onset pH loggers need to be replaced annually so that new instruments are in hand to start each year of sampling to minimize risk of instrument failure.

Recommendation 3. Start each field season with new pH loggers to minimize risk of both logger and electrode failure during the spring to fall field season. Five new pH loggers with new electrodes and six other replacement electrodes should be purchased new to start sampling each year. Three of the loggers will be installed to start in the spring (2 in LAK028, 1 in End Lake). The other two loggers will be carried into the field to be available for swapping out the installed loggers as needed during the field season. Replace the electrode on a given pH logger once every two months (not longer) to avoid electrode error on long term deployments.

Split sample testing of the effect of electrode immersion time on pH showed no significant difference in pH values with the longer electrode immersion times. Other studies have found that immersion times of up to 15 minutes may be needed in low conductivity waters (Busenberg and Plummer 1987) and two lines of evidence from this study in previous years support that finding: a significant test of paired replicates in 2020, and field tests in 2019 that found up to 9 minutes immersion time was needed for a stable instrument reading (Limnotek 2020 and 2021). Despite the finding of no significant difference in pH with immersion time in 2022, this other evidence favours use of the 10-minute electrode immersion period when requesting pH measurement at ALS.

Recommendation 4. When requesting pH measurement at ALS, we recommend selection of the method that provides an electrode immersion period of 10 minutes, not the standard method in which the instrument times out after 3 minutes of electrode immersion. The longer immersion period allows for adequate stabilization of voltage in the low conductivity waters of the BC north coast. Water samples assigned to 10-minute immersion times are handled manually, resulting in a shorter time of sample exposure to air before analysis compared to automated handling that incorporates 3 minute electrode immersion times and relatively long periods during which a sample is uncapped before electrode immersion (C Fuginski, account manager, ALS, Pers. Comm.). This shorter time of sample exposure to air will minimize CO_2 degassing that can increase pH.

While split samples from a common van Dorn haul can be used to measure instrument error only, field duplicates from two separate van Dorn hauls at the same place and time can be used to measure instrument error plus environmental variability. Measurements can be made in water from different lakes or from one lake over time. The multiple measurements by several instruments on Oct 2 included both instrument error and variability among lakes. Hence, the significant mean difference in pH between ALS and BASL and between ALS and the WTW meant that an instrument effect on pH was occurring over and above instrument error and environmental variability. The lack of a significant mean difference in pH between BASL and WTW meant that the combination of instrument error and environmental variability exceeded the instrument effect on pH. Similarly, the significant instrument effect on repeated measurement of pH in LAK006 and in deep waters of LAK028 meant that an instrument effect on pH was occurring over and above instrument error and environmental variability occurring over time.

Tests of instrument effects on pH measurements have included both field instruments (WTW and Onset) and lab instruments (BASL and ALS) over the past three years. Two separate tests have been conducted each year; a test of instrument effect on pH measured in the EEM lakes on a single date in the fall, and time series measurements of pH in LAK006 and LAK028 during May or June through October. The field instruments (Onset logger and WTW) and commonly but not always BASL have generally reported significantly lower pH than ALS (Limnotek 2020 and 2021). In 2022 ALS and BASL reported similar pH values in LAK028 at the surface and at 13m. A similar finding occurred in 2020. At that time, it appeared that the change in electrode immersion time at ALS from 3-minutes to 10-minutes helped reduce the differences in pH values between ALS and other instruments. However, there was no significant difference in pH values at ALS between the two electrode immersion times in 2022, but the tests of instrument effect found that ALS pH values remained significantly greater than pH values measured with the other instruments. This difference suggests another factor was contributing to instrument effects on pH.

One possibility is duration that a sample is exposed to air before a pH measurement is made. The amount of CO_2 lost from degassing can increase with duration of exposure. Loss of CO_2 will raise pH.

A survey was conducted in early 2023 to examine typical times that a sample is exposed to air prior to pH measurement between labs and field instruments. In order from longest to shortest, the exposure times at ALS 10-minute > ALS 3-minute ≥ BASL > WTW > Onset logger (Table 11). This ordering shows that the amount of CO_2 degassing was potentially greatest at ALS and lowest with the field instruments, which is the same ordering of pH results from the Oct 2 annual EEM sampling (Table 6) and the same ordering of pH results from the repeated measures ANOVA for test of instrument effects during time course sampling of LAK028 (Figure 12 and Figure 13) and End Lake (Figure 11). These coincidences are a line of evidence of differences in a degassing effect on pH measured by the different labs and instruments. In this respect the "instrument effect" is actually an "air exposure time effect" (i.e. the amount of time a sample bottle cap is off the bottle prior to pH electrode immersion). In earlier years we were puzzled as to why pH results from the Trent University lab were mostly the same as those from the field instruments despite Trent samples being analysed months after collection (Limnotek 2020). Since the Trent samples were analysed manually with little time exposed to air, it is now evident that the "instrument effect" or more correctly the "air exposure time effect" at Trent was much the same as we now see at BASL. Hence, the pH results were similar.

All statistical analyses of long-term trends in pH throughout the 11 years of the EEM program have been performed using pH measurements from Trent University and BASL. Previous statistical analyses of the two labs showed no significant differences in pH measurements from samples obtained in the 2019 field season (Limnotek 2020). It's appropriate to continue to use BASL measurements of pH for analyses of long-term trends.

Notwithstanding the above conclusion that past methods of statistical analysis can be continued, measurement of pH using the field instruments is the most reliable way to achieve accurate pH measurement in samples from north coast lakes. The samples are both fresh and pH is measured following the smallest possible time of exposure to air. Another conclusion is pH is not affected by time between collection and analysis but rather by time between initial exposure to air after removing the sample bottle cap and immersion of the electrode for measurement of pH.

Table 11. Durations of exposure of a water sample to air before pH measurement between field instruments and labs. Data are from an email survey conducted in January 2023.

Time that a water sample is exposed to air after removing the bottle cap before making a pH measurement (minutes)				
ALS (10 minute electrode immersion method)*	**ALS (routine 3-minute electrode immersion method)***	**BASL****	**Onset pH logger**	**WTW field pH meter**
<30 minutes	<30 minutes then covered with film for up to 72 hours in the que, then up to 12 hours without the film cover while loaded on the autosampler	10 – 120 minutes depending on number of samples in the queue	0 minutes	<3 minutes
*C. Fuginski, account manager, ALS. Personal communication. January 11, 2023. **M. Ma, lab manager, Biogeochemical analytical service laboratory (BASL). Personal communication January 25, 2023.				

These findings support use of the WTW field instrument pH data for long term comparisons of pH among years, as an alternative to using data from Trent University and BASL. It is fortuitous that these field pH data have the longest record in the Rio Tinto SO_2 EEM program among all instruments dating back to the beginning of EEM measurements in 2014. The combined time series of pH measurements from Trent University and BASL go back to 2012, and previous analyses of 2019 data (Limnotek 2020) showed no significant differences between pH measurements from these two laboratories. In contrast, there are only four years of Onset data. We don't consider ALS data useful for showing long term trends despite it also having a long history because of potential upward bias in pH values related to high "air exposure time effect" on pH measurement.

Recommendation 5. pH data from BASL should continue to be used for statistical analyses of long term trends, building on the time series of prior pH measurements from Trent University, and statistical methods used previously. For comparative purposes, pH data from the WTW field instrument could also be used for tracking long term changes. These field data have the smallest sample "air exposure time effect" that can strongly affect pH results and they have the longest record of continuous measurement since the RIO Tinto SO_2 EEM program started.

We do not recommend tracking long term changes in pH values using the ALS data because it can have the strongest upwards bias associated with possible CO_2 degassing during relatively long durations that a sample may be exposed to air in the lab before pH measurement.

Recommendation 6. We recommend running an experiment to test the "air exposure time effect" on sample pH. An experiment is needed because to date our observations are coincidental. The experiment would answer the question as to how the duration of sample exposure to air affects sample pH using water from the north coast lakes. This test can be done with any instrument but the instrument needs to be the same for all measurements. An example experiment that can be done in the field or lab is as follows.

1. 60 water samples with no air space in the bottles are collected from a lake at the same time. The bottles are the same ones used to send water samples to ALS or BASL.
2. 30 of the samples will have caps removed at a given start time in a field or other lab (called "capoff" bottles). The other 30 samples will not have caps removed at that start time (called "capon" bottles).
3. The caps of all 30 capoff bottles are removed at the same time and time noted.
4. The caps of three capon bottles are removed.
5. Immediately measure pH in three of the capoff bottles and the three capon bottles that had caps removed. Recap bottles and set aside in the fridge.
6. Ten minutes later, measure pH in another three of the capoff bottles. Remove caps from three more of the capon bottles and measure pH in each of those bottles. Recap and set aside in the fridge.
7. Repeat step 6 at various time intervals for all remaining capoff and capon bottles over 8 hours.
8. Draw curves to compare mean (±sd) pH change over time of exposure to air (capoff bottles) and pH change over time to no exposure to air (capon bottles). A difference between curves will show the effect of time of exposure to air on sample pH.

4.4 Meromixis in LAK028

LAK028 water chemistry data from 2022 was used to update insight into the influence of meromixis on chemical endpoints used by ESSA to interpret acid loading and acid neutralizing capacity that is part of the SO_2 Environmental Effects Monitoring Program (e.g. ESSA et al. 2022). Accumulation of salts near the lake bottom can be from sediments following decomposition of organic matter that can induce oxygen demand and it can be from release of solutes at the sediment – water interface that do not mix above a chemocline. The lake also has an ample supply of SO_4 originating at the lake surface that eventually is taken up and settles to sediments via assumed bacterial processes. The lake has a pothole shape with small surface area relative to depth and little exposure to wind, which inhibits mixing. As in 2021, the 2022 CTD data showed the mixolimnion is underlain by a strong chemocline lacking oxygen with high conductivity and TDS, relatively high pH and Gran ANC, high soluble phosphorus concentration, and high DOC possibly associated with sulfur-reducing bacteria (bacteria that use sulfur as an electron donor for their metabolism) and possibly phototrophic sulfur bacteria. Increasing concentrations of SO_4 at the lake surface in May – October with little change in lake volume showed increasing supply of sulfur to LAK028 over time in 2022. Emissions from the smelter are a likely source. These conditions favoured high concentrations of reduced chemical species (e.g., sulfides and NH_4-N) in the chemocline. Higher pH at depth compared to the surface can be related to de-oxygenation in the chemocline that can induce chemical reductions in which electron transfer also leads to proton transfer wherein previously free CO_2 is incorporated into bicarbonate, leading to an upward shift in pH (Talling 2006).

Confirmation of types of bacteria in the chemocline would assist in confirming meromixis. Two recommendations follow:

Recommendation 7.
We hypothesize that two types of sulfur bacteria are present in LAK028 based on observations of change in SO_4 and SO_2 concentrations between the mixolimnion and chemocline. They may include phototrophic sulfur bacteria that can take up sulfur in the presence of sufficient light and sulfate-reducing bacteria in the absence of oxygen in the chemocline. It is recommended that bacteria sampling occur in 2023 to confirm the presence of these bacteria or point to other species that may play different roles. These data are needed to further characterize meromixis and to gain insight into sulfur processing following surface loading of SO_4 in LAK028.

Recommendation 8.
If phototrophic bacteria are present, it is recommended that profiles of photosynthetically active radiation (PAR) are completed during regular monthly sampling visits to LAK028 to examine depths where the phototrophic bacteria may be active in taking up sulfur that is loaded at the lake surface.

Presently installed conductivity loggers in LAK028 will show in 2023 if the chemocline is stable year-round and does not mix with the surface water. If the chemocline is stable (non-mixing) in winter, perennial meromixis would be considered present. Stability can occur during isothermal conditions because change in salt content has a greater effect on water density than does temperature (Wetzel 2001). This difference means that temperature stratification may break down, leading to isothermal conditions, but a strong chemocline may coincidentally remain intact due to the dense salinity gradient. This persistence of a chemocline is what characterizes complete meromixis. Conductivity data from the continuously operated mooring that was installed in 2022 are a reasonable surrogate to see if this stability is present year-round.

The 2022 observations of meromixis in LAK028 continue to show that surface chemistry that is used by ESSA for interpretation of potential acidification will not be affected by mixing of higher pH bottom water with lower pH surface water at the time of water sampling in late September or early October. The strong chemocline coupled with large depth relative to surface area prevents higher pH chemocline water from mixing with surface water. In this respect the surface water is much like the other sensitive EEM lakes for interpretation of change in pH and other analytes over time.

To ensure that LAK028 surface chemistry is not confounded by possible future mixing affecting pH, Gran ANC, base cations, etc., monitoring of both layers is required during the course of sampling LAK028 during the SO_2 EEM program. Any future anomaly from LAK028 can then be investigated with respect to potential influence from change in stability of the chemocline. Furthermore, water sampling must always be done at the same time of year (late September to early October) when stratification and concentration stability is present to avoid a time effect on water chemistry.

Recommendation 9. To ensure that LAK028 surface chemistry is not confounded by possible future mixing affecting pH, Gran ANC, base cations, etc., monitoring of the complete water column is required during the course of sampling LAK028. Any future anomaly from LAK028 can then be investigated with respect to potential influence from change in stability of the chemocline.

Recommendation 10. There is uncertainty whether chemical stability occurs in LAK028 in late October through May, as is the case in June through early October. The presence of one or the other of these conditions can affect pH in the surface water in different ways. To resolve this uncertainty, we recommend continued monitoring using a conductivity mooring year-round in LAK028. Resulting data along with data from the temperature mooring will show if perennial meromixis that can affect surface pH needed for the EEM is present.

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6 APPENDIX A: STANDARD FIELD SHEET FOR RIO TINTO WATER SAMPLING

Rio Tinto SO_2 Permit Study-Water Component 2020: Field Data Sheet (Site ID________________)

A: Location

Lake or Stream Name		Site ID (eg.lak053):	
Date:	Time on station:	Time off station:	
Field crew:			
GPS Unit #		Elevation on GPS receiver (m)	
Northing		Easting	

Was a water sample collected from this site? ☐ Y ☐ N
If No, give reasons for not sampling:

Lake Photos
field sheet ☐ facing north ☐ facing south ☐ facing east ☐ facing west ☐ aerial view ☐
Other ______________________________ ☐

Stream Photos
field sheet ☐ upstream ☐ downstream ☐ across site ☐ aerial view ☐
Other ______________________________ ☐

B: Weather

Now: ☐ storm (heavy rain)
☐ rain (steady rain)
☐ showers (intermittent)
☐ overcast
☐ clear/ sunny

Past 24 hours: ☐ storm (heavy rain)
☐ rain (steady rain)
☐ showers (intermittent)
☐ overcast
☐ clear/ sunny

Has there been a heavy rain in the past 7 days? ☐ Y ☐ N

C. Riparian Vegetation (estimate the % of each type, totaling 100%)

Unvegetated (bare soil or bedrock)	%	Deciduous Forest (trees >5m tall)	%
Grasses/Ferns/Herbs	%	Coniferous Forest	%
Shrub (may include grasses/herbs growing beneath	%	wetland	%

D. Lake Site Description

Water depth at sampling station (m):	Instrument used for depth measurement :
Water sampling depth: Surface grab ☐ Other (m):	

E. Water Quality

Field Measurements

Make and model of Sonde	Depth of sample collection (m)	Water Temperature (°C)	pH	Spec. Conductance (µS/cm)	D.O. (mg/L)	Turbidity (NTU)	TDS (mg/L)
YSI model 6920							

Water Samples (check the box once sample is collected on board the helicopter):

☐ 125 mL poly for total cations (metals) (ALS bottle)

☐ 125 mL amber glass for NH_4-N (ALS bottle)

☐ 1 L poly to supply water for filtrations at base (ALS bottle)

☐ 500 mL poly for anions and pH (ALS bottle)

☐ 500 mL poly for Gran ANC and total alkalinity (ALS bottle)

7 APPENDIX B: GRAN-ANC LAB METHODS

Determination of Conductivity, pH, Turbidity and Grans Alkalinity using the PC Titrator plus PC Titrate unit

Theory of pH, Alkalinity and Grans Alkalinity

pH

Pure water dissociates to form hydrogen ions, H^+, and hydroxide ions, OH- :

$$H_2O \rightarrow H^+ + OH^-$$

At equilibrium, $[H^+] \times [OH^-]$ = a constant = the dissociation constant for water = 10^{-14} or 0.00000000000001 at 25°C

For simplicity, $[H^+]$ is expressed as a negative logarithm and is termed the pH. The negative logarithm of the $[OH^-]$ is pOH. For e.g., the negative logarithm of $10^{-7} = 7$. The simplified equilibrium reaction equation is:

$$pH + pOH = 14$$

The pH scale of 0 to 14 indicates the acidity or alkalinity of a water sample, with 7 being the midpoint noting neutrality. As $[H^+]$ increases, the solution becomes more acidic and pH decreases. As $[H^+]$ decreases, the solution becomes more alkaline and pH increases. Since pH is a logarithmic function, as $[H^+]$ increases by a factor of 10, the pH decreases by one unit. Conversely, as $[OH^-]$ increases by a factor of 10, pH increases by one unit.

Changes in pH are caused by the addition of acids (substances that contribute H^+) and bases (substances that accept protons) to the water. Theoretically pure water, such as distilled or deionized water has a pH of 7.0. However, carbon dioxide gas dissolved in water can cause the pH to be 6.5 or lower. Other impurities may also affect the pH.

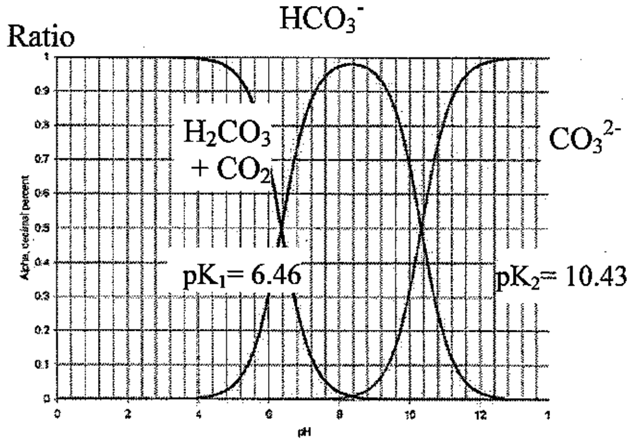
Alkalinity

Alkalinity refers to the acid-neutralizing or buffering capacity of a solution to resist a reduction in pH when H^+ are added. Hydroxides (OH^-), carbonates (CO_3^{2-}), and bicarbonates (HCO_3^-) are the primary contributors to the pH buffering capacity of natural waters. Buffering capacity can be characterized by the absorption of H^+ by CO_3^{2-} and HCO_3^- molecules. This results in a shift in equilibrium without causing a significant change in the pH. A sample with a high alkalinity, and therefore high HCO_3^- will have a greater resistance to changes in pH.

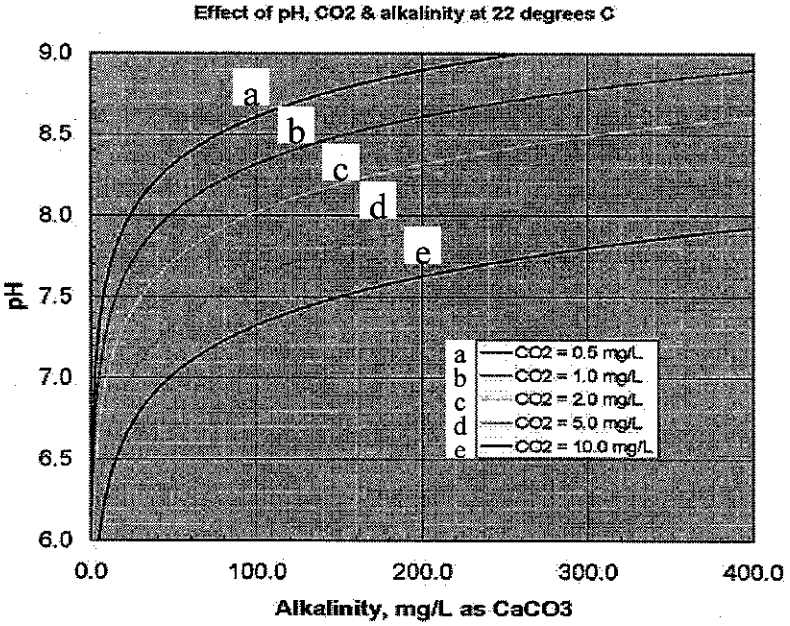
In natural water, the CO_2, CO_3^{2-}, and HCO_3^- alkalinity equilibrium determines and controls the pH:

$$H_2O + CO_2 \Leftrightarrow \underset{\text{carbonic acid}}{H_2CO_3} \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$

The proportion of H_2CO_3 acid to HCO_3^- to CO_3^{2-} varies according to pH:



At 25 °C, the saturation constant of CO_2 in water is about 0.5 mg/L. A body of water at equilibrium with the atmosphere attains 0.5 mg/L dissolved CO_2. At a given temperature, the pH for any alkalinity value depends upon the alkalinity arising from dissolved CO_2.



At 22 °C, water with an alkalinity of 100 mg/L and a pH of 7.6, has dissolved CO_2 of about 5.0mg/L. Since a body of water at equilibrium with the atmosphere has 0.5mg/L CO_2, this means that it will have a pH of 7.6 and the CO_2 level is supersaturated. To remove this excess CO_2, the pH must be driven up.

Alkalinity analysis involves the titration of samples with a standard 0.02N sulphuric acid titrant to endpoints of pH 8.3 and 4.5. To perform a manual titration, phenolphthalein or metacresol purple indicator is used for pH of 8.3 (*palk,* phenolphthalein alkalinity) and bromocresol green indicator is used for pH of 4.5 (*talk,* total alkalinity). The ranges for bromocresol green and methyl orange indicators are pH 3.8 to 5.4.and pH 3.1 to 4.4 respectively.

When the solution is titrated with acid, pH steadily decreases as more and more acid is added. When phenolphthalein is used as the titration indicator, the color of the sample solution changes from pink to colorless when the pH of the sample is decreased to 8.3.

This is the *Palk* or Phenolphthalein alkalinity. It exists when the pH is greater than 8.3 and represents all of the hydroxide alkalinity, ½ of the CO_3^{2-} alkalinity, and $^1/_3$ of the phosphate and any other alkali producing material present in the sample above pH 8.3.

Talk occurs when the pH is greater than 4.3. When bromocresol green indicator is then added to the water sample, it turns blue-green. As more acid is added, the sample will change to a form a pink-purple color when a pH of 4.3 is reached. This is the *Total Alkalinity (talk)* and is a measure of the concentrations of CO_3^{2-}, HCO_3^-, and OH^- expressed as an equivalent concentration (mg/L) of calcium carbonate ($CaCO_3$).

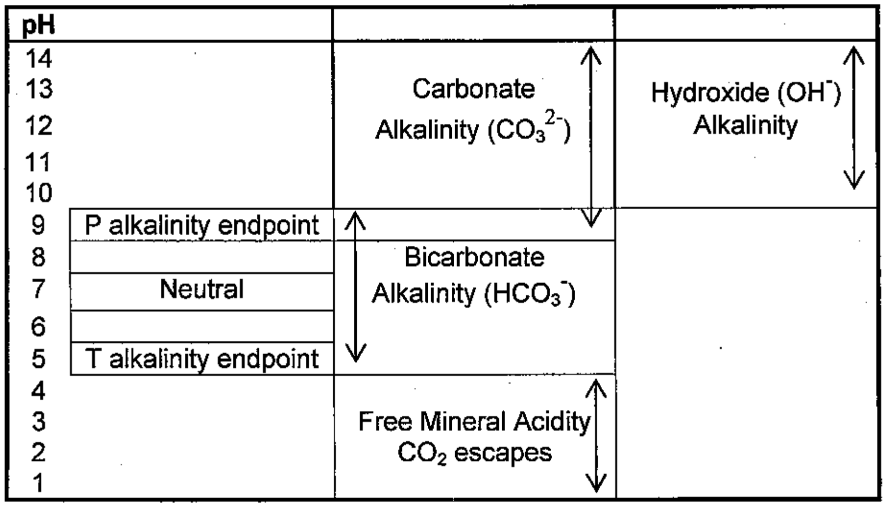
$$Talk = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] + [A_{org}^-] + [B_{inorg}^-]$$

where concentrations are expressed in eq L^{-1}, A_{org} are organic compounds and B_{inorg} are inorganic bases which may accept protons (borate, phosphate, silicate, etc.). In most freshwater and in atmospheric deposition, alkalinity is mainly dependent on the inorganic carbon equilibrium. In the pH range of atmospheric deposition (5.0-7.5) the prevailing form of inorganic carbon are H_2CO_3 and HCO_3^- so it is normally assumed that

$$Talk = [HCO_3^-]$$

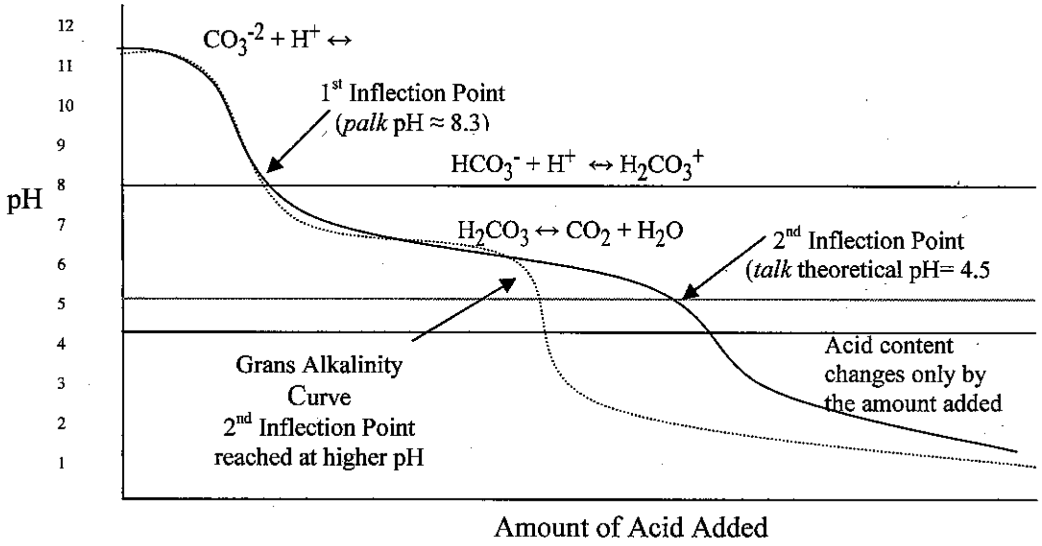
Although the P and T alkalinity do not bear any direct relationship to pH, the readings can be used to determine the CO_3^{2-} and HCO_3^- concentrations in a water sample. The alkalinity determinations represent the following:

If *palk* = 0, all of the alkalinity is HCO_3^-
talk – 2*palk* = CO_3^{2-} alkalinity
2P – *talk* = OH^- alkalinity



The pH of natural waters is normally less than 8.3 so there is no P alkalinity. They also do not normally have a pH below 4.3 so they do not contain strong mineral acids. Waters within the approximate pH range of 4.3 to 8.3 (T alkalinity to P alkalinity) contain HCO_3^- alkalinity and weak acids such as carbonic acid (carbon dioxide in solution) may also exist. In the pH range of approximately 8.3 to 9.6 HCO_3^- and CO_3^{2-} alkalinity can coexist in the absence of carbon dioxide or hydroxide alkalinity. Above a pH of approximately 9.6, hydroxide alkalinity becomes measurable.

Alkalinity is measured using sulphuric acid with a digital titrator. The acid is added to the water sample in measured amounts until the three main forms of alkalinity - OH^-, HCO_3^- and CO_3^{2-} are converted to carbonic acid. At pH 10, hydroxide (if present) reacts to form water. Below this pH, water cannot neutralize the sulphuric acid and there is a linear relationship between the amount of sulphuric acid added to the sample and the change in the pH of the sample.



Inflection Point:
Where the rate of change of pH is the fastest, also indicated by red peaks, called derivatives, in the graph
At pH 8.3, most of the CO_3^{2-} is converted to HCO_3^-. At pH < 8.0, the CO_3^{2-} species becomes negligible. The first inflection point doesn't exist for such a sample.

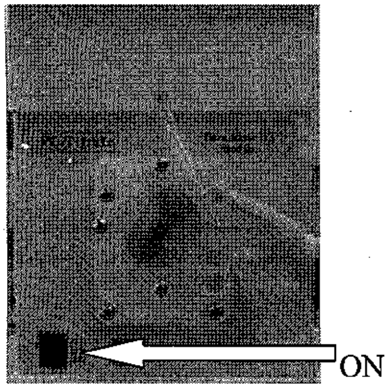
Grans Alkalinity:
At pH 4.5, all CO_3^{2-} and most of the HCO_3^- are converted to carbonic acid. Normal alkalinity equals the amount of acid added to reach a pH of 4.5.
At low conductivity (or ionic strength), the curve is shifted to the left so that the theoretical 2nd inflection point occurs at a pH higher than 4.5. More sulphuric acid is added to the sample to reduce the pH of 4.5 by exactly 0.3 pH units (which corresponds to an exact doubling of the $[H^+]$) to a pH of 4.2. However, the exact pH at which the conversion of bases might have happened, or total alkalinity, is still unknown. This procedure uses an equation derived from the slope of the line described above to extrapolate back to the amount of sulphuric acid that was added to actually convert all the bases to carbonic acid. The multiplier (0.1) then converts this to total alkalinity as mg/L $CaCO_3$.
Grans alkalinity titrates to a pH lower than pH 4.5 (usually 2) and then uses the amount of acid added and the slope of the line after the second inflection point to back calculate to the true inflection point. Lower alkalinity samples have a true inflection point at a higher pH than the theoretical 4.5, thus they require less acid to reach this point resulting in a smaller alkalinity value than that determined for the total carbonate within the sample. Therefore the Grans value will always be equal to or lower than the normal alkalinity.

Instrumentation

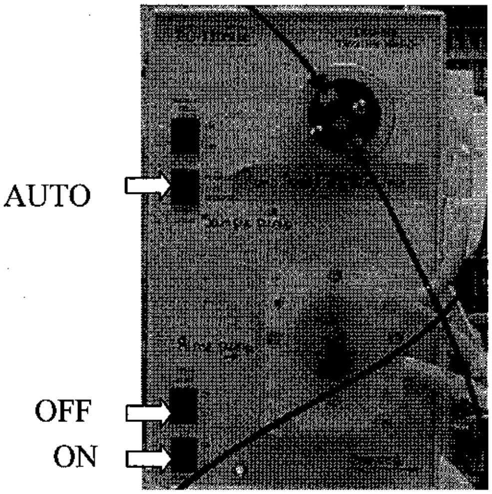
1. PC Titration plus, PC titrate unit, uses electrodes from Mandel Scientific, a Pt conductivity electrode PCE-96-CT1003, pH Titra-Fill electrode PCE-80-PH1013 and PCE-86-Ex1001 cable. Tel. 1-888-883-3636.
2. PC Assay-Plus Turbidity unit

SET-UP FOR AUTOMATED ANALYSIS

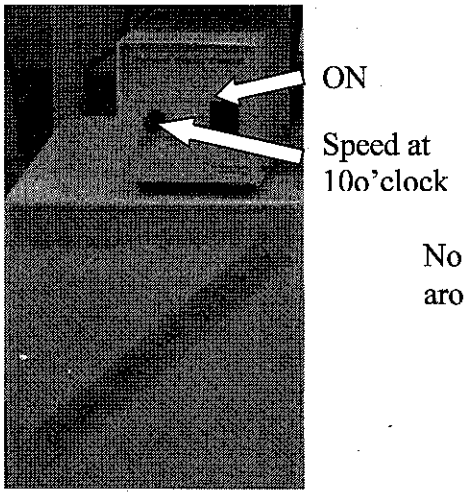
E. Titra-Rinse for Turbidity unit
Top Left



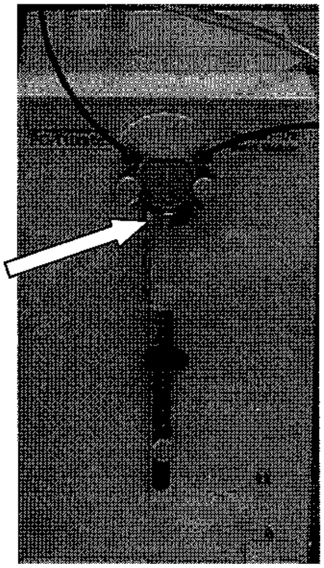
A. Titra-Sip Titration and Rinse station
Top Right



D. Stirrer for Conductivity cell
Bottom Left



B. Burivar Burette for Sulphuric acid
Bottom Right



$M = \mathrm{mol}/L$

$\frac{x}{0.2650} = \frac{200}{250}$

$x = 0.212 \pm 0.0021$

Reagents

1. pH standards – Fisher, pH 3 SB97-500 (case of 4 @ 500mL), 4L each of :
   pH 4 SB101-4, pH 7 SB107-4, pH 10 SB115-4
2. 99.4+% KCl* A.C.S. – VWR BDH0258-500g. For calibration of conductivity and for pH electrode.
3. 99.5+% Na_2CO_3* (anhydrous) A.C.S. - Fisher S263-500
   * Both KCl and Na_2CO_3 are stored in porcelain crucibles, covered with aluminum foil, and stored in an oven at 50°C
4. 0.02N H_2SO_4 – 4L, VWR VW3229-4
5. PC titration Plus Turbidity polysuspension standards – 0.02, 10, 100, 1000 NTU, available as a set, PC-1000-140 (250mL each standard) or PC-1000-150 (1.0L each standard). Note that the standards are very expensive, use wisely.

$74.5513\,\frac{g}{mol} \cdot x = 0.01\,\frac{mol}{L}$

Chemical Preparation

4M KCl (this solution is used to fill the pH electrode)

1. Weigh out $\overset{7.456}{3.728}$ g of KCl and dissolve into 50 ml of Milli-Q water, creating a saturated 4M KCl solution.
2. Prepare on an as-needs basis and update the Reagent Preparation Log.

Conductivity Standard (known conductivity of 1413 µS @ 25°C)

3. Weigh out 0.1863 g of dried KCl and dissolve into 250 ml of Milli-Q water, creating a 0.01M solution, which produces 1413µS conductivity.
4. Prepare on an as-needs basis and update the Reagent Preparation Log. This solution is stable, however, *do not consolidate fresh with existing leftovers.*

Alkalinity Standards and QC

1. Weigh out (0.2650 ± 0.0026) g of dried Na_2CO_3 into a 250 mL Class A volumetric flask and make to mark with B-pure water. Cap and shake contents vigorously. This produces a (1000 ± 10) ppm (wt/vol) stock solution, a ±1.0 % tolerance. Label the expiration date on flask, which is one month after its preparation. Update the Reagent Preparation Log.

2. Dilute the stock solution to the concentrations of 20 ppm and 5 ppm as follows. Weigh (5.000 ± 0.010) g or pipette (5000 ± 10) uL of the 1000ppm stock solution to a 250mL Class A volumetric flask and make to mark with B-pure water. This makes (20.00 + 0.04) ppm, at 0.2% tolerance, 1.02% tolerance when summed with the 1000ppm.

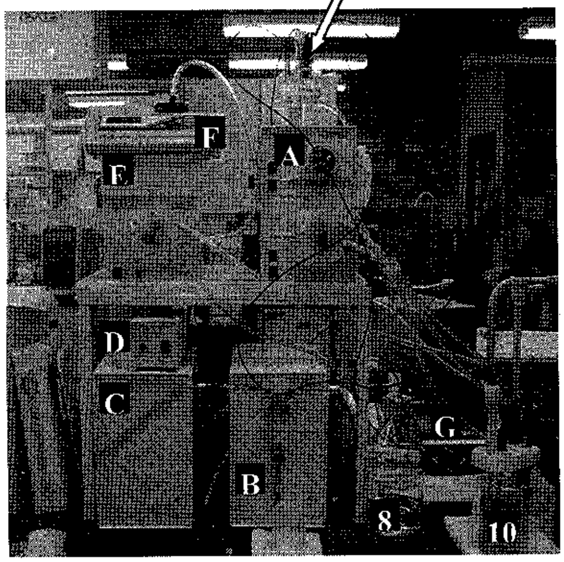
   Weigh (1.000 ± 0.010) g or pipette (5000 ± 10) uL of the 1000ppm stock solution to a 200mL Class A volumetric flask and make to mark with B-pure water. This makes (5.00 + 0.02) ppm standard, at 0.4% tolerance, 1.08 % tolerance when summed with the 1000ppm. This solution is also used to monitor instrument reproducibility during a batch run.

3. Prepare the dilutions on an as-needs basis. Discard old residual solutions when making new dilutions from a fresh 1000ppm standard. Change sampler cup on a weekly basis.

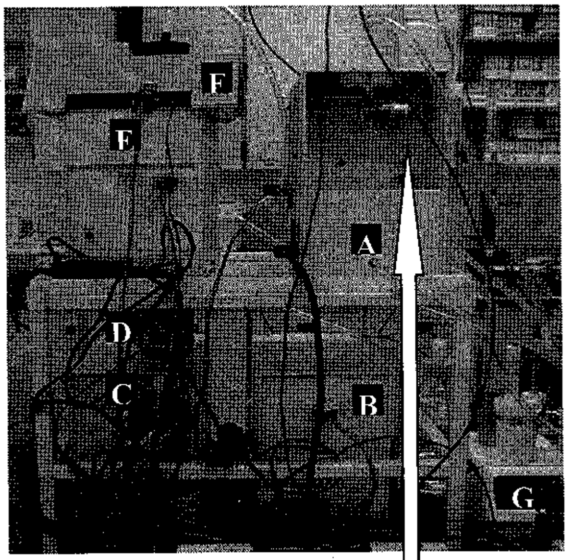
Methods

Start Up Procedure

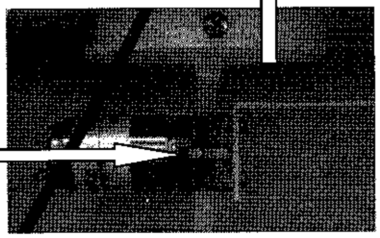
1. If necessary, switch on the computer, the conductivity meter, and all 3 modules of the titration unit.
   Note: A communications error often indicates one or more modules is switched off. If not, reboot the Interface module (C)
2. Fill the rinse carboy with R. O. water (marked as DW on the tap)
3. Click on the PC titrate icon
4. Type the password: "a" in each of both fields
5. When the main screen appears, click on the light bulb icon in the left top corner to connect the titrator to the computer
6. Release the contents of the pH cell to waste using the "Manual Cell Drain" switch (Titra-Sip Titration Module A)



Front



Back

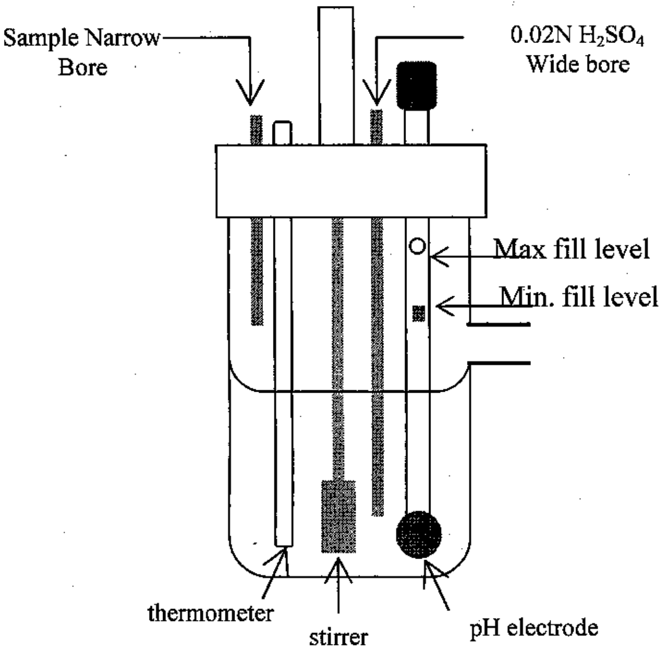


7. Turn on the rinse pump to fill the rinse port then to drain. If the cell won't drain, check the tubing at the back of the Titra-Sip Titration module A. The small white plastic clamps sometimes get stuck to the tubing. Push these apart. If necessary, remove the tubing from the clamps and replace.
8. Flush the turbidity cell if required, the glass sampler probe should be in RO water.
9. The acid bottle should have between 300-400mL 0.02N H_2SO_4. The hose tip must be immersed to the bottom of the bottom to prevent pumping of air into the burette.
10. F-rom the top menu bar, select Titrator/manual control. Click on the "Burette" icon and purge the burette (B) of its contents at least once. When switching acid strength, do this purge at least twice.

Note: Bubbles in the burette cause error in the volume of acid titrated and invalidates results. Bubbles clinging onto the underside of the burette where the dispensing hole is located must be removed. If there are no such bubbles, go to step 12.

11. To remove the bubbles, first the plunger must be all the way down. Loosen the screw from the bottom of the burette and gently push the syringe up by a few cm using the screw. Lift the tubing above the sulphuric acid then pull the syringe down so as to introduce a large bubble into the burette. This large bubble consolidates the smaller ones. Next, push the syringe all the way up. Repeat until all bubbles are removed from the vicinity of the burette opening.
    Note1: If not using the unit for more than a week, empty the burette of acid by pumping air and replace with Milli-Q water. The buret is cleaned every 6 months as described in the Semi-Annual Maintenance section.
    Note2: Condensation on the walls of the burette under the plunger should be removed. First empty the burette. Next remove the burette from the module and gently pry open the bottom black cover. Remove the plunger. Wipe the plunger, black cover, and bottom inner walls of the burette with a clean Kimwipe before reassembling the unit.

12. Ensure that the green stir paddle does not contact the pH electrode and thermometer. The pH electrode must not touch the vessel and the hole must be unplugged. If crusty with KCl crystals, rinse with lots of MilliQ water and refill with 4M KCl.



13. Check the sample uptake rate once a month. It should be (30 ± 2) mL/min. If outside of these tolerance limits, the belt in the Titration module requires replacement, see section on Semi-Annual Maintenance.

14. Calibrate for conductivity and pH. Always make sure a sufficient head of solution is above the sampler probe to avoid pumping air into the buret.

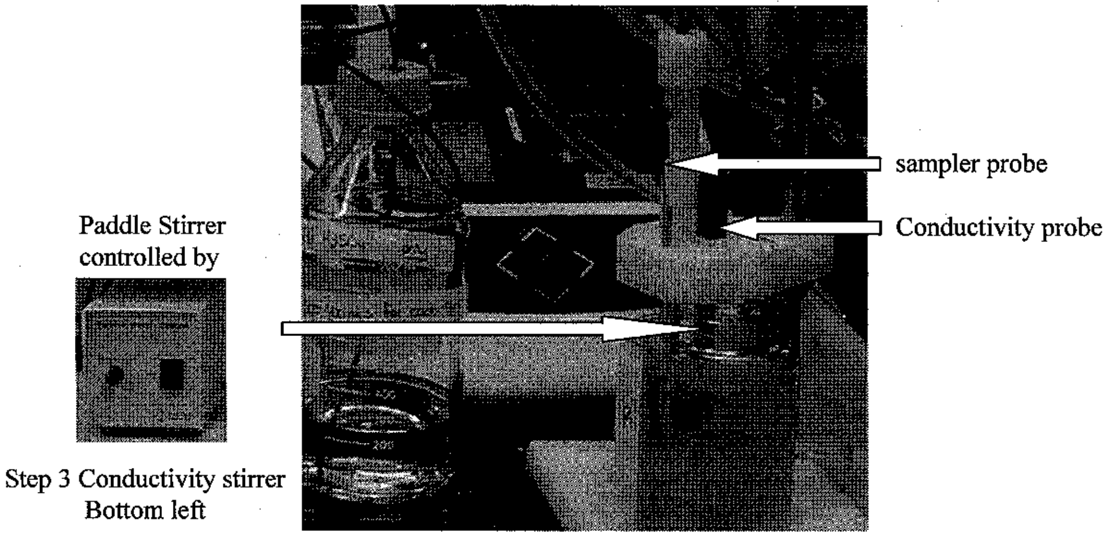
Note1: The pH calibration is also used to indirectly calibrate for alkalinity. Alkalinity standards are measured as QC monitors which do not influence the calibration slope and intercept.

Note2: Fluctuation of pH due to temperature are compensated automatically

Calibration for Conductivity

1. The conductivity probe is sufficiently rinsed when the conductivity reads <1. Otherwise, rinse with methanol or ethanol to remove contaminants from the probe, and gently wipe with a KimWipe. Return the probe to the holder, making sure there is sufficient clearance between the green stirrer paddle and the probe.

Conductivity meter Bottom Far Right



Step 3 Conductivity stirrer Bottom left

2. Place the probes and stirrer in the 0.01 M KCl solution (1413μS).
3. Turn on the stirrer by switching the Variable Control Stirrer Module D to "Manual" and allow a few minutes for the probe to reach equilibrium. The reading is inaccurate if the stirrer is off.
4. On the key pad for the conductivity module G press the right arrow key so that the arrowhead points to the "CAL" function.
5. Once the solution has reached equilibrium, press <enter>. This automatically adjusts the conductivity detector to read 1413 μS.
6. Turn off the stirrer by switching the Variable Control Stirrer Module D to "Auto" and return the probes to the rinse station.
7. Make note of the K value on the pH calibration printout for that day. The K value should fall within an arbitrary ± 0.2 range last measured by the probe. If the K value falls outside this range despite taking the troubleshooting measures, and the pH QC passes, then this indicates that the conductivity probe is gradually degrading with age. If the QC fails and a fresh KCl reads outside of the 1313 to 1513 μS range, then the probe should be replaced.
8. Do this calibration for the day's run.

pH calibration 3,4,7,10

Calibration for pH 3, 4, 7, 10

Check levels of pH probe, if low fill with 4M KCl

1. Click on the pH calibration button along the bottom toolbar, 4th icon from the right of the main screen
2. Click on the start button
3. Follow the steps as listed. The calibration procedure expects the buffers to be delivered in the order of 3, 4, 7 and 10.
4. A calibration report will automatically print off; check that the calibration is valid.
5. Do this calibration for the day's run.
6. Change sampler cup on a weekly basis.

To review a previous calibration,

1. Go to Titrator/Examine Calibration
2. Enter 1 in the field for Port and select the data file using the left or right arrow shown at the bottom left of the screen
3. To print or email the calibration, select Print/Destination/Printer. The "print to file" should be named with the runID followed by CAL.
4. The calibration and sample run files are stored in C:\Program File/Hinterland/ PCTitrate. For email instructions, go to page 14, steps 12 to 13.

Calibration for Turbidity

1. The Turbidity meter requires a 30 minute warm-up.
2. Use the polysuspension standards provided (0.02, 10, 100 NTU). The turbidity meter F automatically returns a large portion to the sample container by reverse pumping before the rinse cycle is initiated. Measure turbidity after conductivity and alkalinity are completed.
3. Use the turbidity cal icon, last icon on the PC titrate screen to begin. This method requires the use of both the computer and the turbidity key pad to complete. Each analysis is separated by a rinse of RO water.
4. Calibrate at the meter and follow the prompts. The unit calibrates in the sequence of 0.02, 100, 10, 0.02 NTU. Press the <enter> key twice on the unit to scroll to the 100NTU standard. The display is faint, and the decimal point is barely visible, so exercise caution.
5. Place the holder consisting of the stir paddle and turbidity sampler into a RO blank. The unit stirs for 30s before pumping in the solution.
6. After approximately 2 minutes, the unit measures and emit a soft beep when done.
7. Press <enter> to save the calibration when done. Do this calibration monthly or more frequently as indicated with QC results

50 ppm: $\frac{50}{100\text{ mL}} = \frac{1000}{X}$ $X = \frac{100000}{50}$ $x = 200$

Running a Sample for Conductivity, pH, and Alkalinity

Run samples directly from clear PET jars.
Do not run samples directly from brown bottles.
Open only when ready to run and pour 80-90mL into a sample cup for mid to moderately high-range samples (up to 300ppm alkalinity)
Run pH first then turbidity

1. In the first column, double left click and select the appropriate method. To globally fill the rows with the same method, highlight the first box, keep the Shift key down and drag the parameters down the column then release. **Cond pH grans alkalinity mid-range** is often used. For the very high range, use **Cond pH alkalinity High.**

Conductivity Range µS	Program	H_2SO_4, N	Sample Size, mL	Alkalinity QCs, ppm
75 +	Very High range	0.02	20	300, 400, 500
75 +	Mod High range	0.02	50	50, 100, 200, 300
25-75	Mid range	0.02	50	5, 20
25 or less	Low range	0.002	40	0.25, 0.5

2. Generate the order number in the second column by clicking "AutoGenerate Order Number"
3. For mid-alkalinity samples, use the following Run Sequence:
   0, 5ppm, 20ppm Na_2CO_3 QC solutions
   The QC tolerances are (0.0 ± 0.2)ppm, (5.00 ± 0.5)ppm, (20 ± 1)ppm. Note the conductivity of the 20ppm QC, let's say it is 32µS for 5ppm Na_2CO_3 QC
   One blank
   Samples
   Run first sample again, use "r" as a suffix
   0ppm, 5ppm Na_2CO_3, 20ppm Na_2CO_3 (32 ± 1) µS QC
4. For moderately high alkalinity samples, use the following Run Sequence:
   0, 50ppm Na_2CO_3, 100ppm Na_2CO_3, 200ppm Na_2CO_3, 300ppm Na_2CO_3 QC solutions
   The QC tolerances are (0 ± 1)ppm, (50.0 ± 2.0)ppm, (100 ± 3)ppm, (200 ± 2)ppm, (300 ± 1)ppm. Note the conductivity of the 200ppm QC, let's say it is 670µS
   200ppm Na_2CO_3 QC
   Samples
   Run first sample again, use "r" as a suffix
   0ppm, 100ppm Na_2CO_3, 200ppm Na_2CO_3 (670 ± 4) µS QC
5. Add samples by right clicking and selecting **add x rows.** To fill globally the same prefix, follow the instructions in step 1.
   Note: Sample numbers have to be unique
6. Press start and follow the prompts as displayed. Make sure a sufficient head of solution is above the sampler probe, otherwise air will be pumped into the titration vessel and results will be erroneous.
   Note: The system measures conductivity first, then it primes the pH cell with sample solution after which it discharges the solution to waste. Next, it pumps the pH cell with sample, turns on the paddle, and proceeds to titrate. This can take from 12 mins. to 22 mins., a longer time is required for higher alkalinity.

7. To view the results during a batch run, click on the bottom tab "**equation results**", go to the far right tab "**water quality equations set**"
8. Inspect QC results. For the **Cond pH grans alkalinity mid-range** method, if these exceed the 5% tolerance limits of 4.5 to 5.5 ?ppm Na_2CO_3 and ? to ?µS, trouble shoot the instrument and standards.
9. The run can be terminated manually by pressing **Stop or paused by pressing <esc>.** "Priority" completes the current measurement and allows insertion of new samples into the batch run. Both actions also remove prior records from the results display, however, these can be viewed under "**How to Obtain a Historical Report**" explained in page 14.
10. When all the samples are completed, a report will pop up. Print this report and also, under the **equation results**, print off the **water quality equations set.**
11. Inspect the results for outliers, unusual values, and QCs. If necessary, re-analyse some samples.
12. To view a titration curve, select Replay Titration. Load and select the dataset and desired sample measurement. The curves should be smooth and not choppy with end points approximately at pH 8.3 and pH 4.5.

print data first!!

Screening Samples for Alkalinity

1. Using the calibrated conductivity meter, make a rough measurement of the samples.
2. For Samples that have a conductivity reading of 250 µS or more, flag for TOC.

Finished for the Day

1. Click on the open door icon from the main screen to end communication with the instrument
2. Fill the pH cell with pH 4 buffer so that the blue bulb of the probe is covered by the solution. Use more solution if the unit is not used for more than 3 days.
3. Pump RO water so as to fill sampler probe and line with water - this takes about 5s.
4. If the unit is not in use the next day, plug the dosing hole with the attached black stopper.
5. Save the results as a "txt" file at the prompt for printing. Name it according to the runID and attached any notes regarding the run when emailing the results. This includes misidentification of sample.

Care of the pH Electrode

Preparation:

1. Remove the bulb protector boot or soaker bottle and immerse the lower end of the electrode into pH4 buffer for 30 minutes. This hydrates the pH bulb and reference junction for optimum performance.

2. Fill refillable electrodes with the reference solution indicated on the electrode (usually 4M KCl) to a level just below the filling hole. It must be above the internal element. Gently shake the electrode downward to remove trapped air bubbles.

Electrode Cleaning:

Electrodes are susceptible to coating by many substances and the response time can deteriorate dramatically. Do not use strong solvents to clean electrodes. If they are mechanically intact, they can often be restored by using one of the following procedures:

1. If coated with salt deposits, rinse with water. If deposits remain, soak in 0.1M KCl for 5 minutes followed by 0.1M NaOH for 5 minutes.
2. If coated with oil or grease, wash the electrode in warm tap water with mild detergent. Rinse the electrode in tap water and then with distilled water. Soak the electrode in a pH4 buffer for 30 minutes after this procedure.
3. If the reference junction is clogged, soak the electrode in 0.1M KCl for 10 minutes.

Electrode Storage:

Do not allow the electrode junction to dry out between measurements.
When taking the electrode out of service for an extended period, rinse the electrode thoroughly and refit the soaker bottle or storage boot.
Ensure there is sufficient solution (pH 4 buffer solution) in the bottle or boot to keep the junction wet.

The electrode should not be stored for a period longer than 6 months