Sulphur Dioxide Environmental Effects Monitoring
for the Kitimat Modernization Project

2017 Annual Report

Package of Technical Memos

Compiled for:

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

Compiled by:

ESSA Technologies Ltd.
Suite 600 – 2695 Granville St., Vancouver, BC, Canada V6H 3H4

The following technical memoranda are cited in the 2017 Annual Report draft, and are provided on the subsequent pages in the order listed below.

Technical Memo P03. Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: Pilot Study Results (September 2016, Trent University)

Technical Memo P04. Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: 2016 (March 2017, Trent University)

Technical Memo P05. Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: 2017 Results (June 2018, Trent University)

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

Technical Memo F01. Atmospheric Sulphur – Filter Pack Measurements of Particulate Sulphate. (June 2018, Trent University)

Technical Memo S06. Long-term Soil Monitoring Plots – Plot Establishment (March 2017, Trent University)

Technical Memo S07. Long-term Soil Monitoring Plots – Laboratory Analysis (June 2018, Trent University)

Technical Memo W03. Aquatic Ecosystems Actions and Analyses (March 2016, ESSA Technologies Ltd.)

Technical Memo W06. Aquatic Ecosystems Actions and Analyses (March 2017, ESSA Technologies Ltd.)

Technical Memo W07. Aquatic Ecosystems Actions and Analyses (April 2018, ESSA Technologies Ltd.)

RioTinto

KMP SO_2 EEM Program – Technical Memo P03

Atmospheric Sulphur Dioxide

Passive Diffusive Sampler Network:
2015 Pilot Study Results

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

Submitted September 2016

Table of Contents

List of Figures

List of Tables

1 Overview

A pilot study to evaluate the performance of passive sulphur dioxide (SO_2) samplers against active (continuous) SO_2 monitors was proposed under the Environmental Effects Monitoring (EEM) program prior to re-establishment of a passive sampler network (see Technical Memo P02: Passive Diffusive Sampler Network: Pilot Study, March 2015).

Passive samplers will be deemed effective, i.e., reliable for network deployment, if they exhibit: (a) a high correlation with continuous SO_2 monitors (e.g., $r \geq 0.8$), and (b) low variability between replicate exposures.

Passive samplers were co-deployed across three monitoring stations (reflecting a gradient in SO_2 air concentrations) during summer 2015. This memo briefly describes the results of the pilot study.

2 Study Design

The objective of the pilot study was to evaluate the performance of passive diffusive SO_2 samplers against continuous SO_2 monitors across a gradient in air concentrations. Specifically, the pilot study evaluated the performance of two commercial samplers (with carbonate-based membrane coatings; see Technical Memo P02) and the variability in replicate exposures.

Passive samplers can be used 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 (see Technical Memo P01 and P02).

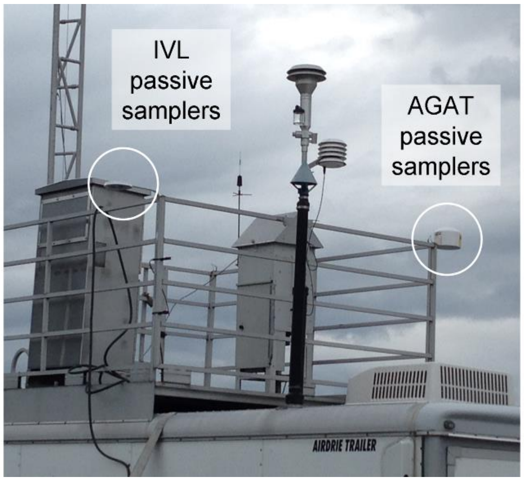


Figure 1. Deployment of passive diffusive samplers (obtained from IVL and AGAT) at continuous sulphur dioxide monitoring station. For further details on passive samplers see: IVL: www.diffusivesampling.ivl.se, and AGAT Laboratories: www.agatlabs.com/energy/air-quality-monitoring/passive-monitoring.cfm.

The pilot study was carried out between 24 July and 16 October 2015 (12 weeks). Two commercial samplers with carbonate-based membrane coatings (IVL and AGAT) were co-located with continuous samplers (Figure 1) at three monitoring stations (Figure 2) spanning a gradient in atmospheric SO_2 (Kitimat Smeltersite [KMP], Haul Road and Riverlodge [highest to lowest SO_2]). Passive samplers were deployed in duplicate at each station for two-week and four-week exposures to evaluate the effect of exposure length on sampler performance. The pilot study included six two-week and three four-week deployments (see Table 1). The study period covered two seasons, summer and autumn, reflecting a range in temperature (Table 1). While temperature (as a surrogate of photochemical activity) plays a dominant role in the atmospheric chemistry of SO_2, given the proximity of the emissions source, aluminium production is the dominant driver of variability in atmospheric SO_2 in the region.

The deployment and collection of passive samplers was carried out by WSP (Jim Young). Following deployment all samplers were returned to their respective manufacturer (or supplier) for analysis.

Figure 2. Location of continuous sulphur dioxide monitoring stations with co-deployment of passive samplers during the 2015 pilot study. Kitimat Smeltersite [KMP] (latitude: 54.01951, longitude: –128.70257, elevation: 2), Haul Road (latitude: 54.02919, longitude: –128.70269, elevation: 11) and Riverlodge (latitude: 54.05389, longitude: –128.67144, elevation: 18).

Table 1. Deployment number and date for the two-week and four-week passive sampler exposures. The average air temperature at the Kitimat Smeltersite and Riverlodge stations is also shown.

Exposure	Deployment #	Deployment date (dd/mm/yyyy)	Temperature (°C)	
			Kitimat Smeltersite	Riverlodge
Two-week	1	24/07/2015	15.9	15.2
	2	07/08/2015	17.2	16.5
	3	21/08/2015	13.4	12.7
	4	08/09/2015	12.3	11.1
	5	18/09/2015	10.5	8.8
	6	02/10/2015	10.1	7.9
Four-week	1	24/07/2015	16.5	15.8
	2	21/08/2015	12.8	11.9
	3	18/09/2015	10.3	8.4

3 Results

Average SO_2 concentrations during the study period (24 July–16 October) measured by the active monitors ranged from 0.3 ppb (Riverlodge) to 3.1 ppb (Smeltersite), with ambient concentrations approximately five times higher at Haul Road compared with Riverlodge, and eight times higher at Smeltersite compared to Riverlodge (Tables 2 and 3). In general, concentrations were higher during the summer months (July and August), with higher temperatures (Figure 1, Tables 1 and 2).

Average SO_2 estimated by the passive samplers (IVL and AGAT) during the study period showed a similar range in air concentrations ranging from 0.2 [0.2] ppb (AGAT [IVL] Riverlodge) to 2.8 [3.1] ppb (AGAT [IVL] Smeltersite). Moreover, average SO_2 estimated by the passive samplers showed a strong linear relationship with the active data during both two-week (IVL $R^2 = 0.99$; AGAT $R^2 = 0.98$) and four-week (IVL $R^2 = 0.99$; AGAT $R^2 = 0.98$) exposures (Figure 4).

While IVL and AGAT passive samplers showed a strong linear relationship to the active data, the difference between replicate samplers was lower for IVL, notably lower for the four-week exposures (see Tables 2 and 3). In addition, the majority of observations at Riverlodge were at the limit detection (0.2 ppb) or below detection for the AGAT samplers (5 of 9 observations were returned as < 0.2 ppb; Table 2 and 3). Overall the two-week and four-week exposures showed a similar relationship to the active data but four-week exposures had a lower difference between replicates and lower difference (%) between active and passive air concentrations (for Smeltersite and Haul Road).

The pilot study was carried out during a period of very low (aluminium production and) emissions under the Kitimat modernisation project. The low emissions resulted in low atmospheric SO_2 concentrations, which was a challenge for the passive samplers. In concert, the proportional (%) variability between replicate samplers under low atmospheric SO_2 concentrations was high, despite their very low absolute difference. However, as SO_2 emissions increase post-modernisation, the level of detection and variation between replicates will improve (for both samplers).

4 Conclusion

Passive samplers showed a strong linear relationship with the active data for ambient SO_2. However, the IVL samplers showed a slightly better relationship, with a lower variation between replicates and lower difference between passive and active observations compared with AGAT samplers (more so for four-week exposures). More importantly, the majority of observations at Riverlodge were below detection for the AGAT samplers. However, the low atmospheric concentrations (< 0.5 ppb) at Riverlodge were also a challenge for the IVL samplers.

It should be noted that the pilot study was carried out during a period of low SO_2 emissions; as emissions (and atmospheric concentrations of SO_2) increase the performance of passive samplers will improve (as evidence by passive sampler performance across the atmospheric concentration gradient in the pilot study). Similarly, under the plume (with elevated atmospheric SO_2 concentrations), the performance of samplers will improve, allowing for the delineation of the areas more likely to influenced by SO_2 emissions. As aluminium production and emissions increase post-modernisation, passive diffusive samplers will provide reliable 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.

5 Recommendations

It is recommend that the passive SO_2 network use the IVL samplers with an exposure period of one month (noting that regions with atmospheric concentrations < 0.5 SO_2 ppb will show greater variability between replicates, and higher uncertainty against active measurements).

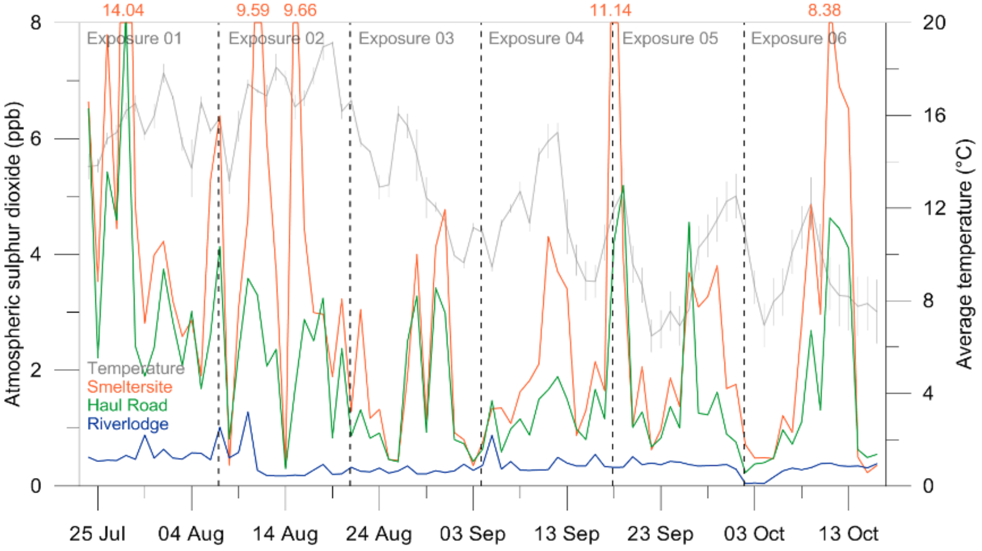


Figure 3. Daily ambient atmospheric sulphur dioxide (ppb) measured at Kitimat Smeltersite (orange), Haul Road (green) and Riverlodge (blue) during the period 24 July–16 October 2015. The average air temperature at Kitimat Smeltersite and Riverlodge is also shown (grey) with daily variation between the stations indicated by the vertical lines.

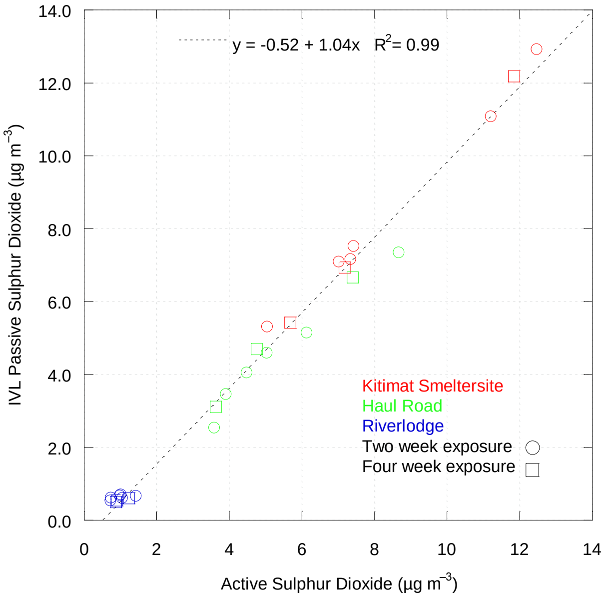


Figure 4. Comparison of IVL passive diffusive samplers for sulphur dioxide against continuous measurements at Kitimat Smeltersite (red), Haul Road (green) and Riverlodge (blue) during 24 July–16 October 2015. Passive samplers were deployed in duplicate at each stations for two-week (open circle) and four-week (open square) exposures.

Table 2. Average ambient sulphur dioxide (ppb) during two-week exposures for active (ACT) and passive (IVL and AGAT) samplers co-deployed at three stations (Kitimat Smeltersite, Haul Road and Riverlodge). See Table 1 for deployment dates. The difference (%) in replicate (n = 2) passive samplers and the difference (%) between active and passive samplers is also given.

Station	Deployment	Sulphur dioxide (ppb)			Replicates (%)		Active (%)	
		ACT	IVL	AGAT	IVL	AGAT	IVL	AGAT
Smeltersite	1	4.62	4.73	4.65	5.5	10.8	2.4	0.7
	2	4.17	4.10	3.75	0.5	2.7	1.8	10.1
	3	1.85	1.96	1.75	3.9	17.1	5.6	5.5
	4	2.72	2.72	2.20	3.1	9.1	0.0	19.0
	5	2.55	2.58	2.15	3.2	14.0	1.1	15.7
	6	2.66	2.62	2.00	2.6	0.0	1.7	24.9
Haul Road	1	3.21	2.69	2.60	17.0	30.8	16.1	18.9
	2	2.28	1.90	1.85	11.6	5.4	16.7	18.9
	3	1.43	1.27	1.10	9.2	18.2	11.3	23.3
	4	1.31	0.92	0.70	13.4	0.0	30.2	46.6
	5	1.82	1.66	1.30	12.4	15.4	8.8	28.7
	6	1.62	1.47	1.20	4.7	0.0	9.2	26.0
Riverlodge	1	0.53	0.24	0.20	0.0	0.0	54.0	62.0
	2	0.39	0.22	0.30	20.9	0.0	42.3	22.8
	3	0.27	0.23	0.20	3.2	0.0	16.5	26.0
	4	0.36	0.24	<0.2	35.4	–	32.2	–
	5	0.37	0.25	<0.2	13.7	–	31.5	–
	6	0.26	0.20	<0.2	0.0	–	26.0	–

Table 3. Average ambient sulphur dioxide (ppb) during four-week exposures for active (ACT) and passive (IVL and AGAT) samplers co-deployed at three stations (Kitimat Smeltersite, Haul Road and Riverlodge). See Table 1 for deployment dates. The difference (%) in replicate (n = 2) passive samplers and the difference (%) between active and passive samplers is also given.

Station	Deployment	Sulphur dioxide (ppb)			Replicates (%)		Active (%)	
		ACT	IVL	AGAT	IVL	AGAT	IVL	AGAT
Smeltersite	1	4.40	4.50	4.35	6.2	6.9	2.3	0.5
	2	2.08	1.97	1.90	8.5	10.5	5.3	4.5
	3	2.61	2.49	2.40	2.9	8.3	4.6	4.1
Haul Road	1	2.74	2.46	2.40	0.3	33.3	10.4	6.7
	2	1.33	1.13	0.95	3.9	10.5	15.2	16.6
	3	1.72	1.68	1.40	4.8	14.3	2.6	10.3
Riverlodge	1	0.46	0.22	0.20	6.1	0.0	51.4	39.2
	2	0.33	0.20	<0.2	5.1	–	40.6	–
	3	0.32	0.18	<0.2	5.9	–	44.3	–

Rio Tinto

KMP SO_2 EEM Program – Technical Memo P04

Atmospheric Sulphur Dioxide
Passive Diffusive Sampler Network: 2016 Results

March 2017

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

1 Overview

A network of sulphur dioxide (SO_2) passive diffusive samplers for was established in the Kitimat Valley during June 2016 following recommendations from a pilot study that evaluated the performance of passive SO_2 samplers (see Technical Memo P03: Passive Diffusive Sampler Network: Pilot Study Results, April 2016).

A second network was established during July 2016, following public consultation during the Kitimat Ambient Air Quality Monitoring Workshop, 23–24 June 2016 (Tamburello and Alexander 2016). The second network was established in urban and residential areas of Kitimat; site selection was informed by public input obtained during the workshop, and also included sites from the 2011—2012 network, e.g., sited close to schools.

This memo describes the establishment of both networks and the results of the SO_2 passive diffusive sampler network during 2016.

2 Study Design

The Kitimat Valley network was established 22–23 June 2016 at 16 monitoring sites primarily located along the Wedeene and Bish roads to capture the plume path, and also included co-location with three ambient stations (Haul Road, Riverlodge and Whitesail). On July 18, an additional site at Highway 37 and the Onion Lake Ski Trail was added to the network. The Kitimat Urban network was established on July 18, with 15 stations located in urban and residential areas of Kitimat (see Appendix Table A1 for exact location of all monitoring sites). Where possible sites were established in close proximity to previous passive sampler monitoring sites, which were operated during 2011–2012 (see Technical Memo P01: Passive Diffusive Sampler Network: 2011–2012) or schools, hospitals, etc. in the urban network.

As recommended under the pilot study, the network employed IVL passive SO_2 samplers (URL: diffusivesampling.ivl.se) with an exposure period of one month (see Technical Memo P03: Passive Diffusive Sampler Network: Pilot Study Results). Both networks operated until 13 October 2016, providing four one-month exposures under the valley network, and three one-month exposures under the urban network. In total, during 2016, there were 32 monitoring sites with 110 sample exposures across both networks, with replicate samplers deployed during 30% of the time (to assess variation in measurements).

Following deployment all samplers were returned to IVL for analysis.

3 Results

The observed data showed elevated atmospheric SO_2 along the plume path (a transect of approximately 45 km; Figure 1 and Appendix Table A2 and Figure A1); notably during June–August plume concentrations were high north of Rio Tinto (concentrations > 10 µg m^{-3} were observed at the Rife Range monitoring site during June and July, 2016), and during August–October higher concentrations were observed south of Rio Tinto (concentrations > 20 µg m^{-3} were observed at Bish Road during September, 2016).

In contrast, all monthly exposures under the urban network were consistently < 1 µg m^{-3} (Figure 1). The lower concentrations observed in the urban areas were explained by the dominant wind directions during the 2016 exposures, which generally directed emissions from the Rio Tinto facilities to west of the Kitimat urban area along the Kitimat Valley (see Figure 2).

The concentration of SO_2 measured by passive samplers was also compared to the active observations at three ambient stations to evaluate sampler performance (Haul Road, Riverlodge and Whitesail; summarised to coincide with the monthly passive sampler exposure periods). In general, there was good correspondence between passive and active (R^2 = 0.98); however, the one-to-one regression slope suggests that passive samplers represented about 80% of the SO_2 concentrations reported by the active samplers (see Figure 3). This difference is similar to the variation between duplicate sampler exposures, i.e., on average there was ~15% variation between duplicate samplers (see Appendix Table A3). Moreover, the comparison against the active stations suggests a larger deviation at stations with low atmospheric SO_2 concentrations (see Whitesail in Figure 3).

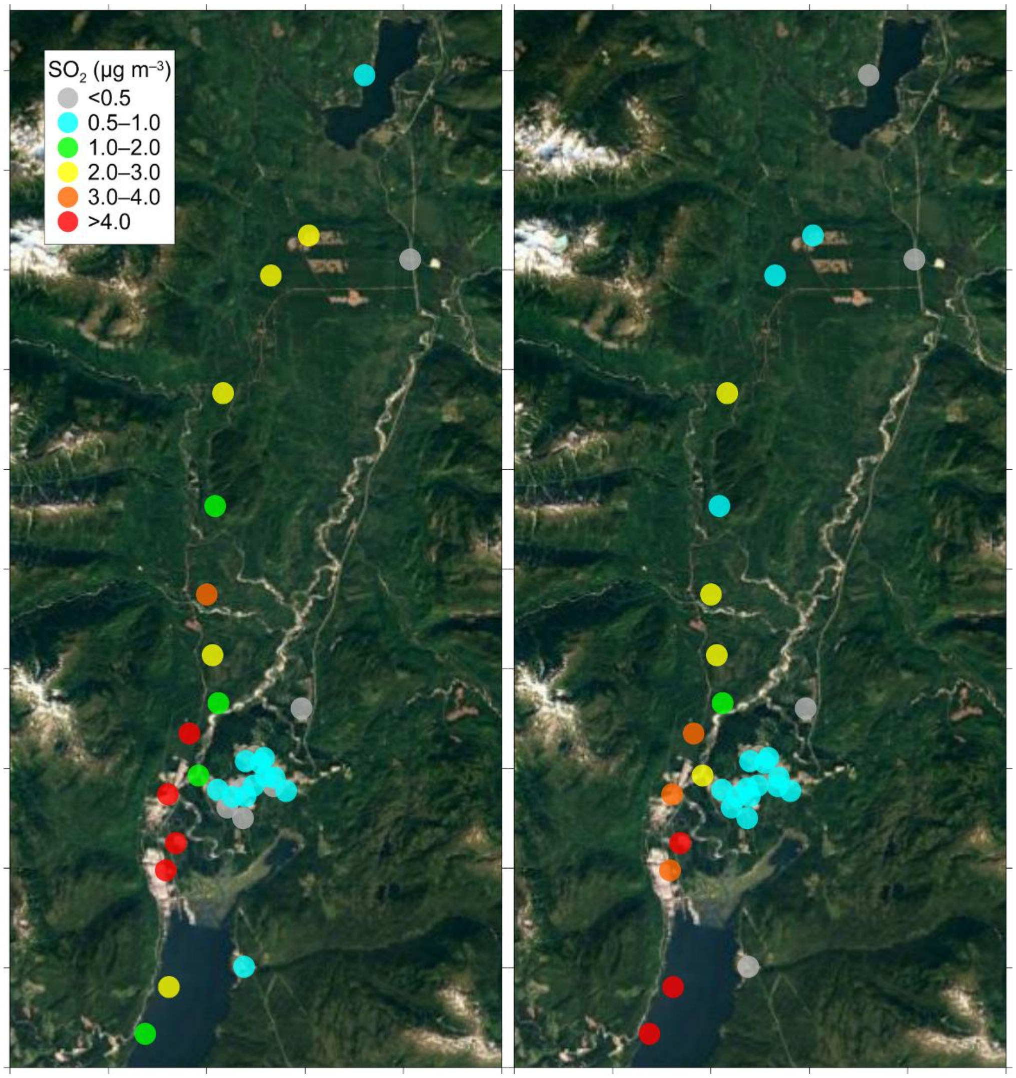


Figure 1. Average atmospheric sulphur dioxide (SO_2) concentration (µg m^{-3} [= ppb × 2.62]) during June–August (left) and August–October (right) 2016 in the Kitimat Valley and urban passive

diffusive monitoring networks. Note: monthly exposures under the Kitimat urban network started mid-July 2016. For further details on passive samplers see: IVL: www.diffusivesampling.ivl.se.

Figure 2. Average atmospheric sulphur dioxide (SO_2) concentration during June–October 2016 (average of three to four monthly exposures) in the Kitimat valley and urban passive diffusive monitoring networks. The image is zoomed-in and centered on the Kitimat urban network; in addition, wind rose plots during the same period are shown for Haul Road (latitude: 54.02919, longitude: –128.70269), Riverlodge (latitude: 54.05389, longitude: –128.67144) and Whitesail (latitude: 54.06691, longitude: –128.63913) meteorological stations. Note: the dominant wind direction explains the low atmospheric SO_2 measured in the urban area.

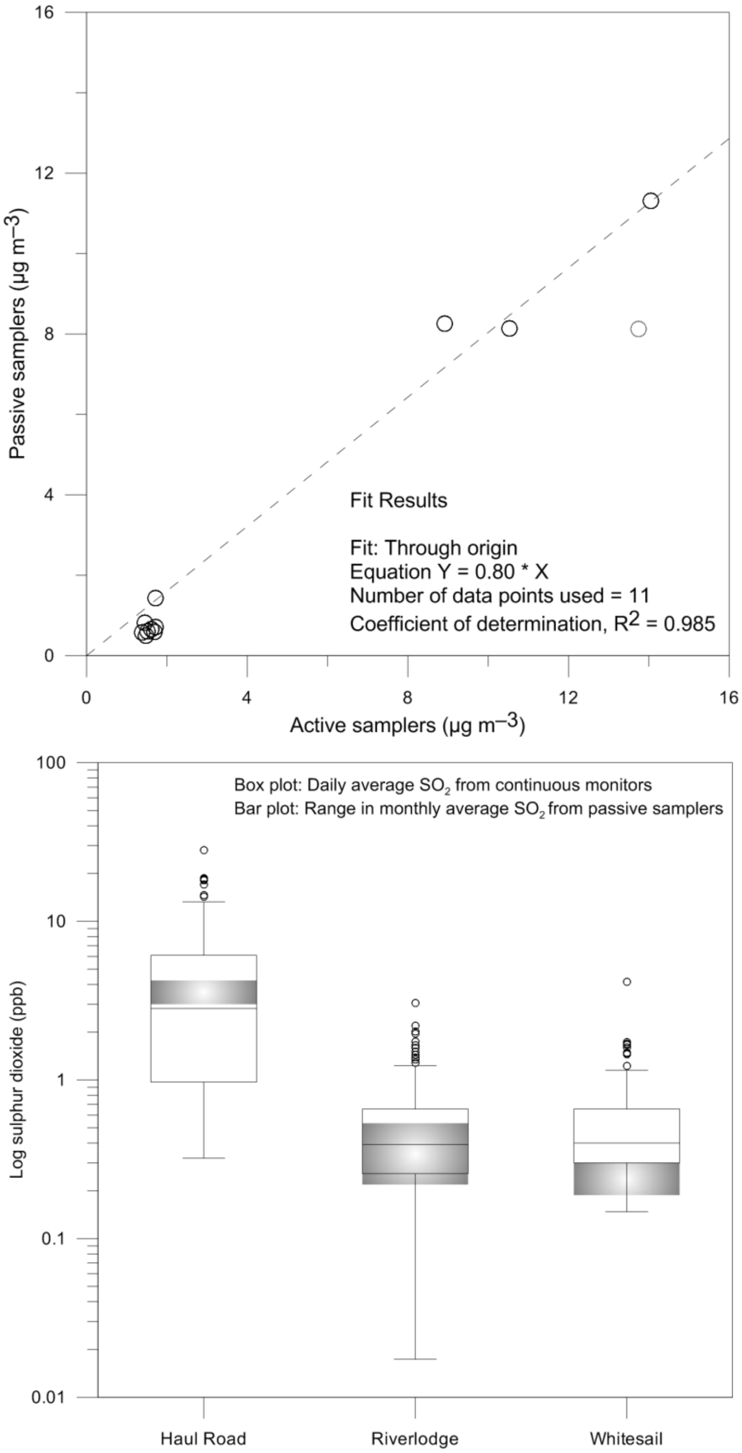


Figure 3. Comparison of IVL passive diffusive samplers for sulphur dioxide (SO_2) against continuous measurements (µg m–3) at Haul Road, Riverlodge and Whitesail during 22 June–13 October 2016. Passive samplers were exposed at each station for four weeks (see Appendix A for exposure dates). The scatter plot (upper) includes a linear regression of active against passive (R2 = 0.98). However, passive SO_2 observations are lower than active, notably at Riverlodge and Whitesail (as show in the scatter [upper] and bar [lower] plots).

4 Conclusion

The 2016 results demonstrate the ability of the passive samplers to map out the plume path along the Kitimat Valley; as such, it is recommended that deployments during 2017 attempt to further define the width and extent of the SO_2 plume.

The low atmospheric SO_2 concentrations at Riverlodge and Whitesail were a challenge for the IVL samplers. As such, it is recommended that a larger number of replicates are deployed at the ambient stations to allow for a more thorough assessment / calibration of passive samplers against the active measurements.

In summary, the results from the 2016 network confirm that passive samplers can be used 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.

5 Literature Cited

Tamburello, N. and C.A.D. Alexander. 2016. Kitimat Air Quality Monitoring Workshop: Optimization of the Ambient Air Quality Monitoring Network. Report to Rio Tinto. Kitimat, B.C. 214 pp. + appendices.

Technical Memo P01: Passive Diffusive Sampler Network: 2011–2012 March 2015. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2013 and 2014 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

Technical Memo P03: Passive Diffusive Sampler Network: 2015 Pilot Study Results, April 2016. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2015 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

Appendix A.

Table A1. Location of passive diffusive sampler monitoring sites established and deployed during June–October (V and A sites) and July–October (U sites) 2016. Note: V denotes Valley, A denotes Ambient stations, and U denotes Urban sites. See Figures A1 and A2 for mapped site locations.

ID	Site Name	Latitude (decimal degrees)	Longitude (decimal degrees)	Elevation (m)
V00	HWY37 at Onion Lake Ski Trail	54.29532	–128.53650	241
V01	Onion Lake Ski Trail North	54.30437	–128.61655	223
V02	Wedeene Road West km 9	54.28593	–128.64471	197
V03	Mound TKTP92	54.23226	–128.67892	127
V04	ENSO	54.18131	–128.68178	112
V05	LNG Muster Station	54.14140	–128.68559	114
V06	Sand Pit	54.11443	–128.67961	70
V07	Wedeene at Powerline	54.09294	–128.67343	26
V08	Claque Mountain Trail at Powerline	54.07872	–128.69531	68
V09	Sand Hill at Powerline	54.05111	–128.71008	170
V10	Rifle Range	54.01693	–128.70958	43
V11	Bish Road 4.1 km	53.96473	–128.70387	35
V12	Bish Road Pullout 4	53.94320	–128.72061	114
A01	Haul Road station	54.02919	–128.70269	11
A02	Riverlodge station	54.05389	–128.67144	18
A03	Whitesail station	54.06691	–128.63913	94
A04	Lakelse Lake NADP station	54.37721	–128.57734	111
U01	Low Channel	54.04629	–128.66356	11
U02	Kitimat City Centre MAML	54.05507	–128.65199	30
U03	Nechako Elementary	54.05655	–128.62810	94
U04	Mount Elizabeth School	54.06028	–128.62775	94
U05	Cable Car residential area	54.09192	–128.60854	50
U06	Kitimat General Hospital	54.05146	–128.64951	19
U07	Blueberry Street	54.04179	–128.65115	12
U08	Anderson Street	54.06731	–128.65057	92
U09	Fulmar Street	54.06102	–128.63463	88
U10	Kitimat Valley Institute	54.06897	–128.63620	98
U11	Kitimat City High	54.05635	–128.64391	86
U12	Industrial area Kitimat Hotel	54.05997	–128.68704	2
U13	St. Anthony's Elementary	54.05471	–128.61835	92
U14	Kildala Elementary	54.05101	–128.65961	16
U15	Haisla Nation Council	53.97498	–128.64581	5

Table A2. Results of the passive diffusive sampler monitoring network for June–October 2016. Atmospheric sulphur dioxide concentrations (µg m–3) are presented for each exposure (E01–E04), the average (AVE) and relative standard deviation (COV) between the four exposures is presented; in addition the average for the first two (JJA: June–July–August) and second two (ASO: August–September–October) exposures is also shown. See Table A1 for site locations and Figure A1 for map of average concentrations over the four exposures.

ID	E01	E02	E03	E04	AVE	COV	JJA	ASO
	(µg m^{-3})					(%)	(µg m^{-3})	
V00		0.366	0.299	0.368	0.34	11.4	0.366	0.334
V01	3.197	1.995	0.896	1.095	1.80	58.4	2.596	0.996
V02	2.316	1.890	1.089	0.590	1.47	52.8	2.103	0.840
V03		4.698	2.342	1.920	2.99	50.1	2.374	2.131
V04	1.310	1.297	0.466	0.597	0.92	48.9	1.304	0.532
V05	4.618	3.316	2.428	2.322	3.17	33.5	3.967	2.375
V06	2.141	2.662	1.742	2.543	2.27	18.4	2.402	2.142
V07	1.406	1.098	1.455	1.459	1.35	12.7	1.252	1.457
V08	4.308	3.850	3.842	3.763	3.94	6.3	4.079	3.803
V09	5.907	5.569	2.729	4.532	4.68	30.5	5.738	3.630
V10	10.009	10.814	3.812	3.875	7.13	53.4	10.411	3.844
V11	1.424	2.888	5.526	20.300	7.53	115.2	2.156	12.913
V12	0.965	2.304	4.683	11.894	4.96	98.2	1.635	8.289
A01	8.006	11.179	7.981	7.957	8.78	18.2	9.593	7.969
A02	0.576	0.650	1.406	0.590	0.81	49.9	0.613	0.998
A03	0.497	0.586	0.700	0.791	0.64	20.0	0.542	0.745
A04	0.844	0.674	0.399	0.535	0.61	31.1	0.759	0.467
U01		0.422	0.785	0.649	0.62	29.7	0.422	0.717
U02		0.484	0.633	0.693	0.60	17.8	0.484	0.663
U03		0.471	0.602	0.685	0.59	18.4	0.471	0.644
U04		0.535	0.531	0.647	0.57	11.5	0.535	0.589
U05		0.264	0.266	0.395	0.31	24.3	0.264	0.331
U06		0.645	0.643	0.907	0.73	20.8	0.645	0.775
U07		0.409	0.694	0.539	0.55	26.1	0.409	0.617
U08		0.594	0.909	0.768	0.76	20.8	0.594	0.839
U09		0.519			0.52		0.519	
U10		0.512	0.827	0.604	0.65	25.0	0.512	0.716
U11		0.603	0.771	0.728	0.70	12.4	0.603	0.749
U12		1.171	2.454	2.705	2.11	39.0	1.171	2.580
U13		0.832	0.562	0.617	0.67	21.3	0.832	0.590
U14		0.562	0.846	0.642	0.68	21.4	0.562	0.744
U15		0.512	0.286	0.610	0.47	35.4	0.512	0.448

E01 22 June to 20 July 2016
E02 20 July to 19 August 2016
E03 19 August to 13 September 2016
E04 13 September to 13 October 2016

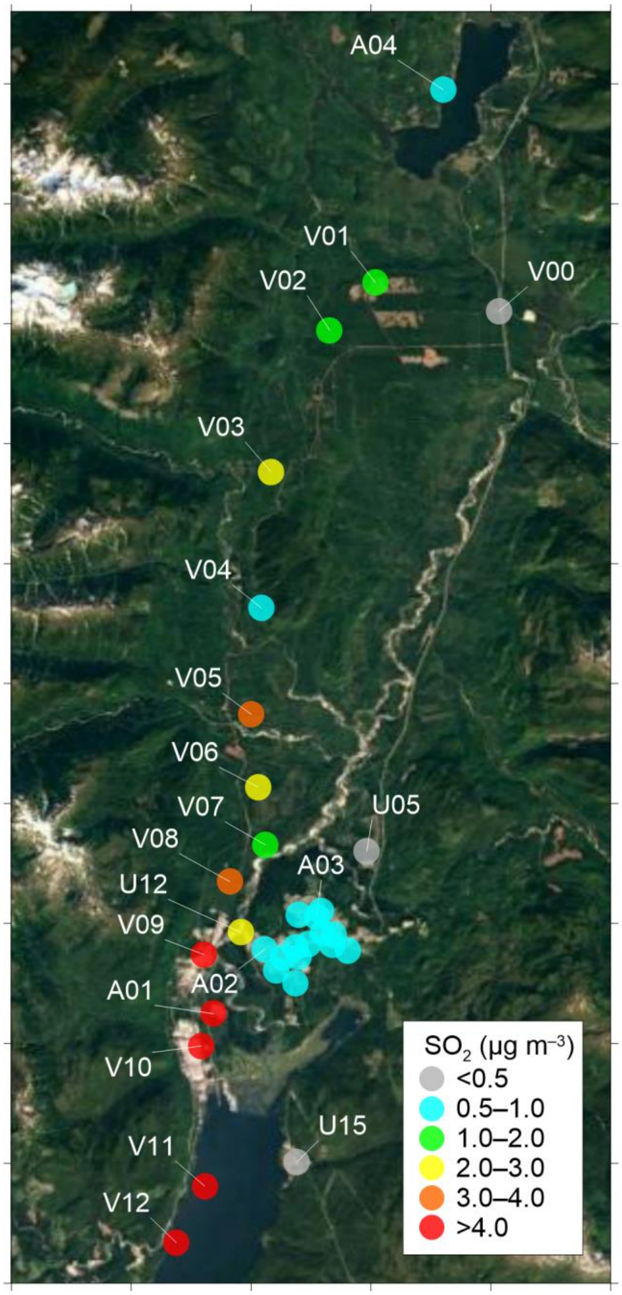


Figure A1. Average atmospheric sulphur dioxide (SO2) concentration (µg m^{-3} [= ppb × 2.62]) during June–October 2016 (average of three to four monthly exposures) in the Kitimat valley and urban passive diffusive monitoring networks (Site IDs are shown for the Kitimat valley network, see Figure A2 for remaining sites). Note: monthly exposures under the Kitimat valley network started mid-June 2016, compared with the urban network, which started mid-July 2016. For further details on passive samplers see: IVL: www.diffusivesampling.ivl.se.

Figure A2. Site locations and IDs for the Kitimat urban passive sampler network (see Table A2 for further details on site locations). Note: monthly exposures under the urban network started mid-July 2016. For further details on passive samplers see: IVL: www.diffusivesampling.ivl.se.

Table A3. Analysis of replicated passive diffusive sampler deployments during exposures 1 to 4. The average and the percent difference between the two replicates are presented. Replicate exposures with a difference greater than 25% are highlighted. See Table A1 for a description of the Site ID (SID).

Exposure	SID	Sampler A	Sampler B (μg m^{-3})	Average	Difference %
1	A04	0.90	0.78	0.84	14.3
1	V02	2.53	2.10	2.32	18.3
1	V07	1.43	1.38	1.41	3.8
1	V09	5.78	6.03	5.91	4.2
1	V11	1.48	1.37	1.42	7.7
2	A01	11.24	11.12	11.18	1.1
2	U01	0.43	0.41	0.42	4.0
2	U02	0.43	0.54	0.48	22.3
2	U06	0.65	0.65	0.65	0.0
2	U07	0.38	0.44	0.41	14.2
2	U12	1.35	0.99	1.17	30.3
2	V03	6.45	2.94	4.70	74.7
2	V08	3.78	3.92	3.85	3.9
2	V10	11.22	10.40	10.81	7.6
2	V12	2.10	2.51	2.30	17.6
3	A03	0.60	0.80	0.70	28.2
3	U03	0.54	0.66	0.60	20.3
3	U11	0.70	0.84	0.77	17.3
3	U13	0.56	0.56	0.56	0.0
3	U14	0.91	0.79	0.85	14.4
3	V00	0.30	0.30	0.30	0.0
3	V04	0.68	0.26	0.47	90.1
3	V09	2.00	3.45	2.73	53.2
3	V11	4.74	6.31	5.53	28.3
4	A01	8.25	7.67	7.96	7.3
4	U04	0.72	0.57	0.65	22.4
4	U05	0.38	0.41	0.40	8.6
4	U10	0.59	0.62	0.60	4.3
4	U15	0.63	0.59	0.61	5.6
4	V01	1.11	1.08	1.10	3.1
4	V05	2.17	2.48	2.32	13.2
4	V06	2.36	2.73	2.54	14.7
4	V12	11.59	12.20	11.89	5.1

E01 22 June to 20 July 2016
E02 20 July to 19 August 2016
E03 19 August to 13 September 2016
E04 13 September to 13 October 2016

Rio Tinto

KMP SO_2 EEM Program – Technical Memo P05

Atmospheric Sulphur Dioxide
Passive Diffusive Sampler Network: 2017 Results

June 2018

DRAFT

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

1 Overview

During 2017, the sulphur dioxide (SO_2) passive diffusive sampler network in the Kitimat Valley began monitoring on 09 June and finished on 26 October, following (approximately) four one-month exposures. The Wedeene Road was closed during the scheduled September sampler change-over, owing to heavy rains, resulting in a 78 day exposure. Further closures on Bish Road delayed collection for sites V11, V12 and V13 until 14 November, resulting in a 97 day exposure. Nonetheless, passive samplers appeared to have performed well, showing similar results to 2016.

The Kitimat Urban SO_2 passive diffusive sampler network was initially to be replaced by a multi-season (year long) study. However, this was delayed until 2018. As such, the urban network was re-established on 10 July and finished on 11 October, following three one-month exposures.

This memo presents the results of the SO_2 passive diffusive samplers during 2017.

2 Study Design

The 2017 monitoring employed the same procedures as 2016, with only minor modifications to the total number of monitoring sites (see Appendix A Table A1); the Valley network added four new sites and decommissioned one (total of 20 sites), and the Urban network was reduced by two sites (total of 13 sites). Sites V04B and V07B were added to the Valley network to assess low and high concentrations observed during 2016, V13 was added to Bish Road to extend the network further south, and V14 (Kitimat Service Centre) was moved from the Urban network (originally U12 in 2016). Sites V00 (HWY37) and U15 (Kitamaat) were removed as they provided limited information (See Appendix A Figure A1 and A2). During 2017, there were 33 monitoring sites with 99 valid sample exposures across both networks, with duplicate samplers deployed >30% of the time.

3 Results

The observed data showed elevated atmospheric SO_2 along the plume path (a transect of approximately 45–50 km; Figure 1 and Appendix Table A2 and Figure A1); notably during June–August plume concentrations were high north of Rio Tinto (concentrations > 10 $\mu g\ m^{-3}$ (> 3ppb) were observed at the Rife Range monitoring site), and during August–October higher concentrations were observed south of Rio Tinto (concentrations > 18 $\mu g\ m^{-3}$ (> 7 ppb) were observed at Bish Road).

In contrast, all monthly exposures under the urban network were consistently < 1.3 $\mu g\ m^{-3}$ (Figure 1). Nonetheless, average air concentrations during 2017 across the Urban network increased by about 30% compared with 2016 observations. Similarly, the average air concentrations during 2017 across the Valley network increased by > 35% compared with 2016 observations (see Technical Memo P04: Passive Diffusive Sampler Network: 2016 Results)

DRAFT

The concentration of SO_2 measured by passive samplers was also compared to the active observations at three ambient stations to evaluate sampler performance (Haul Road, Riverlodge and Whitesail; summarised to coincide with the monthly passive sampler exposure periods). In general, there was good correspondence between passive and active ($R^2 = 0.99$); however, the one-to-one regression slope suggests that passive samplers represented < 80% of the SO_2 concentrations reported by the active samplers (see Figure 2). This difference is similar to the variation between duplicate sampler exposures, i.e., on average there was ~11% variation between duplicate samplers (see Appendix Table A3). Moreover, the comparison against the active stations suggests a larger deviation at stations with low atmospheric SO_2 concentrations (see Whitesail in Figure).

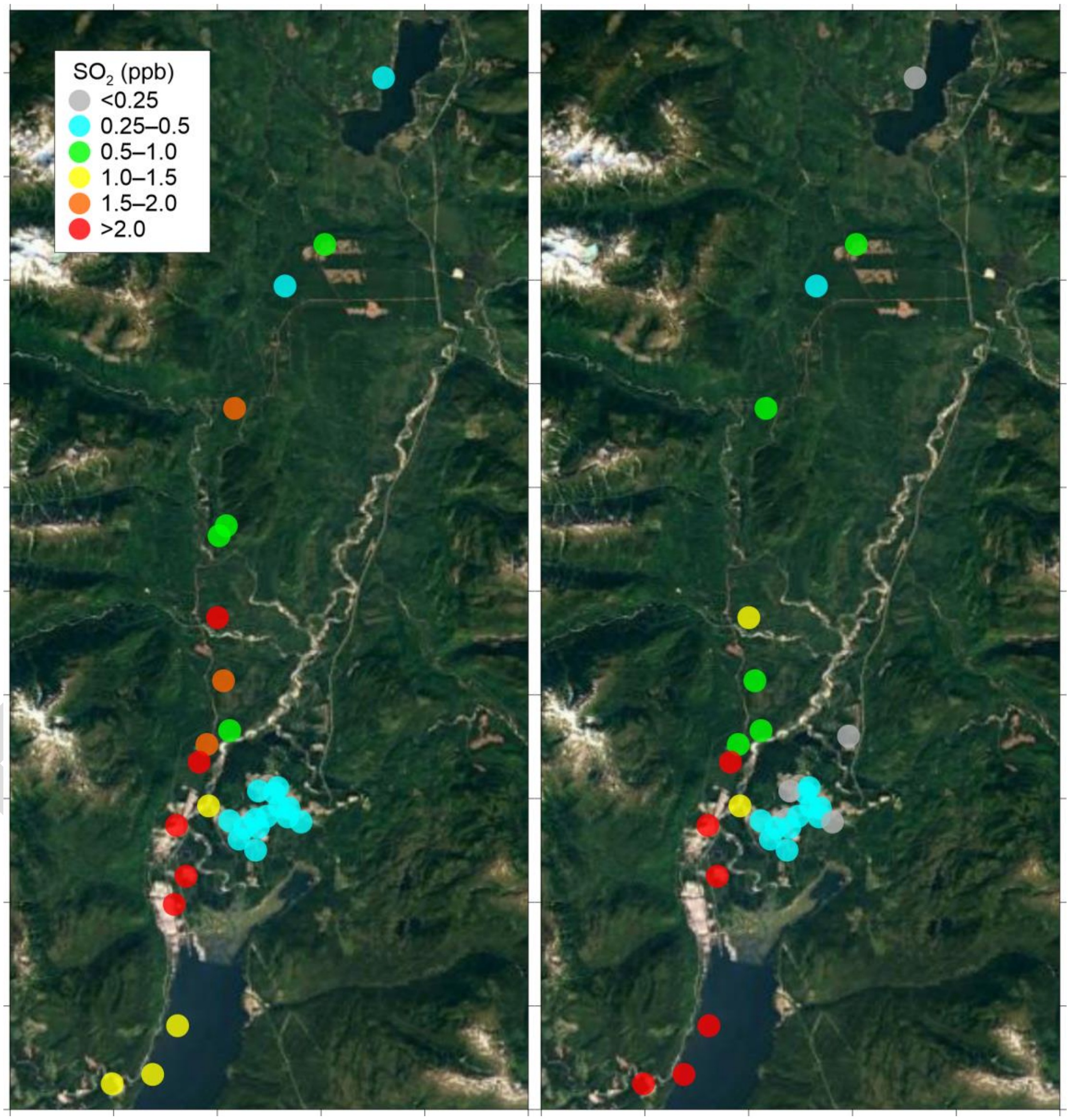


Figure 1. Average atmospheric sulphur dioxide (SO_2) concentration during June–August (left) and August–October (right) 2017 in the Kitimat Valley and Urban passive diffusive monitoring networks (ppb [= µg m^{-3} ÷ 2.62]). Note: monthly exposures under the Kitimat urban network started 10 July during 2017.

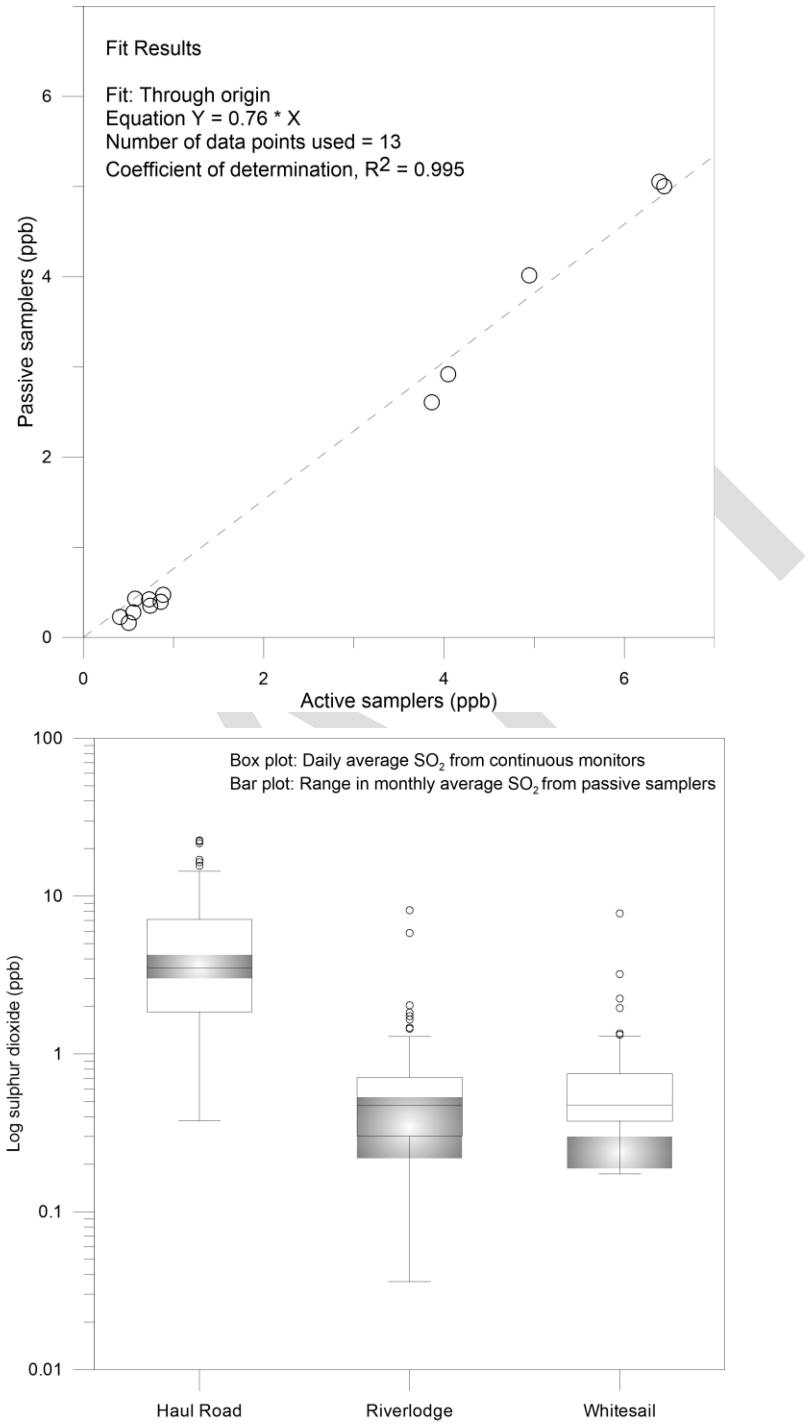


Figure 2. Comparison of IVL passive diffusive samplers for sulphur dioxide (SO_2) against continuous measurements (µg m^{-3}) at Haul Road, Riverlodge and Whitesail during 09 June–27 October 2017. Passive samplers were exposed at each station for one month (see Appendix A for exposure dates). The scatter plot (upper) includes a linear regression of active against passive ($R^2 = 0.99$). However, passive SO_2 observations are lower than active at Riverlodge and Whitesail (as show in the scatter [upper] and bar [lower] plots).

4 Conclusion

The 2017 results demonstrate a similar spatial pattern in SO_2 compared with 2016; however, atmospheric concentrations have increased by > 30% across all sites in 2017 during the same monitoring period.

In summary, the results from the 2017 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 2018.

5 Literature Cited

Technical Memo P04: Passive Diffusive Sampler Network: 2016 Results, March 2017. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2015 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

DRAFT

DRAFT

Appendix A.

Table A1. Location of passive diffusive sampler monitoring sites established and deployed during June–October (V and A sites) and July–October (U sites) 2017. Note: V denotes Valley, A denotes Ambient stations, and U denotes Urban sites. See Figures A1 and A2 for mapped site locations.

ID	Site Name	Latitude	Longitude	Elevation (m)
		(decimal degrees)		
V01	Onion Lake Ski Trail North	54.3044	-128.6166	215
V02	Wedeene Road West km 9	54.2859	-128.6447	197
V03	Mound TKTP92	54.2323	-128.6789	127
V04	ENSO north	54.1813	-128.6818	94
V04B	ENSO south	54.1769	-128.6869	109
V05	LNG Muster Station	54.1414	-128.6856	114
V06	Sand Pit	54.1144	-128.6796	67
V07	Wedeene at Powerline	54.0929	-128.6734	26
V07B	Gravel Pit road at Powerline	54.0865	-128.6899	73
V08	Claque Mountain Trail at Powerline	54.0787	-128.6953	68
V09	Sand Hill at Powerline	54.0511	-128.7101	156
V10	Rifle Range	54.0169	-128.7096	35
V11	Bish Road 4.1 km	53.9647	-128.7039	40
V12	Bish Road Pullout 4	53.9432	-128.7206	114
V13	Bish Road at Chevron LNG	53.9383	-128.7501	76
V14	Industrial area Kitimat Hotel	54.0600	-128.6870	2
A01	Haul Road station	54.0293	-128.7019	10
A02	Riverlodge station	54.0540	-128.6710	17
A03	Whitesail station	54.0669	-128.6391	92
A04	Lakelse Lake NADP station	54.3772	-128.5773	112
U01	Low Channel	54.0463	-128.6636	11
U02	Kitimat City Centre MAML	54.0551	-128.6520	30
U03	Nechako Elementary	54.0566	-128.6281	94
U04	Mount Elizabeth School	54.0603	-128.6278	94
U05	Cable Car residential area	54.0919	-128.6085	50
U06	Kitimat General Hospital	54.0515	-128.6495	19
U07	Blueberry Street	54.0418	-128.6512	12
U08	Anderson Street	54.0673	-128.6506	92
U09	Fulmar Street	54.0610	-128.6346	88
U10	Kitimat Valley Institute	54.0690	-128.6362	98
U11	Kitimat City High	54.0564	-128.6439	86
U13	St. Anthony's Elementary	54.0547	-128.6184	92
U14	Kildala Elementary	54.0510	-128.6596	16

DRAFT

Table A2. Results of the passive diffusive sampler monitoring network for June–October 2017. Atmospheric sulphur dioxide concentrations (µg m^{-3} [= ppb × 2.62]) are presented for each exposure (E01–E04), the average (AVE) and relative standard deviation (COV) between the four exposures is presented; in addition, the averages for the first two (JJA: June–July–August) and second two (ASO: August–September–October) exposures are also shown. See Table A1 for site locations and Figure A1 for map of average concentrations over the four exposures.

ID	E01	E02	E03	E04	AVE	COV	JJA	ASO
			(µg m^{-3})			(%)	(µg m^{-3})	
V01	2.274	1.803	1.840		1.97	13.3	2.039	1.840
V02	0.312	1.834	1.211		1.12	68.4	1.073	1.211
V03	4.819	3.662	2.269		3.58	35.6	4.241	2.269
V04	2.442	1.652			2.05	27.3	2.047	
V04B	2.440	1.852			2.15	19.4	2.146	
V05	6.524	5.909	3.804		5.41	26.4	6.216	3.804
V06	5.114	4.678	1.891		3.89	44.9	4.896	1.891
V07	2.349	2.322	1.572		2.08	21.2	2.335	1.572
V07B	4.336	3.843	2.275		3.48	30.9	4.089	2.275
V08		6.927	5.440		6.18	17.0	6.927	5.440
V09	10.211	8.155	5.267		7.88	31.5	9.183	5.267
V10	11.748	9.052			10.40	18.3	10.400	
V11	1.774	3.512	18.453		7.91	115.9	2.643	18.453
V12	1.778	4.268	10.029		5.36	79.0	3.023	10.029
V13	2.275	3.946	10.282		5.50	76.8	3.111	10.282
V14	4.026	2.845	2.956		3.28	19.9	3.435	2.956
A01	13.744	7.032	13.558	8.054	10.73	28.8	10.388	10.806
A02	1.155	1.168	0.761	1.311	1.01	28.6	1.162	1.036
A03		0.955	0.456	1.090	0.83	40.1	0.955	0.773
A04	0.934	0.913	0.807	0.374	0.76	34.6	0.924	0.590
U01		1.227	0.603	0.903	0.91	34.3	1.227	0.753
U02		1.036	0.481	0.752	0.76	36.7	1.036	0.616
U03		0.956	0.547	0.802	0.77	26.9	0.956	0.674
U04		0.918	0.531	1.115	0.85	34.8	0.918	0.823
U05			0.195	0.458	0.33	56.9		0.327
U06		1.051	0.616	0.961	0.88	26.2	1.051	0.789
U07		1.075	0.565	0.785	0.81	31.7	1.075	0.675
U08		1.173	0.467	0.637	0.76	48.5	1.173	0.552
U09		1.079	0.583	0.951	0.87	29.6	1.079	0.767
U10		0.877	0.477	0.976	0.78	34.0	0.877	0.726
U11		1.156	0.528	1.113	0.93	37.6	1.156	0.821
U13		0.856	0.481	0.813	0.72	28.7	0.856	0.647
U14		1.198	0.645	0.823	0.89	31.8	1.198	0.734

E01 09 June to 10 July 2017 | Valley and Ambient only
E02 10 July to 09 August 2017
E03 U: 09 August to 13 September 2017 | V: 09 August to 26 October 2017[1]
E04 13 September to 11 October 2017 | Urban and Ambient only
E05 11 October to 26 October 2017 | A01 and A02 only (data shown in Table A3)

---

[1] E03 09 August to 14 November 2017 for V11, V12 and V13

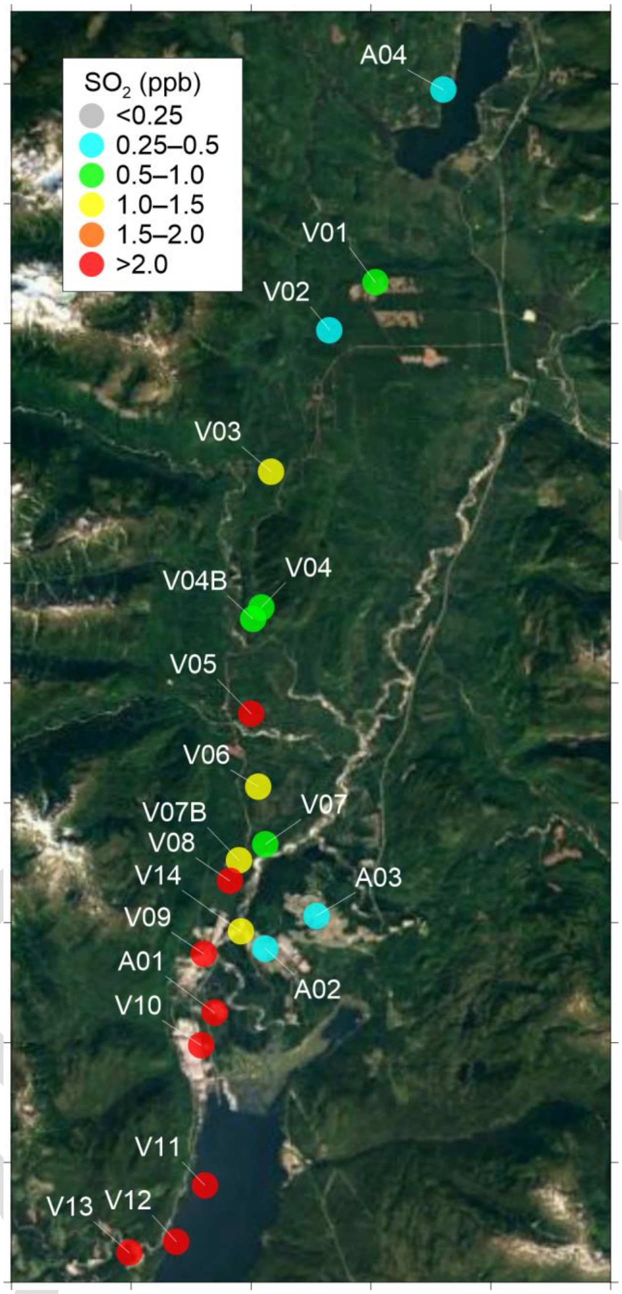


Figure A1. Average atmospheric sulphur dioxide (SO_2) concentration (ppb = [µg m^{-3} ÷ 2.62]) during June–October 2017 (average of three or four monthly exposures) in the Kitimat valley (V) and ambient (A) passive diffusive monitoring networks. Site IDs are shown for the Kitimat valley network, see Figure A2 for remaining sites.

Figure A2. 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.

DRAFT

Table A3. Analysis of replicated passive diffusive sampler deployments during exposures 1 to 5. The average and the percent difference between the two replicates are presented. Replicate exposures with a difference greater than 25% are highlighted. See Table A1 for a description of the Site ID (SID).

Exposure	SID	Sampler A	Sampler B	Average	Difference
			($\mu g\ m^{-3}$)		%
1	A02	1.18	1.13	1.16	3.7
1	A04	1.06	0.81	0.93	26.1
1	V03	5.30	4.34	4.82	20.0
1	V04B	2.39	2.50	2.44	4.5
1	V07B	3.95	4.72	4.34	17.9
1	V13	2.06	2.49	2.28	19.3
2	A03	0.95	0.96	0.95	1.9
2	A04	0.92	0.91	0.91	1.8
2	U03	0.96	0.95	0.96	1.0
2	U11	1.13	1.18	1.16	3.6
2	U14	1.26	1.14	1.20	9.7
2	V04	1.75	1.56	1.65	11.6
2	V07	2.12	2.52	2.32	17.3
2	V09	7.01	9.30	8.16	28.1
2	V12	4.26	4.27	4.27	0.3
3	A01	12.19	14.93	13.56	20.2
3	A02	0.76	0.76	0.76	0.6
3	A03	0.47	0.44	0.46	7.5
3	A04	0.81	0.80	0.81	1.2
3	U01	0.58	0.62	0.60	7.4
3	U04	0.52	0.54	0.53	2.9
3	U05	0.20	0.19	0.20	4.5
3	U09	0.63	0.54	0.58	16.1
3	V02	1.12	1.30	1.21	14.8
3	V05	4.03	3.57	3.80	12.2
3	V11	19.33	17.58	18.45	9.5
3	V14	2.86	3.05	2.96	6.2
4	A01	7.79	8.32	8.05	6.5
4	A02	1.27	1.35	1.31	6.4
4	A03	1.00	1.18	1.09	15.9
4	A04	0.32	0.42	0.37	26.2
4	U02	0.72	0.79	0.75	8.9
5	A01	12.32	10.20	11.26	18.9
5	A02	0.52	0.77	0.64	39.4

E01 09 June to 10 July 2017
E02 10 July to 09 August 2017
E03 U: 09 August to 13 September 2017 | V: 09 August to 26 October 2017
E04 13 September to 11 October 2017
E05 11 October to 26 October 2017

DRAFT

RioTinto

KMP SO_2 EEM Program – Technical Memo D02

Atmospheric Sulphur Dioxide

Method for Estimating Dry Deposition: 2017 Update

(Update to 2016 Technical Memo D01)

June 2018

DRAFT

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

1 Overview

Under the Environmental Effects Monitoring (EEM) program, dry deposition of gaseous and particulate sulphur in the Kitimat valley will be estimated from empirical observations of gaseous sulphur dioxide (SO_2) and particulate sulphate (pSO_4^{2-}; see Technical Memo F01: Filter Pack Network for Particulate Sulphate) combined with modelled dry deposition velocities (V_d). The 'big-leaf' model developed by Environment and Climate Change Canada (ECCC: Zhang et al., (2001; 2003a; 2003b; Zhang and He, 2014) will be used to estimate region-specific V_d (see Technical Memo D01: Method for Estimating Dry Deposition).

This technical memo briefly describes the application of the V_d model in the Kitimat valley.

2 Deposition Velocity Model

The V_d model was obtained from ECCC as a FORTRON code (see Technical Memo D01: Method for Estimating Dry Deposition). This code has been compiled into a Windows executable program and verified, i.e., V_d have been modelled for 31 gaseous species and 3 particulate size classes for a range of land cover types using 'test' meteorological data.

The model requires two sets of input data, site specific variables (such as latitude and land cover) and meteorological forcing variables. While there are several meteorological stations in the Kitimat valley, only one station, i.e., Terrace A (YXT), measures and archives all required model inputs (Table 1). As such, a 'region-specific V_d' will be modelled using hourly data since 2000 from the Terrace A meteorological station, and combined with site-specific observations of gaseous SO_2 (obtained from passive samplers and active monitors) and particulate SO_4^{2-} (obtained from filter packs) to estimate dry deposition.

The V_d model requires thirteen meteorological forcing variables on an hourly resolution for the period of interest (Table 1). While the majority of these variables are available online (URL: climate.weather.gc.ca), several variable, i.e., solar radiation, snow depth and cloud cover, can only be obtained by request from Environment Canada's climate archive (at Climate West). Hourly (and daily) observations for all required variables (Table 1) have been requested from 2000 onwards for the Terrace A station.

Table 1. Meteorological variables required to model deposition velocity, their online availability (URL: climate.weather.gc.ca) and climate archive measurement codes.

Parameter (unit)	Online	Measurement code
Temperature (K)	Y	078 (HLY01)
Windspeed (m s^{-1})	Y	076 (HLY01)
RH fraction (0–1)	Y	080 (HLY01)
Solar irradiance (w m^{-2})		133 (HLY10) until 2002, and 179 (DLY02)
Precipitation rate (mm hr^{-1})	Y	123 (HLY03)
Surface pressure (mb)	Y	077 (HLY01)
Snow depth (cm)		275 (HLY01)
Cloud fraction (0–1)		082 (HLY01)

DRAFT

3 Model Application

The 'big-leaf' model developed by ECCC in combination with hourly meteorological data from the Terrace A station will be used to model gaseous and particulate deposition velocities. These estimates of region-specific V_d will be combined with site-specific observations of gaseous SO_2 (from active and passive samplers) and particulate SO_4^{2-} (from filter pack samplers) under the EEM to estimate dry deposition of sulphur in the Kitimat valley.

The *Terrace A station* is the only location within the Kitimat valley with the required meteorological data for the determination of dry deposition. Moreover, it *provides consistent long-term data since the 1970s, which is essential for the determination of historic hourly deposition velocities*. In the context of the EEM, historic refers to the estimation of dry deposition since 2012 to date. The installation of a new meteorological station will not meet this requirement; the Terrace A station is the only location that can provide consistent long-term data.

4 Literature Cited

Technical Memo F01: Filter Pack Measurements of Particulate Sulphate, June 2018. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2017 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

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

Zhang, L.M., S.L. Gong, J. Padro and L. Barrie. 2001. A size-segregated particle dry deposition scheme for an atmospheric aerosol module, Atmospheric Environment 35, 549–560.

Zhang L., M.D. Moran, P.A. Makar, J.R. Brook and S. Gong. 2002.Modelling gaseous dry deposition in AURAMS: a unified regional air-quality modelling system. Atmospheric Environment 36:3, 537–560.

Zhang, L., J.R. Brook and R.Vet. 2003a. A revised parameterization for gaseous dry deposition in air-quality models, Atmospheric Chemistry and Physics 3, 2067–2082.

Zhang, L., J.R. Brook and R. Vet. 2003b. Evaluation of a non-stomatal resistance parameterization for SO2 dry deposition. Atmospheric Environment, 37:21, 2941–2947.

Zhang, L. and Z. He. 2014. Technical Note: An empirical algorithm estimating dry deposition velocity of fine, coarse and giant particles. Atmospheric Chemistry and Physics 14, 3729–3737.

DRAFT

Rio Tinto

KMP SO_2 EEM Program – Technical Memo F01

Atmospheric Sulphur

Filter Pack Measurements of Particulate Sulphate

June 2018

DRAFT

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

1 Overview

The total deposition of atmospheric sulphur is an essential informative indictor under the Environmental Effects Monitoring (EEM) program (ESSA et al., 2014).

Total deposition refers to the deposition of both wet and dry atmospheric sulphur species. Dry deposition is derived from empirical observations of gaseous and particulate sulphur, i.e., sulphur dioxide (SO_2) and particulate sulphate (pSO_4^{2-}), respectively. Under the EEM, SO_2 and pSO_4^{2-} will be measured using a two-stage filter pack during several discrete campaigns throughout the Kitimat valley. These observations will be used to asses the dominance of pSO_4^{2-} in the region.

This technical memo briefly describes the measurement of pSO_4^{2-} in the Kitimat valley under the EEM during 2017.

2 Study Design

Measurements of particulate and gaseous sulphur can be made using a filter pack system, i.e., a filter holder with successive stages of filters connected to an air flow system (Figure 1). A two-stage filter pack consists of a membrane filter and a hydroxide impregnated filter; particulates are collected on the first filter, and gaseous pollutants on the second. The filter pack is protected from rain by a shelter (Figure 1). Filter pack systems are widely used as they provide reliable measurements of pSO_4^{2-} and SO_2, and are less demanding that alternative methods (NILU, 2001).

The two-stage filter holders were developed by the Norwegian Institute for Air Research (URL: www.innovationnilu.com). The first stage holds a 47 mm Teflon (PTFE) filter to capture particulates, and the second stage holds a 47 mm cellulose filter impregnated with potassium hydroxide to capture SO_2. The holder is connected to a diaphragm pump with a recommend flow rate of 15 L min^{-1} for daily sampling. The filter system, filter preparation, extraction and analysis are described in detail in the 'EMEP Manual for Sampling and Chemical Analysis' (NILU, 2001).

During June and October 2017, filter packs were deployed at Haul Road, Riverlodge, Whitesail and Lakelse Lake monitoring stations to measure daily concentrations of pSO_4^{2-} and SO_2. Site selection was limited to locations with access to power; during 10–20 June, one filter pack was rotated between three locations (Haul Road, Riverlodge, and Lakelse Lake). However, during 21–27 October 2017, four filter packs were operated in parallel across the four stations (using pumps provided by WSP).

3 Results

A total of 29 filter pack measurements were carried during 2017; 9 measurements were carried out between 10–20 June, and 20 measurements between 21–27 October (see Appendix A Table A1). The PTFE filter (first stage) was analysed for range of particulate species including sulphate (SO_4^{2-}) and trace elements (aluminium [Al], lithium [Li], nickel [Ni] and vanadium [V]), and the impregnated filter (second stage) was analysed for major anions including SO_4^{2-} (as a measure of atmospheric SO_2).

Average SO_2 ranged from 0.5 to 10.6 µg m^{-3}, and pSO_4^{2-} ranged from 0.06 to 0.20 µg m^{-3} (Table 1). Atmospheric sulphur species (SO_2 and pSO_4^{2-}) showed the same gradient across the measurement locations; the highest average concentrations were observed at Haul Road and lowest at Lakelse Lake (measurements at Whitesail were carried out only during October, which was heavily influenced high rainfall volumes). To evaluate the performance (reliability) of the filter packs, daily measurements SO_2 (filter pack) were compared with continuous hourly measurements (average to daily observations) at the active monitoring stations (Figure 2). In general, there was good correspondence between filter pack and active daily measurements of SO_2 ($R^2 = 0.93$).

The oxidation of SO_2 to pSO_4^{2-}, which is a secondary pollutant, determines the lifetime of sulphur in the atmosphere. The relative mass ratio of pSO_4^{2-} to total atmospheric sulphur may be used as an indicator of the rate of conversion, e.g., sulphur conversion ratio (see Equation 1). The average sulphur conversion ratio (F_s) showed an opposite gradient to concentration; at Haul Road F_s = 2%, compared with 9% at Riverlodge and Whitesail, and 14% at Lakelse Lake (Table 1), which indicates that pSO_4^{2-} has a longer atmospheric lifetime than SO_2.

$$Sulphur\ conversion\ ratio\ (F_s) = \frac{pSO_4^{2-}}{SO_2 + pSO_4^{2-}} \qquad \text{(Equation 1)}$$

Average SO_2 and pSO_4^{2-} were strongly correlated (r = 0.92), similarly pSO_4^{2-} was strongly correlated to trace elements, e.g., Al (r = 0.91), Li (r = 0.97) and V (r = 0.92). The strong correlations suggest similar emission sources (Table 1).

Table 1. Average gaseous sulphur dioxide (SO_2), particulate sulphate (pSO_4^{2-}), sulphate conversion ratio (Fs), and particulate trace elements (aluminium [Al], lithium [Li], nickel [Ni] and vanadium [V]) during June and October 2017.

Site	n	SO_2	pSO_4^{2-}	F_s	Al	Li	Ni	V[€]
		µg m^{-3}		%	ng m^{-3}			
Haul Road	6	10.607	0.199	1.8	18.703	0.029	0.189	1.203
Riverlodge	9	1.178	0.120	9.2	3.794	0.019	0.083	0.079
Whitesail[$]	6	0.535	0.055	9.3	3.057	0.012	0.145	0.002
Lakelse Lake	8	0.586	0.092	13.6	2.853	0.012	0.089	0.099

[$] Whitesail only has October observations; [€] During October 2017 all observations of V were below detection at Lakelse Lake, and all but one were below detection at Whitesail (<DL set to 0.0005 ng m^{-3}).

4 Conclusion

Gaseous SO_2 and pSO_4^{2-} displayed a similar gradient across the measurement stations; the highest concentrations were observed at Haul Road and lowest at Lakelse Lake. However, sulphur conversion ratios (%) show an inverse relationship. ranging from 2% at Haul Road to 14% at Lakelse Lake indicating a longer atmospheric lifetime for pSO_4^{2-} compared to SO_2.

The 2017 results demonstrate the ability of the filter pack samplers to provide reliable measurements of particulate and gaseous air pollutants. Further measurement campaigns are

DRAFT

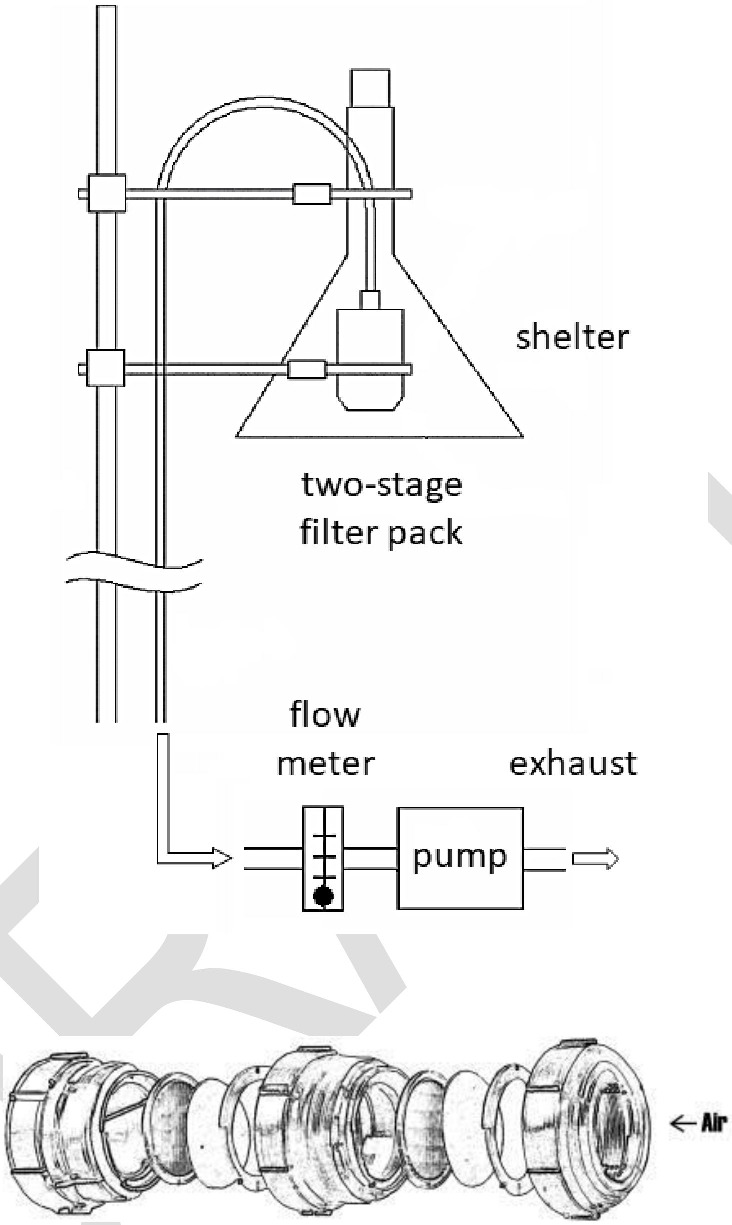
planned for February and June 2018; portable filter packs will be utilised during June 2018 to expand the measurements to seven sites across the Kitimat valley, with the objective to assess the sulphur conversion ratio along the plume path.

5 Literature Cited

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto BC Works, Kitimat, BC. 99 pp.

NILU 2001. EMEP manual for sampling and chemical analysis. Norwegian Institute for Air Research, EMEP/CCC-Report 1/95 (Revision: November 2001).

DRAFT



DRAFT

Figure 1. Upper panel: Filter pack sampling system, with NILU filter holder, shelter, inline flow meter and pump. Lower panel: Two-stage NILU filter holder showing an exploded view of the individual components (see Appendix A Figure A1 for details on holder components).

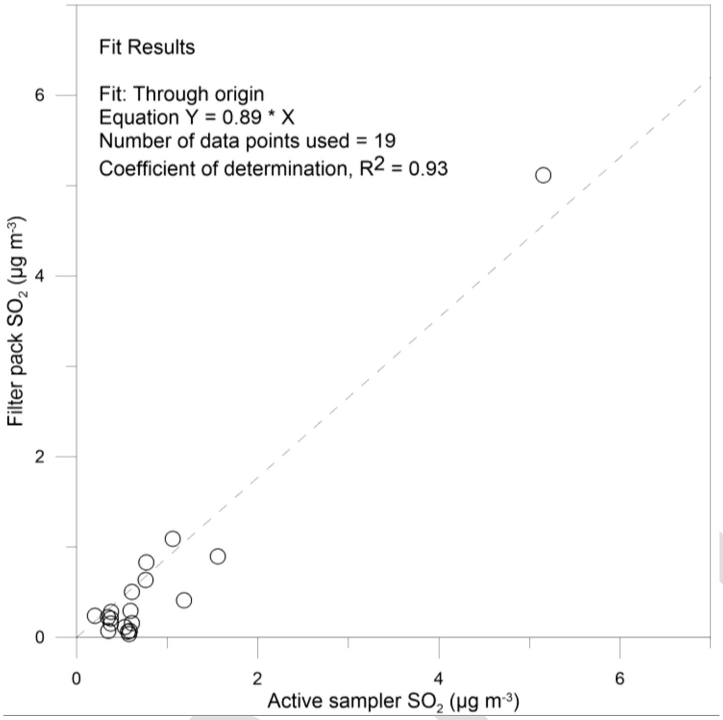


Figure 2. Comparison of active sulphur dioxide (SO_2) against filter pack measurements (µg m^{-3}) at Haul Road, Riverlodge and Whitesail during June and October 2017. Filter pack samplers were exposed at each station for one day (see Appendix A Table A1 for exposure dates). The scatter plot includes a linear regression of active against filter pack (R^2 = 0.93).

DRAFT

Appendix A.

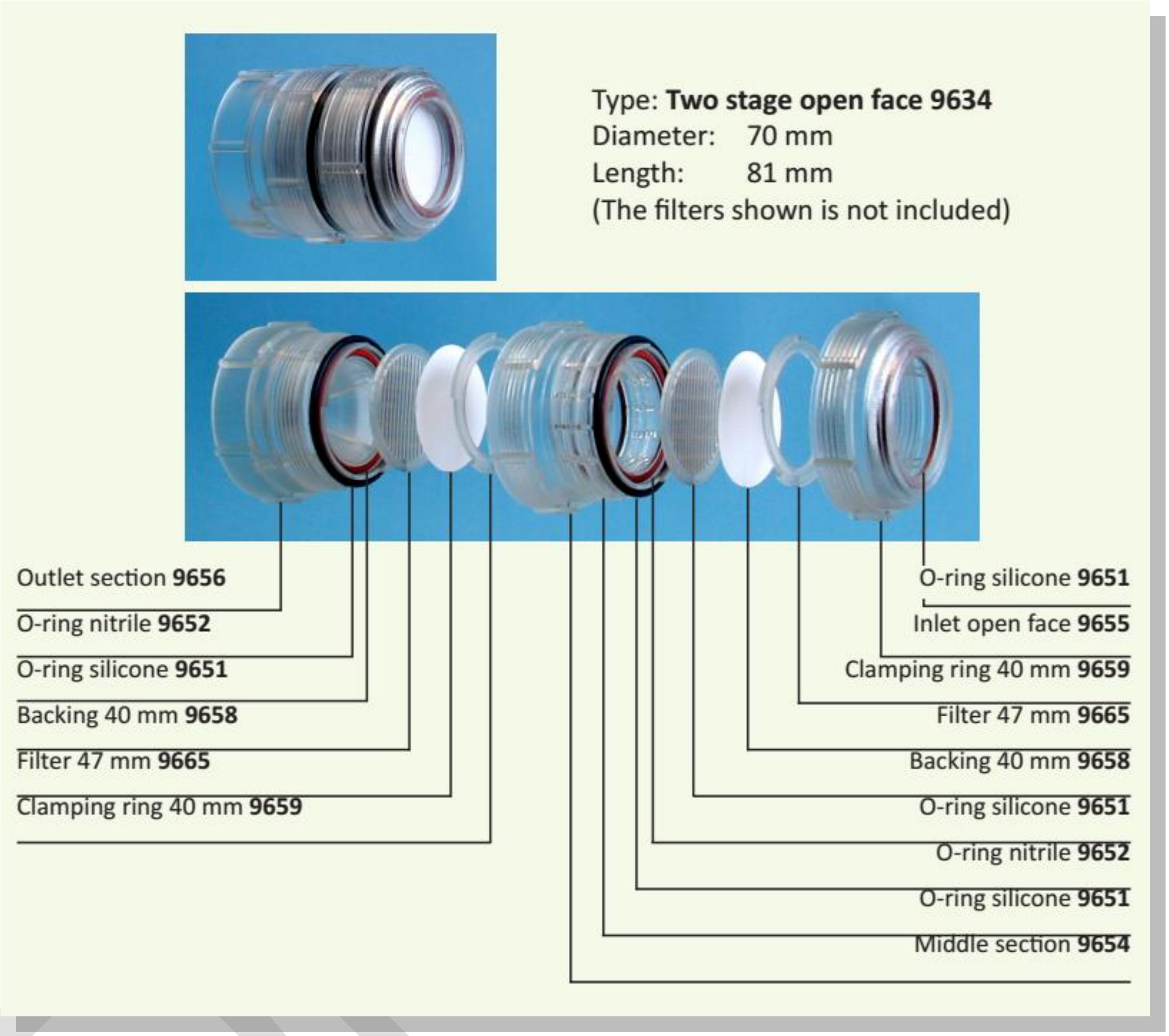


Figure A1. Two-stage open face NILU filter holder system (URL: www.innovationnilu.com).

Table A1. Daily concentrations (µg m^{-3}) of particulate sulphate (pSO_4^{2-}), gaseous sulphur dioxide (SO_2), and the sulphate conversion ratio (F_s) from filter pack measurements during June (n = 3) and October (n = 3–6) 2017.

Site	Start Date yyyy-mm-dd	pSO_4^{2-} µg m^{-3}	SO_2 µg m^{-3}	F_s ratio
Haul Road	2017-06-12	0.319	23.069	0.01
Haul Road	2017-06-13	0.254	14.431	0.02
Haul Road	2017-06-14	0.180	2.534	0.07
Haul Road	2017-10-24	0.230	22.119	0.01
Haul Road	2017-10-25	0.079	1.162	0.06
Haul Road	2017-10-26	0.130	0.327	0.28
Lakelse Lake	2017-06-10	0.134	0.958	0.12
Lakelse Lake	2017-06-18	0.285	1.164	0.20
Lakelse Lake	2017-06-19	0.237	1.112	0.18
Lakelse Lake	2017-10-21	.	0.248	.
Lakelse Lake	2017-10-22	0.059	0.253	0.19
Lakelse Lake	2017-10-23	0.008	0.451	0.02
Lakelse Lake	2017-10-24	.	0.339	.
Lakelse Lake	2017-10-25	.	0.159	.
Riverlodge	2017-06-15	0.116	0.686	0.14
Riverlodge	2017-06-16	0.221	0.801	0.22
Riverlodge	2017-06-17	0.256	3.080	0.08
Riverlodge	2017-10-21	0.050	0.637	0.07
Riverlodge	2017-10-22	0.190	0.591	0.24
Riverlodge	2017-10-23	0.094	0.439	0.18
Riverlodge	2017-10-24	0.036	1.800	0.02
Riverlodge	2017-10-25	0.114	2.353	0.05
Riverlodge	2017-10-26	.	0.215	.
Whitesail	2017-10-21	0.030	0.208	0.13
Whitesail	2017-10-22	0.136	0.833	0.14
Whitesail	2017-10-23	.	0.453	.
Whitesail	2017-10-24	0.012	0.183	0.06
Whitesail	2017-10-25	0.134	1.424	0.09
Whitesail	2017-10-26	0.014	0.106	0.11

DRAFT

RioTinto

KMP SO_2 EEM Program – Technical Memo S06

Long-term Soil Monitoring Plots

Plot Establishment: 2017 Update

(Update to 2016 Technical Memo S04)

March 2017

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

1 Overview

Under the Environmental Effects Monitoring (EEM) Program, long-term soil monitoring plots will address the observation-based KPI: ‘observed change in base cation pool over time’ through repeat sampling and analysis of soils for exchangeable base cations every five years (ESSA et al., 2014).

During October–December 2015 and June–July 2016, long-term soil monitoring plots were established at Coho Flats and at Lakelse Lake, Kitimat Valley, and the reference (background) plots were established at Kemano (far from the smelter emissions plume). This memo describes the establishment of the plots (i.e., plot locations and layout of plot design), the initial collection of soil, and processing of samples (i.e., drying and sieving) during 2015 and 2016. The monitoring plots were re-visited for soil bulk density sampling, and mapping of tree locations during June–July 2016. In addition, the background (control or reference) plots were established at Kemano. Chemical extraction (for exchangeable base cations and exchangeable acidity) was also carried out during 2016.

This memo (S06) updates the March 2016 ‘Long-term Soil Monitoring Plots— Plot Establishment’ memo (S04), with the new information on field sampling and soil analysis carried out during 2016, including the collection of soil bulk density samples, and mapping of tree locations at Coho Flats and Lakelse Lake, and the establishment (i.e., select locations and layout plot design) of the background (control or reference) plots at Kemano (including the initial collection of soil, bulk density samples, and mapping of tree locations).

2 Objective and Rationale

The objective of the long-term soil plots is to monitor changes in soil base cation pools over time through repeated sampling and analysis (every five years). The monitoring plots provide a framework for replicate random sampling of soils, allowing for the statistical assessment of changes between sampling campaigns.

Under the EEM Program, long-term soil monitoring plots will be established in near-field and far-field locations with respect to smelter emissions. In addition a background or reference plot will be established (remote from emissions sources outside the Kitimat Valley) to assess whether a change soil base cation pools (if observed) is causally related to the Kitimat Modernisation Project (KMP). Changes in soil exchangeable base cations will initially evaluated in the upper mineral soil (0–5 cm) between sampling periods. If a statistical change is detected, analysis will be carried out down the soil profile.

3 Plot Location and Design

During October–December 2015, near-field and far-field plots were established at Coho Flats (latitude: 54.07660, longitude: –128.65117) and Lakelse Lake (latitude: 54.37827, longitude: –128.57990), respectively, to reflect the gradient in atmospheric deposition, and during 2016 reference (or background) plots were established at Kemano (latitude: 53.53032, longitude: –127.97384; see Figure 1). The plots in the Kitimat Valley are located in close proximity to, or co-located with, the NADP atmospheric deposition monitoring stations at Haul Road and Lakelse Lake. At each location, primary and secondary (backup) plots were established within forest stands dominated by western Hemlock; secondary plots (located generally within 500 m of the primary plot) provide a backup or replacement to the primary plot if disturbed or destroyed within the lifetime of the monitoring program.

Each long-term soil plot is 32 m by 30 m in size and composed of twenty 8 m by 6 m sub-plots lettered A to T; the A sub-plot is oriented to the north-west corner of each plot (Figure 2). Each sub-plot is further divided into twelve 2 m by 2 m sampling grids (numbered 1 to 12); one numbered grid was randomly sampled from each lettered sub-plot at five depths: litter-fibric (LF), humic (H), and 0–5 cm, 5–15 cm, and 15–30 cm depths in the mineral soil (yielding a total of 100 soil samples for each plot, i.e., 5 soil samples by depth within each of the 20 lettered sub-plots). Every five years one numbered grid within each lettered sub-plot will be randomly sampled (note: individual numbered grids are sampled only once), allowing for a total of twelve sampling campaigns. During the twelve sampling campaigns, each numbered grids is sampled only once. The re-sampling of the primary plots at Coho Flats and Lakelse Lake are scheduled for summer 2018.

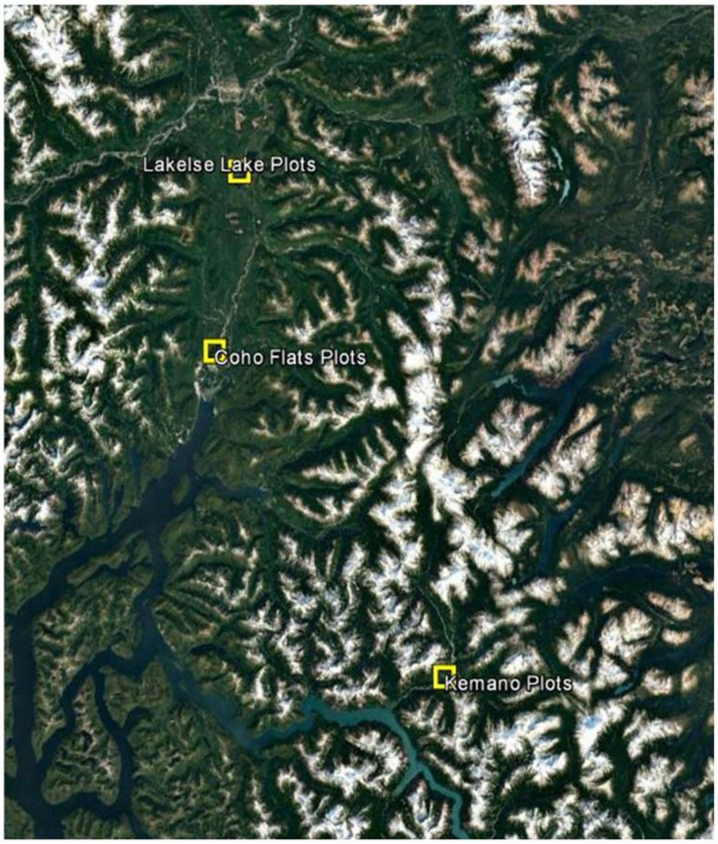


Figure 1. Location of long-term soil monitoring plots at Coho Flats (near-field) and Lakelse Lake (far-field), in the Kitimat Valley, and Kemano (reference). Note: primary and secondary [backup] plots were established at all three locations.

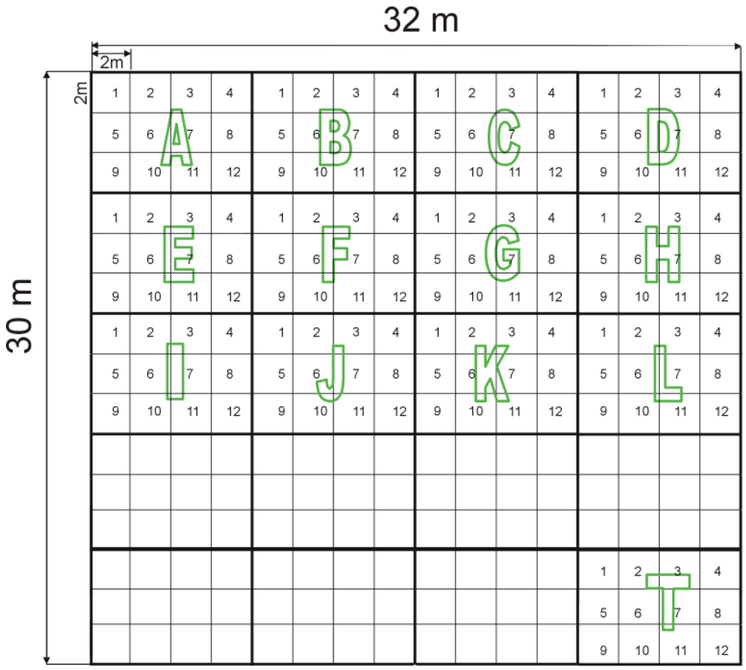


Figure 2. Long-term soil monitoring plot; the plot is divided into twenty 8 m by 6 m sub-plots, lettered A to T; each sub-plot is further divided into twelve 2 m by 2 m sampling grids, numbered 1 to 12. One numbered grid within each lettered sub-plot is randomly selected for sampling during each campaign, allowing for a total of 12 sampling events, with 20 samples per depth.

4 Plot Sampling and Analysis

During October–December 2015, long-term soil monitoring plots (primary and secondary) were established in forest stands dominated by Western Hemlock at Coho Flats and Lakelse Lake, Kitimat Valley (Figure 3). During June–July 2016, the reference long-term soil monitoring plots (primary and secondary) were established at Kemano (Figure 3). Within each plot, one numbered grid was randomly sampled from each lettered sub-plot (see Appendix A for a list of sample grids). In total ~360 mineral soil samples were collected during 2015 and 2016 (6 plots × 20 sub-plots × 3 soil depths). In addition, soil bulk density sampling and tree mapping were carried out at Kemano, and the plots at Lakelse Lake and Coho Flats were revisited to also collect soil samples for bulk density determination, and to map out tree species across all plots. In total ~360 bulk density soil core samples were collected during 2016 (6 plots × 20 sub-plots × 3 soil depths).

Soil samples from the first (2015) and second (2016) sampling campaign have been dried, sieved to < 2 mm and analysed for pH, organic matter content (estimated as % loss on ignition) and bulk density (Figure 4 and Table 1). There is a noticeable difference in organic matter content between depths in the mineral soil (i.e., there is a statistically significant decrease in organic matter between the 0–5 cm and the lower depths at Lakelse Lake, Figure 4) but not between primary and secondary plots (i.e., there is no statistical difference between the 0–5 cm at Lakelse Lake primary compared with the same depth in Lakelse Lake secondary). In contrast, there is no significnat differnce (decreases) in organic matter with depth at the Coho Flats primary plot (see Figure 4 and Table 1)

Tree species were mapped for all plots during 2016 (Figure 5). All primary plots are dominated by Western Hemlock (61% of plot DBH at Kemano, 44% at Lakelse Lake and 96% at Coho Flats;

Figure 5). The total number of trees (> 10 cm DBH) ranged from 47 (Coho Flats), 69 (Kemano) to 108 (Lakelse Lake).

During 2017, the 0–5 cm depth soil samples at the primary plots will be analyzed for exchangeable base cations, and exchangeable acidity (note: laboratory extractions were carried out during 2016, soils are awaiting analysis), and all soils (from the primary and secondary plots) will be archived.

Figure 3. The long-term soil monitoring plots are located at Lakelse Lake beside the NADP monitoring station (A), in a western Hemlock stand (primary plot is shown in B), and east of the Coho Flats Trail, Kitimat (primary plot is shown in C). The reference (or background) plot is located in Kemano (primary plot at Seekwyakin camp is shown in D).

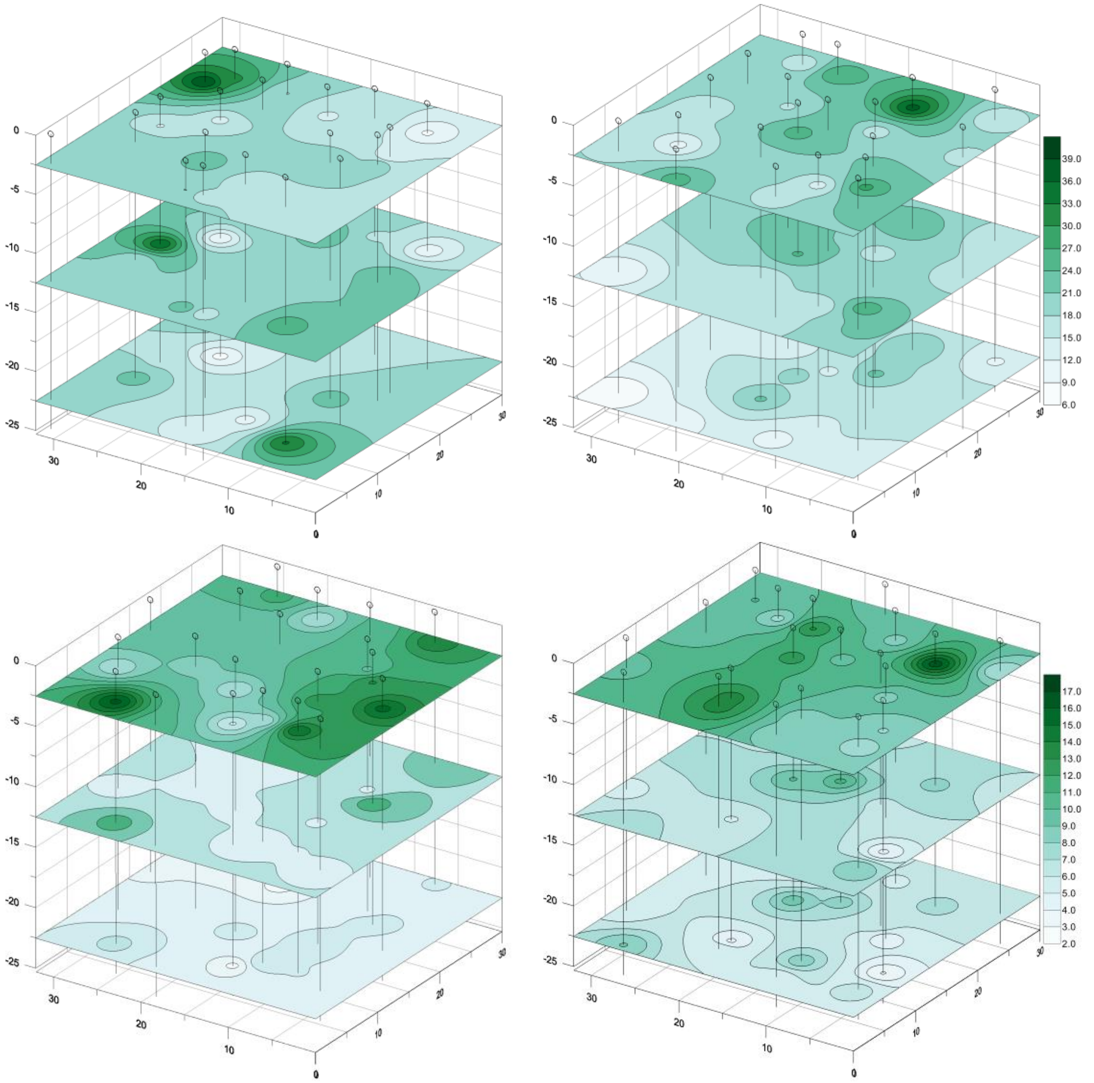


Figure 4. Three-dimensional representation of soil organic matter content (%) in the 0–5 cm, 5–15 cm, and 15–30 cm (mineral) soil depths at the primary (left) and secondary (right) long-term soil monitoring plots at Coho Flats (upper) and Lakelse Lake (lower). The vertical lines indicate the location of the soil sampling pits (n = 20 per plot, with soil sampling at three depths).

Table 1. Average soil data (n = 20 per soil depth) for primary and secondary plots at Coho Flats, Lakelse Lake and Kemano.

Soil Variable	Depth (cm)	Coho Flats Primary	Coho Flats Secondary	Lakelse Lake Primary	Lakelse Lake Secondary	Kemano Primary	Kemano Secondary[$]
Organic matter (%)	0–5	19.04	20.36	10.59	10.07	12.05	3.40
	5–15	20.33	18.62	6.52	6.11	10.88	2.79
	15–30	17.93	14.79	4.50	5.08	10.40	2.03
pH	0–5	4.56	4.62	5.13	4.97	4.95	5.70
	5–15	5.07	4.73	5.41	5.38	5.01	5.73
	15–30	5.33	4.97	5.50	5.49	5.11	5.75
Bulk density ($g\ cm^{-3}$)	0–5	0.664	0.708	0.738	0.828	0.952	1.189
	5–15	0.646	0.708	0.922	0.905	0.906	.
	15–30	0.849	0.664	1.066	0.911	0.814	.
Coarse fragment (%w)	0–5	34.87	30.86	.	.	5.05	3.50
	5–15	39.32	34.26	.	.	9.84	2.66
	15–30	50.62	35.64	.	.	10.95	2.86
Field moisture (%v)	0–5	46.11	41.43	34.09	29.92	15.60	23.19
	5–15	43.46	38.94	32.83	32.02	18.09	.
	15–30	40.39	39.00	32.90	33.00	15.82	.

[$] this is a very sandy site, making collection of bulk density difficult, as such bulk density was only collected from one depth (which was assumed representative of all depths).

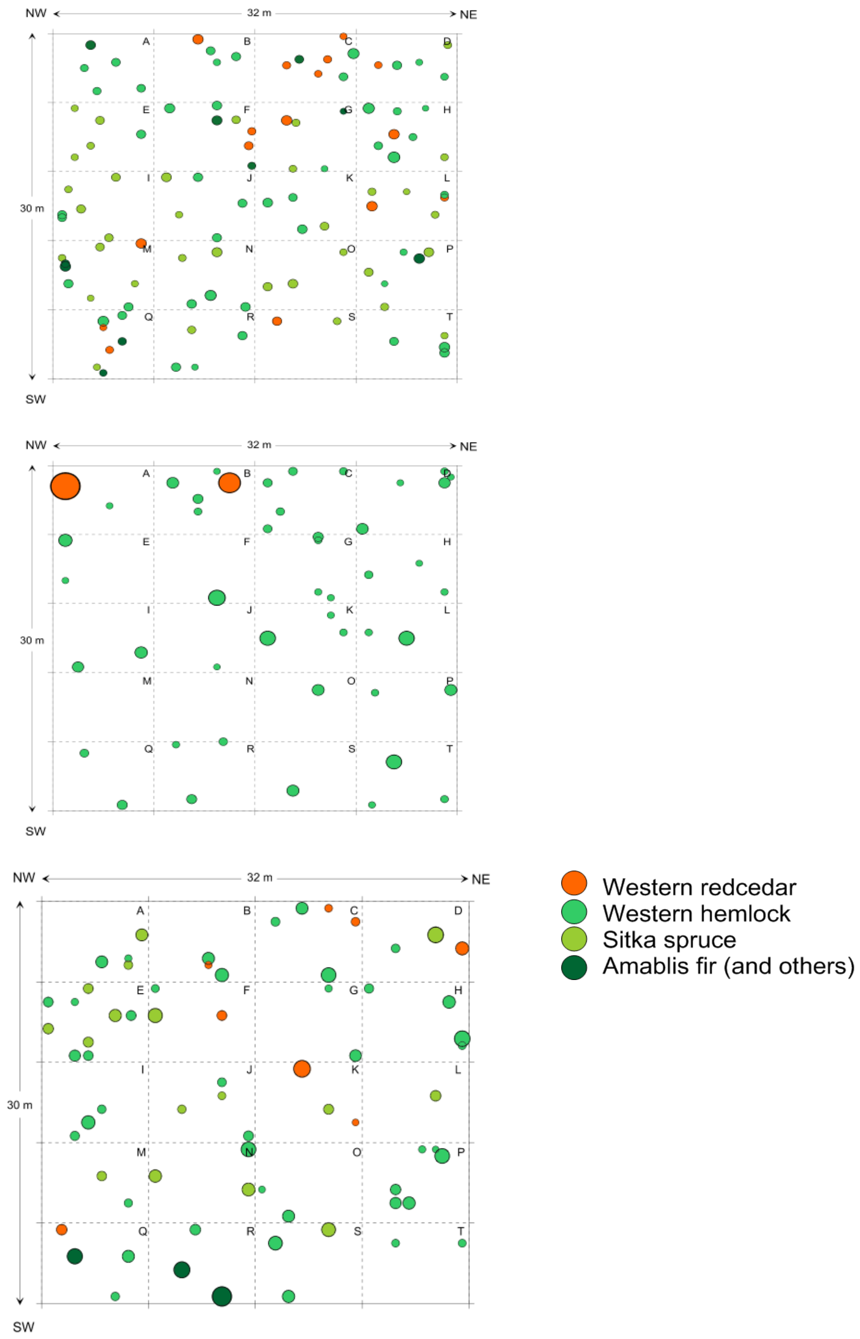


Figure 5. Layout of the primary long-term soil monitoring plots at Lakelse Lake (upper), Coho Flats (middle), and Kemano (lower) showing the location and relative size of each tree species.

5 Literature Cited

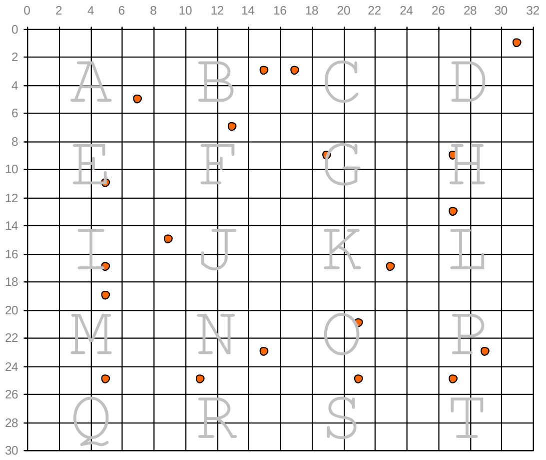
ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Vol.2: Final Technical Report. Prepared for RTA, Kitimat, BC. 450 pp.

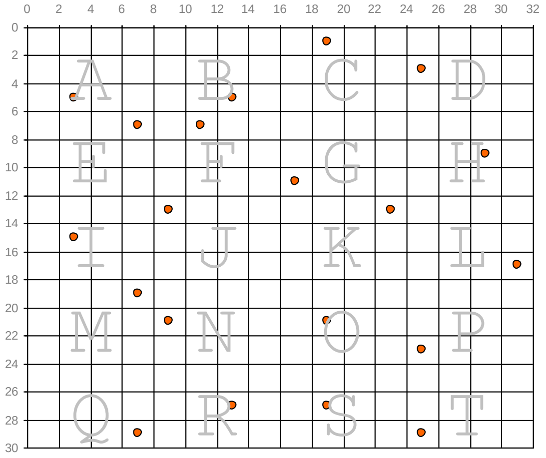
ESSA Technologies, J. Laurence, Risk Sciences International, Trent University, and Trinity Consultants. 2014. Kitimat Airshed Emissions Effects Assessment. Report prepared for BC Ministry of Environment, Smithers, BC. 205 pp. + appendices.

6 Appendix A

Table A1. Soil plot grids sampled (at five depths) during 2015 within the primary and secondary plots located at Coho Flats and Lakelse Lake (see Figure 1). Grids are identified by the sub-plot letter and grid number (see Figure 2). Grid locations for the primary plots are also shown in Figure A1.

#	Coho Flats		Lakelse Lake		Kemano	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
1	A12	A10	A10	A10	A09	A08
2	B08	B06	B11	B06	B02	B12
3	C05	C03	C02	C10	C10	C03
4	D04	D07	D05	D02	D09	D12
5	E11	E07	E04	E06	E03	E04
6	F03	F01	F02	F02	F04	F07
7	G06	G05	G09	G02	G12	G06
8	H06	H01	H07	H04	H03	H11
9	I11	I04	I06	I08	I12	I09
10	J05	J12	J01	J09	J06	J01
11	K12	K05	K04	K10	K09	K09
12	L02	L06	L12	L11	L08	L06
13	M03	M01	M04	M12	M08	M02
14	N12	N02	N05	N04	N09	N04
15	O07	O03	O06	O11	O04	O11
16	P11	P06	P09	P09	P03	P07
17	Q03	Q06	Q12	Q01	Q12	Q02
18	R02	R02	R07	R03	R07	R04
19	S03	S07	S06	S09	S06	S10
20	T02	T05	T09	T03	T09	T04





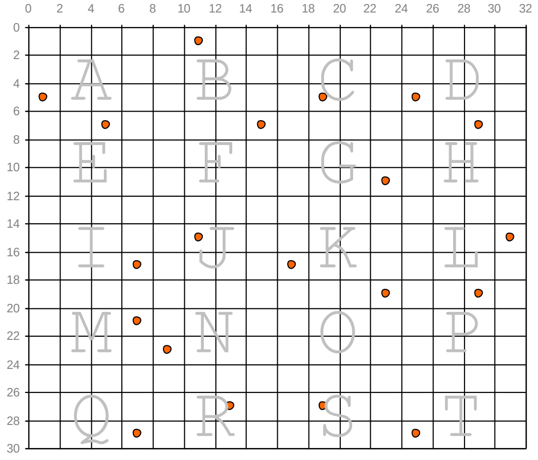


Figure A1. Location of soil sampling grids within letter sub-plots at the primary plots at Coho Flats (upper), Lakelse Lake (middle) and Kemano (lower).

RioTinto

KMP SO_2 EEM Program – Technical Memo S07

Long-term Soil Monitoring Plots

Laboratory Analysis

June 2018

DRAFT

Prepared for:

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

Prepared by:

Trent University
ERS, 1600 West Bank Drive
Peterborough, ON, Canada K9J 7B8

DRAFT

1 Overview

Under the Environmental Effects Monitoring (EEM) Program, long-term soil monitoring plots will address the observation-based KPI: 'observed change in base cation pool over time' through repeat sampling and analysis of soils for exchangeable base cations every five years (ESSA et al., 2014).

During October–December 2015, long-term soil monitoring plots (primary and secondary) were established at Coho Flats and at Lakelse Lake, Kitimat valley, and during June–July 2016 the reference (background or control) plots were established at Kemano. Technical memo S04 (2015) described the establishment of the plots (i.e., plot locations and design), and the initial sampling and processing of soils. Technical memo S06 (2016) described the establishment of the control plots at Kemano, and the sampling of soil bulk density sampling and mapping of trees across all plots during June–July 2016.

This memo (S07) describes the extraction and analysis of the mineral soil samples from the primary plots at Coho Flats and Lakelse Lake for exchangeable base cations and exchangeable acidity, which was carried out during 2017. There are 20 soils samples, collected from three depths, per plot; a total of 120 soil samples.

2 Objective and Rationale

The objective of the long-term soil plots is to monitor changes in soil base cation pools over time through repeated sampling and analysis (every five years). The monitoring plots provide a framework for replicate random sampling of soils, allowing for the statistical assessment of changes between sampling campaigns.

Plot establishment and initial soil sampling was carried out during 2015; the first resampling of soils from the primary plots at Coho Flats and Lakelse Lake is scheduled for June 2018.

3 Plot Location and Design

During October–December 2015, near-field and far-field plots were established at Coho Flats (latitude: 54.07660, longitude: –128.65117) and Lakelse Lake (latitude: 54.37827, longitude: –128.57990), respectively, and during 2016 the control plots were established at Kemano (latitude: 53.53032, longitude: –127.97384; see Appendix Figure A1 and Figure A2). At each location, primary and secondary (backup) plots were established within forest stands dominated by western Hemlock.

Each long-term soil plot is 32 m by 30 m in size and composed of twenty 8 m by 6 m sub-plots lettered A to T; the A sub-plot is oriented to the north-west corner of each plot (see Appendix Figure A3). Each sub-plot is further divided into twelve 2 m by 2 m sampling grids (numbered 1 to 12); one numbered grid was randomly sampled from each lettered sub-plot at five depths (see Appendix Table A1 for a list of sample grids): litter-fibric (LF), humic (H), and 0–5 cm, 5–15 cm, and

15–30 cm depths in the mineral soil (yielding a total of 100 soil samples for each plot, i.e., 5 soil samples by depth within each of the 20 lettered sub-plots).

4 Laboratory Analysis

All soil samples (collected during 2015 and 2016) from the 0–5 cm, 5–15 cm, and 15–30 cm depths have been dried, sieved to < 2 mm and analysed for pH, organic matter content and bulk density. Soils from the primary plots at Coho Flats and Lakelse Lake have been analysed for exchangeable base cations and exchangeable acidity.

Soil bulk density core samples were weighed, oven dried at 105°C for 24 hours, and reweighed. The difference between the wet and oven dry weights provided an estimate of field soil moisture content. The dried soil was sieved to < 2 mm (fine fraction), the volume of the coarse material (>2 mm) was measured by displacement. Bulk density was estimated using the dry weight of the fine fraction (<2 mm) and the volume of the core (adjusted for coarse fragment volume).

Composite mineral soil samples were air dried and sieved (<2 mm). The fine fraction was analysed for organic matter content by loss on ignition (LOI); 5 g of soil was placed into a muffle furnace at 400°C for 10 hours and then reweighed to determine percent loss. Soil pH was measured by mixing 5 g of soil with 20 mL of water and analysed using a pH probe.

Exchangeable acidity was measured using a potassium chloride (KCl) extraction; 5 g of soil was mixed with 25 mL of KCl, the solution was extracted via vacuum filtration. The sample then received five addition washes of 25 mL KCl. The extractant (135 mL) was titrated with sodium hydroxide (NaOH) to determine exchange acidity (H^+ + Al^{3+}). The extractant (15 mL) was also analyzed by ICP–OES to determine exchangeable aluminum (Al^{3+}).

Exchangeable base cations were measured using an ammonium acetate (NH_4OAC) extraction, 5 g of mineral soil was mixed with 25 mL of NH_4OAC, the solution was extracted via vacuum filtration. The sample then received two addition washes of 10 mL NH_4OAC, the extractant was analyzed by ICP–OES for exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Fe^{3+} and Mn^{2+}).

5 Soil Chemistry

Exchangeable base cations were estimated as the sum of calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+). Cation Exchange Capacity (CEC), was estimated as the sum of all cations and exchangeable acidity (which is the sum of exchangeable aluminium (Al^{3+}) and hydrogen (H^+)), this is technically termed effective CEC. Base saturation (%) was estimated as the percentage of effective CEC made up of base cations. Exchangeable base cations pools in the 0–30 cm soil was estimated by multiplying the concentrations of base cations by soil bulk density.

The multiple observations per depth allow the variation in soil properties to be assessed between and within plots. There is a noticeable difference in organic matter content between depths in the mineral soil at Lakelse Lake (i.e., there is a statistically significant decrease in organic matter between the 0–5 cm and the lower depths, Figure 1) but not between primary and secondary

DRAFT

plots (i.e., there is no statistical difference between the 0–5 cm at Lakelse Lake primary compared with the same depth in Lakelse Lake secondary). In contrast, there is no significant difference (decrease) in organic matter with depth at the Coho Flats primary plot (see Figure 1 and **Error! Reference source not found.**)

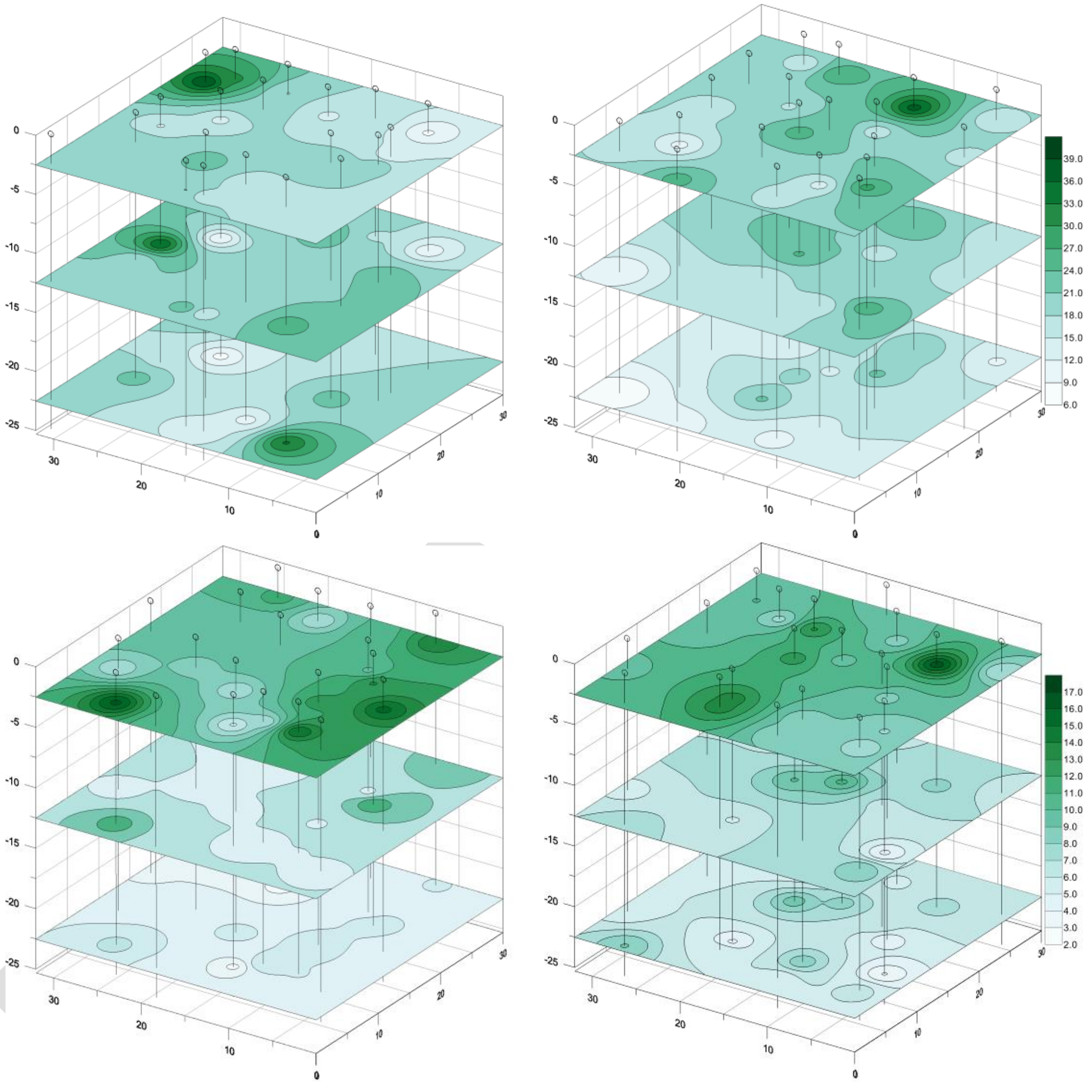


Figure 1. Three-dimensional representation of soil organic matter content (%) in the 0–5 cm, 5–15 cm, and 15–30 cm (mineral) soil depths at the primary (left) and secondary (right) long-term soil monitoring plots at Coho Flats (upper) and Lakelse Lake (lower). The vertical lines indicate the location of the soil sampling pits (n = 20 per plot, with soil sampling at three depths). Note: the difference in scales between plots.

In general, pH and bulk density in forest soils increase with depth and organic matter decreases; however, at Coho Flats both bulk density and organic matter do not show this pattern (Table 1). In contrast, exchangeable base cations, acidity and effective CEC decrease with depth at both plots (Table 1). Lakelse Lake has higher soil pH, bulk density and lower organic matter compared with Coho Flats (Table 1 and Table 2).

Average base saturation (%) at Lakelse Lake is 47%, which is notably higher compared with 17% at Coho Flats. The base saturation is higher throughout all soil depths at Lakelse Lake, especially the 0–5 cm and 5–15 cm soil depths (Figure 2). While total cations (effective CEC) is similar between plots (Table 1), the soils in Lakelse Lake are dominated by base cations (average 2.8 meq $100g^{-1}$) compared with Coho Flats (average 1.3 meq $100g^{-1}$). As a result, base cation pools are > 4 times larger at Lakelse Lake compared with Coho Flats (Table 2), 7217 meq m^{-2} compared with 1667 meq m^{-2}, respectively. It is important to note that the higher bulk density at Lakelse Lake also influences base cation pools (Table 2).

Table 1. Average soil chemistry data per depth (n = 20) for the primary long-term soil monitoring plots at Coho Flats, and Lakelse Lake.

Soil variable (meq $100g^{-1}$)	Coho Flats | Soil depth (cm) 0–5	5–15	15–30	Lakelse Lake | Soil depth (cm) 0–5	5–15	15–30
pH	4.56	5.07	5.33	5.13	5.41	5.50
Organic matter (%)	19.04	20.33	17.93	10.59	6.52	4.50
Bulk density (g cm^{-3})	0.433	0.416	0.509	0.537	0.856	0.982
Exchangeable Ca^{2+}	1.09	0.92	0.97	4.37	2.79	0.88
Exchangeable Mg^{2+}	0.32	0.30	0.24	1.67	1.37	0.26
Exchangeable K^{+}	0.13	0.13	0.10	0.13	0.05	0.11
Exchangeable Fe^{3+}	0.06	0.07	0.07	0.14	0.12	0.03
Exchangeable Mn^{2+}	0.01	0.02	0.01	0.20	0.12	0.03
Exchangeable acidity	7.84	6.77	5.82	3.68	2.86	2.24
Exchangeable base cations$^{\$}$	1.53	1.35	1.30	6.17	4.21	1.25
Cation Exchange Capacity$^{\$}$	9.44	8.20	7.20	10.18	7.31	3.55
Base saturation (%)	16.22	16.44	18.07	60.57	57.61	35.22

$^{\$}$ Exchangeable Base Cations was estimated as the sum of calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^{+}); Cation Exchange Capacity (CEC) was estimated as the sum of all cations and Exchangeable Acidity (which is the sum of exchangeable aluminium (Al^{3+}) and hydrogen (H^{+})), this is also known as effective CEC.

Table 2. Average soil chemistry and relative standard deviation (CV%) for the primary long-term soil monitoring plots at Coho Flats and Lakelse Lake (in the 0–30 cm depth).

Soil variable	Unit	Coho Flats (0–30 cm) Average	CV%	Lakelse Lake (0–30 cm) Average	CV%
Bulk density	g cm^{-3}	0.436	33.7	0.863	16.5
Organic matter	%	18.13	24.2	8.07	32.3
Exchangeable Ca^{2+}	meq $100g^{-1}$	0.91	74.3	1.90	49.9
Exchangeable Mg^{2+}	meq $100g^{-1}$	0.26	43.1	0.80	72.3
Exchangeable K^{+}	meq $100g^{-1}$	0.11	38.8	0.09	39.6
Exchangeable acidity	meq $100g^{-1}$	6.07	41.8	2.59	27.4
Exchangeable base cations	meq $100g^{-1}$	1.27		2.79	
Base cation pool	meq m^{-2}	1667		7217	

DRAFT

DRAFT

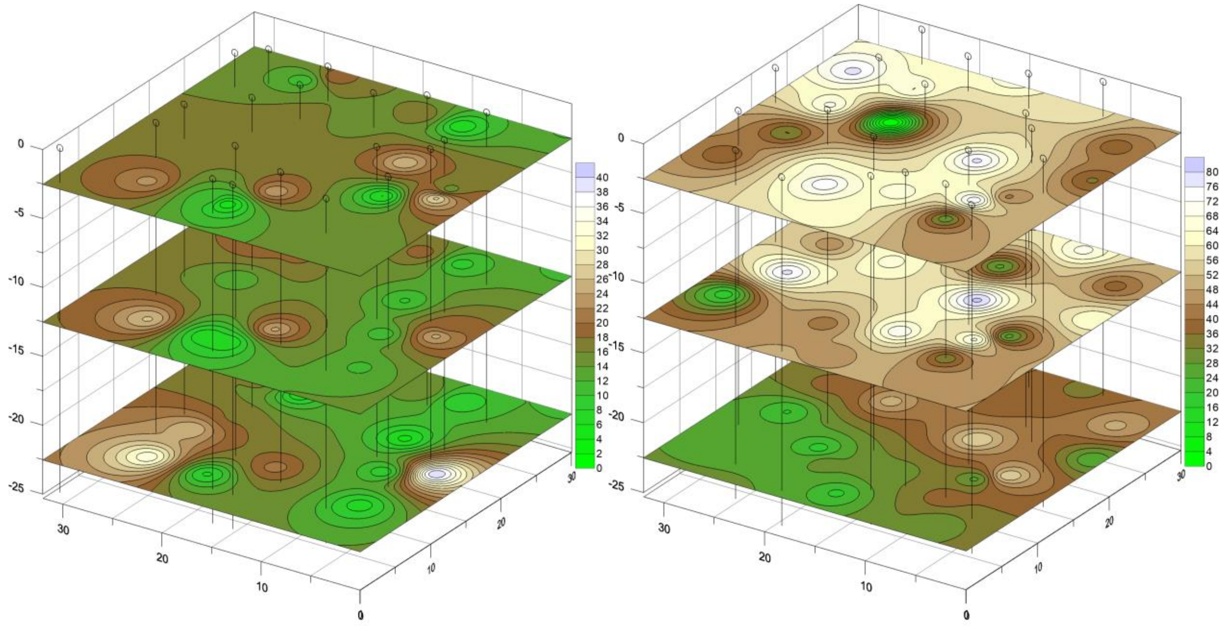


Figure 2. Three-dimensional representation of soil base saturation (%) in the 0–5 cm, 5–15 cm, and 15–30 cm (mineral) soil depths at the primary long-term soil monitoring plots at Coho Flats (left) and Lakelse Lake (right) The vertical lines indicate the location of the soil sampling pits (n = 20 per plot, with soil sampling at three depths). Note: the difference in scales between plots.

6 Literature Cited

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Vol.2: Final Technical Report. Prepared for RTA, Kitimat, BC. 450 pp.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto BC Works, Kitimat, BC. 99 pp.

Technical Memo S04: Long-term Soil Monitoring Plots: Plot Establishment, September 2016. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2015 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

Technical Memo S06: Long-term Soil Monitoring Plots: Plot Establishment— 2017 Update, March 2017. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2016 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

7 Appendix A

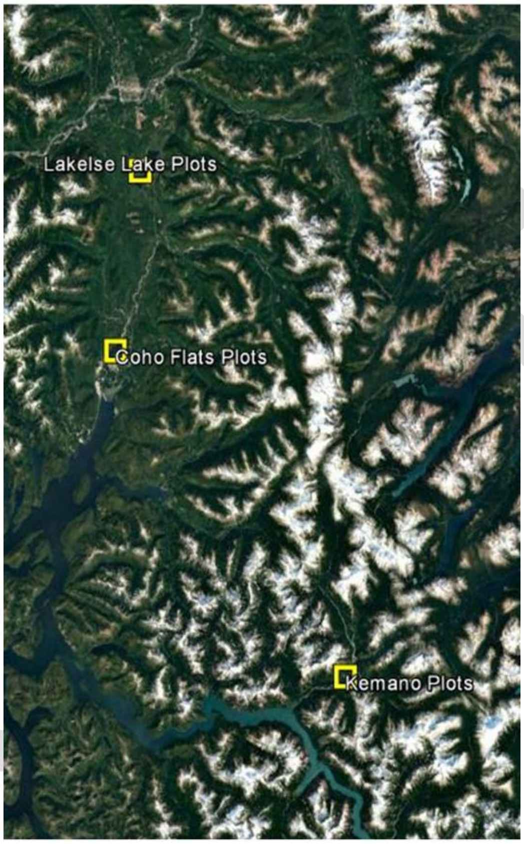


Figure A1. Location of long-term soil monitoring plots at Coho Flats (near-field) and Lakelse Lake (far-field), in the Kitimat Valley, and Kemano (reference). Note: primary and secondary [backup] plots were established at all three locations.

DRAFT

Figure A2. The long-term soil monitoring plots are located at Lakelse Lake beside the NADP monitoring station (A), in a western Hemlock stand (primary plot is shown in B), and east of the Coho Flats Trail, Kitimat (primary plot is shown in C). The reference (or background) plot is located in Kemano (primary plot at Seekwyakin camp is shown in D).

DRAFT

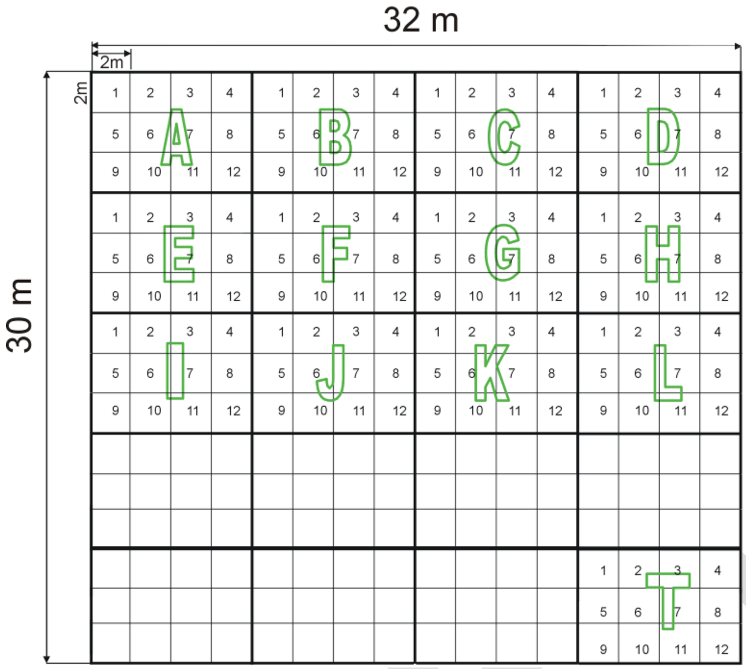


Figure A3. Long-term soil monitoring plot; the plot is divided into twenty 8 m by 6 m sub-plots, lettered A to T; each sub-plot is further divided into twelve 2 m by 2 m sampling grids, numbered 1 to 12. One numbered grid within each lettered sub-plot is randomly selected for sampling during each campaign, allowing for a total of 12 sampling events, with 20 samples per depth.

DRAFT

Table A1. Soil plot grids sampled (at five depths) during 2015 within the primary and secondary plots located at Coho Flats and Lakelse Lake (see Figure A1). Grids are identified by the sub-plot letter and grid number (see Figure). Grid locations for the primary plots are also shown in Figure A1.

#	Coho Flats		Lakelse Lake		Kemano	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
1	A12	A10	A10	A10	A09	A08
2	B08	B06	B11	B06	B02	B12
3	C05	C03	C02	C10	C10	C03
4	D04	D07	D05	D02	D09	D12
5	E11	E07	E04	E06	E03	E04
6	F03	F01	F02	F02	F04	F07
7	G06	G05	G09	G02	G12	G06
8	H06	H01	H07	H04	H03	H11
9	I11	I04	I06	I08	I12	I09
10	J05	J12	J01	J09	J06	J01
11	K12	K05	K04	K10	K09	K09
12	L02	L06	L12	L11	L08	L06
13	M03	M01	M04	M12	M08	M02
14	N12	N02	N05	N04	N09	N04
15	O07	O03	O06	O11	O04	O11
16	P11	P06	P09	P09	P03	P07
17	Q03	Q06	Q12	Q01	Q12	Q02
18	R02	R02	R07	R03	R07	R04
19	S03	S07	S06	S09	S06	S10
20	T02	T05	T09	T03	T09	T04

DRAFT

RioTinto

KMP SO_2 EEM Program – Technical Memo W03

Aquatic Ecosystems Actions and Analyses

March 2016

Prepared for:

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

Prepared by:

ESSA Technologies Ltd.
Suite 600 – 2695 Granville St.
Vancouver, BC, Canada V6H 3H4
(Using data provided by Rio Tinto Alcan)

Table of Contents

Table of Figures

Table of Tables

1 Introduction

This Technical Memo provides extended information on the data and analyses in support of the 2015 requirements for the Aquatic Ecosystems component of the KMP SO_2 Environmental Effects Monitoring (EEM) program (ESSA et al. 2014b). These data and analyses thus provide the foundation for Section 3.5 in the 2015 EEM Annual Report (ESSA et al. 2016).

Table 1-1. Aquatic analyses as specified in the EEM Plan. Extracted from Table 16, Section 6.2.5, "Summary of Lakes, Streams and Aquatic Biota Actions, 2013-2018". The numeric symbols (e.g., ①②③) are used to link sections of the present technical memo with the EEM requirements, and appear throughout this document.

Topic	2015
Steady state water modelling	–
Chemistry: water body sampling	① Annual water sampling, laboratory analysis, and data evaluation. ② Continuation of intensive sampling to determine natural variability.
$[SO_4]_0$; F-factor	–
Fish presence / absence sampling	③ Sampling of the 3 reference lakes. Resample if lake pH change reaches threshold.
Episodic acidification	④ Finalize study design.
Amphibians	⑤ Provide support to existing local community groups who conduct annual amphibian monitoring

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) and the Kitimat Airshed Assessment (KAA) (ESSA et al. 2014a). 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, 2015; Limnotek 2016). Wherever possible, the description of methods in this technical report refers to these reports instead of repeating information that is already well-documented elsewhere.

The following three documents (as described above) are listed here because they are referenced extensively throughout this technical memo, often without their full citation:

- The STAR (ESSA et al. 2013)
- The KAA (ESSA et al. 2014a)
- The EEM Plan (ESSA et al. 2014b)

Figure 1-1 provides a schematic diagram illustrating the relationship among the multiple documents associated with the surface water component of the EEM Program.

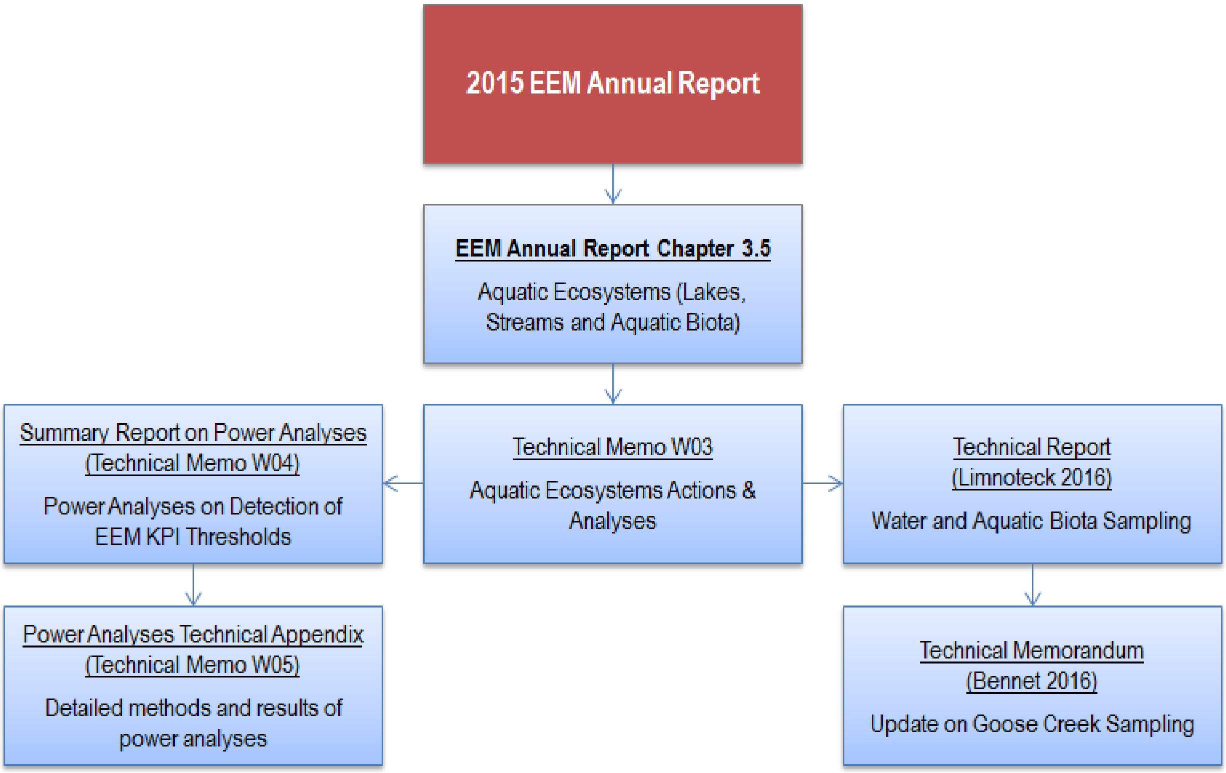


Figure 1-1. Relationship of the multiple technical reports and summaries associated with the aquatic ecosystem component of the EEM Program.

2 Methods

2.1 Annual Monitoring Samples ①

2015 Annual Sampling

In 2015, Limnotek sampled 14 lakes as part of the EEM long-term sampling plan. These lakes included the seven sensitive lakes and three less sensitive lakes identified in the EEM Plan, the high recreational value LAK024 (Lakelse Lake; added to the EEM in 2014), and three additional control lakes added to the EEM in 2015. The three control lakes (NC184, NC194 and DCAS14A) are all located outside of the KMP-influenced airshed and have baseline data for 2013 from sampling as part of the KAA (ESSA et al., 2014a). Sampling was also completed for two sites in the Goose Creek watershed (supplementing the six sites sampled in 2014), to assess whether those sites would be sensitive to increases in sulphur deposition. The sampling methodology is described in detail in Limnotek's technical report on the water quality monitoring (Limnotek 2016). Table 2-1 summarizes all of the EEM sites sampled during 2012-2015. Figure 2-1 shows a map of the lakes sampled in 2015.

Table 2-1. Summary of sites sampled within the EEM Program.

Sample Site	Year of Sampling				Rationale for sampling
	2012	2013	2014	2015	
	During STAR	EEM Program	EEM Program	EEM Program	
Lake 006	✓	✓	✓	✓	EEM sensitive lake
Lake 012	✓	✓	✓	✓	EEM sensitive lake
Lake 022	✓	✓	✓	✓	EEM sensitive lake
Lake 023	✓	✓	✓	✓	EEM sensitive lake
Lake 028	✓	✓	✓	✓	EEM sensitive lake
Lake 042	✓	✓	✓	✓	EEM sensitive lake
Lake 044	✓	✓	✓	✓	EEM sensitive lake
Lake 007	✓	✓	✓	✓	EEM less sensitive lake
Lake 016	✓	✓	✓	✓	EEM less sensitive lake
Lake 034	✓	✓	✓	✓	EEM less sensitive lake
Lake 024	✓		✓	✓	Added to the EEM long-term monitoring lake set due to public importance
MOE3		✓			Potentially sensitive lakes / streams not previously sampled
Cecil Creek 1		✓			
Cecil Creek 2		✓			
Cecil Creek 3		✓			
MOE6			✓		
Goose Creek 1			✓		
Goose Creek 2			✓		
Goose Creek 4			✓		
Goose Creek 5			✓		
Goose Creek 6			✓		
Goose Creek 7			✓		
GNT1 (Goose Creek)				✓	
GNT2 (Goose Creek)				✓	
		KAA Program			
NC184		✓		✓	Control lakes added to EEM in 2015
NC194		✓		✓	
DCAS14A		✓		✓	

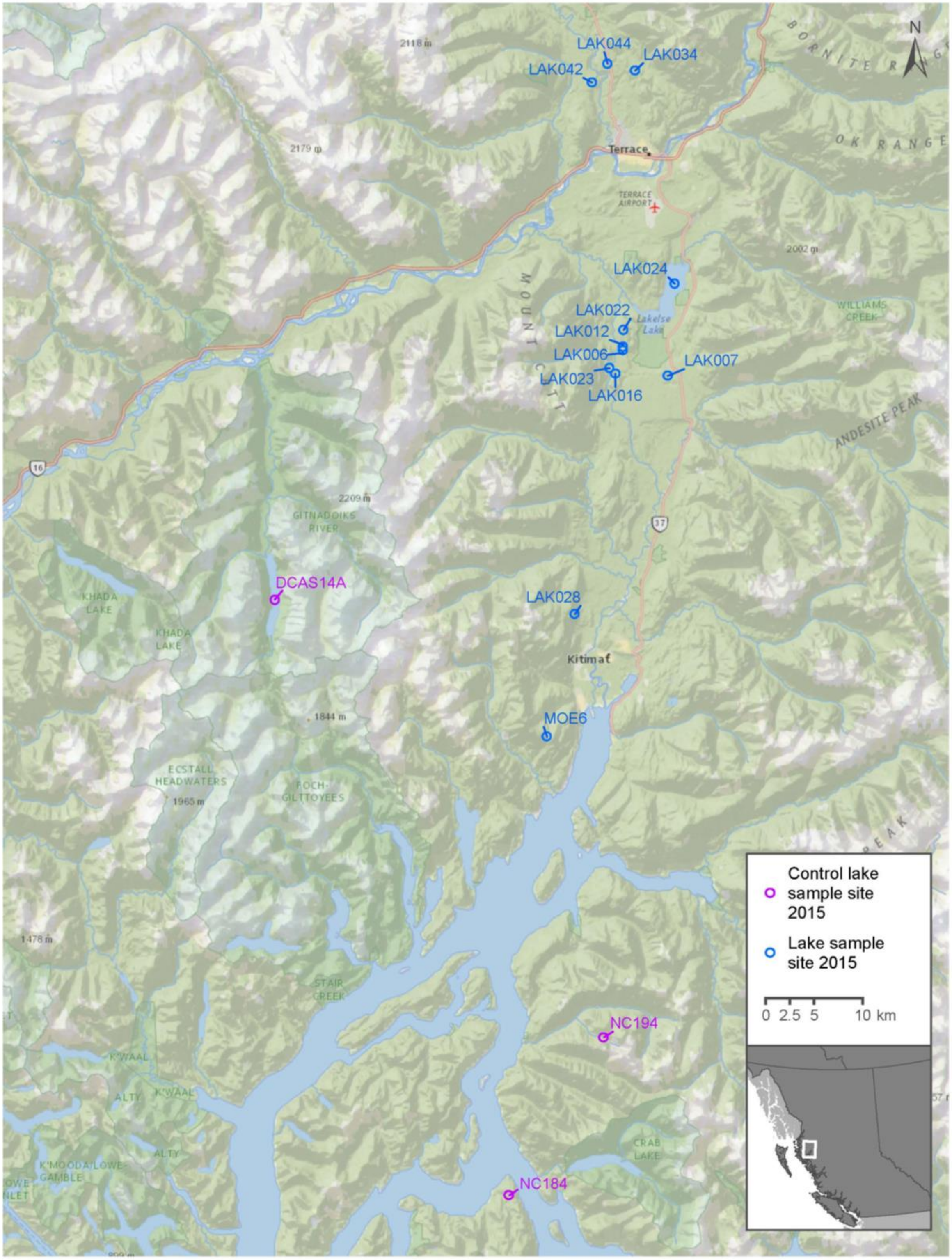


Figure 2-1: Location of the lakes that were sampled in 2015. The lake called MOE6 was not sampled in 2015. The three control lakes are labelled with purple text (Source: Limnotek 2016).

2.2 Intensive Monitoring of Three Lakes ②

Starting in 2014, intensive monitoring was initiated in three of the EEM lakes, End Lake (LAK006), Little End Lake (LAK012) and West Lake (LAK023). These three lakes were selected based on being accessible by road, thus making repeated visits much more feasible than for remote lakes requiring helicopter access. During the fall of 2014, the intensive monitoring included continuous pH monitors and multiple site visits to collect intra-season water samples for additional lab analyses and pH measurements. In 2015, the continuous pH monitors were deployed from mid-April until mid-November. During October 2015, three additional within-season water chemistry samples were taken at these three lakes, subsequent to annual sampling across all of the lakes (i.e., four samples for each of the intensively monitored lakes in 2015). This work was planned, implemented and documented by Limnotek. The methods and results for 2015 are reported in Limnotek (2016).

2.3 Quality of Water Chemistry Data ①②

Sampling and laboratory quality control and quality assurance

The collection, handling, transport, and analyses of water quality samples were conducted with numerous quality checks, to ensure the highest quality data possible. Details on the methods for quality control and quality assurance for the water samples are described in Limnotek (2016).

Analyses of Charge Balance and Estimated vs. Measured Conductivity

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

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

pH measurements

Water quality samples taken in 2015 have multiple measures of pH, including a field measurement and two lab measurements (Trent University and ALS). As described in Section 2.2, three lakes also have additional measurements of pH, in particular from continuous meters. As described in the STAR, lab measurements of pH, rather than field measurements, have been used for the analyses of lake chemistry; lab pH measurements have lower variability, and therefore are more relevant to the detection of long term trends.

The 2012 data collected during the STAR included laboratory measurements of pH only from Trent University. Inter-annual comparisons of trends in pH have therefore been conducted using the Trent pH results. Limnotek (2016) analyzed differences among the different methods of measuring pH for quality assurance purposes.

2.4 Inter-annual Changes

Observed Changes

The EEM Program now has four consecutive years of monitoring data with which to examine inter-annual changes in water chemistry parameters. We calculated the changes in major water chemistry attributes between subsequent years and across the entire period for 2012-2015[1].

Expected Changes and Application of the Evidentiary Framework

The EEM Evidentiary Framework (refer to Section 7.0 and Appendix H of the EEM Plan) provides a weight-of-evidence approach for assessing causality associated with observed changes in water chemistry. The general principles of the evidentiary framework are considered in Section 4.1, but we did not formally apply the framework because the 2015 annual emissions represent a transitional period from the old smelter to KMP, with average SO_2 emissions of only 8.3 tonnes / day, compared to 11.6 tonnes/day in 2014 (Figure 4). It will be more instructive to apply the evidentiary framework once KMP emissions have increased beyond levels observed in 2012-2015.

2.5 Fish Sampling ③

Limnotek conducted fish sampling in LAK006, LAK012, LAK023, and LAK044 in 2013. The goal of this work was to measure the presence/absence of fish in four of the seven sensitive lakes within the EEM Program. Under the EEM Plan, the fish populations in some of these lakes could potentially be resampled if it were determined that a lake's pH had declined by more than 0.3 pH units. In 2015, fish sampling was completed in the three less sensitive lakes: LAK007, LAK016, and LAK034. Details of the fish sampling methodologies for the two years are described in Limnotek's technical reports (Perrin et al. 2013, Section 2.9; Limnotek 2016, Section 2.8).

2.6 Goose Creek (non-EEM sites)

In 2014, six sites within the Goose Creek watershed (not formally part of the EEM Program) were sampled to assess their potential sensitivity. Sampling of these sites was conducted by Limnotek, as described by Bennett (2014). Further analyses of the water chemistry data were conducted in 2014 (ESSA Technologies 2015). In 2015, Limnotek collected samples from two additional sites on northern tributaries of Goose Creek, in a region of the watershed that had not been previously sampled. Full details of the sampling approach and methods are provided in Limnotek's technical report (Limnotek 2016) and a technical memorandum (Bennett 2016).

---

[1] As noted in the 2013/2014 EEM Annual Report (ESSA Technologies 2015), because sampling in 2012 was performed in August and the sampling in subsequent years was performed in October, the observed differences between 2012 and 2013 represent a mixed effect of both changes due to year and changes due to season. For this reason, the observed changes between 2012 and 2013 are harder to interpret than the changes between other sequential years.

2.7 Episodic Acidification Studies ④

The episodic acidification sub-component of the aquatic ecosystems component of the EEM Program is being addressed through two studies: continuous pH monitoring in Anderson Creek, and a research project conducted by Dr. Paul Weidman (School of Resource and Environmental Management & Department of Biology, Simon Fraser University) with supplemental funding provided by RTA.

Continuous pH Monitoring in Anderson Creek

On March 31, 2015, a Manta sampler was installed in Anderson Creek. The sampler has three pH sensors and a temperature probe, and the logging interval on the Manta was set to 30 minutes. The Manta was calibrated once every two weeks, and at the same time the pH of a grab sample of Anderson Creek water was measured using a WTW portable pH meter (same instrument that was used in the intensively sampled lakes). There was a data gap from April 15 to May 15 when the external battery pack was removed for use on a Manta installed in one of the intensively sampled lakes. Further details are provided in Limnotek's technical report (Limnotek 2016).

Research Project by Dr. Paul Weidman

The project title for this research is, "Impacts of industrial sulfur and nitrogen deposition and climate change on salmon stream habitat in the Kitimat watershed". Development of the study design was initiated in 2014 and finalized in 2015. Preliminary sampling activities were conducted in 2015. The following summary has been extracted from Dr. Weidman's project update (Appendix 3):

"The main objective of our project is to determine the cumulative effects of industrial atmospheric emissions of sulfur and nitrogen on salmon stream habitat under hotter and drier conditions due to climate change in the Kitimat watershed. Achieving this objective is critical to anticipating and managing the cumulative effects of industrial activities and climate change on north coastal salmon streams. Moreover, this project will help guide on-going fish habitat restoration projects that are being conducted by the Haisla Fisheries Commission in the Kitimat watershed.

In 2016, we propose to modify our sampling activities from 2015 in order to confirm our preliminary results and to map the potential impacts on salmonid habitat in the Kitimat and Lakelse watersheds from increased industrial emission of sulphur and nitrogen. We used data collected in 2015 to select 12 main project streams to continuing monitoring monthly throughout the entire year in 2016−2017. In this way, we are focusing our efforts on assessing and mapping habitat conditions in fewer streams than in 2015, but over the entire year in order to more efficiently conduct our fish habitat assessment. Streams selected in 2016 will represent the full range of habitat conditions that are relevant to our project. We also propose to measure the lethal and sub-lethal effects on juvenile salmonids of sulphur and nitrogen acid deposition and heat stress due to climate change. These rearing incubations will be conducted either at the Kitimat Hatchery and/or the Cultus Lake Salmon Laboratory."

2.8 Amphibian Monitoring ⑤

No actions were taken in 2015. Moving forward with the action to "provide support to existing local community groups who conduct annual amphibian monitoring" has been postponed and will be revisited next year.

2.9 Power Analyses

As part of the EEM Program in 2015, we conducted power analyses to assess our ability to correctly detect changes of interest in water chemistry in the sensitive lakes within the program. That is, we asked how confidently will the established monitoring program be able to identify lakes that have exceeded their ANC, SO_4^{2-}, and/or pH thresholds?

The power analyses work is presented in its own summary report (Technical Memo W04), which describes the context, rationale, methods, results, and implications for the EEM Program. Further details on the methods and results are included in an additional technical appendix (Technical Memo W05) to that summary report.

To avoid unnecessary duplication, the methods, results and discussion are not repeated in the present report. However, the major recommendations have been included.

2.10 Water Residence Time for Lakes

An estimate of water residence time of all the lakes in the EEM Program was estimated based on a coarse approximation of lake volume. In 2015, bathymetric surveys were done by Limnotek (2016) on the three lakes with continuous monitoring (LAK006, LAK012, LAK023) in order to be able to generate a precise estimate of lake volume and therefore a more accurate estimate of the water residence time for each lake. Water residence time is relevant to understanding one of the possible factors contributing to variability (especially intra-annual variability) within individual lakes – that is, lakes with shorter water residence times would be expected to demonstrate higher variability in water chemistry. The full methods for the bathymetric survey and estimation of lake volume are described in Limnotek (2016).

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

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

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

3 Results

3.1 Quality of Water Chemistry Data ①②

Sampling and laboratory quality control and quality assurance

The results of the sampling and laboratory quality control and quality assurance methods are presented in the associated Limnotek technical report (Limnotek 2016).

Charge Balance Check

The charge balance has been examined for each year of sampling. Table 3-1 shows four diagnostic metrics of the charge balance for the sample sets from 2012, 2013, 2014, 2015 and Goose Creek (2014 and 2015). The charge balance is better for the 2015 sampling data than it had been in 2013 or 2014. In all cases, the average charge balance represents an excess of anions relative to cations. The charge balance can be improved by adjusting the assumptions regarding the charge density of organic anions, which could change across different years (analyses not shown).

The charge balance for the lakes in the EEM Program (sensitive and less sensitive) in each of the four sampling years is shown graphically in Figure 3-1. The figure shows that the charge balance for 2015 demonstrates a markedly closer fit to the 1:1 line (i.e., cations = anions) than for 2013 or 2014. The relationships shown on the graph are heavily influenced by Lake 007 (not shown on the graph), which has cation and anion levels of an order of magnitude greater than the other lakes.

Table 3-1. Measures of the charge balance check for 2012 (STAR lakes), 2013 (EEM lakes, MOE3, Cecil Creek), 2014 (EEM lakes, MOE6), 2015 (EEM lakes and control lakes[2]), 2014-GS (Goose Creek), and 2015-GS (Goose Creek - GNT1, GNT2). Negative (red) values for "Average %Diff" and "Average Difference" indicate less total charge from cations than from anions.

Year	Number of Samples	Average %Diff	Average Abs (%Diff)	Average Difference (µeq/L)	Average Abs(Diff) (µeq/L)
2012	61	-0.7	2.6	-6.5	12.2
2013	14	-8.5	10.1	-28.2	42.8
2014	12	-5.0	5.2	-12.9	14.5
2015	13	-2.9	3.1	-16.6	17.3
Goose Creek sites					
2014-GC	6	-4.7	4.9	-30.4	32.6
2015-GC	2	-1.5	1.5	-25.6	25.6

---

[2] Only NC184 and NC194 are included. DCAS14A has been excluded from this summary because its charge balance is exceptionally poor and the underlying water chemistry data is currently being investigated.

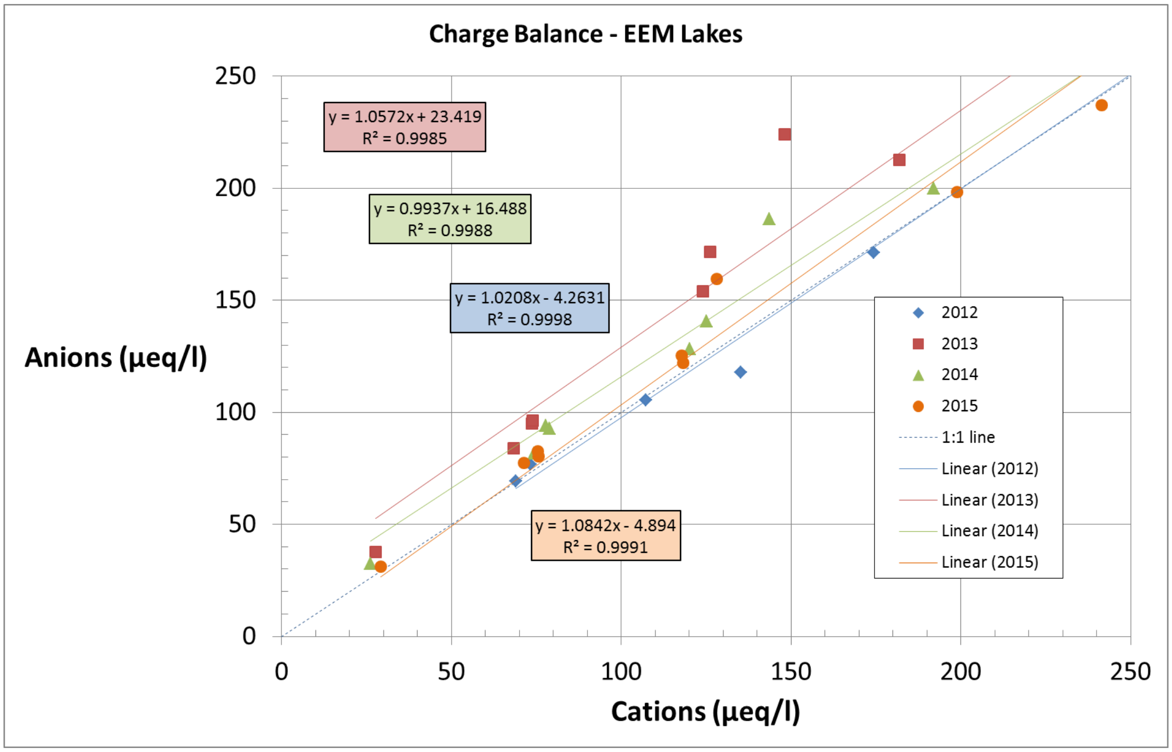


Figure 3-1. Analysis of charge balance for the EEM lakes, 2012-2015. The Y-axis is the sum of all major anions (negatively charged ions); the X-axis the sum of all major cations (positively charged ions).

Measured versus Estimated Conductivity

Measured and estimated conductivity were compared for each year of sampling. Table 3-2 shows two diagnostic metrics of the conductivity check for the sample sets from 2012, 2013, 2014, 2015 and Goose Creek (2014 and 2015). The 2015 Goose Creek data show a substantial difference between the measured and estimated conductivity, indicating a poor performance on this quality control; however, the charge balance for the two sites was very good. All of the other data sets demonstrate an acceptable relationship between measured and estimated conductivity. Estimated conductivity was lower than measured conductivity for the 2015 EEM lakes data, but higher for the Goose Creek sites.

The conductivity check for the EEM lakes (sensitive and less sensitive) in each of the four sampling years is shown graphically in Figure 3-2. The relationships shown on the graph are heavily influenced by Lake 007 (not shown on the graph), which has conductivity values of an order of magnitude greater than the other lakes.

Table 3-2. Measures of the conductivity check for 2012 (STAR lakes), 2013 (EEM lakes, MOE3, Cecil Creek), 2014 (EEM lakes, MOE6), 2015 (EEM lakes, control lakes[3]), 2014-GS (Goose Creek), and 2015-GS (Goose Creek - GNT1, GNT2). Positive values of "Average %Diff" indicate that the estimated conductivity was higher than the measured conductivity.

Year	Number of Samples	Average %Diff	Average Abs (%Diff)
2012	61	4.9	6.0
2013	14	6.8	10.5
2014	12	-5.1	6.4
2015	13	-3.0	6.1
Goose Creek sites			
2014-GC	6	3.4	3.4
2015-GC	2	19.9	19.9

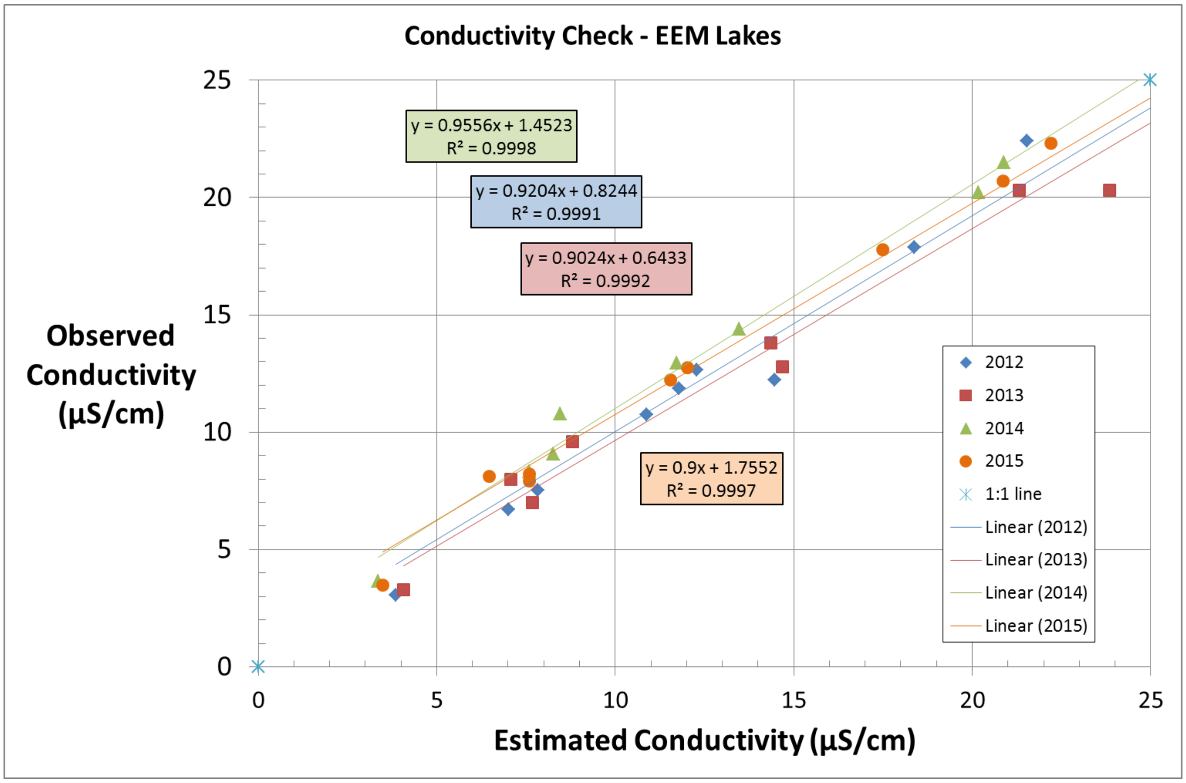


Figure 3-2. Conductivity check for the EEM lakes, 2012-2015. Estimated conductivity is based on laboratory measurements of the concentrations of all ions and literature values for the conductivity of each ion, which is compared to the conductivity observed in field measurements.

---

[3] As per Table 3-1, only NC184 and NC194 are included. DCAS14A is excluded due to data concerns that are being currently explored.

pH measurements

Lab measurements of pH were made at two different labs in 2013, 2014 and 2015. Limnotek (2016) examined the differences in pH measurements for 2015 between the two labs and concluded that the difference was very small relative to the measurement error and not statistically significant. In previous years (see ESSA Technologies 2015), the values measured by ALS were observed to be consistently higher than those measured by Trent University., Both labs apply substantial quality control, quality assurance and equipment calibration procedures; therefore, it is not possible to conclude which lab's measurements are closer to the true pH value. However, the differences were substantially smaller in 2015. For the analyses presented in this technical memo, we used the Trent University measurements to be consistent with the data from the STAR. The 2012 samples were only analyzed by Trent University and not ALS.

3.2 Water Chemistry Results

EEM Lakes – Annual Water Chemistry Data ①

Appendix 1 reports the results of the annual water chemistry sampling for the EEM lakes from the sampling conducted in 2015 (with the data from 2012-2014 included for reference), for major water chemistry metrics (pH, DOC, Gran ANC, base cations, and major anions).

Non-EEM Sites – Water Chemistry Properties

Goose Creek

Goose Creek was the only non-EEM site sampled in 2015. Table 3-3 provides a summary of some of the key water chemistry properties from the 2015 Goose Creek sites, with 2014 Goose Creek sites included for reference.

Table 3-3. Select chemical properties of Goose Creek sites sampled during 2014 and 2015. The 2014 samples were also reported in the 2013/2014 EEM Annual Report. The * indicates that values are corrected for marine influence. Average values for the EEM sensitive lakes and EEM less sensitive lakes are included to provide some context for the values of the other sites.

Site	Sample Year	Gran ANC (μeq/L)	pH	SO4* (μeq/L)	Cl (μeq/L)	F (μeq/L)	BC* (μeq/L)	DOC (mg/L)
Goose Creek 1	2014	93.2	6.4	128.9	18.3	27.6	274.9	6.3
Goose Creek 2	2014	82.5	6.3	139.4	16.6	28.0	251.2	5.6
Goose Creek 4	2014	41.1	5.5	112.1	18.9	42.2	210.1	14.7
Goose Creek 5	2014	332.6	6.7	188.2	18.6	22.4	601.0	4.5
Goose Creek 6	2014	284.9	7.4	185.2	15.2	18.1	488.9	4.5
Goose Creek 7	2014	283.4	6.9	167.6	14.1	12.2	458.0	4.2
GCNT1	2015	247.4	6.8	300.9	29.6	15.6	588.6	6.0
GCNT2	2015	254.6	6.8	620.8	16.6	18.4	872.4	4.6
Average of EEM sensitive lakes	*2015*	*28.0*	*5.84*	*20.5*	*6.7*	*6.7*	*77.6*	*5.2*
Average of EEM less sensitive lakes	*2015*	*574.9*	*7.20*	*30.5*	*24.5*	*4.5*	*609.5*	*3.6*

In the 2013/2014 EEM Annual report, Goose Creek sites 5, 6 and 7 (sampled in 2014) were described as having high pH, high ANC, very high SO_4^{2-} levels, very high F levels, and very high base cations. The two Goose Creek sites sampled in 2015 are similar or even higher than those sites across all of these metrics. GCNT 1 is markedly higher than those three sites for SO_4^{2-} and chloride. GCNT 2 is markedly higher than those sites for SO_4^{2-} and base cations. Notably, the SO_4^{2-} levels are multiple times higher than the levels observed in the other Goose Creek sites sampled in 2014, which were already significantly higher than all but one of the observations across the EEM lakes (i.e., LAK028 in 2013). Despite the high SO_4^{2-} levels, the base cation and ANC levels of sites GCNT 1 and GCNT 2 are indicative of very low sensitivity to acidification.

3.3 Intensive Monitoring of Three Lakes ⑤

Results from the continuous monitoring of pH in West Lake (LAK023), End Lake (LAK006), and Little End Lake (LAK012) are reported in the associated Technical Memo by Limnotek (2016). The Limnotek results for pH monitoring are summarized below in Table 3-4 and Table 3-5. Over the period of continuous monitoring (from April 13 to November 13, 2015), the pH varied by about 1.0 pH unit in End Lake and Little End Lake, and by about 0.8 pH units in West Lake. The mean pH in all three lakes remained very close to or above 6.0, the level used as a biological threshold for analyses of critical loads (see STAR and KAA reports).

The results from these lakes further confirm the results from the first year of continuous monitoring – i.e., that there is high variability in pH, substantially higher than originally expected. Understanding that natural intra-annual variation is very high was one of the primary reasons for conducting the power analyses (see Section 2.9 for brief description and reference to detailed documentation). The power analyses have now shown that continuous monitoring increases the power of the monitoring program to be able to correctly detect changes in pH that exceed the EEM KPI threshold of 0.3 pH units.

Table 3-4. Minimum, maximum, average and range of pH measurements taken every 30 minutes in each of End, Little End and West lakes in April to November 2015.

Lake	Sensor	Number of observations	Minimum pH	Maximum pH	Range of pH	Mean pH ± SD
End	pH1	9501	5.7	6.7	1.0	6.28 ± 0.16
End	pH2	9501	5.7	6.7	1.0	6.28 ± 0.16
End	pH3	9501	5.7	6.7	1.0	6.37 ± 0.15
Little End	pH1	8380	5.5	6.6	1.1	6.02 ± 0.21
Little End	pH2	8380	5.4	6.5	1.1	5.93 ± 0.20
Little End	pH3	8380	5.5	6.6	1.1	5.99 ± 0.20
West	pH1	10163	5.9	6.7	0.8	6.39 ± 0.15
West	pH2	10163	5.8	6.6	0.8	6.27 ± 0.14
West	pH3	10163	5.9	6.7	0.8	6.32 ± 0.14

Table 3-5. Mean (± standard deviation) pH of discrete samples collected on Oct 4, Oct 13, Oct 20, and Oct 27 at each of the three lakes.

Instrument or lab	Mean pH ± sd in October, 2015 (n=4)

	End Lake	**Little End Lake**	**West Lake**
WTW field pH meter	5.96 ± 0.29	5.79 ± 0.16	5.99 ± 0.39
Trent University	6.01 ± 0.13	5.95 ± 0.16	5.94 ± 0.12
ALS	6.42 ± 0.57	6.33 ± 0.30	6.22 ± 0.13
Manta sensors	**6.19 ± 0.13**	**5.94 ± 0.12**	**6.24 ± 0.15**
Instrument/lab effect (*P*)	0.245	0.014	0.185

3.4 Inter-annual Changes

Inter-annual changes in pH, Gran ANC, SO_4^{2-}, DOC, sum of base cations, and chloride are shown in terms of absolute change in Table 3-6 and Table 3-7, and in terms of relative change in Table 3-8 and Table 3-9. Changes are shown for four time periods of comparison: 2012-2013, 2013-2014, 2014-2015, and 2012-2015. The sensitive EEM lakes and less sensitive EEM lakes are presented separately within each of the tables.

Figure 3-3 and Figure 3-4 show the changes in the same water chemistry parameters graphically. These figures allow better visualization of the distribution and variability in the observed changes between 2014 and 2015. Although the tables show changes for other periods as well, these figures have only been included for the changes from 2014 to 2015. Changes from 2014 to 2015 in particular are examined in more detail, in the context of expected changes based on the Evidentiary Framework, in Section 4.1 in the Discussion.

Appendix 2 provides a detailed set of figures showing the inter-annual changes in major water chemistry metrics (Gran ANC, base cations, SO_4^{2-}, chloride, pH and DOC) for each of the EEM lakes across the four years of annual monitoring (2012-2015).

Table 3-6. Inter-annual changes in pH, Gran ANC and SO_4^{2-} for EEM lakes, 2012-2015. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	pH				Gran ANC (ueq/L)				SO4* (μeq/L)			
From	2012	2013	2014	2012	2012	2013	2014	2012	2012	2013	2014	2012
To	2013	2014	2015	2015	2013	2014	2015	2015	2013	2014	2015	2015
Lak006	0.4	0.1	-0.1	0.4	3.3	7.8	-5.4	5.7	3.0	-3.4	-0.3	-0.7
Lak012	0.6	0.0	-0.1	0.5	6.5	16.8	-9.6	13.7	5.2	-5.5	2.7	2.4
Lak022	0.2	0.1	-0.1	0.2	8.5	10.5	-11.3	7.7	16.9	-9.3	-5.3	2.3
Lak023	0.2	0.1	0.0	0.4	4.0	11.7	-8.2	7.6	5.0	-7.4	-3.6	-5.9
Lak028	0.2	0.1	-0.2	0.2	8.8	17.8	-11.8	14.8	71.2	-33.7	-23.3	14.2
Lak042	0.8	-0.4	0.3	0.7	41.4	-8.5	1.3	34.2	-0.5	-1.8	-0.2	-2.4
Lak044	0.3	0.1	0.0	0.4	7.3	-2.7	0.3	4.9	0.0	-1.6	-0.9	-2.5
Average (Sensitive lakes)	**0.39**	**0.02**	**-0.02**	**0.39**	**11.4**	**7.6**	**-6.4**	**12.7**	**14.4**	**-8.9**	**-4.4**	**1.0**

Lak007	0.0	0.1	-0.1	0.0	24.5	-16.4	119.9	128.1	15.1	-35.8	14.9	-5.8
Lak016	0.4	0.0	0.0	0.4	28.3	8.8	7.4	44.4	17.9	-8.7	-7.2	1.9
LAK024	[1]	[1]	-0.2	0.3	[1]	[1]	-29.1	143.5	[1]	[1]	-2.4	9.9
Lak034	0.1	-0.1	-0.1	-0.1	111.0	-5.4	-27.1	78.4	14.0	-21.1	-16.1	-23.2
Average (Less sensitive lakes)	**0.15**	**0.02**	**-0.09**	**0.16**	**54.6**	**-4.3**	**17.8**	**98.6**	**15.7**	**-21.9**	**-2.7**	**-4.3**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-7. Inter-annual changes in DOC, base cations and chloride for EEM lakes, 2012-2015. The differences between subsequent years and across the full record of sampling are shown. DOC = dissolved organic carbon, ΣBC = sum of base cations (i.e., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	DOC (mg/L)				∑ BC* (µeq/L)				Cl (µeq/L)			
From	2012	2013	2014	2012	2012	2013	2014	2012	2012	2013	2014	2012
To	2013	2014	2015	2015	2013	2014	2015	2015	2013	2014	2015	2015
LAK006	-0.4	0.2	0.1	-0.1	-3.0	8.7	1.8	7.5	2.9	-2.2	-0.6	0.2
LAK012	-0.4	0.3	-0.2	-0.3	-11.8	2.7	-1.6	-10.7	10.5	-8.5	0.0	2.1
LAK022	0.9	-0.6	0.6	1.0	11.0	4.9	-6.2	9.7	5.4	-3.3	-1.1	1.0
LAK023	-0.1	0.7	-0.5	0.1	-2.1	7.4	-3.0	2.3	3.0	-1.8	-0.3	0.9
LAK028	2.2	-1.1	2.2	3.2	48.4	4.4	-15.9	36.9	11.7	-6.7	-2.0	3.0
LAK042	-3.5	0.9	-2.3	-4.8	7.6	-5.3	3.7	5.9	1.6	4.1	-5.4	0.3
LAK044	-0.2	0.3	-0.2	-0.1	3.0	0.1	2.9	6.0	3.3	-2.9	0.0	0.3
Average (Sensitive lakes)	**-0.2**	**0.1**	**0.0**	**-0.1**	**7.6**	**3.3**	**-2.6**	**8.2**	**5.5**	**-3.1**	**-1.9**	**1.1**
LAK007	-0.5	0.6	-0.5	-0.4	-51.9	63.5	-7.8	3.8	11.7	-17.1	4.8	-0.6
LAK016	0.5	-0.2	0.3	0.6	0.8	13.7	7.8	22.3	6.0	-3.0	-0.6	2.4
LAK024	[1]	[1]	0.5	0.8	[1]	[1]	-2.8	167.6	[1]	[1]	-6.8	31.7
LAK034	0.1	2.4	0.5	3.0	56.0	8.6	-32.3	32.3	2.5	-1.8	-0.3	0.4
Average (Less sensitive lakes)	**0.0**	**0.9**	**0.2**	**1.0**	**1.6**	**28.6**	**-8.7**	**56.5**	**6.7**	**-7.3**	**-0.7**	**8.5**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-8. Inter-annual changes (%) in pH, Gran ANC and SO_4^{2-} for EEM lakes, 2012-2015. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	pH (TU)				Gran ANC (mg/L)				SO_4^{2-} * (µeq/L)			
From	2012	2013	2014	2012	2012	2013	2014	2012	2012	2013	2014	2012
To	2013	2014	2015	2015	2013	2014	2015	2015	2013	2014	2015	2015
LAK006	6%	1%	-1%	6%	13%	27%	-15%	22%	26%	-24%	-3%	-6%
LAK012	12%	0%	-1%	10%	11%	26%	-12%	24%	84%	-49%	47%	40%
LAK022	4%	2%	-2%	3%	31%	29%	-24%	28%	56%	-20%	-14%	8%
LAK023	4%	2%	1%	7%	20%	49%	-23%	38%	26%	-31%	-22%	-31%
LAK028	5%	2%	-4%	3%	[1]	372%	-52%	[1]	125%	-26%	-25%	25%
LAK042	17%	-6%	6%	15%	[1]	-40%	10%	[1]	-7%	-31%	-5%	-39%
LAK044	5%	2%	0%	7%	576%	-32%	6%	387%	0%	-26%	-19%	-40%
Average (Sensitive lakes)	**7%**	**0%**	**-0.30%**	**7%**	**130%**	**20%**	**-16%**	**120%**	**44%**	**-29%**	**-6%**	**-6%**
LAK007	-1%	2%	-1%	0%	2%	-1%	8%	9%	29%	-54%	49%	-11%
LAK016	6%	1%	0%	7%	41%	9%	7%	65%	46%	-15%	-15%	5%
LAK024	[2]	[2]	-3%	4%	[2]	[2]	-6%	48%	[2]	[2]	-7%	40%
LAK034	2%	-2%	-2%	-2%	112%	-3%	-13%	79%	58%	-55%	-95%	-96%
Average (Less sensitive lakes)	**2%**	**0%**	**-1%**	**2%**	**52%**	**2%**	**-1%**	**50%**	**44%**	**-41%**	**-17%**	**-16%**

[1] LAK028 and LAK042 had negative ANC values in 2012 and therefore the percentage change could not be properly calculated.

[2] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-9. Inter-annual changes (%) in DOC, base cations and chloride for EEM lakes, 2012-2015. The differences between subsequent years and across the full record of sampling are shown. DOC = dissolved organic carbon, ΣBC = sum of base cations (e.g., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	DOC (mg/L)				∑ BC* (μeq/L)				Cl (μeq/L)			
From	2012	2013	2014	2012	2012	2013	2014	2012	2012	2013	2014	2012
To	2013	2014	2015	2015	2013	2014	2015	2015	2013	2014	2015	2015
Lak006	-10%	6%	2%	-3%	-5%	15%	3%	12%	51%	-25%	-9%	3%
Lak012	-9%	7%	-4%	-6%	-10%	2%	-1%	-9%	254%	-58%	0%	49%
Lak022	17%	-9%	11%	18%	11%	5%	-5%	10%	78%	-27%	-13%	14%
Lak023	-3%	18%	-10%	3%	-3%	12%	-4%	3%	67%	-24%	-5%	20%
Lak028	45%	-16%	36%	66%	66%	4%	-13%	51%	193%	-38%	-18%	49%
Lak042	-26%	9%	-21%	-37%	14%	-9%	7%	11%	26%	53%	-45%	6%
Lak044	-12%	17%	-11%	-7%	21%	1%	17%	43%	59%	-33%	0%	6%
Average (Sensitive lakes)	**0%**	**5%**	**0%**	**5%**	**14%**	**4%**	**0%**	**17%**	**104%**	**-22%**	**-18%**	**21%**
Lak007	-84%	610%	-65%	-59%	-3%	4%	-1%	0%	48%	-47%	25%	-3%
Lak016	14%	-4%	8%	17%	0%	8%	4%	13%	95%	-24%	-6%	38%
LAK024	[1]	[1]	30%	59%	[1]	[1]	-1%	49%	[1]	[1]	-10%	116%
Lak034	3%	51%	7%	66%	28%	3%	-12%	16%	42%	-21%	-4%	7%
Average (Less sensitive lakes)	**-22%**	**219%**	**-5%**	**21%**	**8%**	**5%**	**-2%**	**20%**	**62%**	**-31%**	**1%**	**40%**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

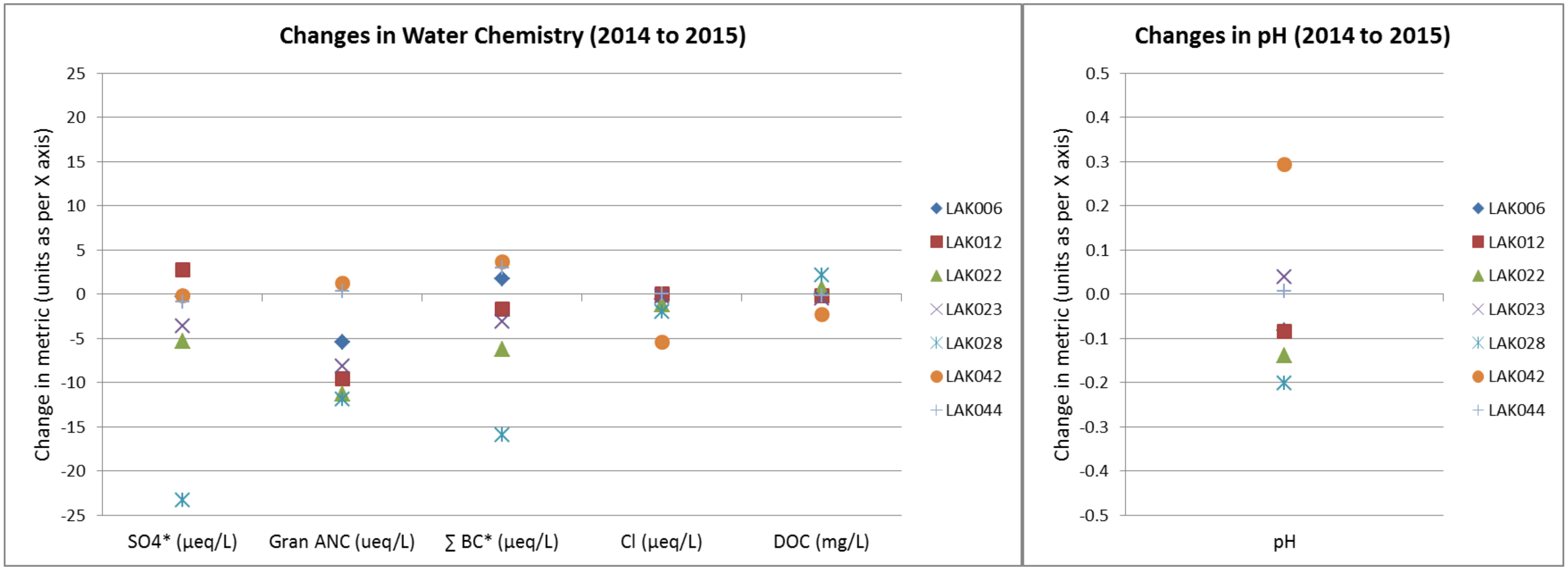


Figure 3-3: Changes in water chemistry parameters (left panel) and pH (right panel) across all of the sensitive EEM lakes, from 2014 to 2015. Values shown are 2015 value minus 2014 value.

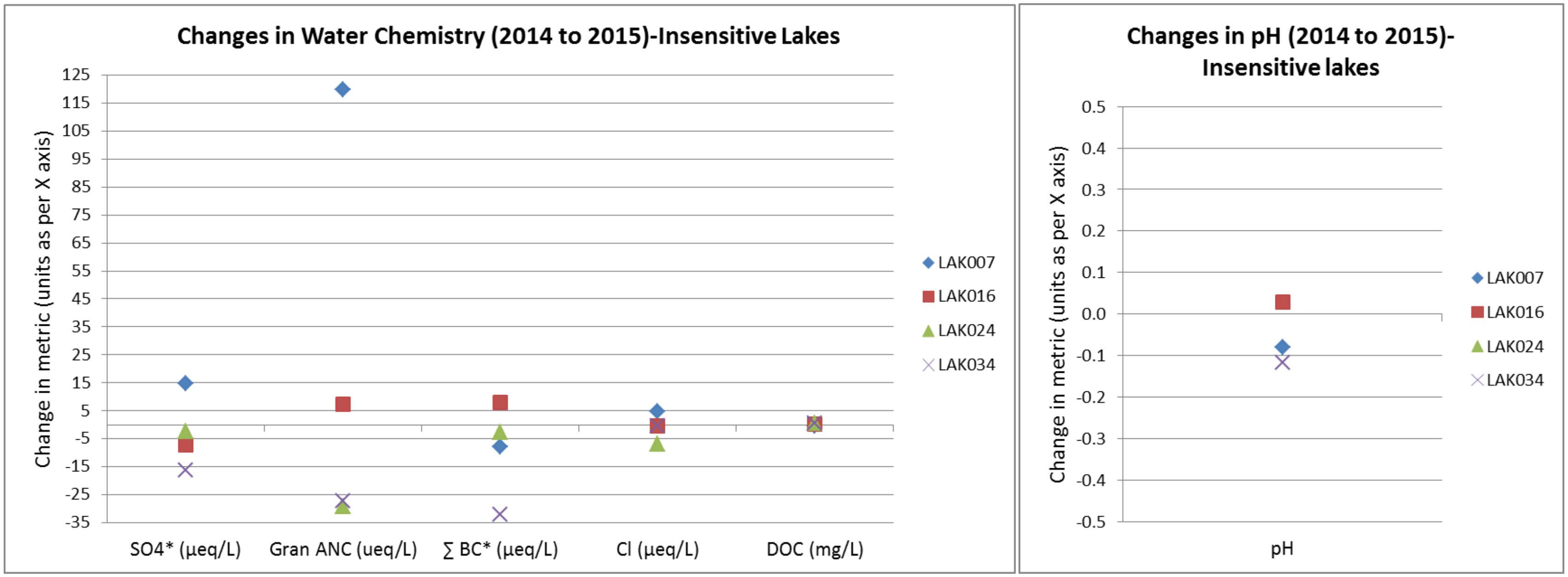


Figure 3-4: Changes in water chemistry parameters (left panel) and pH (right panel) across all of the less sensitive EEM lakes, from 2014 to 2015. Values shown are 2015 value minus 2014 value.

3.5 Fish Sampling ⑦

Fish were sampled from LAK007, LAK016, and LAK034 (less sensitive EEM lakes) in 2015. Limnotek (2016, Section 3.2) provide a detailed description of the fish sampling results. Fish presence was reported in all three lakes and the average values of fish population and biomass metrics were similar between these less sensitive lakes (2015 sampling) and the acid sensitive lakes (2013 sampling), although the variability in the metrics was higher for the less sensitive lakes.

The executive summary of Limnotek (2016) technical report provides a description of fish species distribution in the acid insensitive lakes sampled in 2015:

Six species were found in LAK007, three were found in LAK016, and two were found in LAK034. Coastal cutthroat trout (Oncorhynchus clarkii clarkii, CCT) were common in all three lakes. Both LAK007 and LAK016 had coastal cutthroat trout (Oncorhynchus clarkii clarkii, CCT), Coho salmon (Oncorhynchus kisutch, CO), and Dolly Varden char (Salvelinus malma, DV) whereas LAK034 only had CCT and Threespine Stickleback (Gasterosteus aculeatus, TSB). Large Coho of up to 355 mm in length were captured in LAK016. These large individuals resembled the residualized adult Coho captured in 2013 in West lake and are unique among common life histories of Coho salmon. The presence of these residualized Coho is attributed to periodic inaccessibility to and from waterbodies during certain hydrologic conditions that causes the adults to become "locked" into the lakes.

Limnotek (2016, p. v)

3.6 Episodic Acidification Studies ④

Continuous pH Monitoring in Anderson Creek

There were 199 days of continuous data. The three pH sensors on the Manta showed the same temporal changes, meaning there was no difference among the sensors in detecting ambient pH. There were however large differences in pH between the Manta and two other measurement methods. Results from the other measurement methods corresponded closely to each other, which suggests that the Manta data may not be correct. Further details are provided in Limnotek's technical report (Limnotek 2016).

Research Project by Dr. Paul Weidman

As this project is being conducted by an external organization, the results from this work will be communicated separately as they become available.

3.7 Water Residence Time for Lakes

The bathymetric survey results and lake volume calculations for LAK006, LAK012 and LAK023 are presented in Limnotek (2016). Table 3-10 shows the updated volume calculations compared to the preliminary estimates, along with preliminary interpretation of the implications of these results.

Detailed results on the calculation of water residence time, including accounting for the uncertainty around the volume estimates, are currently not available but will be included in future reporting.

Further investigation of these results and their implications for interpretation and analysis of EEM monitoring data has not yet been completed, but will be incorporated in future analyses.

Table 3-10. Changes in the estimates of lake volume for LAK006, LAK012 and LAK023 along with potential implications for the EEM Program.

Lake	Preliminary estimates of Lake Volume in EEM Plan (m^3)	Precise estimates of Lake Volume (m^3)	Preliminary interpretation of implications
End Lake (LAK 006)	584,232	1,129,350	Lake volume and water residence time underestimated by ~50% in EEM report. Updated residence time is closer to 1.4 years (compared to 1.1 years). This might help to explain why LAK 006 has high power to detect ΔANC and ΔSO_4^{2-}, but does not explain why it has relatively low power to detect ΔpH.
Little End Lake (LAK 012)	80,538	94,455	Lake volume and water residence time underestimated by ~15% in EEM report; still very low water residence time (~0.1 years), which should cause high variability in water chemistry, as is observed for pH (very poor statistical power to detect ΔpH). However, statistical power to detect ΔANC for LAK 012 is much better than for LAK 028 or LAK 042
West Lake (LAK 023)	182,857	185,064	Lake volume and water residence time very close to estimate in EEM report (underestimated by ~1.2% in EEM report).

4 Discussion

This section is divided based on two sets of sample sites: 1) the lakes representing the core of the EEM sampling program, and 2) other sample sites outside of the core EEM lakes that were included in 2015.

4.1 EEM Lakes

Application of the Evidentiary Framework

As noted in Section 2.4, the Evidentiary Framework has not been formally applied in the present EEM Annual Report because 2015 was a transitional period between the old smelter and KMP, with a decline in SO_2 emissions (Figure 4 in main report). However, we did consider the general principles of the evidentiary framework, which suggest that 2015 sulphate concentrations should decrease relative to 2014 (due to declining emissions of SO_2), and that ANC and pH levels should correspondingly increase, if all other constituents and hydrologic conditions remained unchanged. As noted in the EEM Evidentiary Framework, changes in base cations, nitrate or DOC can help to explain observed changes in ANC and pH.

Inter-annual Changes in Lake Chemistry, 2014-2015

Some of the main patterns observed in the changes in lake chemistry between 2014 and 2015:

Sulphate

- 6 of 7 sensitive lakes and 3 of 4 less sensitive lakes showed decreases in SO_4^{2-}, which is generally consistent with the decrease in SO_2 emissions and expectations from the evidentiary framework.
    - 5 of these lakes showed decreases of 10-30%
    - LAK034 decreased by 95%
- Two lakes (LAK012 and LAK007) showed increases in SO_4^{2-} of almost 50%. It's not clear why this occurred in only 2 of the 11 monitored lakes, particularly since both LAK012 and LAK007 showed the expected decreases in SO_4^{2-} between 2013 and 2014 (Table 3-6). Watmough et al. (2005) cite a number of studies describing multiple mechanisms by which watersheds can potentially release sulphate: "Possible (and not mutually exclusive) internal sources, include release from wetland areas within catchments, desorption in response to declining SO4 concentrations in deposition, weathering of S minerals and mineralisation of organic S in soil."

ANC

- For the sensitive lakes, increases in ANC would be expected (based on the evidentiary framework) to accompany decreases in SO_2 emissions and SO_4^{2-} concentrations.
    - This expected pattern was only observed in 2 of 7 sensitive lakes (LAK 042 and LAK 044); both of these lakes also showed increases in total base cations (Table 3-6, Table 3-7). DOC declined by 2.3 mg/l in LAK 042, and that change likely contributed to the observed increase in ANC in LAK 042 through a decrease in organic acids.
    - In the other 5 sensitive lakes ANC decreased (including some significant decreases of 23%, 24%, and 52%) accompanying decreases in SO_4^{2-}, contrary to expectations. Base cations also declined in 4 of these 5 lakes, and likely contributed to the decline in ANC (Table 3-6, Table 3-7). However, since the magnitude of decrease in base cations was less than the magnitude of ANC decline in 3 of these 4 lakes, decreases in base cations are not sufficient to explain all of the ANC declines in these lakes. An increase in DOC of 2.2 mg/l in LAK028 (Table 3-7) might have also contributed to the ANC decline in that lake.
- For the less sensitive lakes, changes in ANC would be expected to be independent of changes in SO_4^{2-} as well as being relatively small
    - Two lakes showed increases in ANC (LAK 007 and LAK 016) and two lakes showed decreases (LAK 024 and LAK 034)
    - Both of the lakes which showed decreases in ANC also showed decreased in total base cations (Table 3-6, Table 3-7), though the magnitudes of change were only comparable in LAK 034.
    - Only 1 of 4 less sensitive lakes demonstrated inverse changes in ANC and SO_4^{2-}
    - Changes in ANC were within the range 8-13%, even for the two lakes with substantial changes in SO_4^{2-}

pH

- For all of the lakes, changes in pH would be expected to be in the same direction as changes in ANC, as per the relationship defined by the pH-alkalinity titration curve (though the magnitude of the pH change would depend on the specific location along the curve)
    - 6 of 7 sensitive lakes demonstrate this expected pattern, including 4 lakes with decreases and 2 lakes with increases in the two metrics

    - 3 of 4 less sensitive lakes demonstrate this expected pattern, including 2 lakes with decreases and 1 lake with increases in the two metrics
    - However, the two lakes that do not follow this pattern had only small changes in pH (+0.0 for LAK023, -0.1 for LAK007)
- pH decreased for 4 of 7 sensitive lakes and 3 of 4 less sensitive lakes

Other metrics

- 5 of 11 EEM lakes decreased in DOC
- 7 of 11 EEM lakes decreased in total base cations
- 10 of 11 EEM lakes decreased (8) or remained the same (2) in chloride.
- The above pattern would be consistent with greater amounts of precipitation in 2015 compared to 2014, which would result in greater dilution of both base cations and chloride. However, precipitation data (Figure 9 in main report) indicate that while there was a slight increase in precipitation at the KMP Campsite location, there was no increase in precipitation at the Lakelse Lake site (in fact a slight decrease).

4.2 Non-EEM Sites

Goose Creek

Goose Creek was sampled at two additional sites in 2015, to supplement the six sites sampled in 2014. Lake chemistry has been assessed for Goose Creek, but not critical loads.

The two new sites show definite influence of the smelter emissions, due to their very high levels of both SO_4^{2-} (much higher than any other observations) and F. However, based on their high pH, high ANC and very high base cations, these sites appear to be insensitive to potential acidification.

5 Recommendations

5.1 Recommendations regarding EEM lakes

The rationale for these recommendations is primarily supported by the power analyses. Please refer to the summary report (Technical Memo W04) and technical appendix (Technical Memo W05) on the power analyses for further details on these recommendations, as well as additional recommendations that are more specific to the power analyses and future analyses of the monitoring data.

- Maintain the continuous monitoring of pH at the three accessible lakes
- Collect water chemistry samples for lab analyses from the three lakes with continuous pH monitors four times during the fall sampling period
- Continue to use multiple metrics to assess potential KMP effect (i.e., ANC, SO_4^{2-} and pH)
- Continue collecting annual water chemistry samples from the three control lakes that were added to the EEM
- Wait until having collected 5 years of post-KMP monitoring data before drawing conclusions about potential changes to lake chemistry, due to the predicted low power and higher false positives (for some scenarios) in the first few years of post-KMP monitoring.

At a minimum, wait until the end of the initial phase of the EEM program (3 years of post-KMP monitoring data).

- Consider using Gran ANC as the primary indicator of KMP induced change in lake chemistry. Gran ANC had a higher power to detect true changes than pH but lower false positive rate than SO_4^{2}-.
- Explore the feasibility of increasing the number of samples for lakes with low power to correctly detect whether the EEM KPI thresholds have been exceeded (in order of priority, with metrics with low power indicated):
    - LAK042 (pH, ANC)
    - LAK028 (ANC, SO_4^{2-})
    - LAK044 (ANC, SO_4^{2-})

5.2 Recommendations regarding non-EEM sites

- No additional activities recommended for non-EEM sites at this time.

6 References Cited

Bennett, S. 2014. Technical Memorandum: Goose Creek Sampling. Limnotek Research & Development Inc., December 2, 2014.

Bennett, S. 2016. Technical Memorandum: Update on Goose Creek Sampling in 2015. Limnotek Research & Development Inc., February 2, 2016.

Bennett, S. and C. Perrin. 2015. Technical Memorandum: Continuous Monitoring of pH in West Lake, End Lake and Little End Lake in fall, 2014 . Limnotek Research & Development Inc., January 19, 2015.

Clow, D.W., J.O. Sickman, R.G. Striegl, D.P. Krabbenhoft, J.G. Elliott, M.Dornblaser, D.A. Roth and D.H. Campbell. 2003. Changes in the chemistry of lakes and precipitation in high-elevation national parks in the western United States, 1985–1999. Water Resources Research. Vol. 39 (6): 1131 http://onlinelibrary.wiley.com/doi/10.1029/2002WR001533/epdf

Driscoll, C.T., G.B. Lawrence, A.J. Bulger, T.J. Butler, C.S. Cronan, C.Eager, K.F. Lambert, G.E. Likens, J.L. Stoddard, and K.C. Weathers. 2001a. Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. BioScience 51(3):180-198.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Vol.2: Final Technical Report. Prepared for RTA, Kitimat, BC. 450 pp.

ESSA Technologies, J. Laurence, Risk Sciences International, Trent University, and Trinity Consultants. 2014a. Kitimat Airshed Emissions Effects Assessment. Report prepared for BC Ministry of Environment, Smithers, BC. 205 pp. + appendices.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014b. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto Alcan, Kitimat, B.C. 99 pp.

ESSA Technologies. 2015. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project – 2013 and 2014 Annual Reports. Prepared for Rio Tinto Alcan, Kitimat, B.C. 27 pp.

ESSA Technologies Ltd. 2016. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project – 2015 Annual Report. Prepared for Rio Tinto Alcan, Kitimat, B.C.

Henriksen A. and M. Posch. 2001. Steady-state models for calculating critical loads of acidity for surface waters. Water, Air and Soil Pollution: Focus 1: 375-398.

Henriksen A., P.J. Dillon, and J. Aherne. 2002. Critical loads of acidity for surface waters in south-central Ontario, Canada: regional application of the steady-state water chemistry (SSWC) model. Canadian Journal of Fisheries and Aquatic Sciences 59: 1287-1295.

Herlihy, A.T., D.H. Landers, R.F. Cusimano, W.S. Overton, P.J. Wigington, Jr., A.K. Pollack, and T.E. Mitchell-Hall. 1990. Temporal Variability in Lakewater Chemistry in the Northeastern United States: Results of Phase II of the Eastern Lake Survey. National Surface Water Survey, Aquatic Effects Research Program, United States Environmental Protection Agency, Washington, DC. 234 pp.

Landers, D.H., J. M. Eilers, D.F. Brakke, W.S. Overton, P.E. Keliar, M.E. Silverstein, R.D. Schonbrod, R.E. Crowe, R.A. Linthurst, J.M. Omernik, S.A. Teague, and E.P. Meier. 1987. Characteristics of Lakes in the Western United States. Volume I. Population Descriptions and Physico-Chemical Relationships. EPA/600/3-86/054a. U.S. Environmental Protection Agency, Washington, DC. 176pp.

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

Moore, R.D., J.W. Trubilowicz, and J.M. Buttle. 2012. Prediction of streamflow regime and annual runoff for ungauged basins using a distributed monthly water balance model. Journal of the American Water Resources Association 48(1): 32–42.

Perrin, C.J and S. Bennett 2015. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lake water quality in 2014. Data report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 20p.

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

Small, M.J. and M.C. Sutton. 1986. A Regional pH-Alkalinity Relationship. Water Research 20(3): 335-343.

UNECE. 2004. Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends. Federal Environment Agency, Texte 52/04, Berlin, Germany, URL: http://www.icpmapping.org/Mapping_Manual

Watmough, S.A., J. Aherne, C. Alewell, P. Arp, S. Bailey, T. Clair, P. Dillon, L. Duchesne, C. Eimers, I. Fernandez, N. Foster, T. Larssen, E. Miller, M. Mitchell and S. Page. 2005. Sulphate, nitrogen and base cation budgets at 21 forested catchments in Canada, the United States and Europe. Environmental Monitoring and Assessment (2005) 109: 1–36

7 Cited EEM Technical Memos

Technical Memo W04. Summary Report on Power Analyses (March 2016, ESSA Technologies)

Technical Memo W05. Power Analyses Technical Appendix (March 2016, ESSA Technologies)

Appendix 1: Water Chemistry Data from Annual Sampling, 2012-2014

The table below shows the sample results for each of the EEM lakes from annual monitoring conducted in 2012, 2013, 2014 and 2015. including pH, dissolved organic carbon (DOC), Gran ANC, and the concentration of major anions and cations, as well as the sum of all base cations (BC). In 2013-2015, the pH of the water samples was measured by two different laboratories (Trent University and ALS).

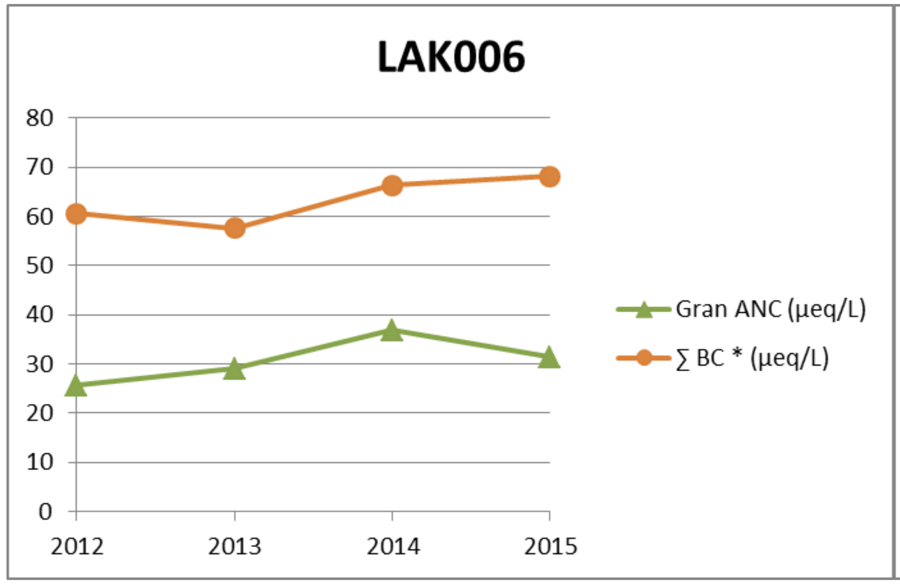
Lake	Year	Lab pH (Trent)	Lab pH (ALS)	DOC (mg/L)	Gran ANC (µeq/L)	SO4 (µeq/L)	Cl (µeq/L)	F (µeq/L)	Ca (µeq/L)	Mg (µeq/L)	K (µeq/L)	Na (µeq/L)	∑ BC (µeq/L)
LAK006	2012	5.8		3.6	25.7	12.0	5.8	4.5	30.5	13.6	3.0	19.8	67.0
LAK007	2012	8.0		0.6	1437.6	53.9	24.6	2.8	1273.1	161.8	19.8	76.5	1531.2
LAK012	2012	5.6		4.6	57.0	6.6	4.2	5.0	74.7	21.6	5.3	23.6	125.2
LAK016	2012	6.3		3.7	68.7	39.7	6.3	7.8	117.9	21.8	7.4	26.2	173.3
LAK022	2012	5.9		5.3	27.8	30.9	6.9	6.1	58.4	17.4	3.3	26.7	105.8
LAK023	2012	5.7		4.2	19.8	19.5	4.5	5.6	39.6	12.9	3.7	14.7	70.9
LAK024	2012	7.1		1.4	299.5	27.6	27.3	1.6	274.2	38.4	4.7	53.0	370.3
LAK028	2012	5.0		4.9	-4.0	57.5	6.1	20.7	47.8	10.7	3.2	18.0	79.6
LAK034	2012	6.7		4.5	99.4	24.7	5.8	5.8	119.5	32.8	5.9	49.9	208.1
LAK042	2012	4.7		13.2	-20.4	6.8	6.1	3.2	7.6	23.9	3.2	25.5	60.2
LAK044	2012	5.4		1.7	1.3	6.8	5.6	2.9	7.0	4.3	4.2	4.8	20.4
LAK006	2013	6.2	6.1	3.2	29.0	15.3	8.7	5.6	27.4	14.7	5.4	19.7	67.2
LAK007	2013	7.9	8.1	0.1	1462.1	70.3	36.3	3.7	1227.3	163.7	22.6	78.8	1492.4
LAK012	2013	6.3	6.1	4.2	63.5	12.8	14.7	8.2	65.4	23.2	9.5	27.2	125.2
LAK016	2013	6.7	7.2	4.2	96.9	58.2	12.3	11.5	114.9	26.3	11.4	28.1	180.8
LAK022	2013	6.2	6.1	6.2	36.4	48.3	12.4	8.7	65.6	21.7	6.2	29.4	122.8
LAK023	2013	6.0	6.0	4.0	23.8	24.8	7.5	7.4	37.4	14.8	5.3	14.7	72.2
LAK028	2013	5.2	5.5	7.1	4.8	129.9	17.7	32.0	85.8	21.8	5.3	28.2	141.0
LAK034	2013	6.9	7.4	4.7	210.4	39.0	8.2	10.0	153.0	43.3	9.3	61.2	266.9
LAK042	2013	5.5	5.4	9.7	21.0	6.5	7.7	3.2	16.3	23.8	3.6	25.9	69.6
LAK044	2013	5.7	6.0	1.5	8.6	7.1	8.9	3.8	8.1	5.3	6.0	5.6	25.1
LAK006	2014	6.2	6.7	3.4	36.8	11.7	6.5	5.1	31.8	15.9	4.3	21.5	73.5
LAK007	2014	8.1	8.0	0.7	1445.7	32.7	19.2	1.9	1277.5	160.5	20.6	78.3	1536.9
LAK012	2014	6.3	6.7	4.6	80.3	6.5	6.2	5.7	65.4	21.4	6.2	25.5	118.5
LAK016	2014	6.7	6.7	4.0	105.7	49.1	9.3	9.5	122.8	26.8	10.2	31.3	191.1
LAK022	2014	6.3	6.4	5.7	46.9	38.7	9.0	6.9	68.9	20.7	5.3	29.1	124.1
LAK023	2014	6.1	6.2	4.8	35.5	17.3	5.6	6.7	42.4	15.6	3.9	15.6	77.5
LAK024	2014	7.6	7.5	1.7	472.1	43.9	65.7	2.3	404.7	63.1	9.0	106.6	583.4
LAK028	2014	5.3	5.7	5.9	22.6	95.6	11.0	23.3	86.3	19.9	4.6	27.1	137.9
LAK034	2014	6.7	7.0	7.0	205.0	17.7	6.5	7.7	161.7	44.8	9.5	57.4	273.5
LAK042	2014	5.1	5.4	10.6	12.5	5.2	11.8	2.6	10.9	25.9	3.9	28.1	68.8
LAK044	2014	5.8	5.6	1.8	5.9	5.2	5.9	2.8	8.0	5.1	5.4	5.5	23.9

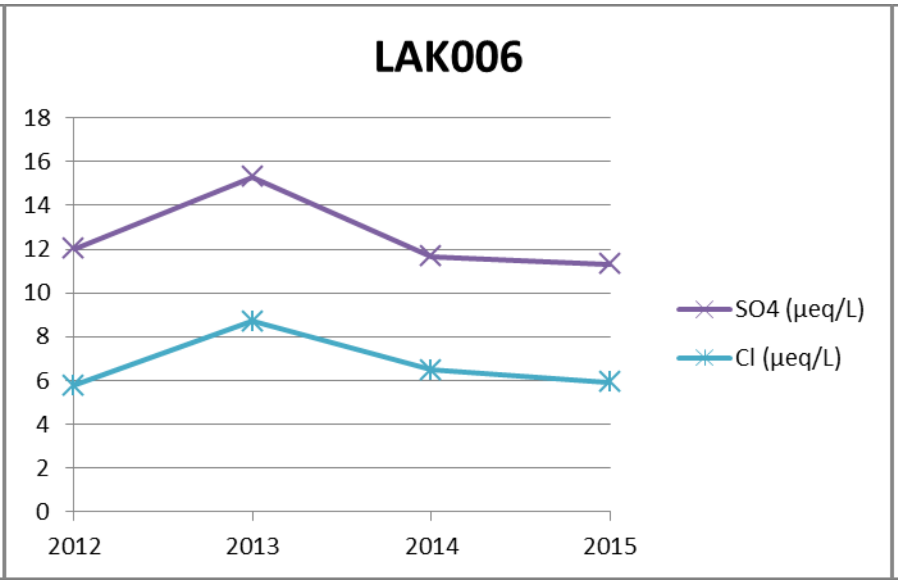
Lake	Year	Lab pH (Trent)	Lab pH (ALS)	DOC (mg/L)	Gran ANC (µeq/L)	SO4 (µeq/L)	Cl (µeq/L)	F (µeq/L)	Ca (µeq/L)	Mg (µeq/L)	K (µeq/L)	Na (µeq/L)	∑ BC (µeq/L)
Lak006	2015	6.2	6.2	3.5	31.4	11.3	5.9	4.7	32.7	16.3	4.0	21.7	74.7
Lak007	2015	8.0	7.9	0.3	1565.6	48.1	24.0	2.6	1267.5	166.2	21.5	79.2	1534.4
Lak012	2015	6.2	6.2	4.4	70.7	9.2	6.2	5.0	63.4	21.9	6.2	25.4	116.8
LAK016	2015	6.8	6.9	4.3	113.1	41.8	8.7	8.6	131.2	26.7	9.9	30.4	198.3
LAK022	2015	6.1	6.2	6.3	35.6	33.3	7.9	5.9	64.4	19.7	4.6	28.0	116.6
Lak023	2015	6.1	6.2	4.3	27.4	13.7	5.4	5.6	42.0	14.2	3.7	14.2	74.1
Lak024	2015	7.4	7.5	2.2	443.0	40.8	59.0	2.1	402.7	61.0	9.8	99.6	573.1
LAK028	2015	5.1	5.3	8.1	10.8	72.0	9.0	20.5	76.9	17.4	3.4	22.2	119.9
LAK034	2015	6.6	6.7	7.6	177.8	1.5	6.2	4.7	146.7	38.3	5.4	50.5	240.9
LAK042	2015	5.4	5.5	8.3	13.8	4.5	6.5	2.3	11.0	24.4	2.7	28.5	66.5
LAK044	2015	5.8	5.8	1.6	6.2	4.3	5.9	2.7	10.0	5.6	5.6	5.6	26.8

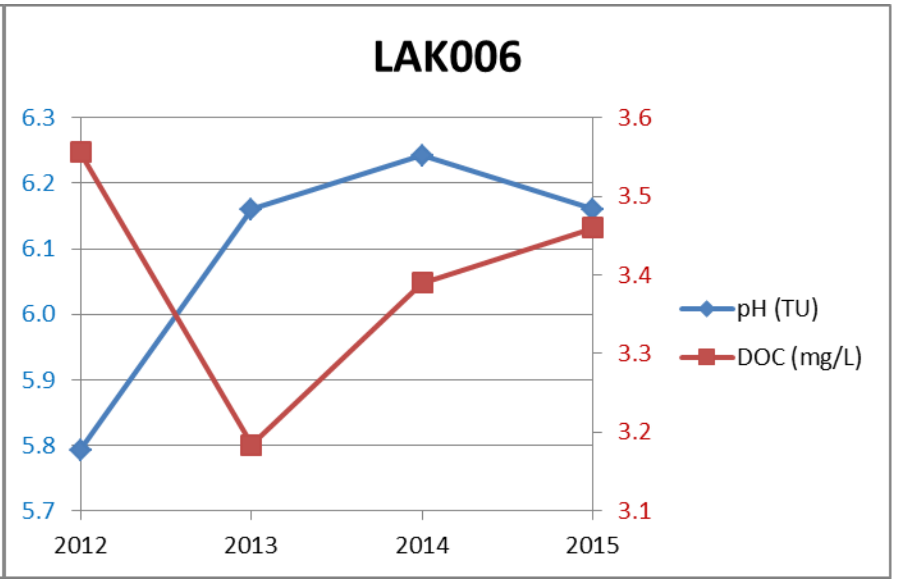
Appendix 2: Changes in Ion Concentrations from 2012 to 2015

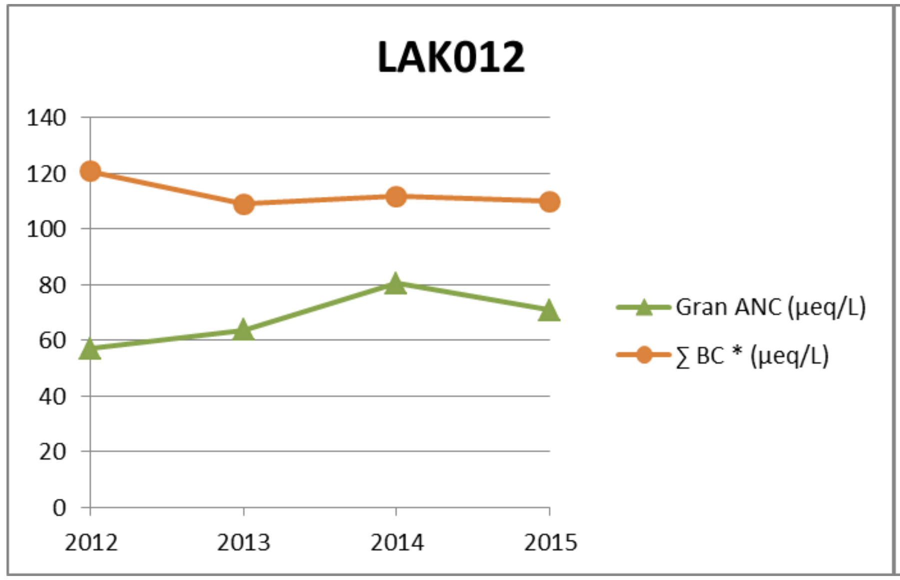
For each of the EEM lakes, the figures in this appendix show the inter-annual changes in six major water chemistry metrics from 2012 to 2015: Gran ANC and base cations (left panel), sulfate and chloride (centre panel), and pH and dissolved organic carbon (right panel). The selection of each pair of metrics is solely based on optimizing graphical representation across all metrics and lakes (i.e., metrics with somewhat similar numeric ranges are shown together). The right panel has two Y-axes, neither of which start at zero – be aware that this can make relatively minor changes appear to be much more substantial than they are. Due to large variation among the lakes for some of the metrics, the Y-axis is not consistent across the lakes, therefore extra caution is required for making comparisons among lakes with respect to the magnitude of changes. However, these graphs are especially useful for looking at the patterns of changes across the sampling record and determining whether similar patterns are observed across lakes and/or metrics.

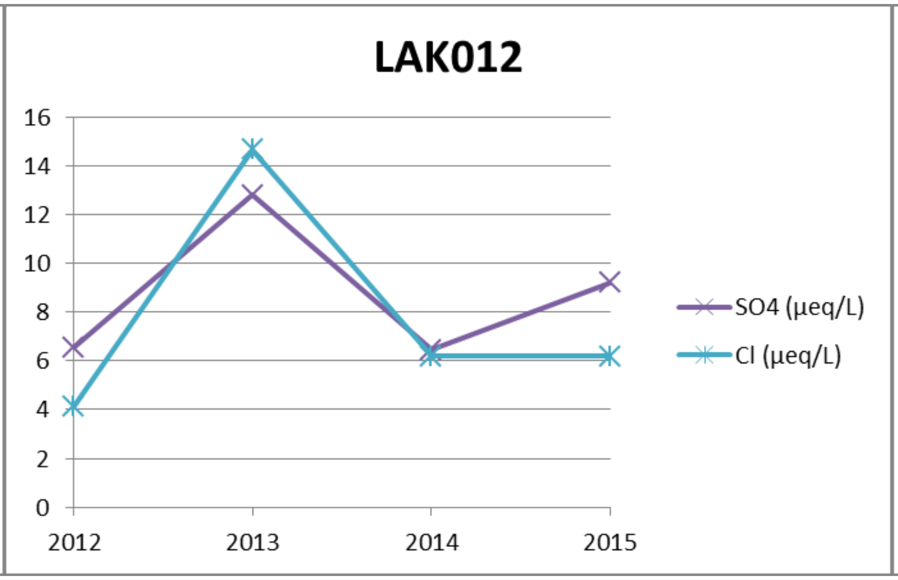
Sensitive Lakes

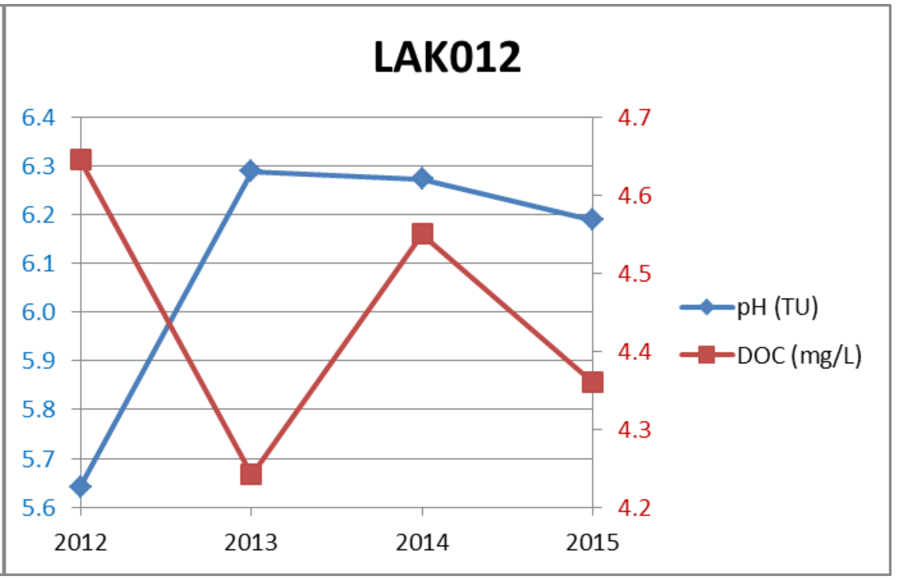


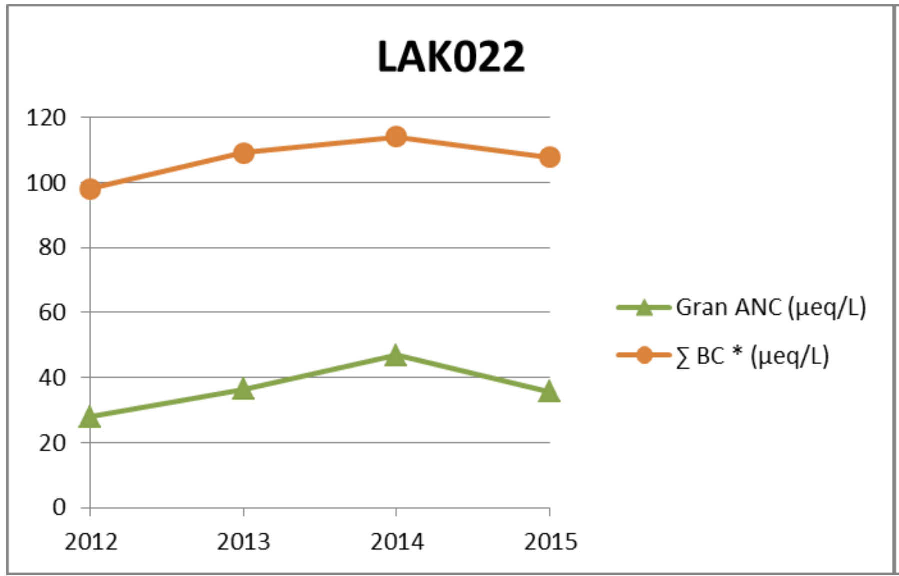


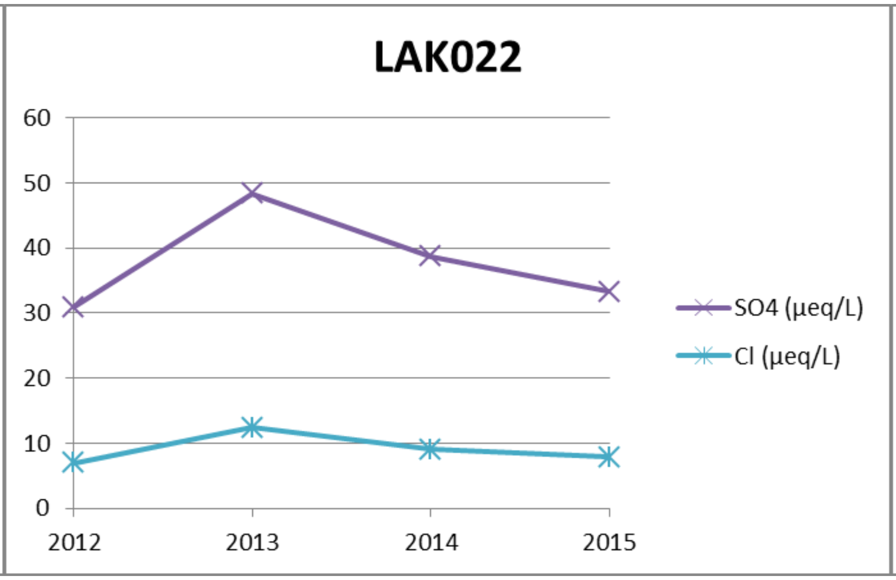


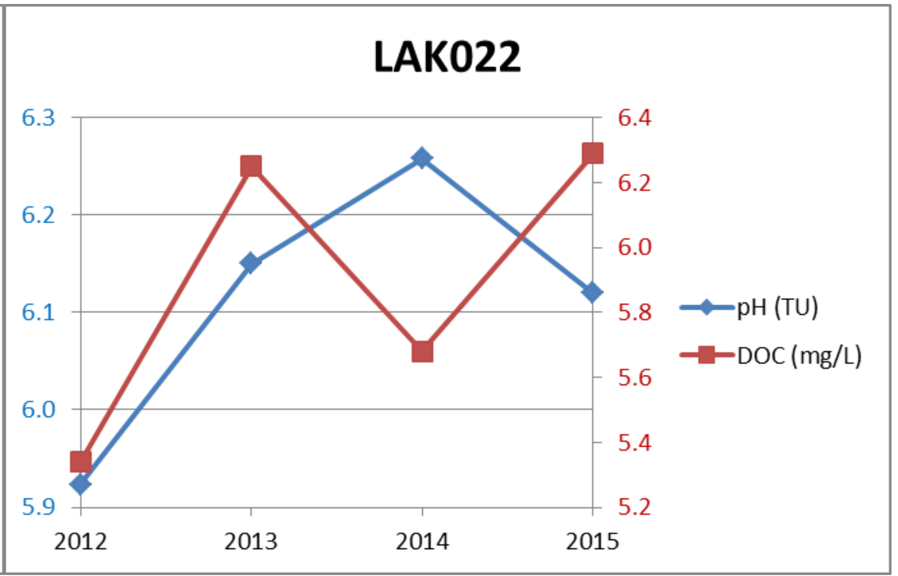


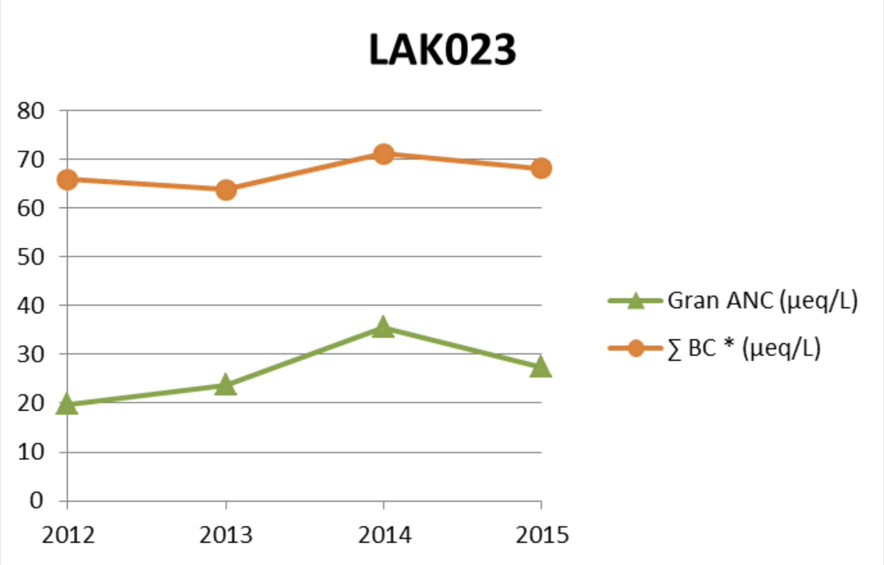


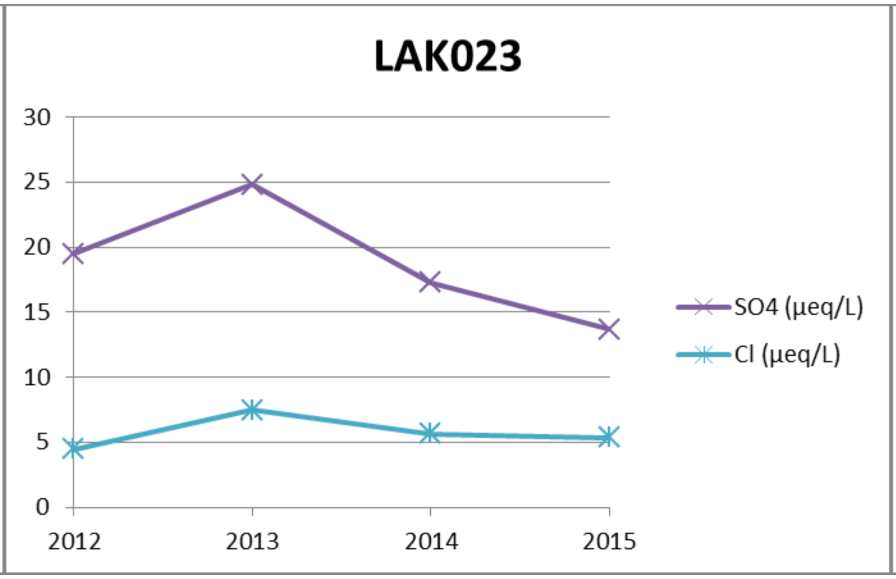


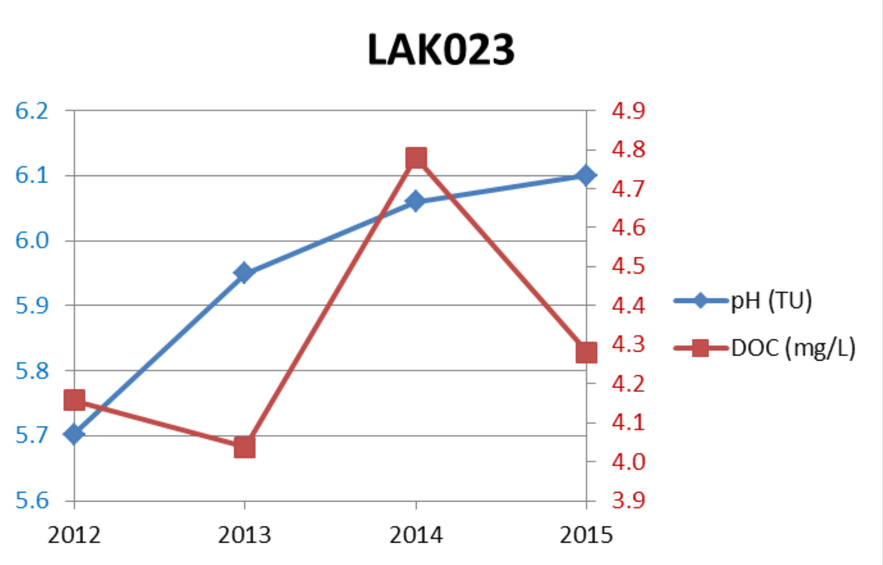

LAK022
120
100
80
60
40
20
0
2012
2013
2014
2015
Gran ANC (µeq/L)
∑ BC * (µeq/L)

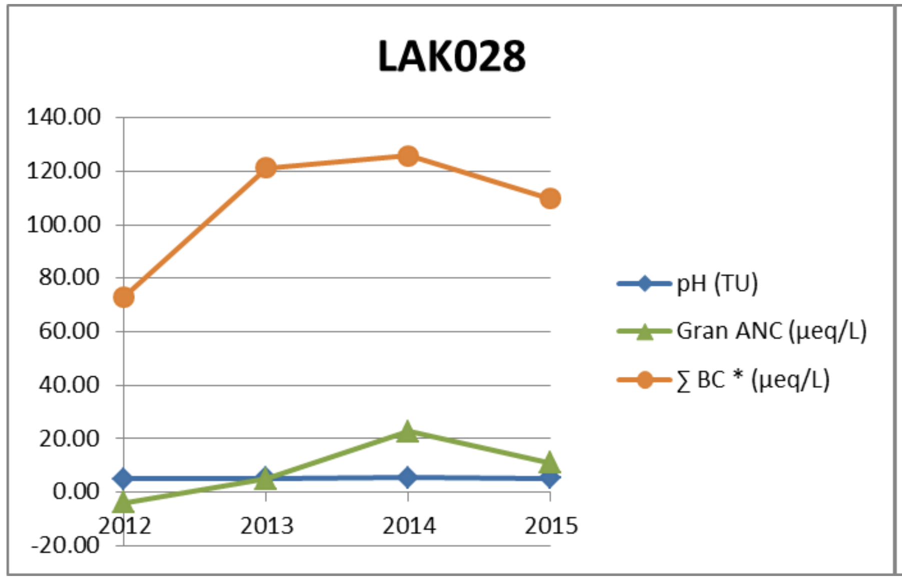

LAK022
60
50
40
30
20
10
0
2012
2013
2014
2015
SO4 (µeq/L)
Cl (µeq/L)

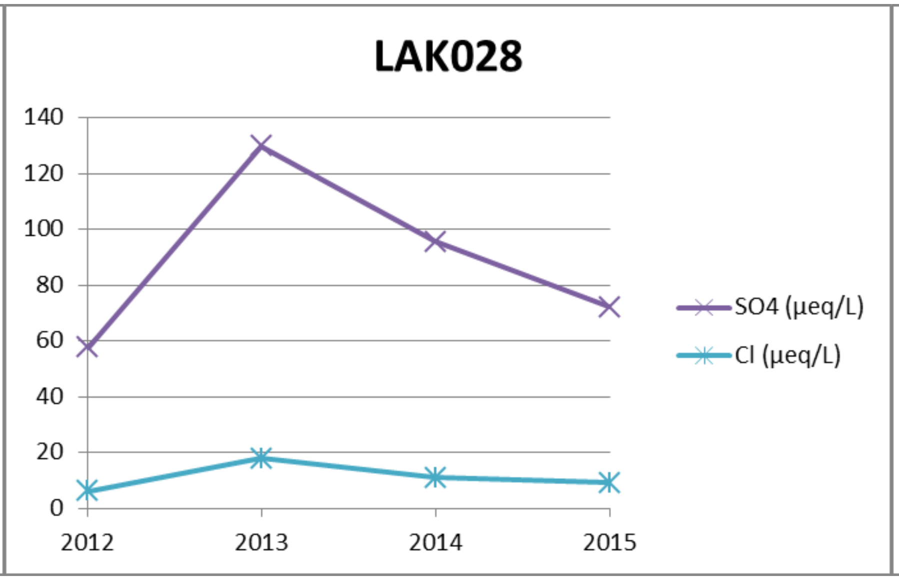

LAK022
6.3
6.2
6.1
6.0
5.9
6.4
6.2
6.0
5.8
5.6
5.4
5.2
2012
2013
2014
2015
pH (TU)
DOC (mg/L)

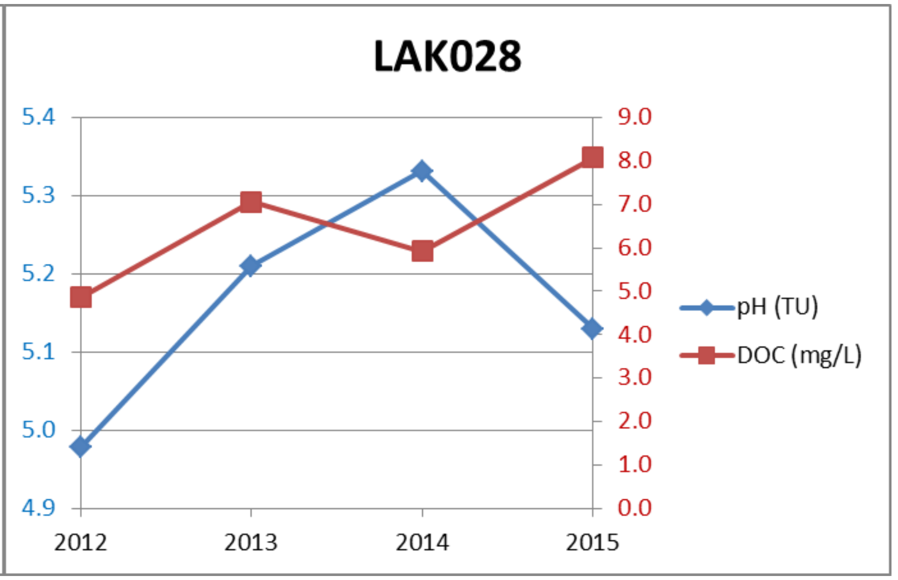

LAK023
80
70
60
50
40
30
20
10
0
2012
2013
2014
2015
Gran ANC (µeq/L)
∑ BC * (µeq/L)

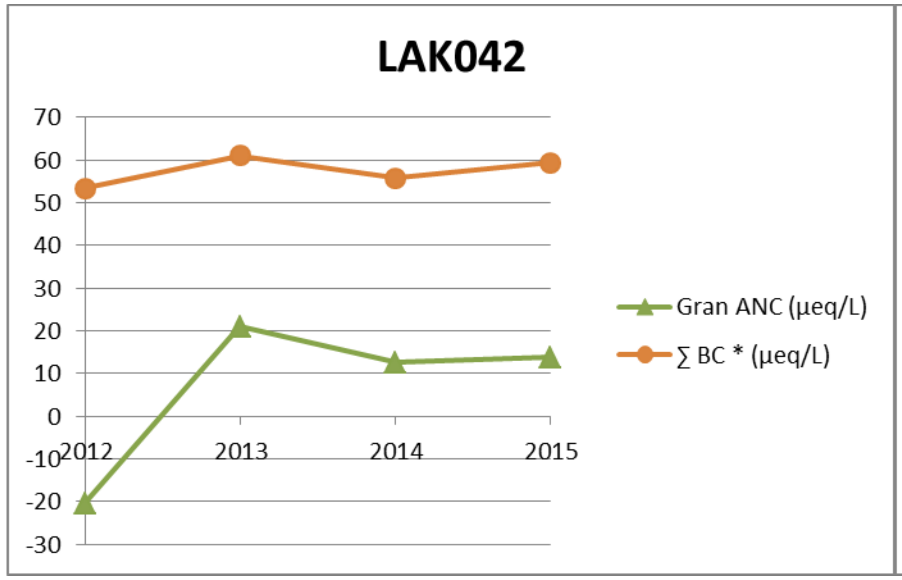

LAK023
30
25
20
15
10
5
0
2012
2013
2014
2015
SO4 (µeq/L)
Cl (µeq/L)

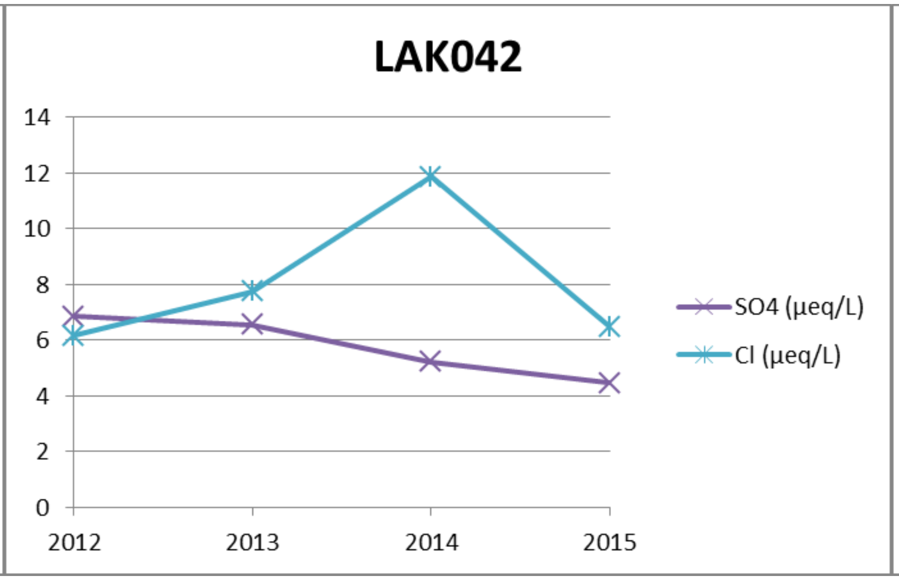

LAK023
6.2
6.1
6.0
5.9
5.8
5.7
5.6
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
2012
2013
2014
2015
pH (TU)
DOC (mg/L)

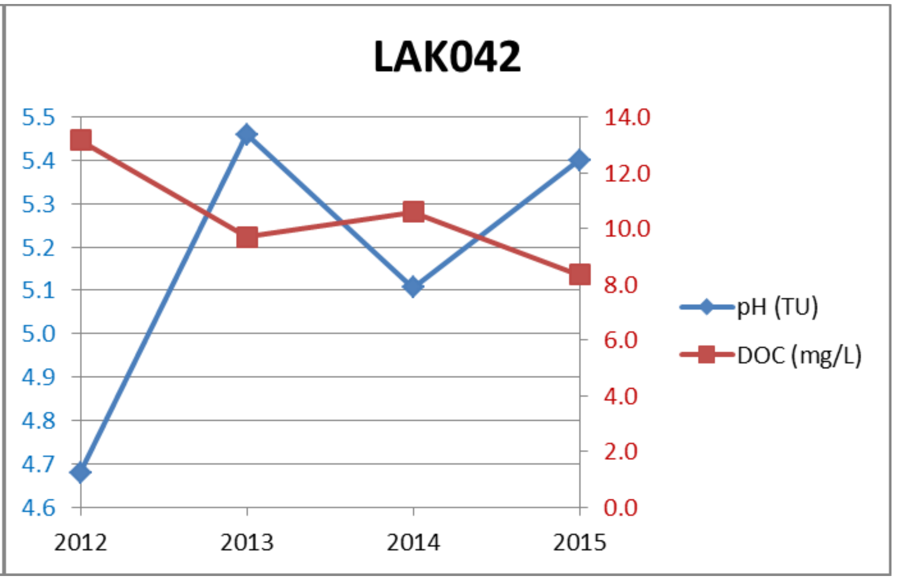

LAK028
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
2012
2013
2014
2015
pH (TU)
Gran ANC (μeq/L)
∑ BC * (μeq/L)

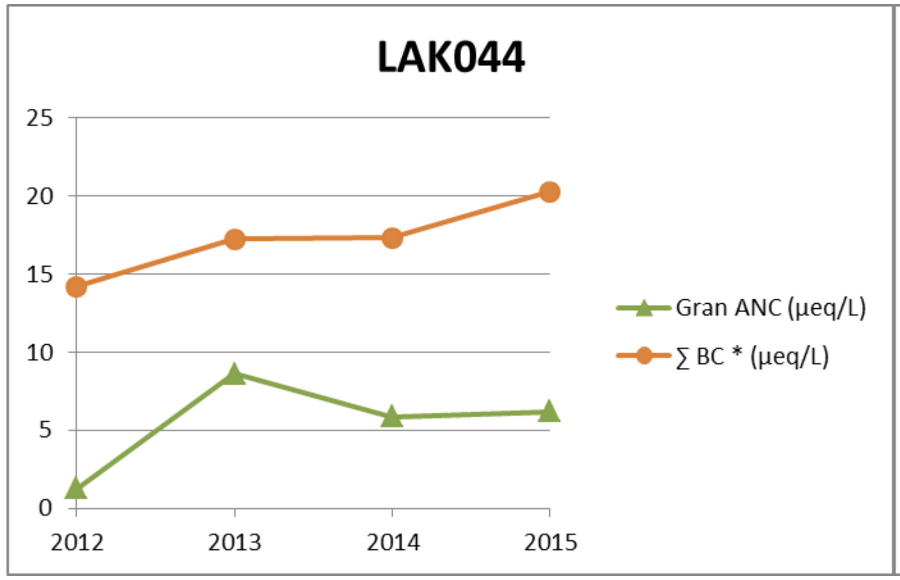

LAK028
140
120
100
80
60
40
20
0
2012
2013
2014
2015
SO4 (μeq/L)
Cl (μeq/L)

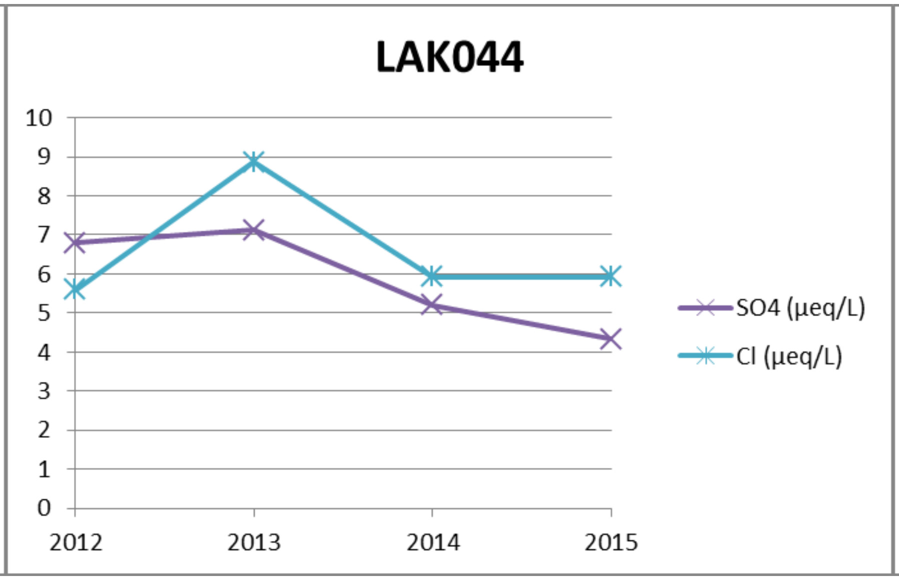

LAK028
5.4
5.3
5.2
5.1
5.0
4.9
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
pH (TU)
DOC (mg/L)

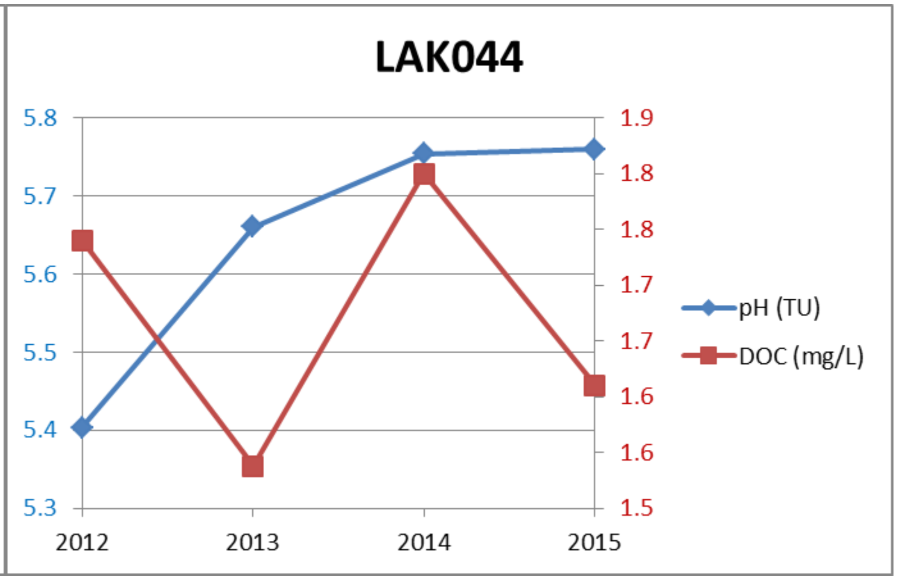

LAK042
70
60
50
40
30
20
10
0
-10
-20
-30
2012
2013
2014
2015
Gran ANC (μeq/L)
∑ BC * (μeq/L)


LAK042
14
12
10
8
6
4
2
0
2012
2013
2014
2015
SO4 (μeq/L)
Cl (μeq/L)

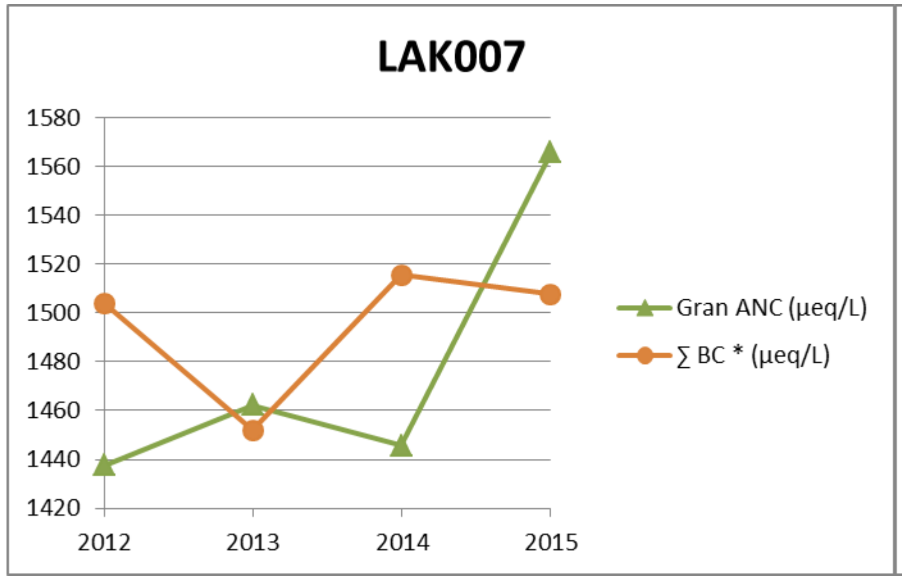

LAK042
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2012
2013
2014
2015
pH (TU)
DOC (mg/L)

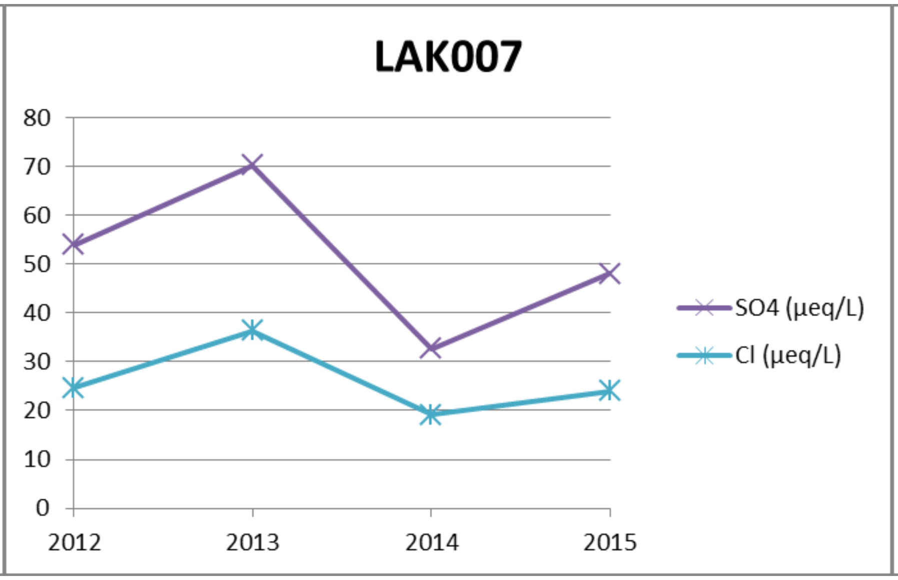

LAK044
25
20
15
10
5
0
2012
2013
2014
2015
Gran ANC (µeq/L)
∑ BC * (µeq/L)

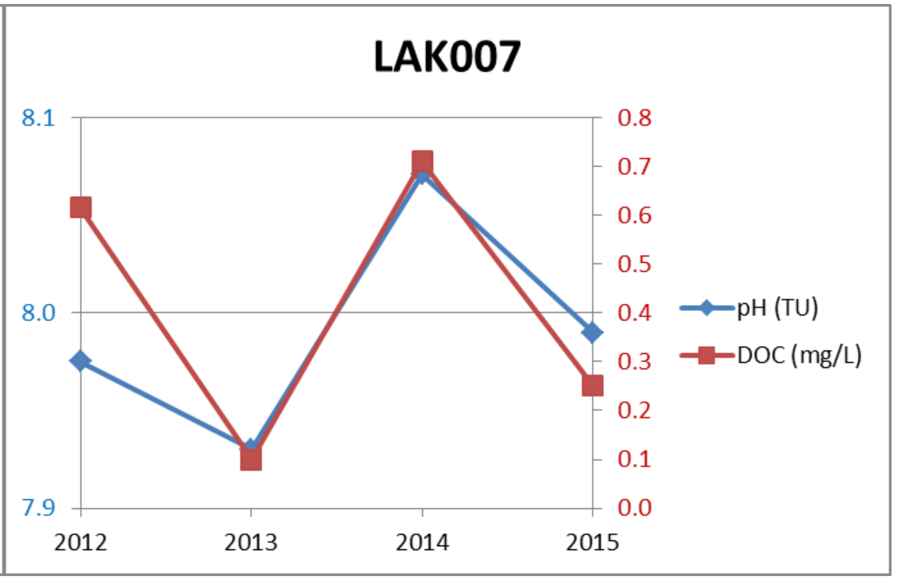

LAK044
10
9
8
7
6
5
4
3
2
1
0
2012
2013
2014
2015
SO4 (µeq/L)
Cl (µeq/L)

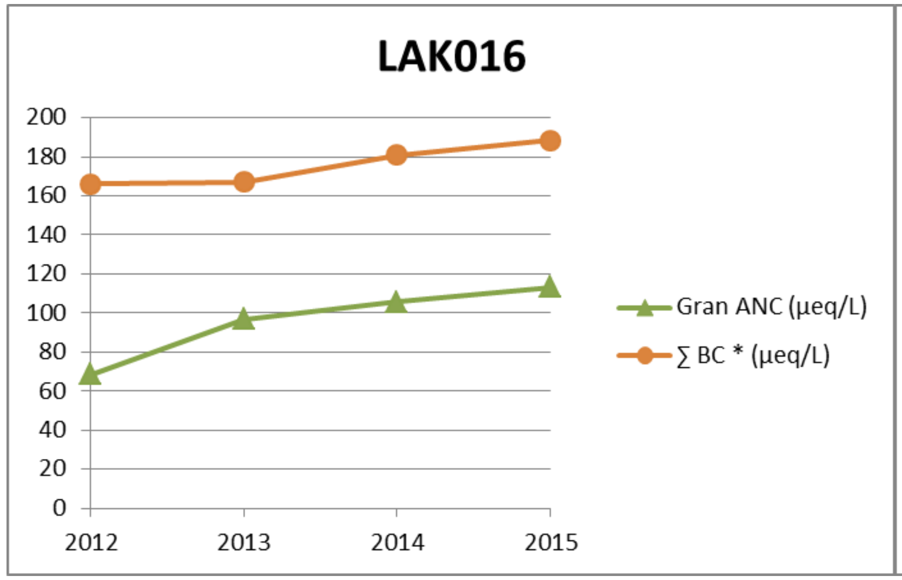

LAK044
5.8
5.7
5.6
5.5
5.4
5.3
1.9
1.8
1.8
1.7
1.7
1.6
1.6
1.5
2012
2013
2014
2015
pH (TU)
DOC (mg/L)

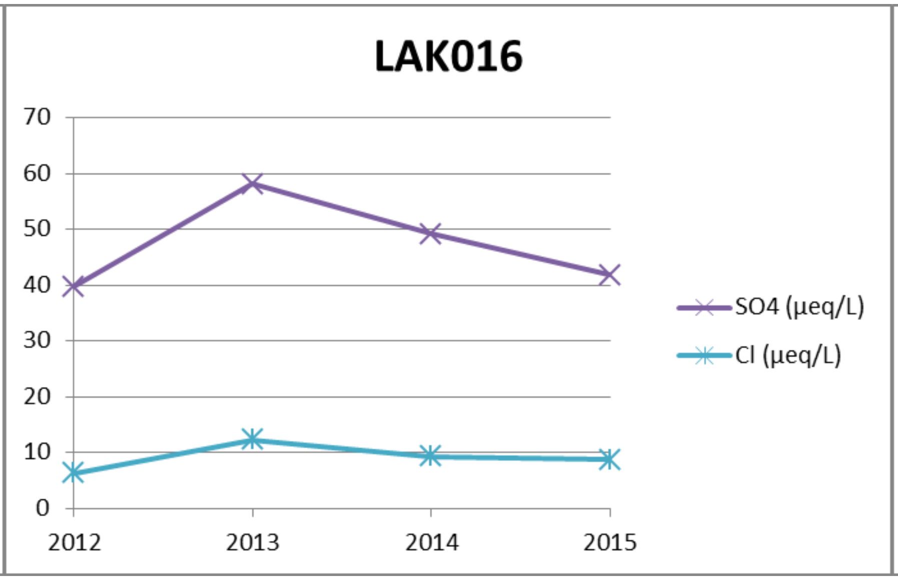
Less Sensitive Lakes

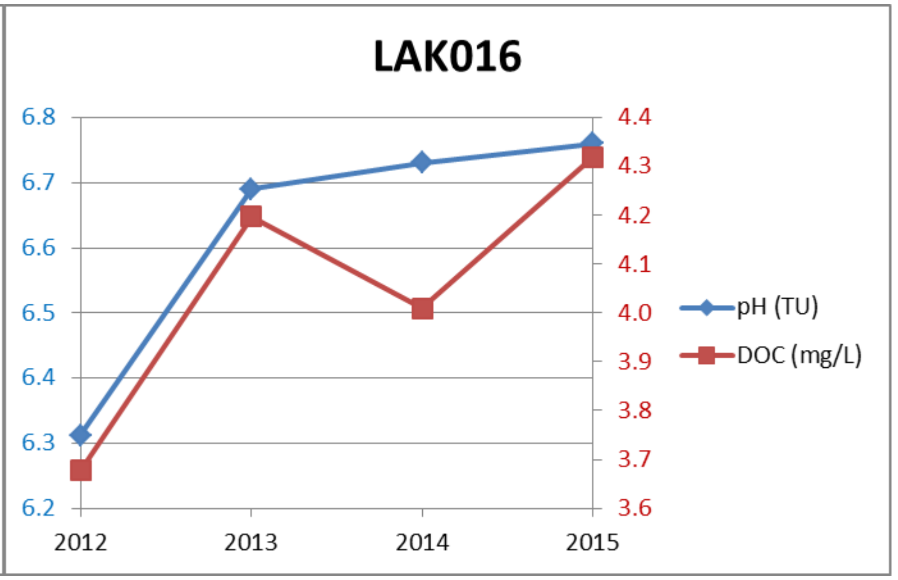


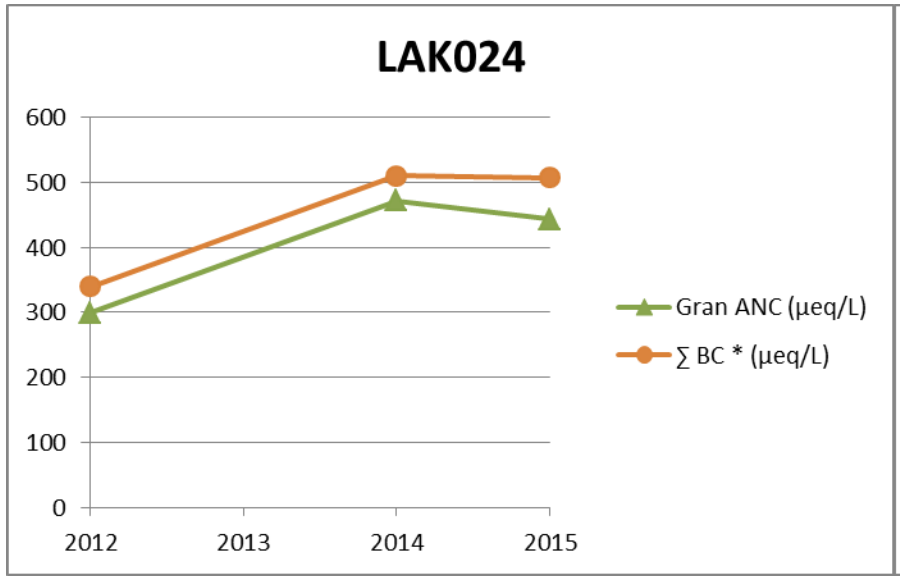


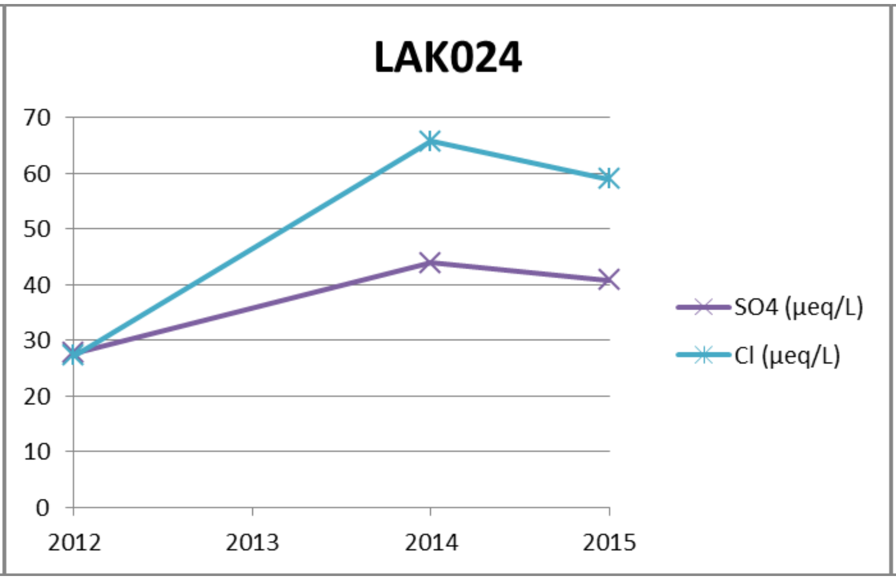


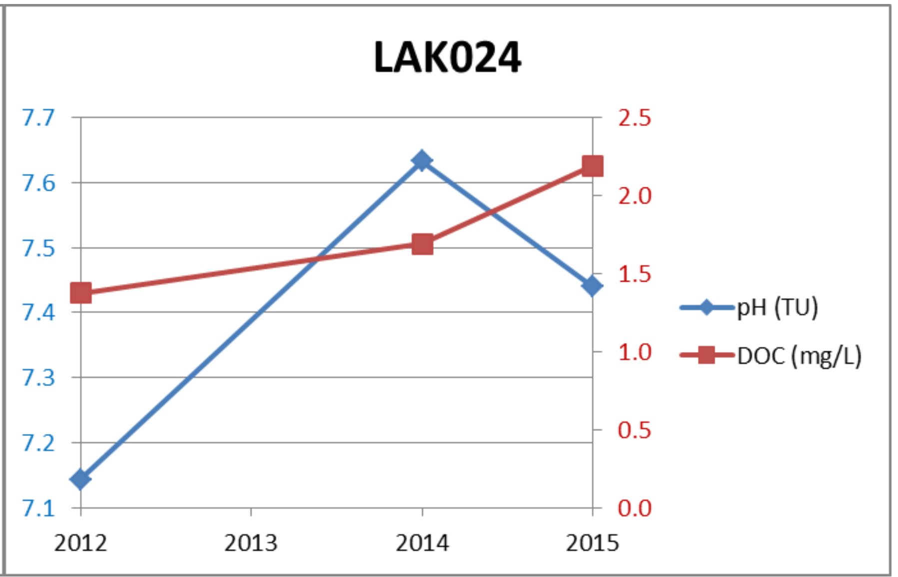




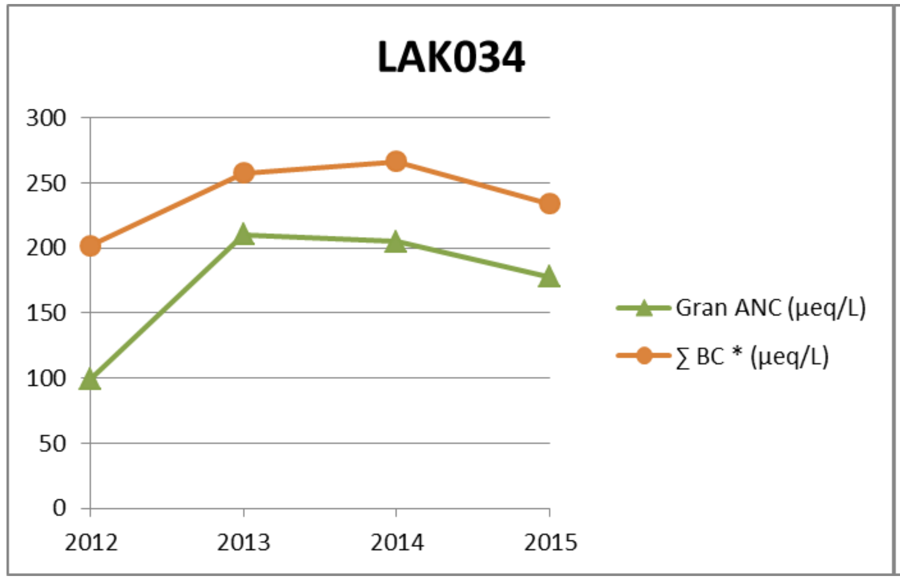


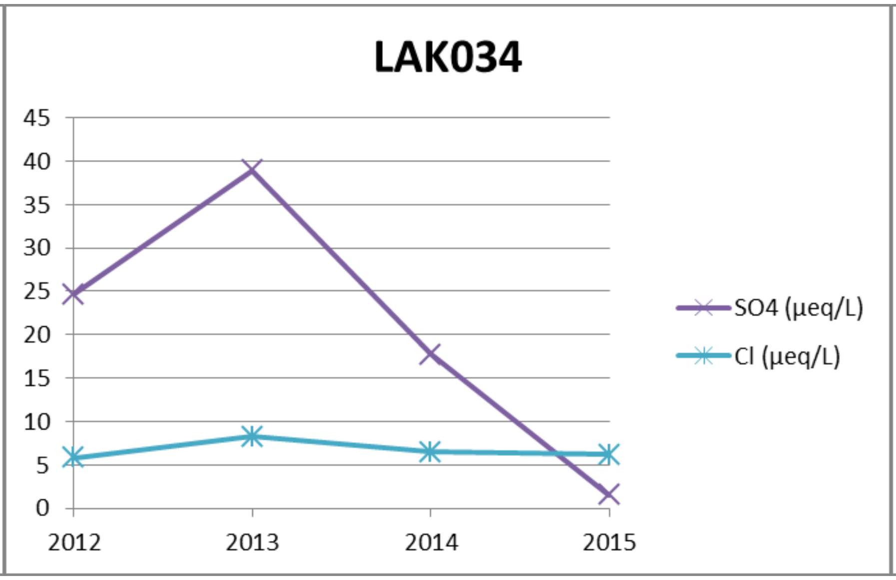


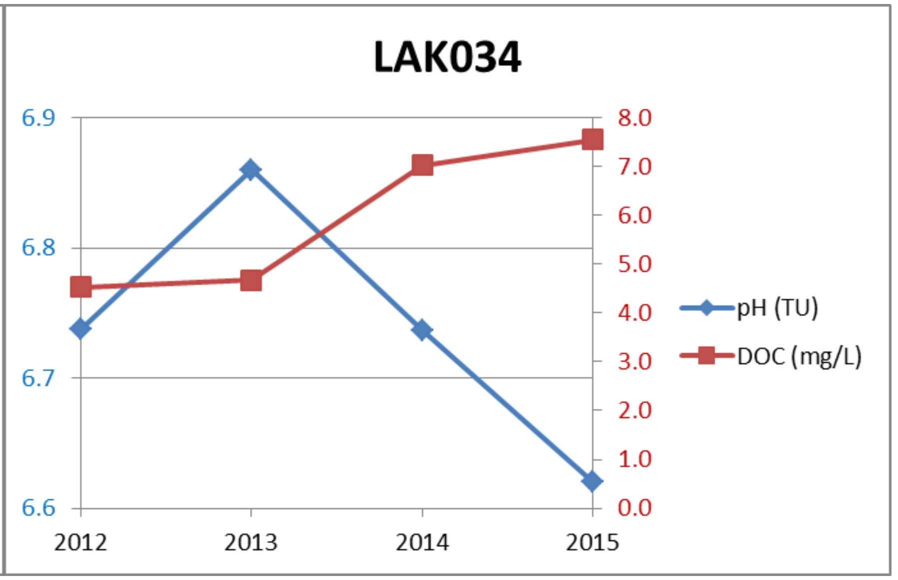




NOTE: Because LAK024 was not sampled in 2013, the implied trend between 2012 and 2014 may misrepresent the true pattern. For example, for most of the other lakes, SO_4^{2-} was highest in 2013, which could be the same for LAK024 but the lack of data point from 2013 masks that potential pattern.







Appendix 3: Project Update from Dr. Paul Weidman

Impacts of Industrial Sulfur and Nitrogen Deposition and Climate Change on Salmon Stream Habitat in the Kitimat Watershed

Paul Weidman, Ph.D. (Postdoctoral Fellow & Lead for Project #1) School of Resource and Environmental Management & Department of Biology, Simon Fraser University

15-March-2016

Brief Summary

The main objective of our project is to determine the cumulative effects of industrial atmospheric emissions of sulfur and nitrogen on salmon stream habitat under hotter and drier conditions due to climate change in the Kitimat watershed. Achieving this objective is critical to anticipating and managing the cumulative effects of industrial activities and climate change on north coastal salmon streams. Moreover, this project will help guide on-going fish habitat restoration projects that are being conducted by the Haisla Fisheries Commission in the Kitimat watershed.

In 2016, we propose to modify our sampling activities from 2015 in order to confirm our preliminary results and to map the potential impacts on salmonid habitat in the Kitimat and Lakelse watersheds from increased industrial emission of sulphur and nitrogen. We used data collected in 2015 to select 12 main project streams to continuing monitoring monthly throughout the entire year in 2016−2017. In this way, we are focusing our efforts on assessing and mapping habitat conditions in fewer streams than in 2015, but over the entire year in order to more efficiently conduct our fish habitat assessment. Streams selected in 2016 will represent the full range of habitat conditions that are relevant to our project. We also propose to measure the lethal and sub-lethal effects on juvenile salmonids of sulphur and nitrogen acid deposition and heat stress due to climate change. These rearing incubations will be conducted either at the Kitimat Hatchery and/or the Cultus Lake Salmon Laboratory.

Description of Activities

Part 1: Stream Water Quality

- Continue to survey water quality and water chemistry in 12 main project streams monthly throughout 2016 and 2017.
- Re-install and continue to monitor data loggers for pH, water temperature, and water depth throughout the year in order to determine the extent of episodic acidification in late fall, winter and early spring.
- Continue to sample benthic algae and benthic invertebrates as bioindicators of industrial impacts every four months.
- Re-assess the presence of all salmonid species in all 12 streams using a minnow traps and seine nets in summer.

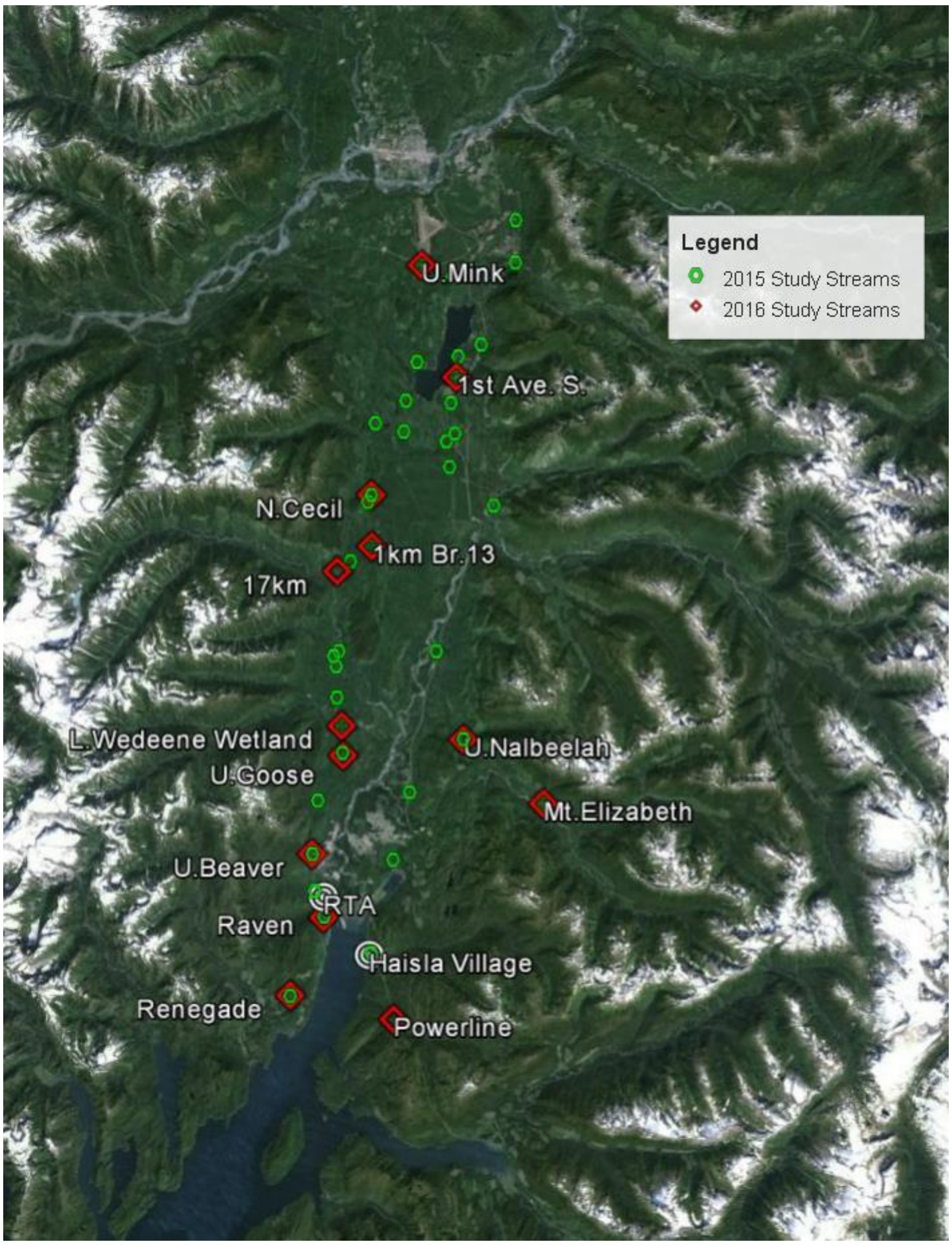
Part 2: Fish Stress Rearing Incubations

- Collect live juvenile salmonids (coho, chum, chinook, and steelhead) from streams in the Kitimat watershed where these populations spawn and rear.
- Incubate juveniles in containers at either the Kitimat Hatchery and/or the Cultus Lake Salmon Laboratory (to be determined).
- Subject juveniles to a 2-week period of stress due to inorganic acid (sulphur, pH 5.0), organic acid (from wetlands, pH 5.0), and heat stress (20oC).
- Continue to incubate juveniles for 2 months and monitor survival.
- At the end of the 2-month incubation, sacrifice individuals and measure growth and sub-lethal stress response indicators, including ion concentration and enzyme activity in blood and gill tissue.

Table 1. Average Chemical Conditions among 37 Study Streams in the Kitimat Valley, June−November 2015, measured with a YSI ProDSS multi-parameter probe.

	Water Temperature (^oC)	Turbidity (NTU)	Conductivity (µS/cm)	pH (*in situ*)	Dissolved Oxygen (%)	Sample size (#)
Mean	11.1	2.2	50	7.00	91	14
SD	3.6	8.1	29	0.37	14	6
Min	7.7	0.0	16	6.10	34	6
Max	27.2	43.7	147	7.55	105	21

Figure 1. Study Sites in 2015 and 2016.



Reports provided to DFO:

- We will produce a peer-reviewed scientific publication that will summarize the historical and expected future impacts of industrial atmospheric sulphur and nitrogen emissions on salmon stream habitat in the Kitimat watershed.
- We will produce a peer-reviewed scientific publication that will summarize the cumulative impacts on salmonid survival as the result of expected changes in fish habitat due to industrial atmospheric sulphur and nitrogen emissions and warming due to climate change.
- We will share both of these scientific publications with our main project partners who are responsible for monitoring and regulating the impacts of industrial activities on fish populations and fish habitat in the region, including Fisheries and Oceans Canada and the BC Ministry of Environment.
- A public summary of findings from both these publications will be produced for the Haisla Nation Council and the general public.

First Nation Communities Involved:

- Haisla First Nation

Other Partners Involved:

- Dr. Paul Weidman (Postdoctoral Fellow and Lead for Project #1), Department of Biology & School of Resource and Environmental Management, Simon Fraser University, Burnaby
- Mr. Michael Jacobs (Fisheries Manager) & Ms. Brenda Bouzane (Fisheries Administrative Technician), Haisla Fisheries Commission, Haisla Nation Council, Kitamaat Village
- Mr. Mitch Drewes (Environmental Specialist), Hidden River Environmental Management Ltd., Terrace
- Dr. Daniel Selbie (Head), Cultus Lake Salmon Research Laboratory, Fisheries and Oceans Canada, Cultus Lake
- Dr. Jonathan Moore (Associate Professor), Department of Biology & School of Resource and Environmental Management, Simon Fraser University, Burnaby
- Mr. Markus Feldhoff (Hatchery Manager) & Mr. Vince Sealy (Hatchery Manager), Kitimat River Hatchery, Fisheries and Oceans Canada, Kitimat
- Mr. Erland MacIssac (Fisheries Biologist - retired), Cooperative Resource Management Institute, Fisheries and Oceans Canada, Simon Fraser University, Burnaby
- Mr. Patrick Williston (Environmental Impact Assessment Biologist), Ministry of Environment, Smithers

RioTinto

KMP SO_2 EEM Program – Technical Memo W06

Aquatic Ecosystems Actions and Analyses

March 2017

Prepared for:

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

Prepared by:

ESSA Technologies Ltd.
Suite 600 – 2695 Granville St.
Vancouver, BC, Canada V6H 3H4
(Using data provided by Rio Tinto BC Works)

Table of Contents

Table of Figures

Table of Tables

1 Introduction

This Technical Memo provides extended information on the data and analyses in support of the 2016 requirements for the Aquatic Ecosystems component of the KMP SO_2 Environmental Effects Monitoring (EEM) program (ESSA et al. 2014b). These data and analyses thus provide the foundation for Section 3.5 in the 2016 Annual Report (ESSA et al. 2017).

Table 1-1. Aquatic analyses as specified in the EEM Plan. Extracted from Table 16, Section 6.2.5, "Summary of Lakes, Streams and Aquatic Biota Actions, 2013-2018". The numeric symbols (e.g., ①②③) are used to link sections of the present technical memo with the EEM requirements, and appear throughout this document.

Topic	2016
Steady state water modelling	*No work planned for 2016 on this task*
Chemistry: water body sampling	① Annual water sampling, laboratory analysis, and data evaluation. ② Continuation of intensive sampling to determine natural variability.
$[SO_4]_0$; F-factor	*No work planned for 2016 on this task*
Fish presence / absence sampling	③ Resample if lake pH change reaches threshold.
Episodic acidification	④ Implement study.
Amphibians	⑤ Provide support to existing local community groups who conduct annual amphibian monitoring

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) and the Kitimat Airshed Assessment (KAA) (ESSA et al. 2014a). 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). Wherever possible, the description of methods in this technical report refers to these reports instead of repeating information that is already well-documented elsewhere.

The following three documents (as described above) are listed here because they are referenced extensively throughout this technical memo, often without their full citation:

- The STAR (ESSA *et al.* 2013)
- The KAA (ESSA *et al.* 2014a)
- The EEM Plan (ESSA *et al.* 2014b)

2 Methods

2.1 Annual Monitoring Samples ①

2016 Annual Sampling

In 2016, Limnotek sampled 14 lakes as part of the EEM long-term sampling plan. These lakes included the seven sensitive lakes and three less sensitive lakes identified in the EEM Plan, the high recreational value LAK024 (Lakelse Lake; added to the EEM in 2014), and three additional control lakes added to the EEM in 2015. The three control lakes (NC184, NC194 and DCAS14A) are all located outside of the KMP-influenced airshed and have baseline data for 2013 from sampling as part of the KAA (ESSA et al., 2014a). The sampling methodology is described in detail in

Limnotek’s technical report on the water quality monitoring (Bennett and Perrin 2017). Table 2-1 summarizes all of the EEM sites sampled during 2012-2016. Figure 2-1 shows a map of the lakes sampled in 2016.

Table 2-1. Summary of sites sampled within the EEM Program.

Sample Site	Year of Sampling					Rationale for sampling
	2012	2013	2014	2015	2016	
	STAR	EEM	EEM	EEM	EEM	
Lake 006	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 012	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 022	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 023	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 028	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 042	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 044	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 007	✓	✓	✓	✓	✓	EEM less sensitive lake
Lake 016	✓	✓	✓	✓	✓	EEM less sensitive lake
Lake 034	✓	✓	✓	✓	✓	EEM less sensitive lake
Lake 024	✓		✓	✓	✓	Added to the EEM long-term monitoring lake set due to public importance
MOE3		✓				Potentially sensitive lakes / streams not previously sampled
Cecil Creek 1		✓				
Cecil Creek 2		✓				
Cecil Creek 3		✓				
MOE6			✓			
Goose Creek 1			✓			
Goose Creek 2			✓			
Goose Creek 4			✓			
Goose Creek 5			✓			
Goose Creek 6			✓			
Goose Creek 7			✓			
GNT1 (Goose Creek)				✓		
GNT2 (Goose Creek)				✓		
NC184		✓[1]		✓	✓	Control lakes added to EEM in 2015
NC194		✓[1]		✓	✓	
DCAS14A		✓[1]		✓	✓	

---

[1] Sampled as part of the Kitimat Airshed Assessment (ESSA *et al.* 2014a)

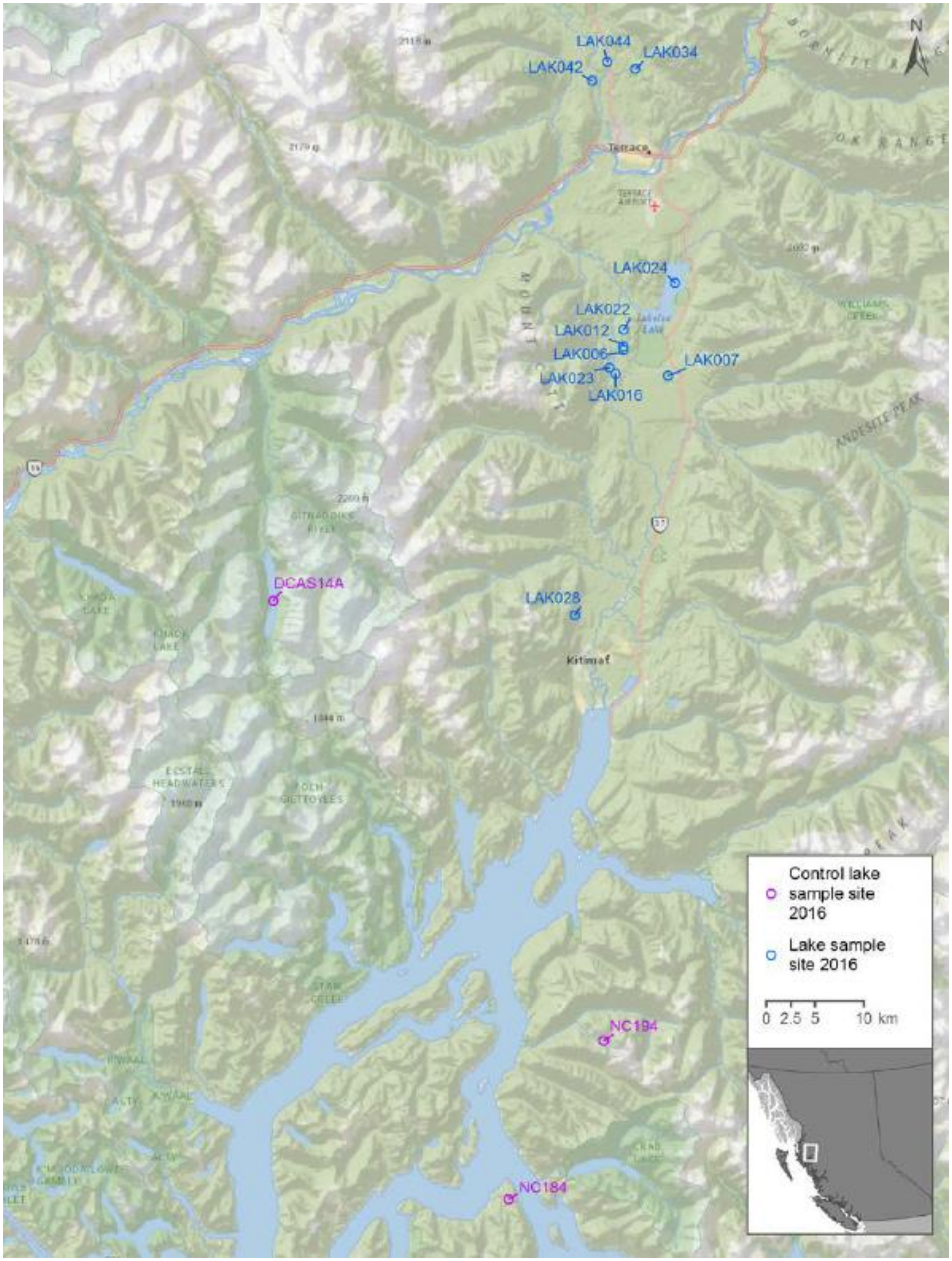


Figure 2-1: Location of the lakes that were sampled in 2016. The three control lakes are labelled with purple text (Source: Bennett and Perrin 2017).

2.2 Intensive Monitoring of Three Lakes ②

Starting in 2014, intensive monitoring was implemented in three of the EEM lakes – End Lake (LAK006), Little End Lake (LAK012) and West Lake (LAK023). These three lakes were selected based on being accessible by road, thus making repeated visits much more feasible than for remote lakes requiring helicopter access. During the fall of 2014, the intensive monitoring included continuous pH monitors and multiple site visits to collect intra-season water samples for additional lab analyses and pH measurements. In 2015, the continuous pH monitors were deployed from mid-April until mid-November. During October 2015, three additional within-season water chemistry samples were taken at these three lakes, subsequent to annual sampling across all of the lakes (i.e., four samples in total for each of the intensively monitored lakes in 2015). In October 2016, this was repeated for the same three lakes (LAK006, LAK012 and LAK023) as well as being expanded to LAK028, LAK042 and LAK044. The three additional lakes were added in 2016 based on the recommendation in the 2015 EEM Annual Report to explore the feasibility of increasing the number of samples for lakes with low power to correctly detect whether the EEM KPI thresholds have been exceeded. The power analyses (see ESSA Technologies Ltd. 2016) demonstrated that the existing monitoring plan (i.e., annual samples only for these lakes) would have low power to detect changes in some of the primary metrics for water chemistry in LAK028 (for ANC, SO_4^{2-}), LAK042 (for pH, ANC), or LAK044 (for ANC, SO_4^{2-}). Additional sampling was conducted in 2016 to provide insight into the natural variability in pH, Gran ANC and SO_4^{2-} in these lakes near the time of the annual water sampling. Finally, lake levels were monitored in End Lake, Little End Lake, and West Lake to provide an accurate, local measure of the timing of storm events, so as to better explain observed variation in pH (monitored continuously) and other water quality parameters of interest monitored during October (particularly sulphate, nitrate, DOC, ANC, and base cations).

This work was planned, implemented and documented by Limnotek. The methods and results for 2016 are reported in Bennett and Perrin (2017).

For the lakes with more than one sample per year, the data from the multiple within-season samples have been used to determine mean annual values. In previous Annual Reports, only the sample taken on the first day of the monitoring season (i.e., the day(s) of sampling all lakes) was designated as the “annual sampling” value. Starting in this year’s Annual Report, the mean annual values are used for all years in which additional within-season samples were taken.

2.3 Quality of Water Chemistry Data ①②

Sampling and laboratory quality control and quality assurance

The collection, handling, transport, and analyses of water quality samples were conducted with numerous quality checks, to ensure the highest quality data possible. Details on the methods for quality control and quality assurance for the water samples are described in Bennett and Perrin (2017).

Analyses of Charge Balance and Estimated vs. Measured Conductivity

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

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

pH measurements

Water quality samples taken in 2016 have multiple measures of pH, including a field measurement and two lab measurements (Trent University and ALS). As described in Section 2.2, three lakes also have additional measurements of pH from continuous meters. As described in the STAR, lab measurements of pH, rather than field measurements, have been used for the analyses of lake chemistry; lab pH measurements have lower variability, and therefore are more relevant to the detection of long term trends.

The 2012 data collected during the STAR included laboratory measurements of pH only from Trent University. Inter-annual comparisons of trends in pH have therefore been conducted using the pH measurements from Trent University. Limnotek (Bennett and Perrin 2017) analyzed differences among the different methods of measuring pH for quality assurance purposes, repeating similar comparisons conducted in previous years (Perrin and Bennett 2015, Limnotek 2016).

2.4 Inter-annual Changes

Observed Changes

The EEM Program now has five consecutive years of monitoring data with which to examine inter-annual changes in water chemistry parameters. The monitoring data from 2016 represents the first year of true post-KMP sampling. The years 2012 to 2014 were prior to the implementation of KMP and 2015 was a transition year that included decreases in production in preparation for the transition then ramping production as KMP was phased in during the year.

We calculated the changes in major water chemistry attributes between subsequent years and across the entire period for 2012-2016[2]. However, the power analyses conducted and reported in the 2015 EEM Annual Report illustrated that the power to detect annual changes in pH, Gran ANC and SO_4 is very low due to high variability and/or measurement error. Therefore annual changes should be interpreted very cautiously.

---

[2] As noted in the 2013/2014 EEM Annual Report (ESSA Technologies 2015), because sampling in 2012 was performed in August and the sampling in subsequent years was performed in October, the observed differences between 2012 and 2013 represent a mixed effect of both changes due to year and changes due to season. For this reason, the observed changes between 2012 and 2013 are harder to interpret than the changes between other sequential years. However, to better understand this potential seasonal effect, We analyzed pH data from 2015 and 2016 for the 3 intensively monitored lakes to test if there were any consistent differences in mean August pH vs mean October pH.

Expected Changes and Application of the Evidentiary Framework

The EEM Evidentiary Framework (refer to Section 7.0 and Appendix H of the EEM Plan) provides a weight-of-evidence approach for assessing causality associated with observed changes in water chemistry. The principles of the framework are considered and applied in Section 4. More years of data will be required to achieve statistically reliable comparisons of pre-KMP and post-KMP conditions, as demonstrated by the statistical power analyses conducted in 2015.

2.5 Fish Sampling ③

No new fish sampling was conducted in 2016.

Limnotek conducted fish sampling in LAK006, LAK012, LAK023, and LAK044 in 2013 to measure the presence/absence of fish in four of the seven sensitive lakes within the EEM Program. Under the EEM Plan, the fish populations in some of these lakes could potentially be resampled if there were convincing evidence that a lake’s pH had declined by more than 0.3 pH units. In 2015, fish sampling was completed in the three less sensitive lakes: LAK007, LAK016, and LAK034. Details of the fish sampling methodologies for the two years are described in Limnotek’s previous technical reports (Perrin et al. 2013, Section 2.9; Limnotek 2016, Section 2.8).

2.6 Episodic Acidification Studies ④

Three studies are directly relevant to the episodic acidification sub-component of the aquatic ecosystems component of the EEM Program. First, the three intensively monitored lakes include continuous monitoring of pH during the ice free season. Second, there have been substantial efforts to establish a continuous pH monitoring station on Anderson Creek. In 2015, there was a Manta monitor installed by Limnotek, but the data collected suggested that the instrument may not have been functioning properly. Due to such concerns, the monitor was removed and set up alongside the Manta monitor in West Lake in 2016 to test for instrument issues (Limnotek 2016). Independently, Rio Tinto had a continuous pH monitor in place in Anderson Creek during 2016; however, the instrument was not properly re-calibrated through the season and therefore the data were unusable due to measurement drift. In 2017, a Manta monitor was installed in Anderson creek for 4 weeks in 2017 to validate the Rio Tinto data from their Foxboro instrument which was installed in Anderson Creek in July 2017. Third, Dr. Paul Weidman (School of Resource and Environmental Management & Department of Biology, Simon Fraser University) has been conducting a research project on episodic acidification and climate change. Dr. Weidman’s research is highly relevant to the work of the EEM program although it is not a formal component of the EEM program. Rio Tinto will provide an update on Dr. Weidman’s research once his report is publicly available.

Research Project by Dr. Paul Weidman

The project title for this research is, “Impacts of industrial sulfur and nitrogen deposition and climate change on salmon stream habitat in the Kitimat watershed”. Development of the study design was initiated in 2014 and finalized in 2015. Preliminary sampling activities were conducted in 2015. The following summary has been extracted from Dr. Weidman’s project summary provided in the 2015 EEM Annual Report:

> *"The main objective of our project is to determine the cumulative effects of industrial atmospheric emissions of sulfur and nitrogen on salmon stream habitat under hotter and drier conditions due to climate change in the Kitimat watershed. Achieving this objective is critical to anticipating and managing the cumulative effects of industrial activities and climate change on north coastal salmon streams. Moreover, this project will help guide on-going fish habitat restoration projects that are being conducted by the Haisla Fisheries Commission in the Kitimat watershed.*
>
> *In 2016, we propose to modify our sampling activities from 2015 in order to confirm our preliminary results and to map the potential impacts on salmonid habitat in the Kitimat and Lakelse watersheds from increased industrial emission of sulphur and nitrogen. We used data collected in 2015 to select 12 main project streams to continuing monitoring monthly throughout the entire year in 2016−2017. In this way, we are focusing our efforts on assessing and mapping habitat conditions in fewer streams than in 2015, but over the entire year in order to more efficiently conduct our fish habitat assessment. Streams selected in 2016 will represent the full range of habitat conditions that are relevant to our project. We also propose to measure the lethal and sub-lethal effects on juvenile salmonids of sulphur and nitrogen acid deposition and heat stress due to climate change. These rearing incubations will be conducted either at the Kitimat Hatchery and/or the Cultus Lake Salmon Laboratory."*

2.7 Amphibian Monitoring ⑤

No actions were taken in 2016. Moving forward with the action to "provide support to existing local community groups who conduct annual amphibian monitoring" had been postponed and is presently being revisited. A literature review of acidification impacts on amphibians and potential pathways of effects is currently planned for 2017.

3 Results

3.1 Quality of Water Chemistry Data ①②

Sampling and laboratory quality control and quality assurance

The results of the sampling and laboratory quality control and quality assurance methods are presented in the associated technical report by Limnotek (Bennet and Perrin 2017). The laboratory data show high precision and accuracy, with no apparent problems. Measurements of pH from ALS were statistically significantly different from pH measurements in the field, and from pH measurements in the laboratory at Trent University, but these differences were still within the specified limits of ± 0.3 pH units for the equipment used by ALS.

Charge Balance Check

The charge balance has been examined for each year of sampling, based on the data from annual sampling event. Table 3-1 shows four diagnostic metrics of the charge balance for the annual sample sets from 2012 to 2016. The charge balance is better for the 2016 sampling data than it had been in during the previous three years.

The charge balance for the lakes in the EEM Program (sensitive and less sensitive), as sampled in 2016, is shown graphically in Figure 3-1. The linear trend line shown on the graph is heavily influenced by Lake 007 (not shown on the graph), which has cation and anion levels of an order of magnitude greater than the other lakes.

Table 3-1. Measures of the charge balance check for 2012 (STAR lakes), 2013 (EEM lakes, MOE3, Cecil Creek), 2014 (EEM lakes, MOE6), 2015 (EEM lakes, control lakes[3]), and 2016 (EEM lakes, control lakes). Negative (red) values for "Average %Diff" and "Average Difference" indicate less total charge from cations than from anions.

Year	Number of Samples	Average %Diff	Average Abs (%Diff)	Average Difference (µeq/L)	Average Abs(Diff) (µeq/L)
2012	61	-0.7	2.6	-6.5	12.2
2013	14	-8.5	10.1	-28.2	42.8
2014	12	-5.0	5.2	-12.9	14.5
2015	13[3]	-2.9	3.1	-16.6	17.3
2016	14	-1.7	2.3	1.7	12.6

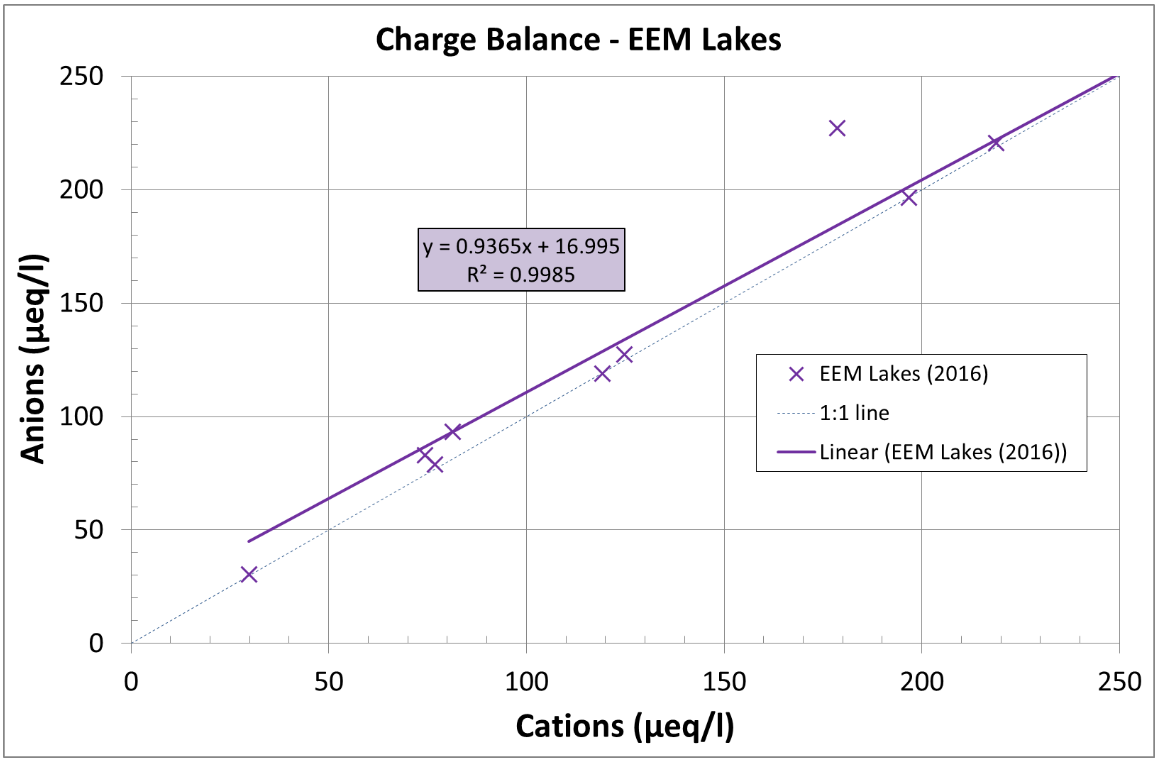


Figure 3-1. Analysis of charge balance for the EEM lakes in 2016. The Y-axis is the sum of all major anions (negatively charged ions); the X-axis the sum of all major cations (positively charged ions).

For each of the lakes with multiple within-season samples, Table 3-2 shows the measures of the charge balance check. In 2016, the average charge balance discrepancy was greater for this data set than for the single annual samples across all of the lakes, but still within acceptable limits for data quality.

---

[3] Only NC184 and NC194 are included. DCAS14A has been excluded from this summary because its charge balance is exceptionally poor and the underlying water chemistry data is currently being investigated.

Table 3-2. Measures of the charge balance check for lakes with multiple within-season samples. In 2014 and 2015, these included (LAK06, LAK12 and LAK023). In 2016, these included those same three lakes plus LAK028, LAK042 and LAK044. Negative (red) values for "Average %Diff" and "Average Difference" indicate less total charge from cations than from anions.

Year	# Lakes	Number of Samples	Average %Diff	Average Abs (%Diff)	Average Difference (µeq/L)	Average Abs(Diff) (µeq/L)
2014	3	15	-5.6	5.6	-11.1	11.1
2015	3	12	-3.5	3.5	-6.8	6.8
2016	6	24	-4.3	4.9	-10.4	11.6

Measured versus Estimated Conductivity

Measured and estimated conductivity were compared for each year of sampling, based on the data from annual sampling. Table 3-3 shows two diagnostic metrics of the conductivity check for the annual sample sets from 2012 to 2016. The data for 2016 demonstrate an acceptable relationship between measured and estimated conductivity. Estimated conductivity was lower than measured conductivity for all but one of the lakes sampled in 2016.

The conductivity check for the lakes in the EEM Program (sensitive and less sensitive), as sampled in 2016, is shown graphically in Figure 3-2. The linear trend line shown on the graph is heavily influenced by Lake 007 (not shown on the graph), which has conductivity values of an order of magnitude greater than most of the other lakes.

Table 3-3. Measures of the conductivity check for 2012 (STAR lakes), 2013 (EEM lakes, MOE3, Cecil Creek), 2014 (EEM lakes, MOE6), 2015 (EEM lakes, control lakes[4]), and 2016 (EEM lakes, control lakes). Positive values of "Average %Diff" indicate that the estimated conductivity was higher than the measured conductivity. Negative values (shown in red) indicate that the estimated conductivity was lower than the measured conductivity.

Year	Number of Samples	Average %Diff	Average Abs (%Diff)
2012	61	4.9	6.0
2013	14	6.8	10.5
2014	12	-5.1	6.4
2015	13 [4]	-3.0	6.1
2016	14	-7.5	9.1

---

[4] As per Table 3-1, only NC184 and NC194 are included. DCAS14A is excluded due to data concerns that are being currently explored.

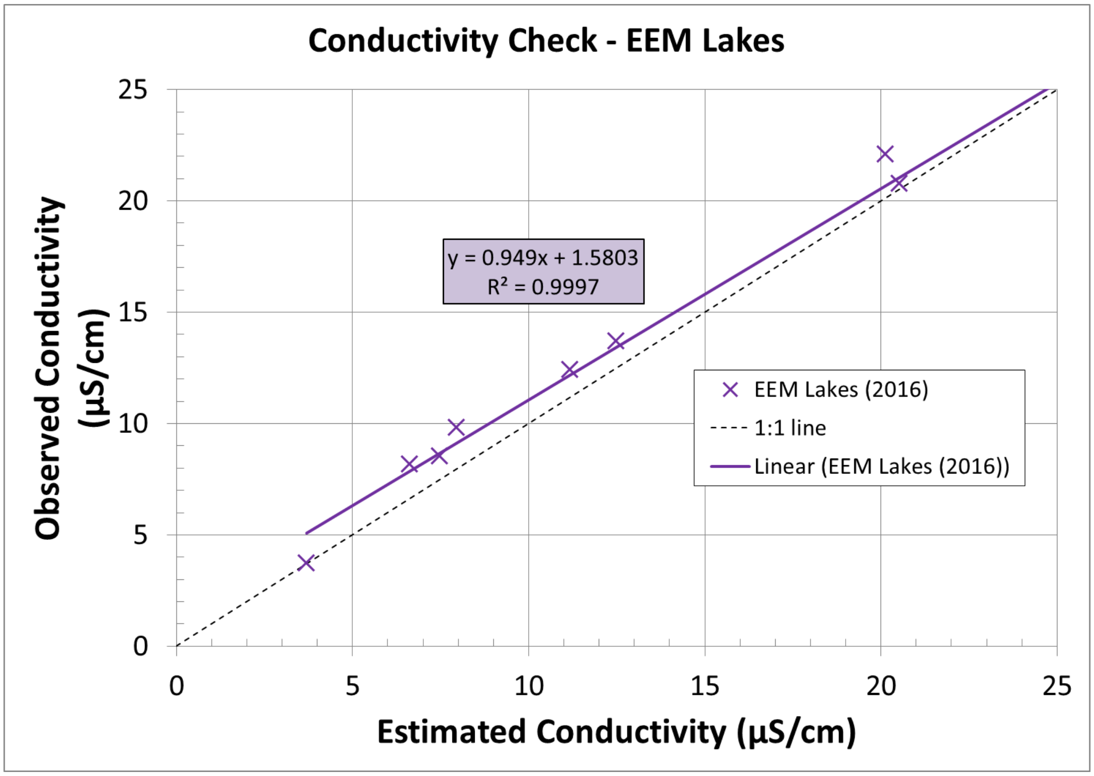


Figure 3-2. Conductivity check for the EEM lakes in 2016. Estimated conductivity is based on laboratory measurements of the concentrations of all ions and literature values for the conductivity of each ion, which is compared to the conductivity observed in field measurements.

For each of the lakes with multiple within-season samples, Table 3-4 shows the measures of the charge balance check. In 2016, the average conductivity difference was less for this data set than for the single annual samples across all of the lakes, but greater for the average of the absolute differences. However, the 2016 data still fall within acceptable limits for data quality. As explained in the footnote to Table 3-4, it appears that in 2015 the measured conductivity was erroneous for the three additional within-season samples taken at all three lakes, but that the ion measurements still showed acceptable charge balance (Table 3-2).

Table 3-4. Measures of the conductivity check for lakes with multiple within-season samples. In 2014 and 2015, these included (LAK06, LAK12 and LAK023). In 2016, these included those same three lakes plus LAK028, LAK042 and LAK044. Positive values of "Average %Diff" indicate that the estimated conductivity was higher than the measured conductivity.

Year	Lakes	Number of Samples	Average %Diff	Average Abs (%Diff)
2014	3	15	-3.2	6.2
2015	3	12	43.4 [5]	46.3
2016	6	24	-6.5	11.9

pH measurements

Lab measurements of pH were made at two different labs in 2013 to 2016. Limnotek examined the differences in pH measurements for 2016 among the two labs and the field measurement and concluded that the differences were within the expected ranges (i.e., factory/lab specified measurement error associated with each instrument; Bennett and Perrin 2017). In 2016, the values measured by ALS were higher than those measured by Trent University for all lakes and the mean difference between the labs was greater than previous years. However, both labs apply substantial quality control, quality assurance and equipment calibration procedures; therefore, it is not possible to conclude which lab's measurements are closer to the true pH value. For the analyses presented in this technical memo, we used the Trent University measurements to be consistent with the data from the STAR – the 2012 samples were only analyzed by Trent University and not ALS.

3.2 Annual Water Chemistry Sampling Results ①

Appendix 1 reports the results of the annual water chemistry sampling for the EEM lakes and control lakes from the sampling conducted in 2016 (with the data from 2012-2015 included for reference), for major water chemistry metrics (pH, DOC, Gran ANC, base cations, and major anions).

3.3 Intensive Monitoring of Three Lakes ⑤

Results from the continuous monitoring of pH in West Lake (LAK023), End Lake (LAK006), and Little End Lake (LAK012) are reported in the associated Technical Memo by Limnotek (Bennett and Perrin 2017). The Limnotek results for pH monitoring are summarized below in Table 3-5 and Table 3-6. Over the period of continuous monitoring (from April 10 to November 10, 2016), the pH varied by about 1.1 pH units in End Lake and by about 1.3 pH units in both Little End Lake and West Lake. The mean pH in all three lakes remained at or above 6.0, the level used as a biological threshold for analyses of critical loads (see STAR and KAA reports).

---

[5] It appears that for all 3 lakes the measured conductivity values for samples taken October 13, 20, and 27 are in error. Based on the first sample taken at each lake (October 4), the average % difference in conductivity was only -5.8%, which is within the range of other years and within the range of acceptable limits. Measured conductivity dropped substantially after the first sample, while the estimated conductivity remained relatively similar. Further examination confirmed that estimated conductivity was calculated correctly and there were no suspect data in the ion concentrations. The ion measurements are the most important data for the EEM Program – the ion measurements for these samples appear to be consistent with the data from the first sample, and the charge balances for all of the samples are within the range of acceptable limits. These errors appear to be limited only to the conductivity measurements for these three dates.

The results from these lakes further confirm the results from the first two years of continuous monitoring – i.e., that these data show a high degree of variation in the half-hourly pH within each year, substantially higher than originally expected, but not in the mean annual pH. Understanding that natural intra-annual variation is very high was one of the primary reasons for conducting the power analyses as part of the 2015 EEM Annual Report (ESSA Technologies Ltd 2016) and the resultant recommendation that changes in primary lake chemistry metrics will need to be assessed within a probabilistic analytical framework rather than simple deterministic comparisons between years[6]. The power analyses showed that continuous monitoring will increase the power of the monitoring program to be able to correctly detect changes in pH that exceed the EEM KPI threshold of 0.3 pH units (i.e., when the comprehensive review of the monitoring data is conducted in 2019).

A sharp drop in pH was observed in Little End Lake and West Lake at the very end of the monitoring period (Figure 6 in Bennett and Perrin 2017), coinciding with a large rainstorm (100mm of rainfall on November 8th and 9th) after a relatively dry October. During the first 10 days of November, Lake levels increased by about 0.25 m in End Lake and Little End Lake, and by about 0.45 m in West Lake (Figure 11 in Bennett and Perrin 2017). In End Lake, there was no sharp drop in pH following the storm, indicating hydrologic and biogeochemical differences between the End Lakes. There were no analyses of full lake chemistry in the three intensively monitored lakes on or following Nov 8 and 9, so it isn't possible to determine what chemical changes were associated with this pH decline. However, sampling of Lake 028 on Nov. 9th showed declines in pH, all base cations and sulphate since the previous sampling on October 31st, suggesting that base cation dilution is the most likely explanation for the pH decline in Lake 028 associated with the November 9th storm event.

---

[6] As described in the power analysis, there is a high degree of variability in pH (the KPI) within most of the sensitive lakes and for Gran ANC and SO_4^{2-} (the informative indicators) within some of the sensitive lakes . In 2019, as part of the comprehensive evaluation of EEM monitoring data, we will therefore generate a probability distribution for the change in each primary metric (pH, ANC, SO_4^{2-}), based on the 2012-2018 monitoring data, explicitly accounting for natural variability and measurement error. We will then compare those distributions to the evaluation thresholds for each indicator within each lake. The results will be expressed as the *probability that a particular lake has exceeded a particular threshold*. .

Table 3-5. Minimum, maximum, average and range of pH measurements taken every 30 minutes in each of End, Little End and West lakes in April to November 2016. Source: Table 9 in Bennett and Perrin (2017)

Lake	Sensor	Number of observations	Minimum pH	Maximum pH	Range of pH	Mean pH ± SD
End	pH1	10254	5.9	6.8	1.0	6.3 ± 0.1
End	pH2	10254	5.9	7.1	1.2	6.2 ± 0.1
End	pH3	10253	5.8	8.7*	2.9	6.3 ± 0.1
Little End	pH1	9726	5.6	7.0	1.4	6.1 ± 0.2
Little End	pH2	9726	5.4	6.7	1.2	6.0 ± 0.2
Little End	pH3	9726	5.6	6.9	1.3	6.1 ± 0.2
West	pH1	10253	5.6	7.0	1.4	6.3 ± 0.2
West	pH2	10253	5.5	6.8	1.3	6.2 ± 0.2
West	pH3	10253	5.5	6.8	1.3	6.2 ± 0.2

* Extreme values on sensor pH3 in End Lake were possibly due to instrument error (Bennett and Perrin 2017).

Table 3-6. Variation in mean pH (± standard deviation) between instruments, by lake, during sampling in October 2016. Source: Table 10 in Bennett and Perrin (2017).

Instrument or lab	Mean pH ± sd in October, 2016 (n=4)		
	End Lake	Little End Lake	West Lake
WTW field pH meter	6.1 ± 0.1	6.1 ± 0.1	6.1 ± 0.1
Trent University	6.0 ± 0.1	6.2 ± 0.0	5.9 ± 0.0
ALS	6.3 ± 0.2	6.5 ± 0.2	6.2 ± 0.1
Manta sensors	6.3 ± 0.1	6.2 ± 0.1	6.0 ± 0.2
Instrument/lab effect (*P*)	0.005	0.001	0.015

Analyses of 2015 and 2016 data from the 3 intensively monitored lakes with continuous monitoring of pH show that the difference in mean August pH and mean October pH varies across years within lakes, and across lakes within years (Table 3-7). Across all lakes and years, the mean August pH was 0.05 pH units higher than the mean October pH, but there does not appear to be any consistent pattern. The results in Table 3-7 provide a preliminary indication that samples taken in August are not biased relative to samples taken in October in a particular year and therefore it appears reasonable to use data from August 2012 (without any bias correction) together with data from October 2013 and October 2014 as estimates of pre-KMP conditions. However, this analysis is only based on two years and should be repeated in subsequent years to confirm the finding.

Table 3-7. Mean pH in August vs. mean pH in October, for each of the three intensively monitored lakes with continuous pH monitoring. These values represent an averaging of all measurements from the three Manta probes within each lake during each monthly period. None of the differences are greater than the measurement error (+/- 0.2 pH units for Manta instrument). Note: the monthly averages and differences reported in this table appear not to match in some places due to rounding errors (pH values are reported to nearest 0.1 pH units, but the calculations were conducted with more significant digits).

Year	Month	Metric	Lake		
			West Lake (LAK023)	End Lake (LAK006)	Little End (LAK012)
2015	Aug	COUNT	4455	4458	4101
		MEAN pH	6.2	6.4	6.2
		SD	0.1	0.1	0.2
	Oct	COUNT	4455	4455	4458
		MEAN pH	6.3	6.2	5.9
		SD	0.1	0.1	0.1
		DIFF (Aug-Oct pH)	**-0.0**	**0.1**	**0.2**
2016	Aug	COUNT	4452	4449	4452
		MEAN pH	6.2	6.3	6.0
		SD	0.1	0.1	0.2
	Oct	COUNT	4455	4455	4245
		MEAN pH	6.1	6.3	6.2
		SD	0.1	0.1	0.0
		DIFF (Aug-Oct pH)	**0.1**	**-0.0**	**-0.2**
		AVG. DIFF (Aug-Oct pH)	**0.05**		

3.4 Inter-annual Changes

Inter-annual changes in pH, Gran ANC, SO_4^{2-}, DOC, sum of base cations, and chloride are shown in terms of absolute change in Table 3-8 and Table 3-9, and in terms of relative change in Table 3-10 and Table 3-11. Changes are shown for five time periods of comparison: 2012-2013, 2013-2014, 2014-2015, 2015-2016, and 2012-2016. 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 taken for a given lake in a given year[7].

Figure 3-3 and Figure 3-4 show the changes in the same water chemistry parameters graphically. These figures allow better visualization of the distribution and variability in the observed changes between 2015 and 2016. Although the tables show changes for other periods as well, these figures have only been included for the changes from 2015 to 2016. Changes from 2015 to 2016 in

---

[7] This represents a change in practice from previous years, in which annual sampling values (and therefore intra-annual changes) were based only on the single samples taken on the day(s) in which sampling was conducted across all of the lakes. When the monitoring plan was expanded to include additional intra-annual sampling for some lakes in October (and sometimes November), these data were used to better understand intra-annual variability and help provide context for the inter-annual patterns observed.

particular are examined in more detail, in the context of expected changes based on the Evidentiary Framework, in the Discussion (Section 4).

Appendix 2 provides a detailed set of figures showing the inter-annual changes in major water chemistry metrics (Gran ANC, base cations, SO_4^{2-}, chloride, pH and DOC) for each of the EEM lakes across the five years of annual monitoring (2012-2016). Similar figures are also included for the three control lakes based on their three years of annual monitoring (2013, 2015, 2016).

However, as stated in Section 2.4, annual changes should be interpreted with substantial caution due to the combination of large natural variation (both within and between years) and limitations on measurement precision. The power analyses conducted and reported in the 2015 EEM Annual Report illustrated that *multiple* years of observations are required to reliably detect changes in mean pH, Gran ANC and SO_4; it is risky to draw conclusions based only on annual changes. We provide further discussion of these results in section 4.

Table 3-8. Inter-annual changes in pH, Gran ANC and SO_4^{2-} for EEM lakes, 2012-2016. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	pH (TU)					Gran ANC (µeq/L)					SO4* (µeq/L)				
From	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012
To	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016
LAK006	0.4	-0.1	-0.1	0.0	0.2	3.3	9.9	-6.5	-5.5	1.2	3.0	-2.3	-0.7	0.4	0.4
LAK012	0.6	-0.3	-0.1	0.3	0.6	6.5	5.2	-2.9	-0.1	8.8	5.2	4.5	1.7	-8.0	3.4
LAK022	0.2	0.1	-0.1	-0.1	0.1	8.5	10.5	-11.3	-1.1	6.6	16.9	-9.3	-5.3	1.7	4.0
LAK023	0.2	0.0	0.0	0.0	0.2	4.0	8.3	-2.1	-2.1	8.1	5.0	-5.1	-3.8	-2.4	-6.3
LAK028	0.2	0.1	-0.2	-0.2	0.0	8.8	17.8	-11.8	-15.7	-0.9	71.2	-33.7	-23.3	56.7	70.9
LAK042	0.8	-0.4	0.3	0.0	0.7	41.4	-8.5	1.3	0.2	34.4	-0.5	-1.8	-0.2	-0.5	-2.9
LAK044	0.3	0.1	0.0	-0.2	0.1	7.3	-2.7	0.3	-2.1	2.8	0.0	-1.6	-0.9	0.4	-2.1
Lakes with Increase	**7**	**3**	**3**	**1**	**6**	**7**	**5**	**2**	**1**	**6**	**5**	**1**	**1**	**4**	**4**
Lakes with Decrease	**0**	**4**	**4**	**6**	**1**	**0**	**2**	**5**	**6**	**1**	**2**	**6**	**6**	**3**	**3**

LAK007	0.0	0.1	-0.1	0.0	0.0	24.5	-16.4	119.9	-197.0	-69.0	15.1	-35.8	14.9	1.1	-4.7
LAK016	0.4	0.0	0.0	-0.2	0.3	28.3	8.8	7.4	-19.2	25.2	17.9	-8.7	-7.2	4.0	5.9
LAK024	[1]	[1]	-0.2	0.1	0.4	[1]	[1]	-29.1	20.1	163.6	[1]	[1]	-2.4	4.5	14.4
LAK034	0.1	-0.1	-0.1	-0.1	-0.3	111.0	-5.4	-27.1	-26.2	52.2	14.0	-21.1	-16.1	-0.9	-24.1
Lakes with Increase	**2**	**2**	**1**	**1**	**2**	**3**	**1**	**2**	**1**	**3**	**3**	**0**	**1**	**3**	**2**
Lakes with Decrease	**1**	**1**	**3**	**3**	**2**	**0**	**2**	**2**	**3**	**1**	**0**	**3**	**3**	**1**	**2**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-9. Inter-annual changes in DOC, base cations, chloride, and calcium for EEM lakes, 2012-2016. The differences between subsequent years and across the full record of sampling are shown. DOC = dissolved organic carbon, ΣBC = sum of base cations (i.e., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	DOC (mg/L)					∑ BC* (µeq/L)					Cl (µeq/L)					Ca* (µeq/L)				
From	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012
To	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016
LAK006	-0.4	0.6	0.1	0.3	0.7	-3.0	8.0	1.2	2.1	8.2	2.9	-0.6	-1.5	-1.1	-0.2	-3.2	4.6	0.6	0.3	2.3
LAK012	-0.4	2.0	1.2	-2.4	0.4	-11.8	7.3	8.1	-11.2	-7.6	10.5	-4.4	0.8	-5.4	1.5	-9.7	4.5	5.5	-10.2	-9.9
LAK022	0.9	-0.6	0.6	0.4	1.3	11.0	4.9	-6.2	6.7	16.4	5.4	-3.3	-1.1	0.0	1.0	7.0	3.4	-4.4	4.0	10.0
LAK023	-0.1	1.6	-0.3	0.5	1.7	-2.1	15.2	-5.5	-1.2	6.4	3.0	-1.3	0.1	-1.3	0.5	-2.3	12.2	-3.2	-3.6	3.1
LAK028	2.2	-1.1	2.2	0.0	3.2	48.4	4.4	-15.9	31.8	68.7	11.7	-6.7	-2.0	1.0	3.9	37.6	0.8	-9.4	18.2	47.2
LAK042	-3.5	0.9	-2.3	1.5	-3.3	7.6	-5.3	3.7	8.1	14.0	1.6	4.1	-5.4	0.7	1.0	8.7	-5.5	0.2	5.9	9.3
LAK044	-0.2	0.3	-0.2	0.4	0.3	3.0	0.1	2.9	-2.1	4.0	3.3	-2.9	0.0	0.2	0.5	0.9	0.0	2.0	-1.6	1.4
Lakes with Increase	**2**	**5**	**4**	**6**	**6**	**4**	**6**	**4**	**4**	**6**	**7**	**1**	**2**	**3**	**6**	**4**	**5**	**4**	**4**	**6**
Lakes with Decrease	**5**	**2**	**3**	**1**	**1**	**3**	**1**	**3**	**3**	**1**	**0**	**6**	**4**	**3**	**1**	**3**	**2**	**3**	**3**	**1**

LAK007	-0.5	0.6	-0.5	0.5	0.2	-51.9	63.5	-7.8	35.1	38.9	11.7	-17.1	4.8	1.4	0.8	-46.2	50.8	-10.2	34.9	29.3
LAK016	0.5	-0.2	0.3	0.8	1.5	0.8	13.7	7.8	-2.1	20.2	6.0	-3.0	-0.6	-0.3	2.1	-3.2	8.0	8.5	-3.5	9.8
LAK024	[1]	[1]	0.5	0.5	1.3	[1]	[1]	-2.8	57.7	225.3	[1]	[1]	-6.8	11.0	42.7	[1]	[1]	-1.7	46.0	173.4
LAK034	0.1	2.4	0.5	0.0	3.0	56.0	8.6	-32.3	-21.8	10.6	2.5	-1.8	-0.3	-0.8	-0.4	33.4	8.7	-15.0	-16.4	10.7
Lakes with Increase	**2**	**2**	**3**	**4**	**4**	**2**	**3**	**1**	**2**	**4**	**3**	**0**	**1**	**2**	**3**	**1**	**3**	**1**	**2**	**4**
Lakes with Decrease	**1**	**1**	**1**	**0**	**0**	**1**	**0**	**3**	**2**	**0**	**0**	**3**	**3**	**2**	**1**	**2**	**0**	**3**	**2**	**0**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-10. Inter-annual changes (%) in pH, Gran ANC and SO_4^{2-} for EEM lakes, 2012-2016. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	pH (TU)					Gran ANC (mg/L)					SO4* (µeq/L)				
From	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012
To	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016
LAK006	6%	-1%	-1%	0%	4%	13%	34%	-17%	-17%	5%	26%	-16%	-5%	3%	4%
LAK012	12%	-5%	-1%	5%	10%	11%	8%	-4%	0%	15%	84%	40%	11%	-46%	56%
LAK022	4%	2%	-2%	-1%	2%	31%	29%	-24%	-3%	24%	56%	-20%	-14%	5%	13%
LAK023	4%	-1%	0%	0%	4%	20%	35%	-7%	-7%	41%	26%	-21%	-20%	-16%	-33%
LAK028	5%	2%	-4%	-3%	0%	[1]	372%	-52%	-146%	[1]	125%	-26%	-25%	80%	125%
LAK042	17%	-6%	6%	0%	15%	[1]	-40%	10%	1%	[1]	-7%	-31%	-5%	-13%	-47%
LAK044	5%	2%	0%	-4%	2%	576%	-32%	6%	-34%	220%	0%	-26%	-19%	11%	-34%
Lakes with Increase	**7**	**3**	**3**	**1**	**6**	**5**	**5**	**2**	**1**	**5**	**5**	**1**	**1**	**4**	**4**
Lakes with Decrease	**0**	**4**	**4**	**6**	**1**	**0**	**2**	**5**	**6**	**0**	**2**	**6**	**6**	**3**	**3**
LAK007	-1%	2%	-1%	0%	0%	2%	-1%	8%	-13%	-5%	29%	-54%	49%	2%	-9%
LAK016	6%	1%	0%	-3%	4%	41%	9%	7%	-17%	37%	46%	-15%	-15%	10%	15%
LAK024	[2]	[2]	-3%	1%	5%	[2]	[2]	-6%	5%	55%	[2]	[2]	-7%	13%	58%
LAK034	2%	-2%	-2%	-2%	-4%	112%	-3%	-13%	-15%	53%	58%	-55%	-95%	-100%[3]	-100%
Lakes with Increase	**2**	**2**	**1**	**1**	**2**	**3**	**1**	**2**	**1**	**3**	**3**	**0**	**1**	**3**	**2**
Lakes with Decrease	**1**	**1**	**3**	**3**	**2**	**0**	**2**	**2**	**3**	**1**	**0**	**3**	**3**	**1**	**2**

[1] LAK028 and LAK042 had negative ANC values in 2012 and therefore the percentage change could not be properly calculated.

[2] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

[3] The resulting SO_4^{2-} concentration for LAK034 for 2016 after correcting for marine influence was calculated as less than zero. Therefore the relative change from 2015 to 2016 was calculated as -104%. This value has been adjusted to -100%.

Table 3-11. Inter-annual changes (%) in DOC, base cations and chloride for EEM lakes, 2012-2016. The differences between subsequent years and across the full record of sampling are shown. DOC = dissolved organic carbon, ΣBC = sum of base cations (e.g., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	DOC (mg/L)					∑ BC* (µeq/L)					Cl (µeq/L)					Ca* (µeq/L)				
From	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012	2012	2013	2014	2015	2012
To	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016	2013	2014	2015	2016	2016
LAK006	-10%	19%	3%	8%	19%	-5%	14%	2%	3%	14%	51%	-7%	-18%	-16%	-3%	-11%	17%	2%	1%	8%
LAK012	-9%	47%	20%	-32%	9%	-10%	7%	7%	-9%	-6%	254%	-30%	8%	-49%	36%	-13%	7%	8%	-14%	-13%
LAK022	17%	-9%	11%	6%	25%	11%	5%	-5%	6%	17%	78%	-27%	-13%	0%	14%	12%	5%	-6%	6%	17%
LAK023	-3%	40%	-5%	9%	40%	-3%	24%	-7%	-2%	10%	67%	-18%	1%	-20%	10%	-6%	33%	-6%	-8%	8%
LAK028	45%	-16%	36%	0%	66%	66%	4%	-13%	29%	94%	193%	-38%	-18%	11%	65%	79%	1%	-11%	24%	99%
LAK042	-26%	9%	-21%	18%	-25%	14%	-9%	7%	14%	26%	26%	53%	-45%	11%	17%	118%	-35%	2%	55%	126%
LAK044	-12%	17%	-11%	27%	17%	21%	1%	17%	-10%	28%	59%	-33%	0%	4%	10%	14%	0%	26%	-16%	21%
Lakes with Increase	**2**	**5**	**4**	**6**	**6**	**4**	**6**	**4**	**4**	**6**	**7**	**1**	**2**	**3**	**6**	**4**	**5**	**4**	**4**	**6**
Lakes with Decrease	**5**	**2**	**3**	**1**	**1**	**3**	**1**	**3**	**3**	**1**	**0**	**6**	**4**	**3**	**1**	**3**	**2**	**3**	**3**	**1**
LAK007	-84%	610%	-65%	208%	25%	-3%	4%	-1%	2%	3%	48%	-47%	25%	6%	3%	-4%	4%	-1%	3%	2%
LAK016	14%	-4%	8%	19%	40%	0%	8%	4%	-1%	12%	95%	-24%	-6%	-3%	34%	-3%	7%	7%	-3%	8%
LAK024	[1]	[1]	30%	23%	96%	[1]	[1]	-1%	11%	66%	[1]	[1]	-10%	19%	157%	[1]	[1]	0%	11%	63%
LAK034	3%	51%	7%	0%	67%	28%	3%	-12%	-9%	5%	42%	-21%	-4%	-14%	-8%	28%	6%	-9%	-11%	9%
Lakes with Increase	**2**	**2**	**3**	**4**	**4**	**2**	**3**	**1**	**2**	**4**	**3**	**0**	**1**	**2**	**3**	**1**	**3**	**1**	**2**	**4**
Lakes with Decrease	**1**	**1**	**1**	**0**	**0**	**1**	**0**	**3**	**2**	**0**	**0**	**3**	**3**	**2**	**1**	**2**	**0**	**3**	**2**	**0**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

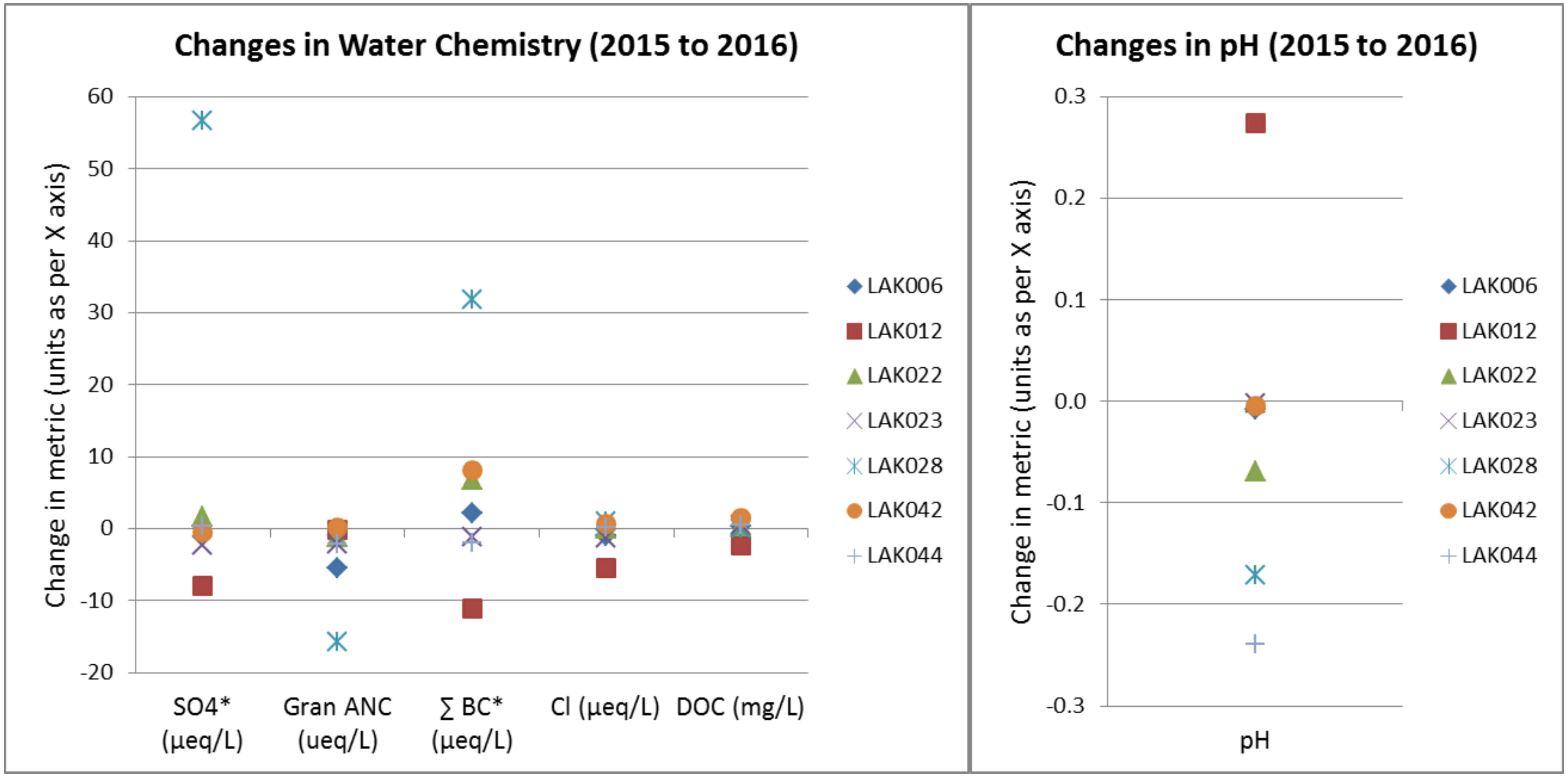


Figure 3-3: Changes in water chemistry metrics (left panel) and pH (right panel) across all of the sensitive EEM lakes, from 2015 to 2016. Values shown are 2016 value minus 2015 value.

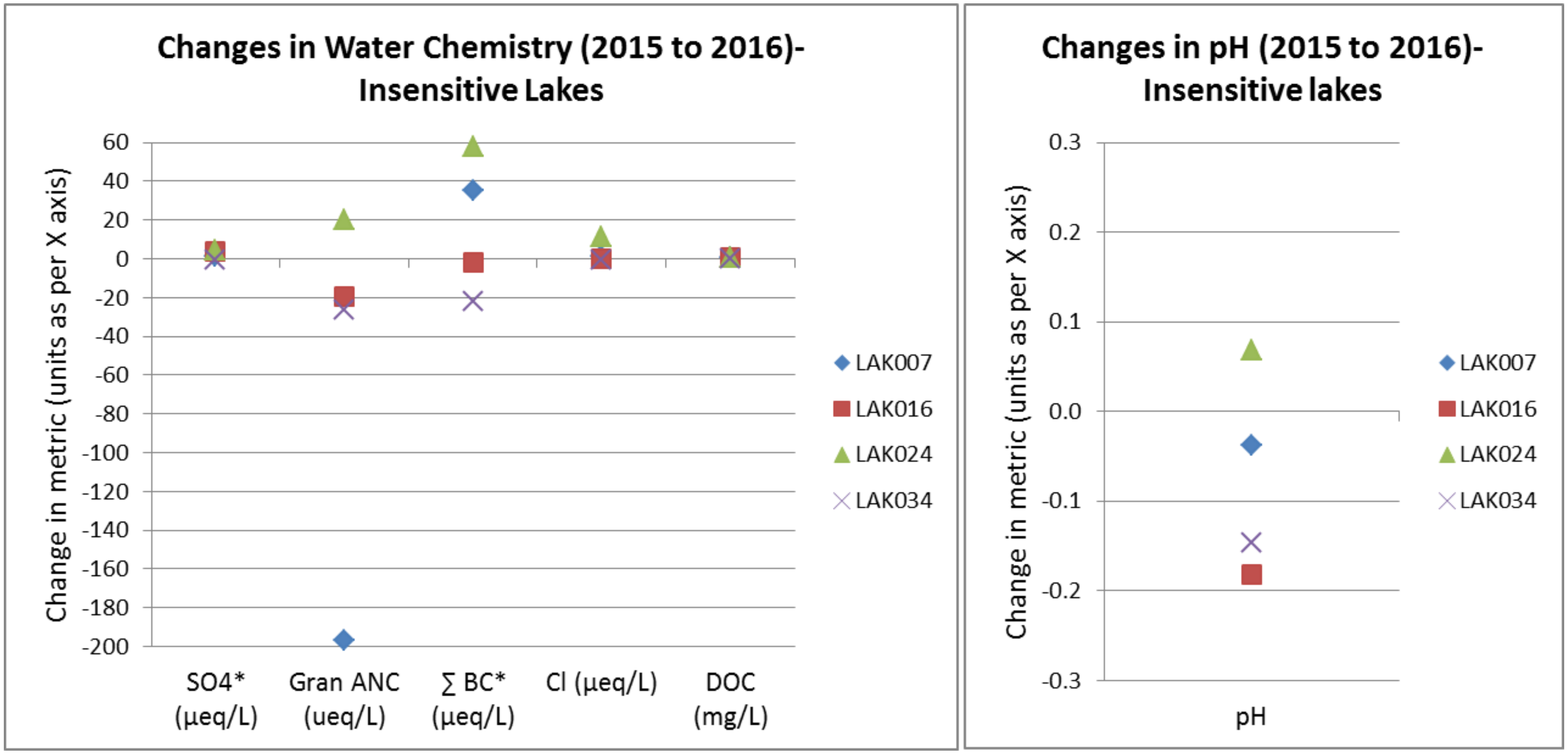


Figure 3-4: Changes in water chemistry metrics (left panel) and pH (right panel) across all of the less sensitive EEM lakes, from 2015 to 2016. Values shown are 2016 value minus 2015 value.

3.5 Episodic Acidification Studies ④

Research Project by Dr. Paul Weidman

As this project is being conducted by an external organization, the results from this work will be communicated separately as they become available.

4 Discussion

4.1 Application of the Evidentiary Framework

The principles of the evidentiary framework are applied in the interpretation of the results in the subsequent two sections. The evidentiary framework suggests that 2016 sulphate concentrations should increase relative to 2015 (due to increased emissions of SO_2), and that if changes in sulphate are driving acidification then ANC and pH levels should correspondingly decrease, if all other constituents and hydrologic conditions remained unchanged. As noted in the EEM Evidentiary Framework, changes in base cations, nitrate or DOC can also help to explain observed changes in ANC and pH.

4.2 Inter-annual Changes in Lake Chemistry, 2015-2016

Some of the main patterns observed in the changes in lake chemistry between 2015 and 2016 are reported in this section. These patterns are reported in two ways:

- By water chemistry metric across lakes (i.e., how do the general patterns for sulphate, ANC and pH align with changes that would be expected if acidification were occurring), and
- By lake across metrics (i.e., how do the patterns observed in each lake align with changes that would be expected if acidification driven by smelter emissions were occurring).

As emphasized in Sections 2.4 and 3.4, annual changes should be interpreted with great caution due to the high degree of natural variation (both within and between years) and measurement precision, which result in a low power to accurately detect annual changes in lake chemistry.

The following recommendation was put forth in the 2015 EEM Annual Report (based on the results of the power analyses):

- Wait until having collected 5 years of post-KMP monitoring data before drawing conclusions about potential changes to lake chemistry, due to the predicted low power and higher false positives (for some scenarios) in the first few years of post-KMP monitoring. At a minimum, wait until the end of the initial phase of the EEM program (3 years of post-KMP monitoring data).

In accordance with this recommendation and previously emphasized cautions about interpreting the annual changes in measured values, the observed changes discussed in the following two sections should be considered as preliminary indicators of potential changes that may be occurring rather than definitive patterns of change. We are reporting on the annual changes that have been measured thus far but have not yet conducted analyses on the long-term trends. The comprehensive review in 2019 will rigorously analyses the multi-year, pre-/post-KMP trends and patterns in the data.

4.2.1 Observed Changes by Metric, 2015-2016

Sulphate

- Sulphate would be expected to increase in lakes (if they are responsive on an annual time scale) to increases in SO_2 emissions from KMP
- 4 of 7 sensitive lakes and 3 of 4 less sensitive lakes showed increases in SO_4^{2-} (corrected for influence of marine ions)
    - In LAK028, sulphate increased by approximately 80% (70.9 μeq/L)
    - The other 3 sensitive lakes with increases in SO_4^{2-} had small increases of 0.4 to 4 μeq/L (5-11%)
    - The less sensitive lakes with increases in SO_4^{2-} had increases of 2-13%
- Despite the increased emissions, 3 sensitive lakes and 1 less sensitive lake showed decreases in SO_4^{2-}
    - In LAK012, LAK023 and LAK042, SO_4^{2-} decreased by 8.0, 2.4 and 0.5 μeq/L (respectively)
    - LAK034 decreased by 0.9 μeq/L to zero
    - For LAK023, LAK042 and LAK034, 2016 represented the third consecutive year of decreases, suggesting that if the lakes are in fact responsive to changes in smelter emissions, the response has a lag of greater than 1 year, or that the spatial pattern of sulphate deposition has changed under KMP, with less sulphate deposition occurring in these lakes
    - Two of these lakes (LAK034 and LAK042) are located at the northern extent of the study area and therefore receive lower levels of deposition. Further distance from the plume should mean greater dilution of emissions and could also mean that deposition levels vary more with changing wind patterns. However, the data from the other EEM lakes does not provide evidence for the distance from the smelter being a driving factor for lakes that had decreases in sulphate:
        - The other "far north" sensitive lake (LAK044), located near LAK034 and LAK044 showed little change in SO_4^{2-} (an increase of 0.4 μeq/L)
        - LAK012 had a considerably larger decrease in SO_4^{2-} (8 μeq/L) than both LAK034 and LAK042 despite being located much closer to the smelter
        - The two sensitive lakes near LAK012 and LAK023 (i.e., LAK006, LAK022) experienced small increases in SO_4^{2-} (+0.4 and +1.7 μeq/L, respectively)
        - We conclude that more years of data will be required to sort out the spatial pattern of changes in sulphate deposition.

ANC

- For the sensitive lakes, decreases in ANC would be expected (based on the evidentiary framework) to accompany increases in SO_2 emissions and resultant increases in SO_4^{2-} concentrations
    - This expected pattern of decreased ANC was observed in 6 of 7 sensitive lakes, and 4 of these 6 lakes also showed increased SO_4^{2-}
    - The 1 sensitive lake that showed an increase in ANC (LAK042), demonstrated only a very small increase (0.2 μeq/L)
    - Base cations are expected to increase ANC, whereas sulphate is expected to decrease ANC. The 3 sensitive lakes with a negative value for {[Δ base cations] – [Δ sulphate]} also showed a decrease in ANC, which is what would be expected (LAK012, LAK028 and LAK044). LAK042 showed positive values for both {[Δ base cations] – [Δ sulphate]} and ΔANC, which would also be expected (although

    the increase in ANC was very small). However, 3 sensitive lakes (LAK006, LAK022 and LAK023) had positive values for {[Δ sum of base cations] – [Δ sulphate]} but showed declines in ANC, which would not be expected. However, the decreases in ANC were very small in LAK022 and LAK023 (-1.1 and -2.1 µeq/l, respectively), so one should not over-interpret these patterns.
  - 5 of the 7 sensitive lakes demonstrated the pattern of inverse changes in ANC and SO_4^{2-} that would be expected if ANC is associated with changes in sulphate
    - The 2 lakes showing patterns contrary to expectations had only small decreases in ANC (-0.1 and -2.1 µeq/l) associated with their decreases in SO_4^{2-} – these small changes over only one year do not provide strong evidence of truly contrary pattern
- For the less sensitive lakes, changes in ANC would be expected to be independent of changes in SO_4^{2-} as well as being relatively small
  - ANC and SO_4^{2-} changed in the same direction for 2 of the less sensitive lakes and in opposite directions for the other 2 less sensitive lakes (although that alone does not mean that ANC is being influenced by SO_4^{2-})
  - 3 lakes showed decreases in ANC and 1 lake showed an increase (LAK024)
  - Of the 3 lakes that showed decreases in ANC, 2 of them also showed decreased in total base cations (Table 3-8, Table 3-9), though the magnitudes of change were only comparable in LAK034.
  - Decreases in ANC were within the range 13-17%; LAK024 increased in ANC by 5%

pH

- For all of the lakes, changes in pH would be expected to be in the same direction as changes in ANC, as per the relationship defined by the pH-alkalinity titration curve (though the magnitude of the pH change would depend on the specific location along the curve)
  - 5 of 7 sensitive lakes demonstrate this expected pattern, with all 5 of those lakes showing decreases in the two metrics (although the magnitude of decrease in pH was negligible for 3 of the lakes)
  - All 4 less sensitive lakes demonstrate this expected pattern, including 3 lakes with decreases and 1 lake with increases in the two metrics
- pH decreased for 6 of 7 sensitive lakes and 3 of 4 less sensitive lakes; all of these decreases were within the accuracy of the pH meter used at Trent University (± 0.2 pH units)

Other metrics

- 10 of 11 EEM lakes increased in DOC
  - LAK042 increased by 1.5 mg/L; all other lakes changed by ≤1.0 mg/L
  - LAK028 and LAK034 had negligible increases in DOC
  - LAK012 decreased by 2.4 mg/L
- 6 of 11 EEM lakes increased in total base cations, so there was not a consistent pattern
- 6 of 11 EEM lakes decreased (5) or remained the same (1) in chloride.
  - 4 lakes increased in chloride by 0.2 to 1.4 µeq/l (4-11%) and 1 lake (less sensitive) increased by 11.0 µeq/l (19%)

4.2.2 Observed Changes by EEM Lake, 2015-2016

The observed changes for 2015 to 2016 for each lake in major lake chemistry metrics are summarized here. We then consider whether these changes are consistent with the expectations of a potential KMP-driven acidification impact (as per the patterns of changed outlined in the evidentiary framework).

After a 9-year trend in generally declining SO_2 emissions, 2016 represented a substantial increase in emissions and therefore a strong reversal of this longer term trend. Emissions in 2016 provide a very strong contrast with previous years. This provides an opportunity to understand how responsive the EEM lakes are to changes in emissions, based on if and when this strong signal in emissions is reflected in changes in sulphate concentrations. With the 2016 sampling data, we can see which lakes are responsive on annual timescale to changes in emissions. Lakes that do not show an increase in sulphate concentrations in 2016 may simply be responsive on a longer timescale (which may be confirmed by sampling in future years) or are not particular responsive to changes in emissions (due to the spatial distribution of sulphate deposition, or other factors). In previous years of the EEM program it was not possible to assess whether the generally observed decreases in sulphate were due to decreases in emission in the same year (i.e., highly responsive, little lag in effect) or a result of the many previous years of continuing decreases in emissions (i.e., less responsive, multi-year lag in effect).

However, as emphasized throughout this report, changes between individual years should be interpreted with a very high degree of caution given high natural variation and measurement error. Definitive conclusions should therefore not be drawn based on these simple inter-annual comparisons. The observed changes between 2015 and 2016 should be considered preliminary indications of the patterns that may be occurring, but it will not be possible to draw stronger conclusions about these patterns and potential mechanisms until more data are collected and analyzed in the comprehensive EEM review in 2019.

Control Lakes

Monitoring results for the three control lakes (DCAS14A, NC184, NC194; see Appendices 1 and 2) show that there were minimal changes (i.e., ± 4%) in sulphate concentrations between 2015 and 2016, which provides initial confirmation that these lakes are outside the area of deposition (a critical attribute for their suitability as control lakes). The control lakes have not been extensively analyzed at this point but will be an invaluable component of the comprehensive statistical analyses that will be conducted in 2019. Including reference samples from beyond the predicted SO_2 plume is an important component of the monitoring design for determining whether or not observed effects are related to smelter emissions. The control lakes will increase the power to accurately detect changes in the EEM lakes and will help advance our understanding of natural inter-annual variability in lake chemistry.

Sensitive EEM Lakes

LAK006. SO_4^{2-} increased, and ANC and pH decreased (by <0.05 pH units, well within the ± 0.2 pH units accuracy of laboratory pH measurements), as expected with increased sulphate emissions. The minor increase in DOC could also be contributing to decreased ANC.

- ➢ CONSISTENT with expectations from evidentiary framework

LAK012. Decrease in SO_4^{2-} (-8.0 µeq/l; -46%), which is highly unexpected if the lake is in fact receiving higher levels of sulphate deposition, and is responsive on annual scale to increased sulphate emissions. ANC decreased by a very small margin while pH increased (by 0.3 pH units, greater than the ± 0.2 pH units accuracy of laboratory pH measurements), which is contrary to expected relationship between pH and ANC, but consistent with a decrease in sulphate concentrations.

- ➢ INCONSISTENT with expectations from evidentiary framework

LAK022. SO_4^{2-} increased, and ANC and pH decreased (by 0.1 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), as expected with increased sulphate (albeit only a small increase). Decrease in ANC could be being mitigated by increase in base cations.

- ➢ CONSISTENT with expectations from evidentiary framework

LAK023. Decrease in SO_4^{2-} (2.4 µeq/L; -16%), which is not expected if lake is responsive on annual scale to increased sulphate emissions. ANC and pH decreased (by <0.05 pH units, well within the ± 0.2 pH units accuracy of laboratory pH measurements), which is consistent with the expected relationship between pH and ANC; however, the decrease in SO_4^{2-} suggests that the changes in pH and ANC are not being driven by SO_4^{2-}. Decrease in ANC could be affected by a decrease in base cations. LAK023 also shows a very small increase in DOC, which should generally contribute to reduced ANC.

- ➢ INCONSISTENT with expectations from evidentiary framework

LAK028. Large increase in SO_4^{2-}, as expected with increased sulphate emissions and indicating that the lake is responsive on an annual scale to such emissions. Among the acid-sensitive lakes, LAK028 demonstrated the most substantial changes between 2015 and 2016, including an 80% increase in sulphate concentrations (70.9 µeq/L), and a 29% increase in the concentration of base cations (31.8 µeq/L). ANC decreased (by 15.7 µeq/l) and pH decreased (by 0.2 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), as expected for sensitive lakes with increased sulphate concentration. The large increase in base cations appears to be mitigating the magnitude of the decrease in ANC. DOC remained unchanged.

- ➢ CONSISTENT with expectations from evidentiary framework

LAK042. Decrease in SO_4^{2-} (-13%, but only -0.5 µeq/L), which is not expected if the lake is responsive on annual scale to increased sulphate emissions. However, LAK042 is one of the most distant from the smelter and therefore may have a limited and/or lagged response in sulphate concentrations to increases in emissions, or may in fact not have received increased deposition between 2015 and 2016 due to variations in wind patterns. ANC remained virtually unchanged (+ 0.2 µeq/l) and pH also remained unchanged (accuracy of laboratory pH measurements is ± 0.2 pH units).

Over the entire period from 2012 to 2016, LAK042 has shown an increase of 34.4 µeq/L in Gran ANC (Table 3-8), which was associated with an increase in base cations of 14 µeq/L, and a decrease in DOC of 3.3 mg/L (equivalent to a decrease in organic anions of 25 µeq/L if charge density were 7.5 µeq per mg of DOC); Table 3-9. Sulphate only decreased by 2.9 µeq/L over this period (Table 3-8), so it appears that the increase in GranANC was mostly related to an increase in base cations and a decrease in organic anions.

- ➢ INCONSISTENT with expectations from evidentiary framework[8]

LAK044. SO_4^{2-} increased by 0.4 µeq/l, , ANC decreased by 2.1 µeq/l and pH decreased (by 0.2 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), as expected with increased sulphate emissions, albeit the increase in SO_4^{2-} was very small. LAK044 is also one of the most distant lakes from the smelter and therefore may have a limited and/or lagged response in

---

[8] In absolute terms, the changes in pH, ANC and SO_4^{2-} are very small and therefore do not indicate any change, which is in itself unexpected given increased SO_2 emissions.

sulphate concentrations to increases in emissions. However, given the relatively small increase in sulphate, the 5-fold greater change in ANC is likely not being driven by increased sulphate. The change in ANC could potentially be influenced by the small decrease in base cations and moderate increase in DOC. The changes in SO_4^{2-}, ANC and pH are consistent with the evidentiary framework, but the small magnitude of the increase in sulphate does not align with the expectations associated with KMP-driven acidification.

- ➢ NOT CONSISTENT with expectations from evidentiary framework

Less Sensitive EEM Lakes

The evidentiary framework is intended to identify patterns of change associated with the potential for an acidification effect driven by the increased sulphate emissions. The less sensitive lakes in the zone of increased sulphate deposition are expected to show an increase in sulphate concentrations, but are not expected to experience any acidification effect (i.e., declines in ANC and pH). Changes in ANC are expected to be relatively small and independent of changes in sulphate concentration and therefore our expectation is that the less sensitive lakes *should* be inconsistent with the evidentiary framework.

LAK007. ANC decreased by 13% (which resulted in the largest absolute decrease in ANC because the ANC of LAK007 is more than an order of magnitude larger than any of the sensitive lakes). The small increase in SO_4^{2-} is consistent in direction with the decrease in ANC, but far too small in magnitude to explain the observed decline (ANC decreased by 197.0 µeq/l and SO_4^{2-} increased by 1.1 µeq/l). Furthermore, the increase in base cations is inconsistent with the observed change in ANC. Although ANC decreased substantially, pH did not change at all (accuracy of laboratory pH measurements is ± 0.2 pH units), which is consistent with the lake being very high on the pH-ANC curve (i.e., changes in ANC are not expected to result in much change in pH). LAK007 has an ANC of about 1400 µeq/l so it is highly insensitive to acidification.

- ➢ CONSISTENT with expectations for an insensitive lake

LAK016. SO_4^{2-} increased, and ANC and pH decreased (by 0.2 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), as would be expected for a *sensitive* lake under increased sulphate emissions, but would not be expected for a less sensitive lake. Decreased base cations and increased DOC could also be contributing to the decrease in ANC, albeit the change in base cations is relatively insignificant and change in DOC is very small in absolute terms. For a less sensitive lake, pH is not expected to change much in association with changes in ANC. However, LAK016 has an ANC of about 100 µeq/l so it is moderately sensitive to acidification.

- ➢ CONSISTENT with expectations for a moderately sensitive lake

LAK024. SO_4^{2-} increased, as expected with increased sulphate emissions. ANC and pH both increased (pH increased by 0.1 pH units, laboratory accuracy is ± 0.2 pH units), which is the opposite of what would occur if the lake were sensitive to acidification. The increase in ANC is proportionally small and could potentially be associated with the corresponding increase in base cations. LAK024 has an ANC of about 500 µeq/l so it is insensitive to acidification.

- ➢ CONSISTENT with expectations for an insensitive lake

LAK034. SO_4^{2-} decreased (from very low in 2015 to zero), which is not expected with increased sulphate emissions. However, LAK034 is one of the most distant lakes from the smelter and therefore may have limited/lagged response in sulphate concentrations to increases in emissions. ANC and pH both decreased (by 0.1 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), but given lack of sulphate and minimal change from the previous year, the decrease in ANC could not be driven by sulphate. The decrease in ANC (-15%) could potentially be associated with the corresponding decrease in base cations. LAK024 has an ANC of about 150 µeq/l so it can be considered relatively insensitive to acidification (compared to the seven acid-sensitive lakes).

- ➢ CONSISTENT with expectations for a relatively insensitive lake distant from the smelter

4.2.3 Observed Changes in LAK028

The data and analyses from the STAR and EEM program have thus far suggested that LAK028 has the highest potential risk of acidification due to KMP. The data do not show that acidification is presently occurring, but the patterns observed remain consistent with the possibility of acidification occurring in the future. With only one year of post-KMP observations, high natural variability and measurement error, it is not possible to make any conclusions about trends at this point. However, if the observations from this year accurately represent underlying changes in lake chemistry, as opposed to simply reflecting the high degree of variability and uncertainty, then these changes would be consistent with the patterns associated with acidification – that is, a large increase in SO_4^{2-} concurrent with decreases in ANC and pH (although within the limits of the laboratory accuracy), and offsetting increases in base cations. For this reason, we have provided some further exploration of LAK028 in the current annual report.

As part of the STAR, the results of the Steady State Water Chemistry model showed that LAK028 had the highest predicted exceedance of critical loads of acidity for all the STAR lakes, and was one of only 5 lakes with a predicted steady state pH that represents a decrease in pH of greater than 0.3 pH units. Geographically, it is located much closer to the smelter than any of the other sensitive lakes. In fact, the data collected in 2012 suggested that the chemistry of LAK028 had already been influenced by exposure to emissions of the pre-KMP smelter (see section 9.4.1.2.3 of STAR report, ESSA et al. 2013). The anion composition analyses showed that among lakes with pH<6, LAK028 was the only lake with an anion composition signature that was strongly consistent with a hypothesis of smelter influence. LAK028 had the highest levels of sulphate (51% of total anions) and by far the highest level of fluoride (18% of total anions), providing strong evidence of smelter effects.

We have compared LAK028 to acid-sensitive lakes from the northeast U.S. that had been acidified by sulphate deposition, as analyzed by Sullivan et al. (1988). Figure 4-1 shows that the sulphate and ANC levels for LAK028 are comparable to those acid-sensitive lakes, except that LAK028 has slightly lower ANC than many of those lakes due to organic acids. One indicator of acidification is the ratio of SO_4^{2-} * to total base cations (a ratio > 1 is indicative of acidification), as described in Sullivan et al. (1988). In LAK028, this ratio was < 1 in all years except for 2013 (Table 4-1). The monitoring data collected thus far shows that base cations are increasing as sulphate increases, neutralizing much of the H+ associated with the SO_4^{2-} *.

There are two ways of estimating the proportion of deposited acidity that was neutralized between 2015 and 2016. First, one can compute the F-factor (Δ Base Cations$_{2015\text{-}2016}$ / Δ Sulphate$_{2015\text{-}2016}$). From Table 4-1, F is estimated at 0.56[9]. From this method, one can infer that 56% of the deposited acidity was neutralized through increases in base cations. This is higher than the F-factor that was assumed for the STAR (0.44), indicating a higher level of acid neutralization by cation exchange, but the two values are still roughly comparable. However, this estimate is only based on the changes between two individual years and is therefore highly sensitive to variability in the sample

---

[9] F-factor$_{2015\text{-}2016}$ = [Δ Base Cations$_{2015\text{-}2016}$] / [Δ Sulphate$_{2015\text{-}2016}$] = [31.76 µeq/l] / [56.68 µeq/l]= 0.56

measurements used. The second way of estimating the proportion of deposited acidity that was neutralized between 2015 and 2016 is to compare the decrease in Gran ANC (15.72 μeq/l) to the increase in SO_4^{2-} (56.68 μeq/l). If there were no mechanisms of acid neutralization, the decrease in Gran ANC would equal the increase in SO_4^{2-}. This comparison implies that 72%[10] of the deposited acidity was neutralized through one neutralizing process or another. One possible explanation for the difference between the two methods described above is that some of the deposited sulphate was neutralized by sulphate reduction, which has been described by Baker et al. (1986) and Kelly et al. (1987), and used in acidification modelling by Marmorek et al. (1990). Further investigations are required as to the potential significance of this mechanism in LAK028.

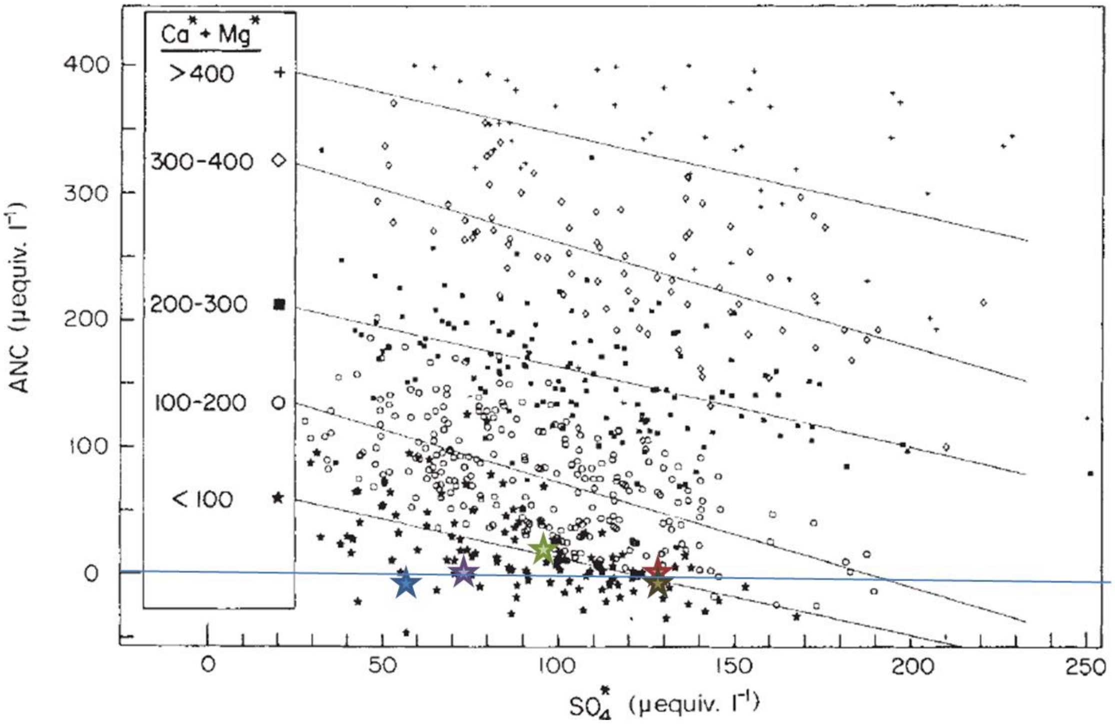


Figure 4-1. ANC and SO_4^{2-} * for LAK028 compared to acid sensitive lakes in the northeast U.S. The underlying figure is from Sullivan et al. (1988), showing the relationship between ANC and SO_4^{2-} * as stratified by the sum of marine-adjusted Ca and Mg cations. The stars represent the data for LAK028 from each of the annual sampling events (blue = 2012, red = 2013, green = 2014, purple = 2015, brown = 2016). The * (e.g., Ca*, Mg*) signifies that concentrations have been adjusted to account for marine influence.

---

[10] $(\Delta SO_4^{2-\,*} - \Delta \text{Gran ANC}) / \Delta SO_4^{2-\,*} = (56.68\ \mu eq/l - 15.72\ \mu eq/l) / 56.68\ \mu eq/l = 0.72$

Table 4-1. Sulphate and base cation concentrations for LAK028. Values in 2016 are mean annual values; previous years only had annual samples.

Year	SO4 * (µeq/L)	Ca * (µeq/L)	Mg * (µeq/L)	Ca*+Mg*	∑ BC * (µeq/L)	Gran ANC	SO4 * / ∑ BC *	pH
2012	56.90	47.54	9.50	57.05	72.91	-3.98	0.78	4.98
2013	128.12	85.11	18.27	103.38	121.31	4.80	1.06	5.21
2014	94.43	85.92	17.74	103.66	125.71	22.64	0.75	5.33
2015	71.11	76.52	15.66	92.17	109.83	10.79	0.65	5.13
2016	127.79	94.69	23.75	118.45	141.59	-4.93	0.90	4.96

Changes over 2012-2016. LAK028 showed a 70.9 µeq/l increase in the $SO_4^{2-\,*}$ anion over 2012-2016 (Table 3-8), which was almost completely balanced by a 68.7 µeq/l increase in total base cations (Table 3-9). The increase in base cations over 2012-2016 likely reflects more than just cation exchange (possibly greater weathering rates or less dilution of base cations with reduced runoff), since much of the increase occurred between 2012 and 2013 (Table 4-1). Though DOC increased by 3.2 mg/L between 2012 and 2016 (Table 3-9), contributing possibly up to 24 µeq/l in organic anions[11], there has been a negligible change over 2012-2016 in both Gran ANC (-0.9 µeq/l, Table 3-8) and pH (0.0 pH units, Table 3-8). Our preliminary conclusion is that the acidity contributed by increases in SO_4^{2} over 2012-2016 appears to have been balanced by increases in base cations (as well as possibly other mechanisms discussed above, such as sulphate reduction), and increases in DOC do not appear to have resulted in any further acidification. Due to the many sources of variability in lake chemistry data (i.e., between-year variation, within-year natural variation, measurement errors), it is fortunate to observe an approximate match of the changes in sulphate and base cations over 2012-2016 in LAK028. It will be important to reassess this conclusion with more years of data.

5 Recommendations

The 2017 sampling plan should follow the 2016 sampling plan. Changes that were implemented in 2016 were justified based on recommendations in the 2015 EEM Annual Report, which still hold. No additional changes are recommended at this time. Additional information on within-season variability in lake chemistry for LAK028, LAK042 and LAK044 will be valuable for analyzing trends over time, as will continued sampling of the control lakes, and the intensively monitored lakes.

Some of the reviews of this year's report have suggested some additional analyses that should be considered in future years. The primary analysis of interest will be comparisons (in the 2019 report) of observed changes in pH and ANC to the thresholds of interest. The EEM report (ESSA et al. 2014b, pg. 32) recommended that laboratory Gran ANC titrations be used to estimate lake-specific ANC thresholds that correspond to a pH decline of 0.3, thereby taking into account the unique mix of organic anions found in each lake. Recent work by ESSA has demonstrated how past lab reports of Gran ANC titrations can be used to derive ANC thresholds. We recommend that the lab reports from all past lake samples be retrieved from Trent University in 2018, and used to estimate the mean ANC threshold (and its variation) for each EEM lake. Other secondary analyses suggested by the KPAC will also be explored in future years (e.g., analyses of changes in calcium, as per recent literature; further analyses of charge balance to investigate potential explanations for changes in ANC or total base cations; exploration of snowmelt data to help identify the timing potential acidic

---

[11] assuming a charge density of 7.5 µeq/l of organic anion per mg of DOC, consistent with the STAR and Oliver et al (1983)

episodes). In addition, we recommend an exploration of the potential role of sulphate reduction in LAK028, applying simple models from the literature based on estimated runoff, depth, watershed area and lake area.

6 References Cited

Baker, L. A., P.L. Brezonik, and C.D. Pollman. 1986. Model of internal alkalinity generation: sulfate retention component. Water Air Soil Pollut. 31: 89-94

Bennett, S. and C.J. Perrin. 2017. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lakes in 2016. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 40pp. plus appendices.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Vol.2: Final Technical Report. Prepared for RTA, Kitimat, BC. 450 pp.

ESSA Technologies, J. Laurence, Risk Sciences International, Trent University, and Trinity Consultants. 2014a. Kitimat Airshed Emissions Effects Assessment. Report prepared for BC Ministry of Environment, Smithers, BC. 205 pp. + appendices.

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014b. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto Alcan, Kitimat, B.C. 99 pp.

ESSA Technologies. 2015. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project – 2013 and 2014 Annual Reports. Prepared for Rio Tinto Alcan, Kitimat, B.C. 27 pp.

ESSA Technologies Ltd. 2016. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project – 2015 Annual Report. Prepared for Rio Tinto Alcan, Kitimat, B.C.

Kelly, C.A., J.W.M. Rudd, R.H. Hesslein, D.W. Schindler, P.J. Dillon, C.T. Driscoll, S.A. Gherini and R.E. Hecky. 1987. Prediction of biological acid neutralization in acid-sensitive lakes. Biogeochemistry 3: 129-140.

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

Marmorek, D.R., M.L. Jones, C.K. Minns, and F.C. Elder. 1990. Assessing the potential extent of damage to inland lakes in eastern Canada due to acidic deposition. I. Development and evaluation of a simple "site" model. Can. J. Fish. Aquat. Sci. 47: 55-66.

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

Perrin, C.J and S. Bennett 2015. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lake water quality in 2014. Data report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 20p.

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

Sullivan, T.J., J.M. Eilers, M.R. Church, D.J. Blick, K.N. Eshleman, D.H. Landers, and M.S. DeHann. 1988. Atmospheric wet sulphate deposition and lakewater chemistry. Nature 331:607-609.

Appendix 1: Water Chemistry Data from Annual Sampling, 2012-2016

The three tables below shows the sample results for each of the EEM lakes and control lakes from annual monitoring conducted from 2012 to 2016, including pH, dissolved organic carbon (DOC), Gran ANC, and the concentration of major anions and cations, as well as the sum of all base cations (BC). In 2013-2016, the pH of the water samples was measured by two different laboratories (Trent University and ALS).

The first table follows the convention of previous EEM Annual Reports, designating only the first sample (for lakes with multiple within-season samples), taken on the day(s) in which annual sampling was conducted across all EEM lakes, as the "annual sampling" value. The second table provides the mean annual value and standard deviation 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 third lake 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.

Values from the "annual sampling" site visits

Lake	Year	Lab pH (Trent)	Lab pH (ALS)	DOC (mg/L)	Gran ANC (µeq/L)	SO4 (µeq/L)	Cl (µeq/L)	F (µeq/L)	Ca (µeq/L)	Mg (µeq/L)	K (µeq/L)	Na (µeq/L)	∑ BC (µeq/L)
LAK006	2012	5.8		3.6	25.7	12.0	5.8	4.5	30.5	13.6	3.0	19.8	67.0
LAK007	2012	8.0		0.6	1437.6	53.9	24.6	2.8	1273.1	161.8	19.8	76.5	1531.2
LAK012	2012	5.6		4.6	57.0	6.6	4.2	5.0	74.7	21.6	5.3	23.6	125.2
LAK016	2012	6.3		3.7	68.7	39.7	6.3	7.8	117.9	21.8	7.4	26.2	173.3
LAK022	2012	5.9		5.3	27.8	30.9	6.9	6.1	58.4	17.4	3.3	26.7	105.8
LAK023	2012	5.7		4.2	19.8	19.5	4.5	5.6	39.6	12.9	3.7	14.7	70.9
LAK024	2012	7.1		1.4	299.5	27.6	27.3	1.6	274.2	38.4	4.7	53.0	370.3
LAK028	2012	5.0		4.9	-4.0	57.5	6.1	20.7	47.8	10.7	3.2	18.0	79.6
LAK034	2012	6.7		4.5	99.4	24.7	5.8	5.8	119.5	32.8	5.9	49.9	208.1
LAK042	2012	4.7		13.2	-20.4	6.8	6.1	3.2	7.6	23.9	3.2	25.5	60.2
LAK044	2012	5.4		1.7	1.3	6.8	5.6	2.9	7.0	4.3	4.2	4.8	20.4
LAK006	2013	6.2	6.1	3.2	29.0	15.3	8.7	5.6	27.4	14.7	5.4	19.7	67.2
LAK007	2013	7.9	8.1	0.1	1462.1	70.3	36.3	3.7	1227.3	163.7	22.6	78.8	1492.4
LAK012	2013	6.3	6.1	4.2	63.5	12.8	14.7	8.2	65.4	23.2	9.5	27.2	125.2
LAK016	2013	6.7	7.2	4.2	96.9	58.2	12.3	11.5	114.9	26.3	11.4	28.1	180.8
LAK022	2013	6.2	6.1	6.2	36.4	48.3	12.4	8.7	65.6	21.7	6.2	29.4	122.8
LAK023	2013	6.0	6.0	4.0	23.8	24.8	7.5	7.4	37.4	14.8	5.3	14.7	72.2
LAK028	2013	5.2	5.5	7.1	4.8	129.9	17.7	32.0	85.8	21.8	5.3	28.2	141.0
LAK034	2013	6.9	7.4	4.7	210.4	39.0	8.2	10.0	153.0	43.3	9.3	61.2	266.9
LAK042	2013	5.5	5.4	9.7	21.0	6.5	7.7	3.2	16.3	23.8	3.6	25.9	69.6

Lake	Year	Lab pH (Trent)	Lab pH (ALS)	DOC (mg/L)	Gran ANC (µeq/L)	SO4 (µeq/L)	Cl (µeq/L)	F (µeq/L)	Ca (µeq/L)	Mg (µeq/L)	K (µeq/L)	Na (µeq/L)	∑ BC (µeq/L)
LAK044	2013	5.7	6.0	1.5	8.6	7.1	8.9	3.8	8.1	5.3	6.0	5.6	25.1
LAK006	2014	6.2	6.7	3.4	36.8	11.7	6.5	5.1	31.8	15.9	4.3	21.5	73.5
LAK007	2014	8.1	8.0	0.7	1445.7	32.7	19.2	1.9	1277.5	160.5	20.6	78.3	1536.9
LAK012	2014	6.3	6.7	4.6	80.3	6.5	6.2	5.7	65.4	21.4	6.2	25.5	118.5
LAK016	2014	6.7	6.7	4.0	105.7	49.1	9.3	9.5	122.8	26.8	10.2	31.3	191.1
LAK022	2014	6.3	6.4	5.7	46.9	38.7	9.0	6.9	68.9	20.7	5.3	29.1	124.1
LAK023	2014	6.1	6.2	4.8	35.5	17.3	5.6	6.7	42.4	15.6	3.9	15.6	77.5
LAK024	2014	7.6	7.5	1.7	472.1	43.9	65.7	2.3	404.7	63.1	9.0	106.6	583.4
LAK028	2014	5.3	5.7	5.9	22.6	95.6	11.0	23.3	86.3	19.9	4.6	27.1	137.9
LAK034	2014	6.7	7.0	7.0	205.0	17.7	6.5	7.7	161.7	44.8	9.5	57.4	273.5
LAK042	2014	5.1	5.4	10.6	12.5	5.2	11.8	2.6	10.9	25.9	3.9	28.1	68.8
LAK044	2014	5.8	5.6	1.8	5.9	5.2	5.9	2.8	8.0	5.1	5.4	5.5	23.9
Lak006	2015	6.2	6.2	3.5	31.4	11.3	5.9	4.7	32.7	16.3	4.0	21.7	74.7
Lak007	2015	8.0	7.9	0.3	1565.6	48.1	24.0	2.6	1267.5	166.2	21.5	79.2	1534.4
Lak012	2015	6.2	6.2	4.4	70.7	9.2	6.2	5.0	63.4	21.9	6.2	25.4	116.8
LAK016	2015	6.8	6.9	4.3	113.1	41.8	8.7	8.6	131.2	26.7	9.9	30.4	198.3
LAK022	2015	6.1	6.2	6.3	35.6	33.3	7.9	5.9	64.4	19.7	4.6	28.0	116.6
Lak023	2015	6.1	6.2	4.3	27.4	13.7	5.4	5.6	42.0	14.2	3.7	14.2	74.1
Lak024	2015	7.4	7.5	2.2	443.0	40.8	59.0	2.1	402.7	61.0	9.8	99.6	573.1
LAK028	2015	5.1	5.3	8.1	10.8	72.0	9.0	20.5	76.9	17.4	3.4	22.2	119.9
LAK034	2015	6.6	6.7	7.6	177.8	1.5	6.2	4.7	146.7	38.3	5.4	50.5	240.9
LAK042	2015	5.4	5.5	8.3	13.8	4.5	6.5	2.3	11.0	24.4	2.7	28.5	66.5
LAK044	2015	5.8	5.8	1.6	6.2	4.3	5.9	2.7	10.0	5.6	5.6	5.6	26.8
Lak006	2016	6.0	6.5	4.2	25.8	12.4	5.6	4.3	16.3	3.4	22.4	75.7	78.9
Lak007	2016	8.0	8.1	0.8	1368.6	49.3	25.4	2.6	167.9	20.7	80.0	1571.0	1480.3
LAK012	2016	6.2	6.7	5.1	64.8	9.0	5.4	4.5	22.2	5.1	26.4	118.0	119.1
LAK016	2016	6.6	6.9	5.2	93.9	45.8	8.5	8.2	28.1	9.1	31.0	195.9	196.6
LAK022	2016	6.1	6.4	6.7	34.4	35.0	7.9	5.8	20.7	4.3	29.9	123.3	127.4
LAK023	2016	6.0	6.3	6.1	31.0	12.8	5.1	4.9	15.5	3.9	15.4	79.8	93.4
LAK024	2016	7.5	7.6	2.7	463.1	46.4	70.0	2.3	69.1	10.8	114.0	643.0	634.9
LAK028	2016	5.1	5.2	7.9	0.2	140.7	9.0	29.2	29.5	3.9	28.4	168.0	227.1
LAK034	2016	6.5	7.1	7.6	151.6	0.5	5.4	4.4	35.4	3.9	48.7	218.2	220.5
LAK042	2016	5.4	5.6	9.3	11.7	3.4	6.8	2.2	25.8	2.5	29.4	69.5	83.1
LAK044	2016	5.5	5.9	2.3	2.3	4.6	5.9	2.3	5.2	5.8	5.9	26.4	30.3

Lake	Year	Lab pH (Trent)	Lab pH (ALS)	DOC (mg/L)	Gran ANC (μeq/L)	SO4 (μeq/L)	Cl (μeq/L)	F (μeq/L)	Ca (μeq/L)	Mg (μeq/L)	K (μeq/L)	Na (μeq/L)	∑ BC (μeq/L)
NC184	2013	5.7		11.6	16.2	8.1	24.0	0.3	51.4	22.2	4.9	34.4	112.8
NC194	2013	6.6		0.7	28.0	4.4	7.6	0.3	23.5	4.9	5.4	13.9	47.7
DCAS14A	2013	6.5		1.4	50.6	34.4	9.2	0.6	64.2	12.1	10.5	14.0	100.8
NC184	2015	5.5	5.6	9.8	18.4	8.0	21.7	0.5	49.7	20.4	3.3	29.4	102.8
NC194	2015	6.5	6.5	0.8	33.0	3.1	7.3	0.5	27.1	5.8	4.4	14.2	51.5
DCAS14A	2015	6.6	6.7	0.9		36.4	7.3	0.5	77.8	13.8	11.3	16.2	119.2
NC184	2016	5.8	6.2	10.6	27.3	7.7	21.2	0.5	63.4	23.5	3.1	33.7	123.6
NC194	2016	6.4	6.6	1.6	28.7	3.1	7.9	0.5	26.7	5.9	4.0	14.7	51.2
DCAS14A	2016	6.6	6.8	1.5	57.5	37.7	8.5	0.5	77.8	13.5	10.7	17.0	119.0

Mean Annual Values

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

Lake	Year	pH TU	SD[1]	pH ALS	SD	DOC mg/L	SD	Gran ANC µeq/L	SD	SO4 µeq/L	SD	Cl µeq/L	SD	F µeq/L	SD	Ca µeq/L	SD	Mg µeq/L	SD	K µeq/L	SD	Na µeq/L	SD	∑ BC µeq/L
LAK006	**2012**	5.8				3.6		25.7		12.0		5.8		4.5		30.5		13.6		3.0		19.8		67.0
LAK007	**2012**	8.0				0.6		1437.6		53.9		24.6		2.8		1273.1		161.8		19.8		76.5		1531.2
LAK012	**2012**	5.6				4.6		57.0		6.6		4.2		5.0		74.7		21.6		5.3		23.6		125.2
LAK016	**2012**	6.3				3.7		68.7		39.7		6.3		7.8		117.9		21.8		7.4		26.2		173.3
LAK022	**2012**	5.9				5.3		27.8		30.9		6.9		6.1		58.4		17.4		3.3		26.7		105.8
LAK023	**2012**	5.7				4.2		19.8		19.5		4.5		5.6		39.6		12.9		3.7		14.7		70.9
LAK024	**2012**	7.1				1.4		299.5		27.6		27.3		1.6		274.2		38.4		4.7		53.0		370.3
LAK028	**2012**	5.0				4.9		-4.0		57.5		6.1		20.7		47.8		10.7		3.2		18.0		79.6
LAK034	**2012**	6.7				4.5		99.4		24.7		5.8		5.8		119.5		32.8		5.9		49.9		208.1
LAK042	**2012**	4.7				13.2		-20.4		6.8		6.1		3.2		7.6		23.9		3.2		25.5		60.2
LAK044	**2012**	5.4				1.7		1.3		6.8		5.6		2.9		7.0		4.3		4.2		4.8		20.4
LAK006	**2013**	6.2		6.1		3.2		29.0		15.3		8.7		5.6		27.4		14.7		5.4		19.7		67.2
LAK007	**2013**	7.9		8.1		0.1		1462.1		70.3		36.3		3.7		1227.3		163.7		22.6		78.8		1492.4
LAK012	**2013**	6.3		6.1		4.2		63.5		12.8		14.7		8.2		65.4		23.2		9.5		27.2		125.2
LAK016	**2013**	6.7		7.2		4.2		96.9		58.2		12.3		11.5		114.9		26.3		11.4		28.1		180.8
LAK022	**2013**	6.2		6.1		6.2		36.4		48.3		12.4		8.7		65.6		21.7		6.2		29.4		122.8
LAK023	**2013**	6.0		6.0		4.0		23.8		24.8		7.5		7.4		37.4		14.8		5.3		14.7		72.2
LAK024	**2013**																							
LAK028	**2013**	5.2		5.5		7.1		4.8		129.9		17.7		32.0		85.8		21.8		5.3		28.2		141.0
LAK034	**2013**	6.9		7.4		4.7		210.4		39.0		8.2		10.0		153.0		43.3		9.3		61.2		266.9
LAK042	**2013**	5.5		5.4		9.7		21.0		6.5		7.7		3.2		16.3		23.8		3.6		25.9		69.6
LAK044	**2013**	5.7		6.0		1.5		8.6		7.1		8.9		3.8		8.1		5.3		6.0		5.6		25.1
Lak006	**2014**	6.1	*0.1*	6.6	*0.6*	3.8	*1.0*	38.8	*2.5*	12.9	*2.2*	8.1	*0.6*	4.8	*0.5*	32.0	*8.7*	16.2	*0.8*	4.9	*0.2*	21.5	*0.7*	74.6
LAK007	**2014**	8.1		8.0		0.7		1445.7		32.7		19.2		1.9		1277.5		160.5		20.6		78.3		1536.9
LAK012	**2014**	6.0	*0.2*	6.7	*0.4*	6.3	*2.2*	68.8	*15.2*	16.9	*11.7*	10.3	*4.9*	5.2	*0.5*	69.7	*3.7*	23.3	*1.7*	7.5	*1.2*	27.1	*1.5*	127.5
LAK016	**2014**	6.7		6.7		4.0		105.7		49.1		9.3		9.5		122.8		26.8		10.2		31.3		191.1
LAK022	**2014**	6.3		6.4		5.7		46.9		38.7		9.0		6.9		68.9		20.7		5.3		29.1		124.1
LAK023	**2014**	5.9	*0.1*	6.7	*0.6*	5.7	*1.0*	32.1	*2.5*	19.6	*2.2*	6.1	*0.6*	6.2	*0.5*	49.5	*8.7*	16.1	*0.8*	4.1	*0.2*	16.1	*0.7*	85.9
LAK024	**2014**	7.6		7.5		1.7		472.1		43.9		65.7		2.3		404.7		63.1		9.0		106.6		583.4
LAK028	**2014**	5.3		5.7		5.9		22.6		95.6		11.0		23.3		86.3		19.9		4.6		27.1		137.9
LAK034	**2014**	6.7		7.0		7.0		205.0		17.7		6.5		7.7		161.7		44.8		9.5		57.4		273.5
LAK042	**2014**	5.1		5.4		10.6		12.5		5.2		11.8		2.6		10.9		25.9		3.9		28.1		68.8
LAK044	**2014**	5.8		5.6		1.8		5.9		5.2		5.9		2.8		8.0		5.1		5.4		5.5		23.9
LAK006	**2015**	6.0	*0.1*	6.4	*0.6*	3.9	*0.3*	32.4	*0.7*	12.1	*0.7*	6.6	*0.6*	4.4	*0.2*	32.6	*0.6*	16.1	*0.3*	4.0	*0.1*	21.4	*0.2*	74.1
LAK007	**2015**	8.0		7.9		0.3		1565.6		48.1		24.0		2.6		1267.5		166.2		21.5		79.2		1534.4
LAK012	**2015**	6.0	*0.2*	6.3	*0.3*	7.5	*2.1*	65.9	*4.2*	18.7	*6.4*	11.1	*3.3*	4.7	*0.3*	75.2	*7.9*	25.4	*2.4*	8.3	*1.7*	27.5	*1.5*	136.5
LAK016	**2015**	6.8		6.9		4.3		113.1		41.8		8.7		8.6		131.2		26.7		9.9		30.4		198.3
LAK022	**2015**	6.1		6.2		6.3		35.6		33.3		7.9		5.9		64.4		19.7		4.6		28.0		116.6

Lake	Year	pH TU	SD[1]	pH ALS	SD	DOC mg/L	SD	Gran ANC µeq/L	SD	SO4 µeq/L	SD	Cl µeq/L	SD	F µeq/L	SD	Ca µeq/L	SD	Mg µeq/L	SD	K µeq/L	SD	Na µeq/L	SD	∑ BC µeq/L
LAK023	**2015**	5.9	*0.1*	6.2	*0.1*	5.4	*0.7*	30.0	*2.0*	15.8	*1.5*	6.2	*0.6*	5.2	*0.3*	46.4	*3.0*	15.1	*0.7*	3.9	*0.2*	15.0	*0.6*	80.4
LAK024	**2015**	7.4		7.5		2.2		443.0		40.8		59.0		2.1		402.7		61.0		9.8		99.6		573.1
LAK028	**2015**	5.1		5.3		8.1		10.8		72.0		9.0		20.5		76.9		17.4		3.4		22.2		119.9
LAK034	**2015**	6.6		6.7		7.6		177.8		1.5		6.2		4.7		146.7		38.3		5.4		50.5		240.9
LAK042	**2015**	5.4		5.5		8.3		13.8		4.5		6.5		2.3		11.0		24.4		2.7		28.5		66.5
LAK044	**2015**	5.8		5.8		1.6		6.2		4.3		5.9		2.7		10.0		5.6		5.6		5.6		26.8
LAK006	**2016**	6.0	*0.1*	6.3	*0.2*	4.2	*0.2*	26.9	*2.0*	12.4	*0.4*	5.6	*0.4*	4.2	*0.2*	32.8	*1.0*	15.9	*1.2*	4.3	*1.2*	22.0	*1.6*	75.0
LAK007	**2016**	8.0		8.1		0.8		1368.6		49.3		25.4		2.6		1302.5		167.9		20.7		80.0		1571.0
LAK012	**2016**	6.2	*0.0*	6.5	*0.2*	5.1	*0.5*	65.8	*2.3*	10.1	*1.1*	5.6	*0.3*	4.6	*0.2*	64.9	*1.7*	21.9	*1.2*	6.1	*1.2*	26.4	*1.4*	119.3
LAK016	**2016**	6.6		6.9		5.2		93.9		45.8		8.5		8.2		127.8		28.1		9.1		31.0		195.9
LAK022	**2016**	6.1	*0.0*	6.4	*0.1*	6.7	*0.2*	34.4	*3.8*	35.0	*0.4*	7.9	*0.4*	5.8	*0.2*	68.4	*1.8*	20.7	*0.8*	4.3	*1.1*	29.9	*1.3*	123.3
LAK023	**2016**	5.9		6.2		5.8		27.9		13.2		4.9		5.1		42.7		15.1		4.8		15.2		77.8
LAK024	**2016**	7.5		7.6		2.7		463.1		46.4		70.0		2.3		449.1		69.1		10.8		114.0		643.0
LAK028	**2016**	5.0	*0.2*	5.1	*0.2*	8.1	*0.6*	-4.9	*12.5*	128.8	*16.2*	10.0	*1.1*	26.8	*1.7*	95.1	*16.6*	25.7	*3.3*	3.8	*0.4*	28.1	*2.4*	152.7
LAK034	**2016**	6.5		7.1		7.6		151.6		0.5		5.4		4.4		130.2		35.4		3.9		48.7		218.2
LAK042	**2016**	5.4	*0.0*	5.7	*0.1*	9.8	*0.4*	14.0	*3.1*	4.0	*0.5*	7.2	*0.5*	2.2	*0.2*	16.9	*3.4*	26.1	*0.8*	2.9	*0.4*	29.5	*0.6*	75.4
LAK044	**2016**	5.5	*0.0*	6.0	*0.3*	2.0	*0.2*	4.1	*2.6*	4.8	*0.2*	6.1	*0.3*	2.3	*0.1*	8.4	*0.7*	5.3	*0.1*	5.6	*0.2*	5.6	*0.2*	25.0
NC184	**2013**	5.7				11.6		16.2		8.1		24.0		0.3		51.4		22.2		4.9		34.4		112.8
NC194	**2013**	6.6				0.7		28.0		4.4		7.6		0.3		23.5		4.9		5.4		13.9		47.7
DCAS14A	**2013**	6.5				1.4		50.6		34.4		9.2		0.6		64.2		12.1		10.5		14.0		100.8
NC184	**2015**	5.5		5.6		9.8		18.4		8.0		21.7		0.5		49.7		20.4		3.3		29.4		102.8
NC194	**2015**	6.5		6.5		0.8		33.0		3.1		7.3		0.5		27.1		5.8		4.4		14.2		51.5
DCAS14A	**2015**	6.6		6.7		0.9				36.4		7.3		0.5		77.8		13.8		11.3		16.2		119.2
NC184	**2016**	5.8		6.2		10.6		27.3		7.7		21.2		0.5		63.4		23.5		3.1		33.7		123.6
NC194	**2016**	6.4		6.6		1.6		28.7		3.1		7.9		0.5		26.7		5.9		4.0		14.7		51.2
DCAS14A	**2016**	6.6		6.8		1.5		57.5		37.7		8.5		0.5		77.8		13.5		10.7		17.0		119.0

[1] SD = standard deviation

Sampling Data in “Raw” Units

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

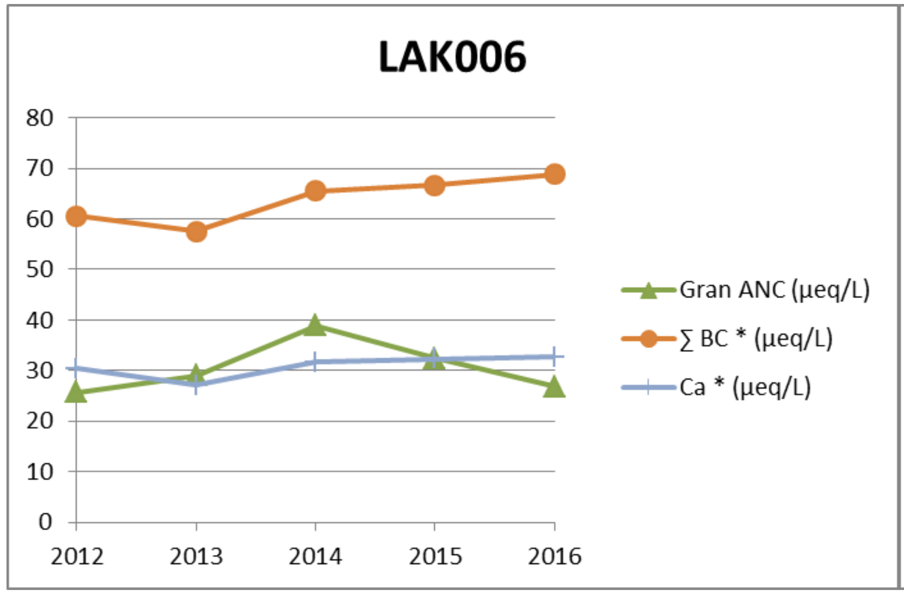
Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (µS/s)	SO4 (mg/L)	Cl (mg/L)	F (mg/L)	NO3 (µg/L)	NH4 (µg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
Lak006	2012	5.8		3.6	1.3	6.7	0.6	0.2	0.1	0.1	3.0	0.6	0.2	0.1	0.5	0.0	0.1	0.0
Lak007	2012	8.0		0.6	71.9	148.9	2.6	0.9	0.1	4.7	1.8	25.5	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2012	5.6		4.6	2.9	12.7	0.3	0.1	0.1	0.7	3.4	1.5	0.3	0.2	0.5	0.7	0.1	0.2
LAK016	2012	6.3		3.7	3.4	17.9	1.9	0.2	0.1	0.8	3.9	2.4	0.3	0.3	0.6	0.0	0.1	0.0
LAK022	2012	5.9		5.3	1.4	10.7	1.5	0.2	0.1	0.7	3.7	1.2	0.2	0.1	0.6	0.0	0.1	0.0
LAK023	2012	5.7		4.2	1.0	7.5	0.9	0.2	0.1	0.3	3.3	0.8	0.2	0.1	0.3	0.0	0.1	0.0
LAK024	2012	7.1		1.4	15.0	40.0	1.3	1.0	0.0	0.4	2.4	5.5	0.5	0.2	1.2	0.0	0.0	
LAK028	2012	5.0		4.9	-0.2	12.2	2.8	0.2	0.4	1.5	3.4	1.0	0.1	0.1	0.4	0.1	0.4	0.0
LAK034	2012	6.7		4.5	5.0	22.4	1.2	0.2	0.1	1.6	4.9	2.4	0.4	0.2	1.1	0.0	0.0	0.0
LAK042	2012	4.7		13.2	-1.0	11.9	0.3	0.2	0.1	0.7	8.5	0.2	0.3	0.1	0.6	0.6	0.4	0.0
LAK044	2012	5.4		1.7	0.1	3.1	0.3	0.2	0.1	0.4	3.0	0.1	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2013	6.2	6.1	3.2	1.5	7.0	0.7	0.3	0.1	2.5	2.5	0.5	0.2	0.2	0.5	0.0	0.0	0.0
Lak007	2013	7.9	8.1	0.1	73.2	147.0	3.4	1.3	0.1	2.5	2.5	24.6	2.0	0.9	1.8	0.0	0.0	0.0
LAK012	2013	6.3	6.1	4.2	3.2	12.8	0.6	0.5	0.2	2.5	2.5	1.3	0.3	0.4	0.6	0.4	0.1	0.0
LAK016	2013	6.7	7.2	4.2	4.9	20.3	2.8	0.4	0.2	22.7	7.1	2.3	0.3	0.4	0.6	0.0	0.0	0.0
LAK022	2013	6.2	6.1	6.2	1.8	13.8	2.3	0.4	0.2	2.5	2.5	1.3	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	2013	6.0	6.0	4.0	1.2	9.6	1.2	0.3	0.1	30.1	2.5	0.7	0.2	0.2	0.3	0.0	0.1	0.0
LAK024	2013																	
LAK028	2013	5.2	5.5	7.1	0.2	20.3	6.2	0.6	0.6	20.4	2.5	1.7	0.3	0.2	0.6	0.2	0.6	0.0
LAK034	2013	6.9	7.4	4.7	10.5	28.3	1.9	0.3	0.2	2.5	2.5	3.1	0.5	0.4	1.4	0.0	0.0	0.0
LAK042	2013	5.5	5.4	9.7	1.1	8.0	0.3	0.3	0.1	2.5	2.5	0.3	0.3	0.1	0.6	0.3	0.3	0.0
LAK044	2013	5.7	6.0	1.5	0.4	3.3	0.3	0.3	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2014	6.1	6.6	3.8	1.9	8.5	0.6	0.3	0.1	7.7	40.5	0.6	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2014	8.1	8.0	0.7	72.4	154.2	1.6	0.7	0.0	2.5	2.5	25.6	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2014	6.0	6.7	6.3	3.4	13.9	0.8	0.4	0.1	7.6	5.3	1.4	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	2014	6.7	6.7	4.0	5.3	21.5	2.4	0.3	0.2	2.5	6.7	2.5	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2014	6.3	6.4	5.7	2.3	14.4	1.9	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	2014	5.9	6.7	5.7	1.6	9.3	0.9	0.2	0.1	10.9	5.3	1.0	0.2	0.2	0.4	0.0	0.1	0.0
LAK024	2014	7.6	7.5	1.7	23.6	63.1	2.1	2.3	0.0	5.1	2.5	8.1	0.8	0.4	2.5	0.0	0.0	0.0
LAK028	2014	5.3	5.7	5.9	1.1	20.2	4.6	0.4	0.4	2.5	2.5	1.7	0.2	0.2	0.6	0.1	0.5	0.0
LAK034	2014	6.7	7.0	7.0	10.3	27.5	0.9	0.2	0.1	2.5	2.5	3.2	0.5	0.4	1.3	0.1	0.0	0.0
LAK042	2014	5.1	5.4	10.6	0.6	10.8	0.3	0.4	0.1	2.5	2.5	0.2	0.3	0.2	0.6	0.4	0.3	0.0
LAK044	2014	5.8	5.6	1.8	0.3	3.6	0.3	0.2	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2015	6.0	6.4	3.9	1.6	5.6	0.6	0.2	0.1	3.4	5.4	0.7	0.2	0.2	0.5	0.1	0.1	0.0
Lak007	2015	8.0	7.9	0.3	78.4	151.2	2.3	0.9	0.0	5.6	2.5	25.4	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2015	6.0	6.3	7.5	3.3	10.1	0.9	0.4	0.1	8.3	8.0	1.5	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	2015	6.8	6.9	4.3	5.7	20.7	2.0	0.3	0.2	7.9	2.5	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2015	6.1	6.2	6.3	1.8	12.8	1.6	0.3	0.1	2.5	2.5	1.3	0.2	0.2	0.6	0.1	0.1	0.0

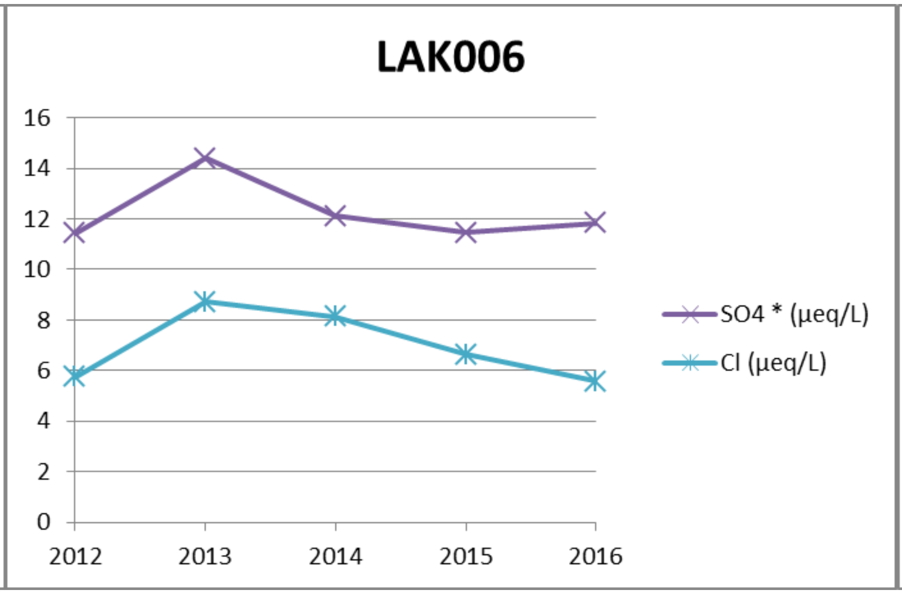
Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (µS/s)	SO4 (mg/L)	Cl (mg/L)	F (mg/L)	NO3 (µg/L)	NH4 (µg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)
LAK023	**2015**	5.9	6.2	5.4	1.5	5.9	0.8	0.2	0.1	6.3	2.5	0.9	0.2	0.2	0.3	0.0	0.1	0.0
LAK024	**2015**	7.4	7.5	2.2	22.2	58.7	2.0	2.1	0.0	8.1	2.5	8.1	0.7	0.4	2.3	0.1	0.0	0.0
LAK028	**2015**	5.1	5.3	8.1	0.5	17.8	3.5	0.3	0.4	2.5	2.5	1.5	0.2	0.1	0.5	0.2	0.6	0.0
LAK034	**2015**	6.6	6.7	7.6	8.9	22.3	0.1	0.2	0.1	2.5	2.5	2.9	0.5	0.2	1.2	0.1	0.0	0.0
LAK042	**2015**	5.4	5.5	8.3	0.7	8.1	0.2	0.2	0.0	2.5	2.5	0.2	0.3	0.1	0.7	0.2	0.3	0.0
LAK044	**2015**	5.8	5.8	1.6	0.3	3.5	0.2	0.2	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	**2016**	6.0	6.3	4.2	1.3	7.8	0.6	0.2	0.1	2.5	2.5	0.7	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	**2016**	8.0	8.1	0.8	68.5	153.7	2.4	0.9	0.1	6.5	2.5	26.1	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	**2016**	6.2	6.5	5.1	3.3	12.4	0.5	0.2	0.1	5.0	4.7	1.3	0.3	0.2	0.6	0.3	0.1	0.0
LAK016	**2016**	6.6	6.9	5.2	4.7	20.8	2.2	0.3	0.2	10.9	2.5	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	**2016**	6.1	6.4	6.7	1.7	13.7	1.7	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	**2016**	5.9	6.2	5.8	1.4	9.1	0.6	0.2	0.1	2.5	5.1	0.9	0.2	0.2	0.4	0.0	0.1	0.0
LAK024	**2016**	7.5	7.6	2.7	23.2	66.3	2.2	2.5	0.0	20.7	2.5	9.0	0.8	0.4	2.6	0.1	0.0	0.0
LAK028	**2016**	5.0	5.1	8.1	-0.2	23.7	6.2	0.4	0.5	21.5	2.5	1.9	0.3	0.2	0.6	0.1	0.7	0.0
LAK034	**2016**	6.5	7.1	7.6	7.6	22.1	0.0	0.2	0.1	2.5	2.5	2.6	0.4	0.2	1.1	0.1	0.0	0.0
LAK042	**2016**	5.4	5.7	9.8	0.7	8.8	0.2	0.3	0.0	2.5	3.7	0.3	0.3	0.1	0.7	0.2	0.3	0.0
LAK044	**2016**	5.5	6.0	2.0	0.2	3.9	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
NC184	**2013**	5.7		11.6	0.8	10.0	0.4	0.9	0.0	0.0	0.0	1.0	0.3	0.2	0.8			
NC194	**2013**	6.6		0.7	1.4	3.9	0.2	0.3	0.0	0.0	0.0	0.5	0.1	0.2	0.3			
DCAS14A	**2013**	6.5		1.4	2.5	10.6	1.7	0.3	0.0	52.6	2.5	1.3	0.1	0.4	0.3	0.0	0.0	0.0
NC184	**2015**	5.5	5.6	9.8	0.9	11.6	0.4	0.8	0.0	2.5	2.5	1.0	0.2	0.1	0.7	0.2	0.3	0.0
NC194	**2015**	6.5	6.5	0.8	1.7	5.4	0.1	0.3	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	**2015**	6.6	6.7	0.9	48.6	14.0	1.8	0.3	0.0	6.8	2.5	1.6	0.2	0.4	0.4	0.0	0.0	0.0
NC184	**2016**	5.8	6.2	10.6	1.4	12.8	0.4	0.8	0.0	2.5	2.5	1.3	0.3	0.1	0.8	0.1	0.3	0.0
NC194	**2016**	6.4	6.6	1.6	1.4	5.9	0.1	0.3	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	**2016**	6.6	6.8	1.5	2.9	14.8	1.8	0.3	0.0	2.5	2.5	1.6	0.2	0.4	0.4	0.0	0.0	0.0

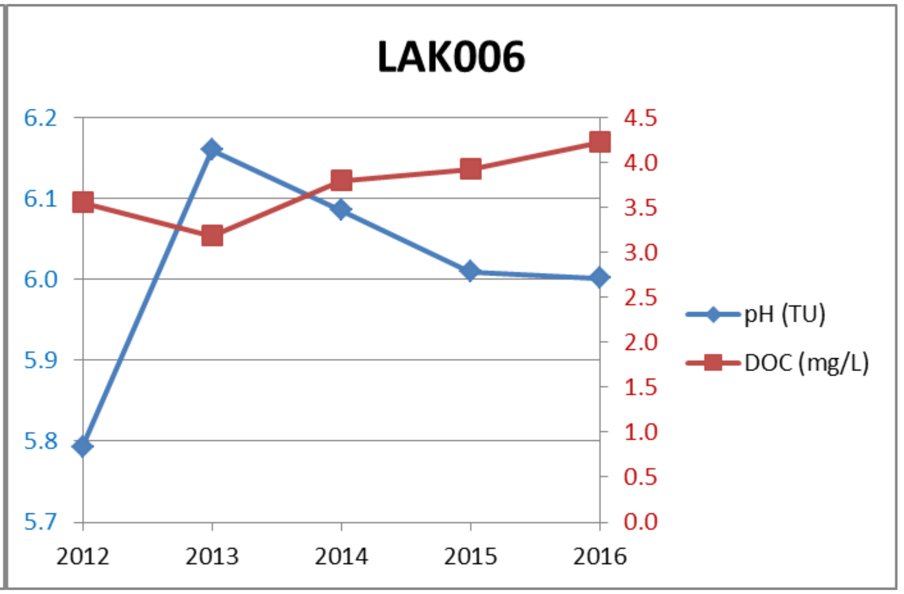
Appendix 2: Changes in Ion Concentrations from 2012 to 2016

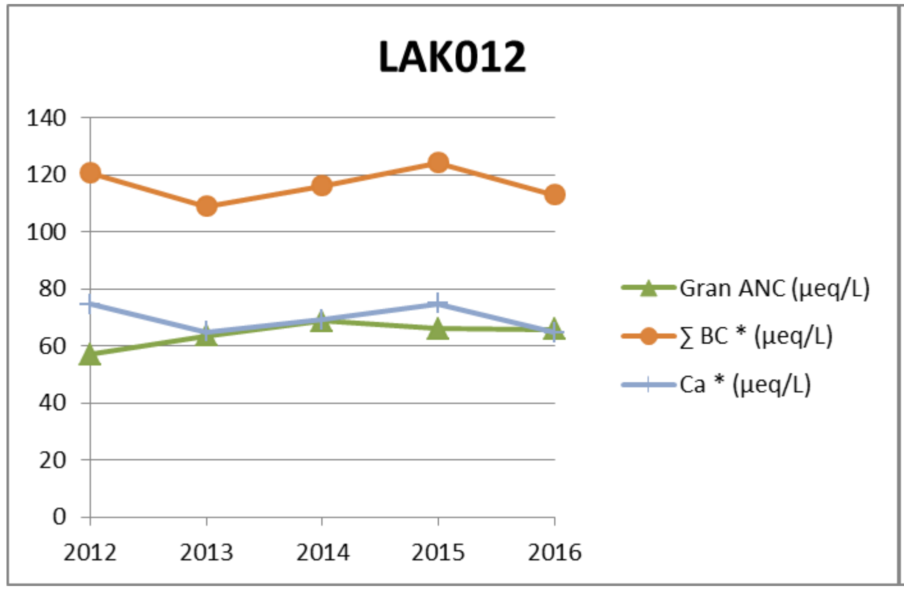
For each of the EEM lakes, the figures in this appendix show the inter-annual changes in six major water chemistry metrics from 2012 to 2016: Gran ANC, base cations and calcium (left panel), sulfate and chloride (centre panel), and pH and dissolved organic carbon (right panel). The selection of each pair of metrics is solely based on optimizing graphical representation across all metrics and lakes (i.e., metrics with somewhat similar numeric ranges are shown together). The right panel has two Y-axes, neither of which start at zero – be aware that this can make relatively minor changes appear to be much more substantial than they are. Due to large variation among the lakes for some of the metrics, the Y-axis is not consistent across the lakes, therefore extra caution is required for making comparisons among lakes with respect to the magnitude of changes. However, these graphs are especially useful for looking at the patterns of changes across the sampling record and determining whether similar patterns are observed across lakes and/or metrics.

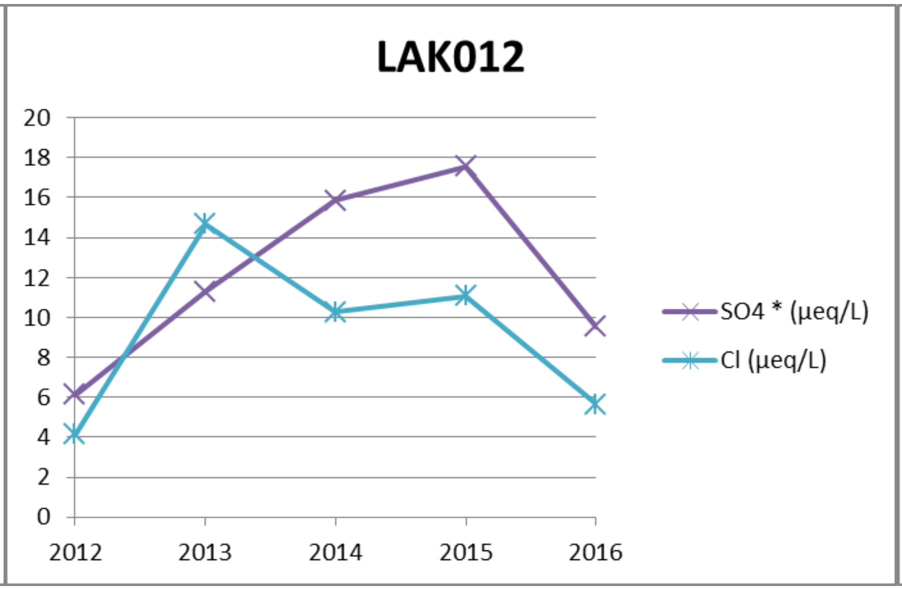
Sensitive Lakes

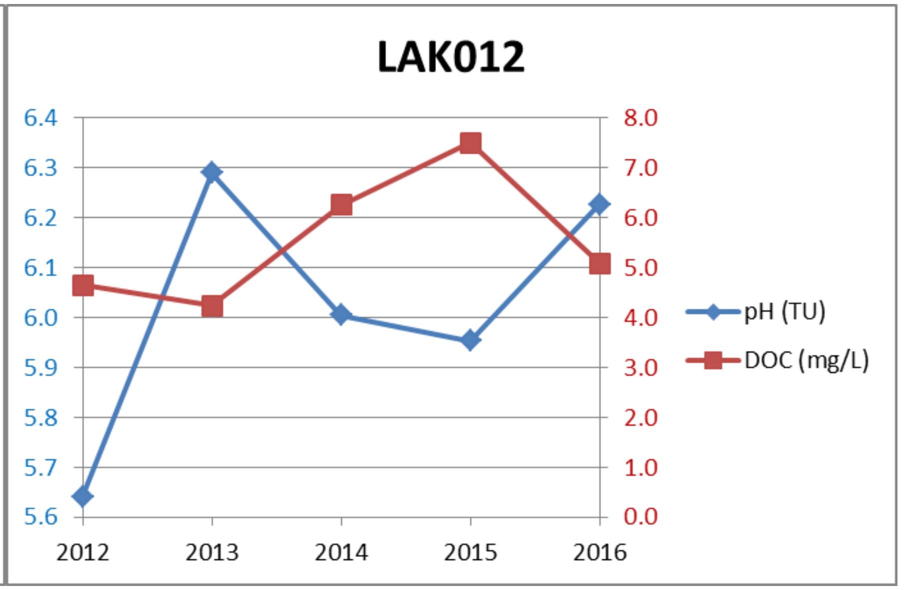


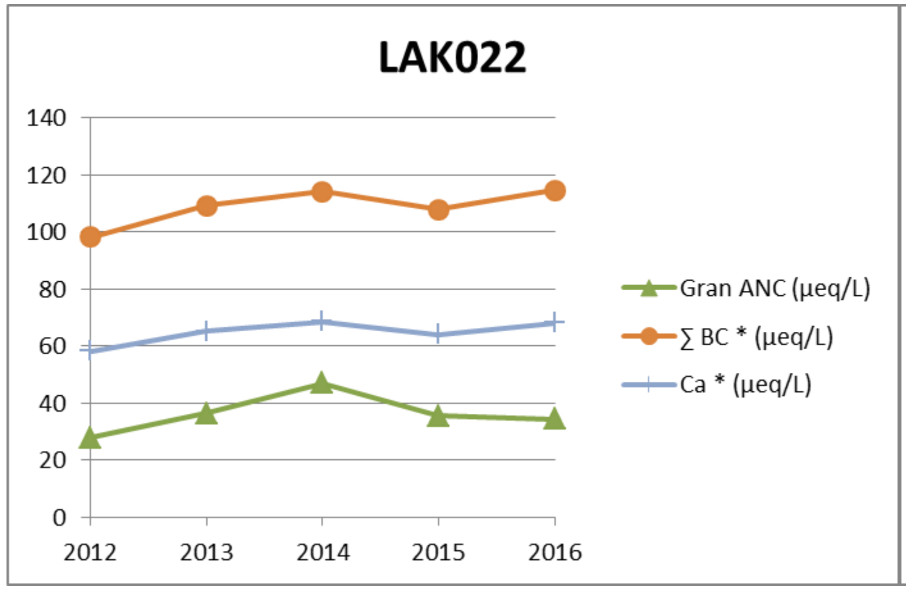




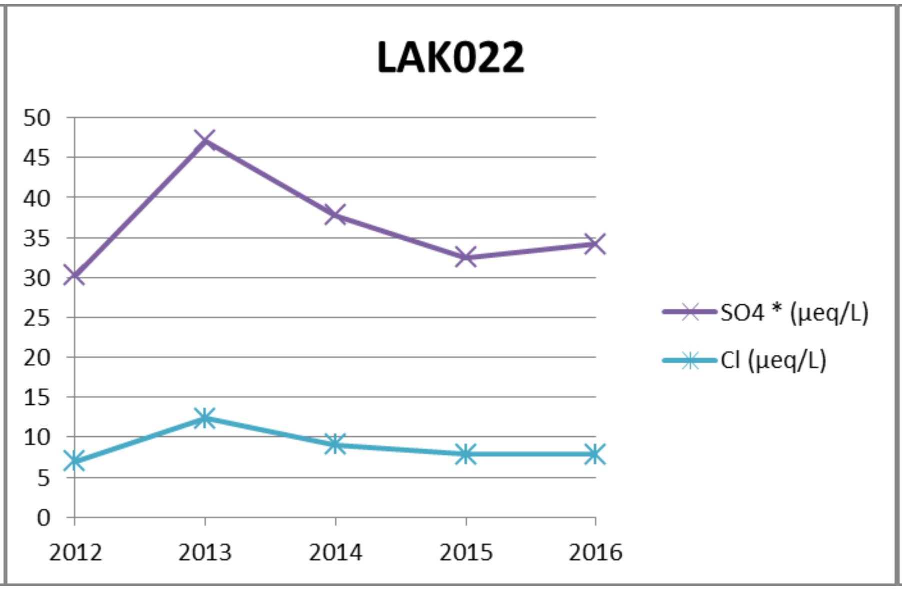




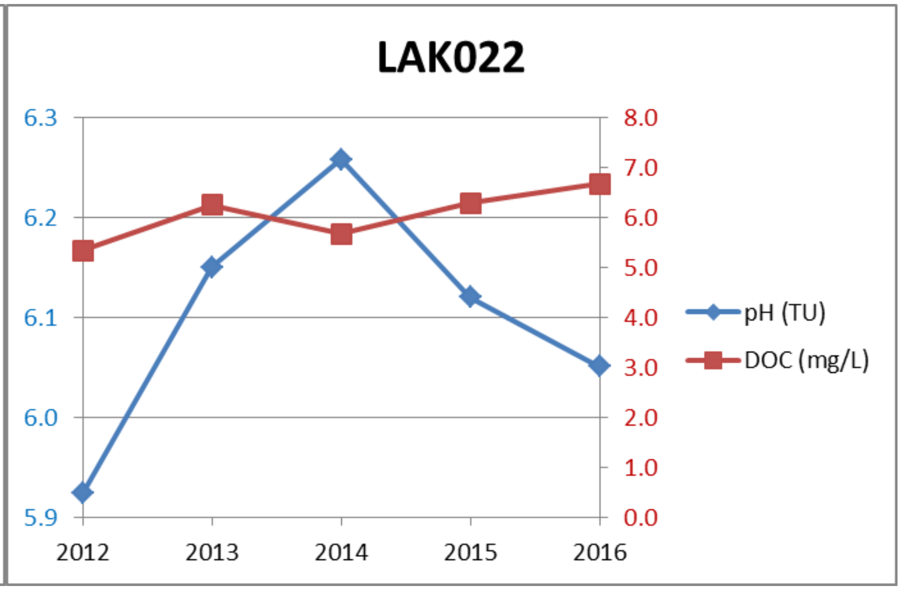




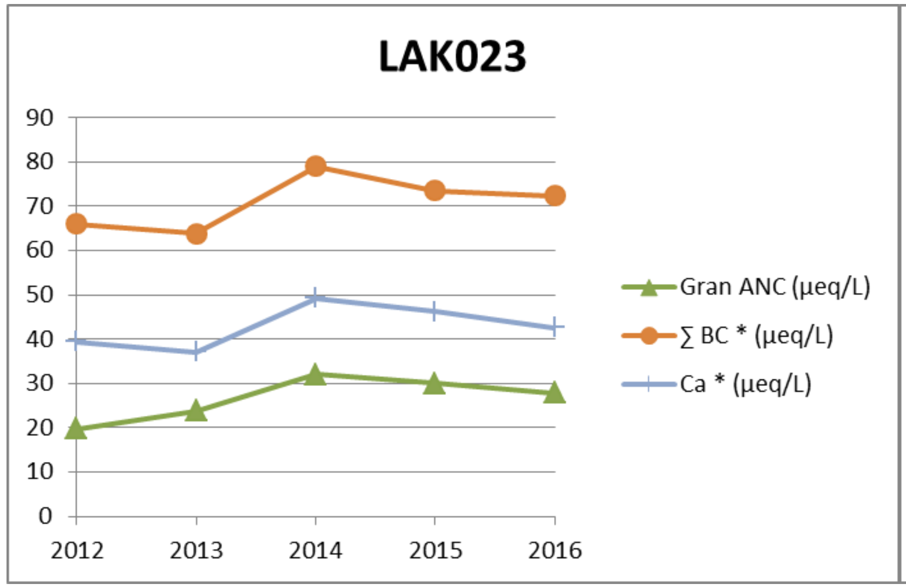
LAK022



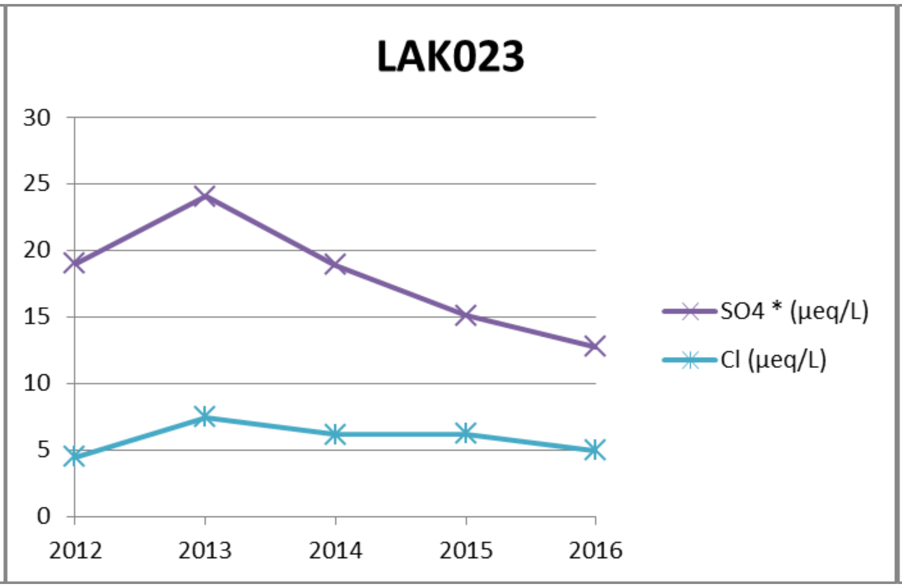
LAK022



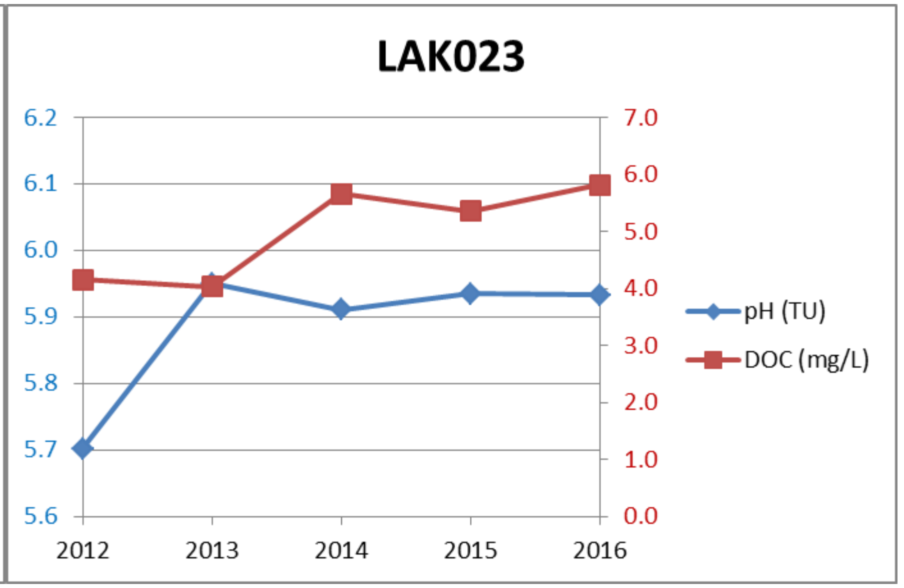
LAK022



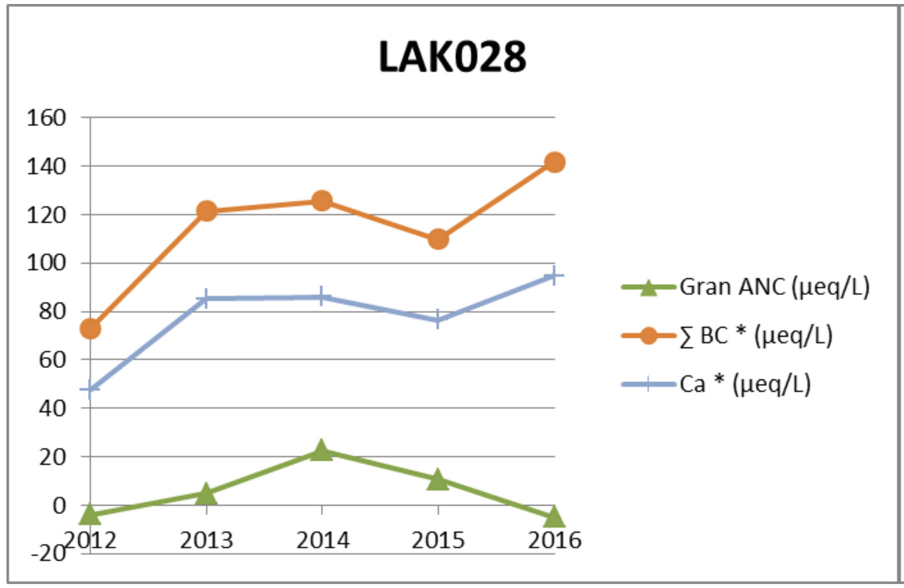
LAK023

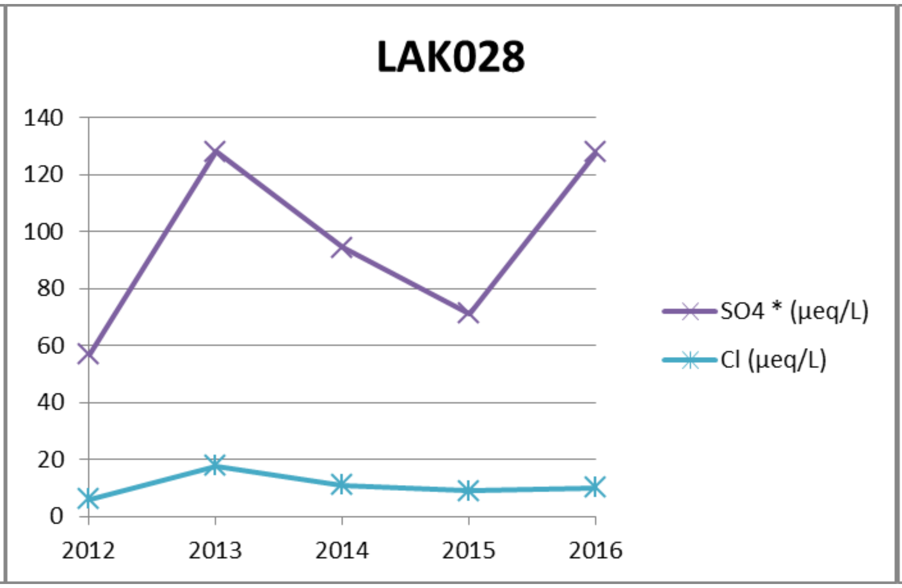


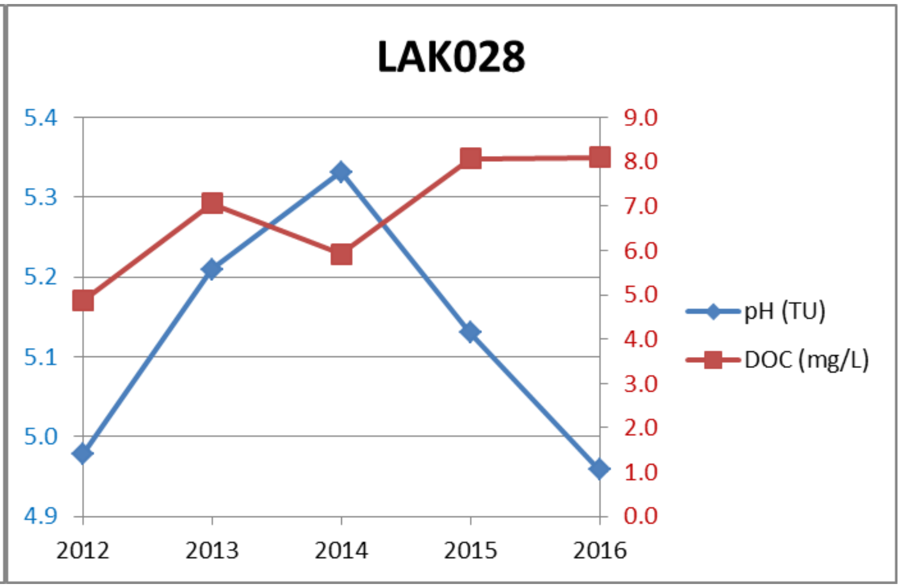
LAK023

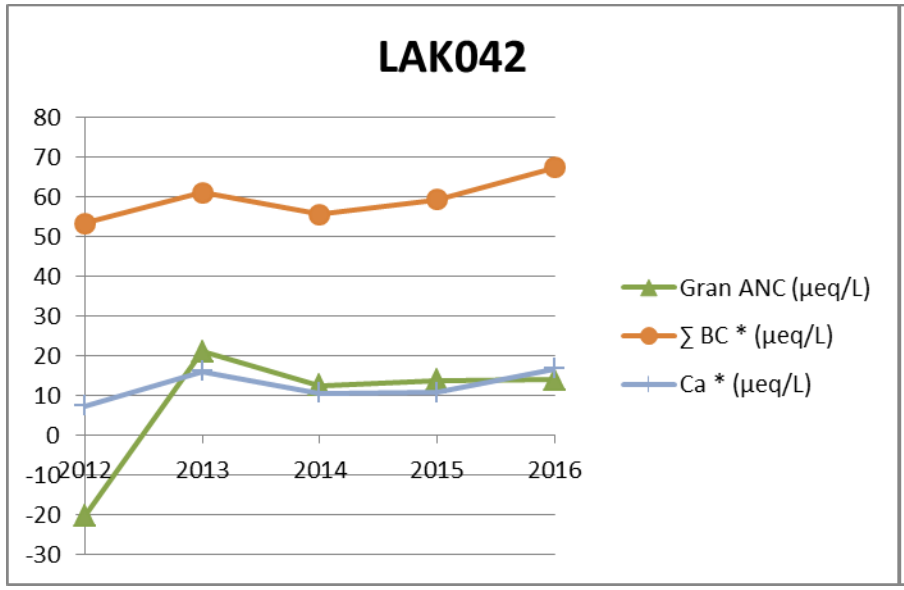


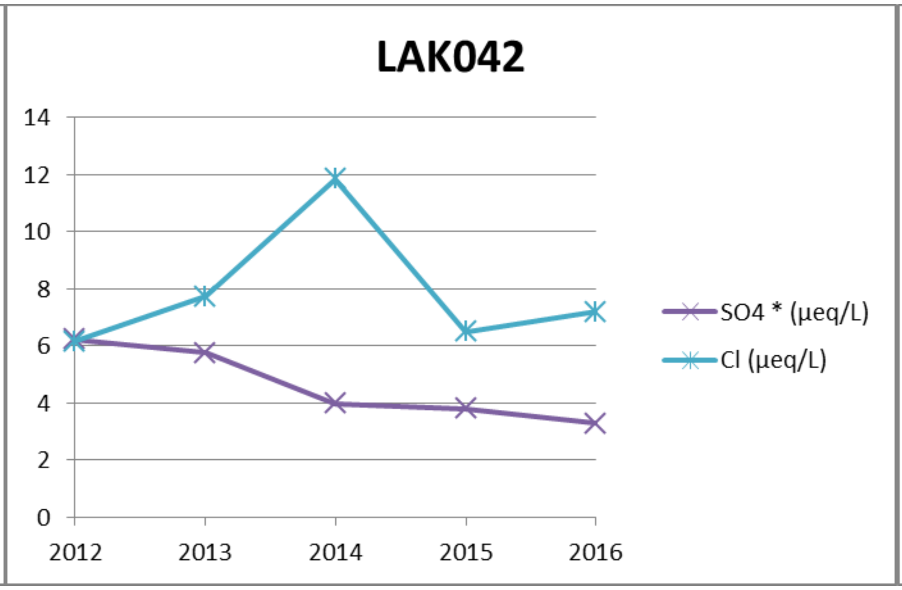
LAK023

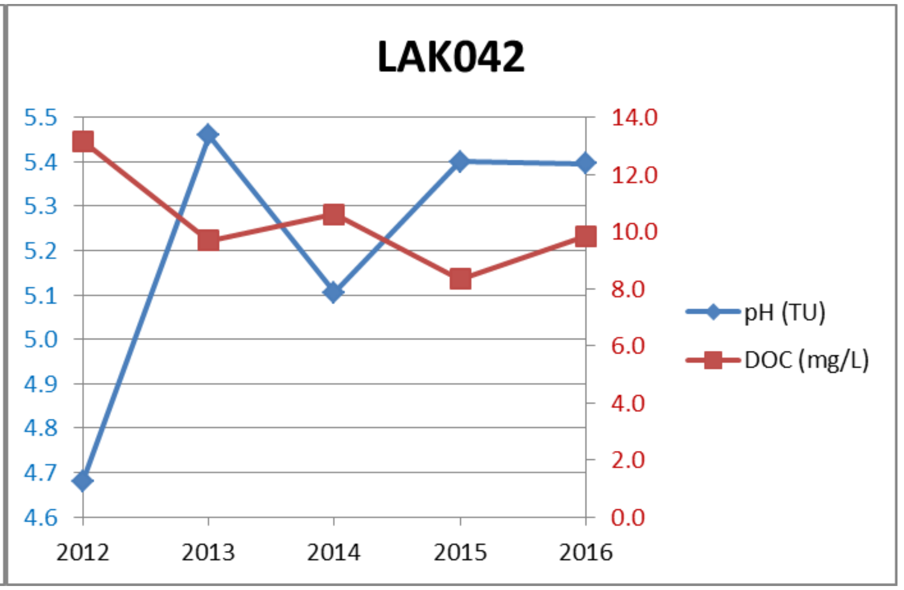

LAK028
160
140
120
100
80
60
40
20
0
-20
2012
2013
2014
2015
2016
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)

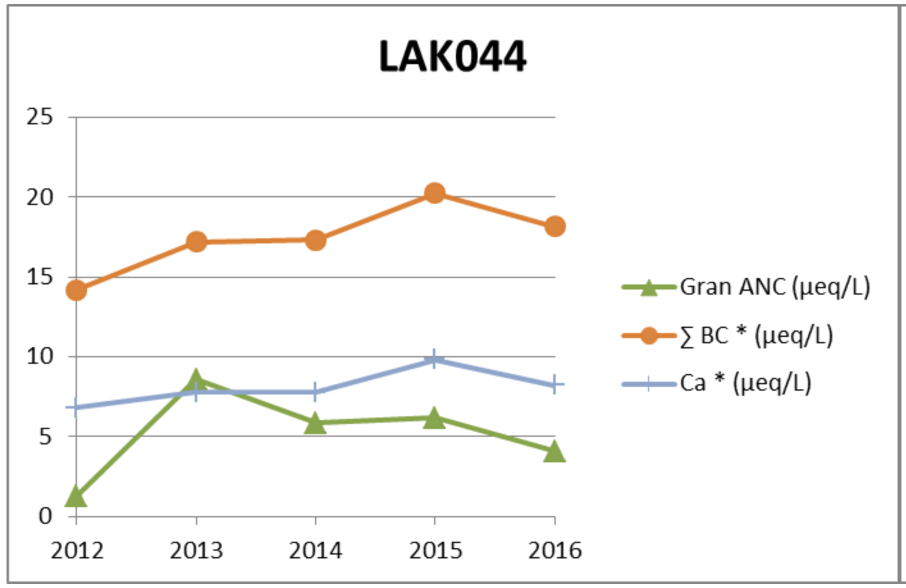

LAK028
140
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
SO4 * (μeq/L)
Cl (μeq/L)

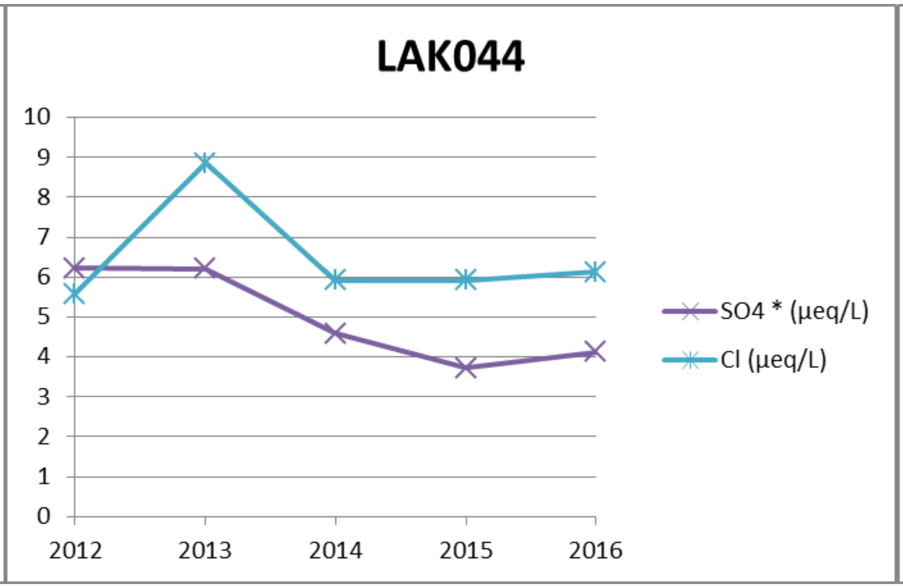

LAK028
5.4
5.3
5.2
5.1
5.0
4.9
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
pH (TU)
DOC (mg/L)

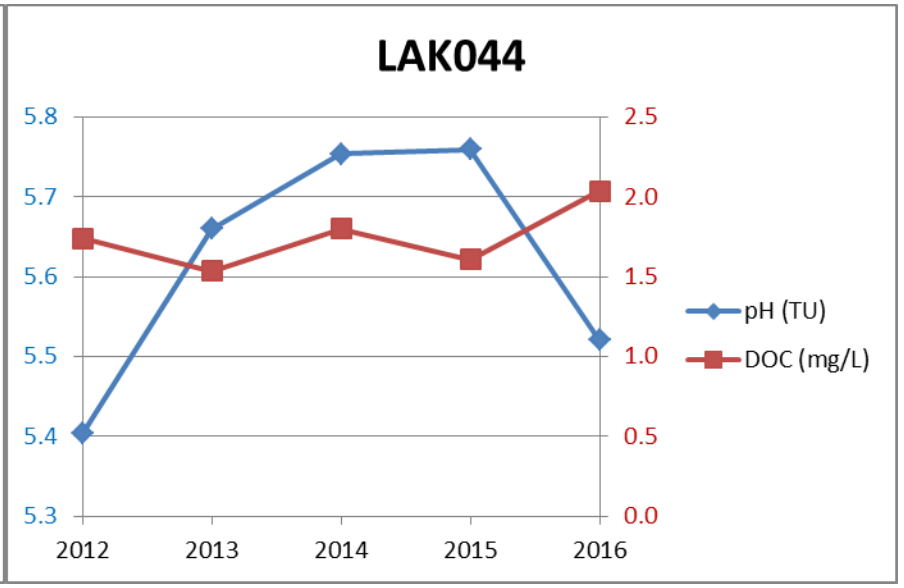

LAK042
80
70
60
50
40
30
20
10
0
-10
-20
-30
2012
2013
2014
2015
2016
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)


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

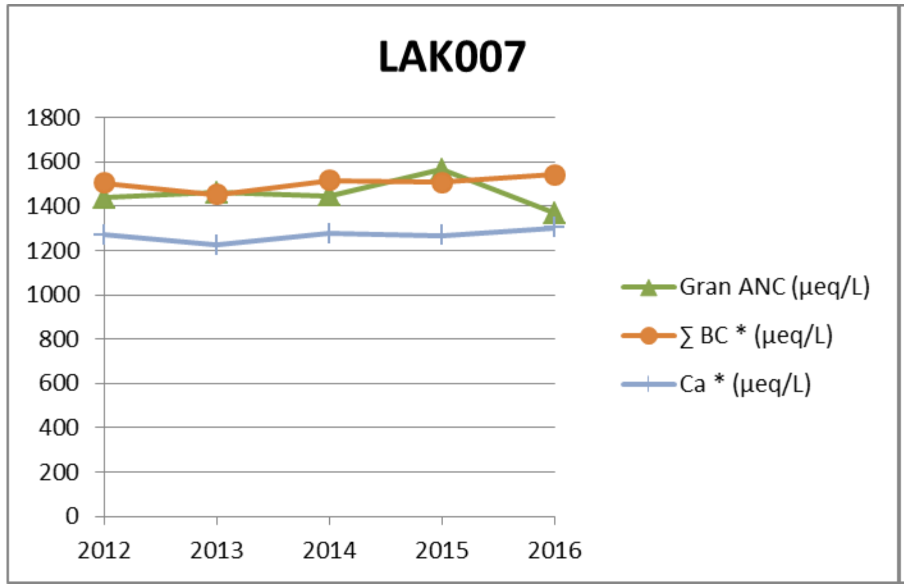

LAK042
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2012
2013
2014
2015
2016
pH (TU)
DOC (mg/L)

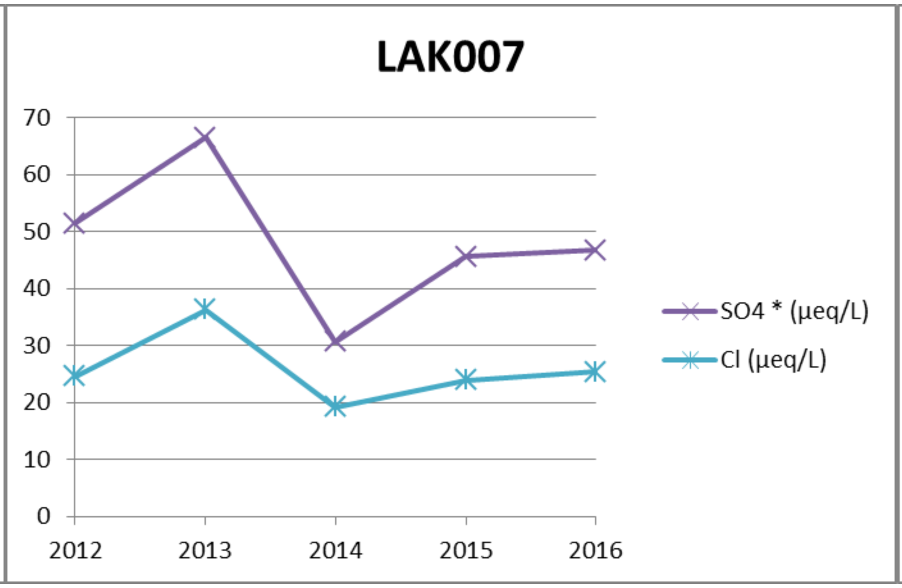

LAK044
25
20
15
10
5
0
2012
2013
2014
2015
2016
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)

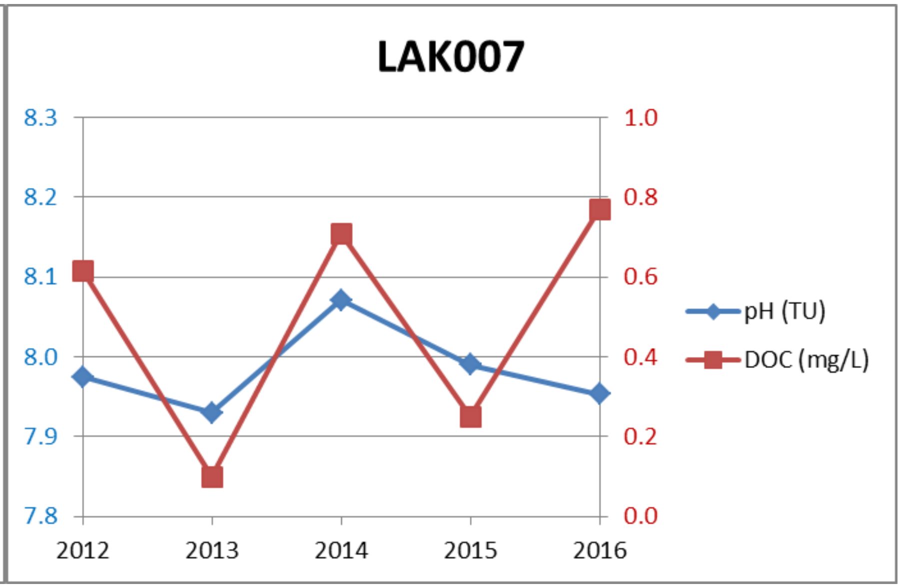

LAK044
10
9
8
7
6
5
4
3
2
1
0
2012
2013
2014
2015
2016
SO4 * (µeq/L)
Cl (µeq/L)

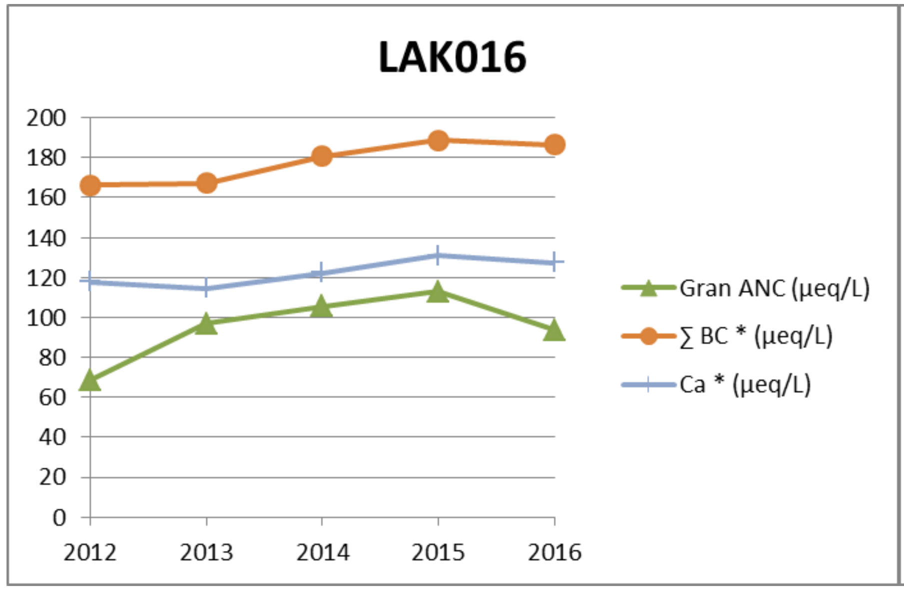

LAK044
5.8
5.7
5.6
5.5
5.4
5.3
2.5
2.0
1.5
1.0
0.5
0.0
2012
2013
2014
2015
2016
pH (TU)
DOC (mg/L)

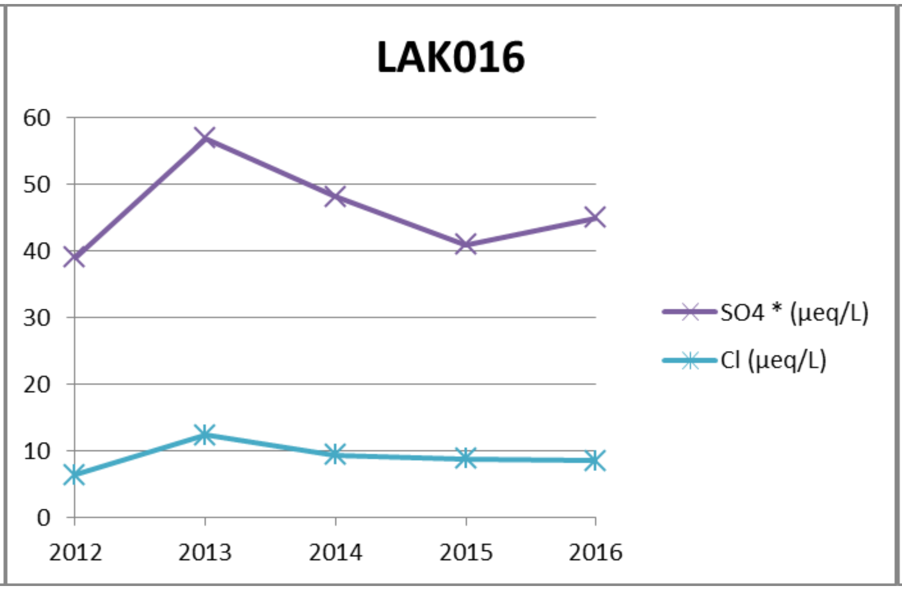
Less Sensitive Lakes

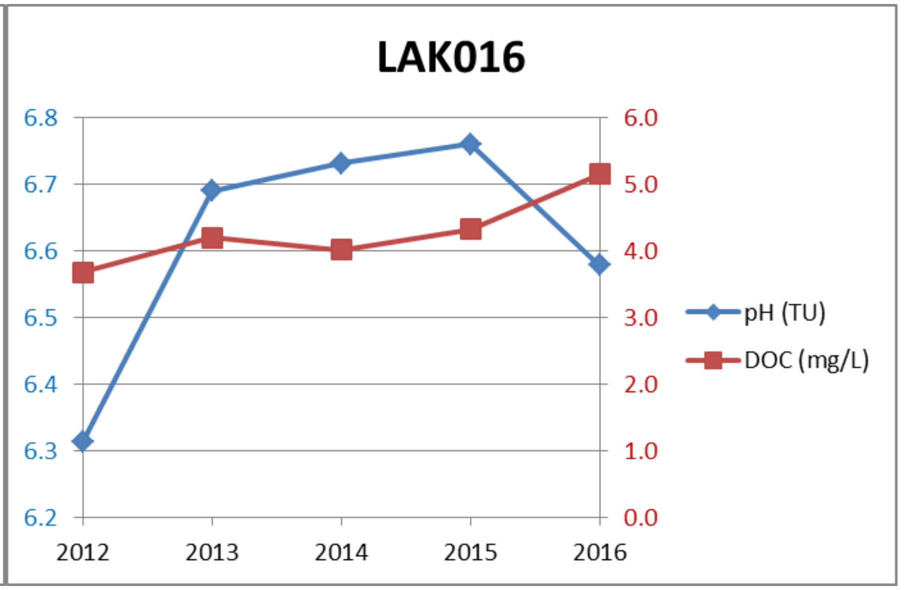


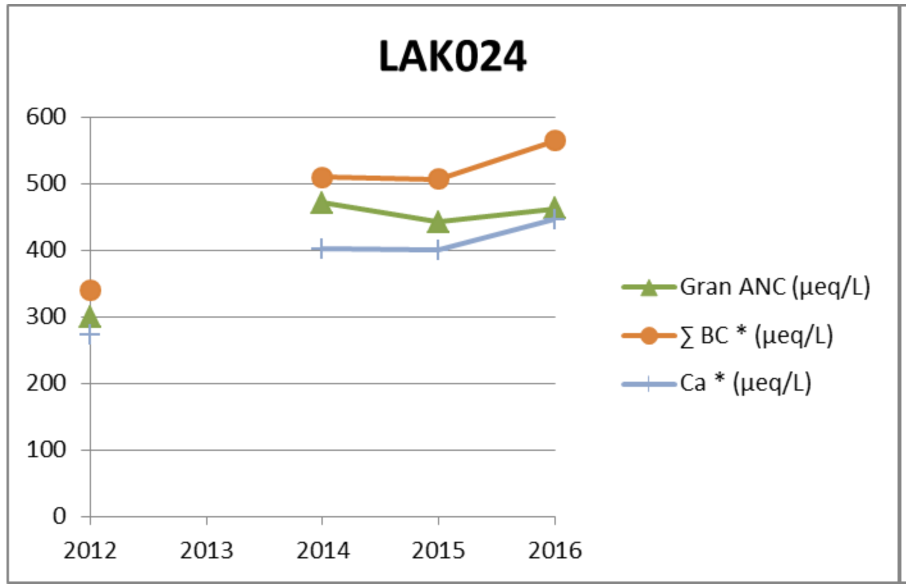


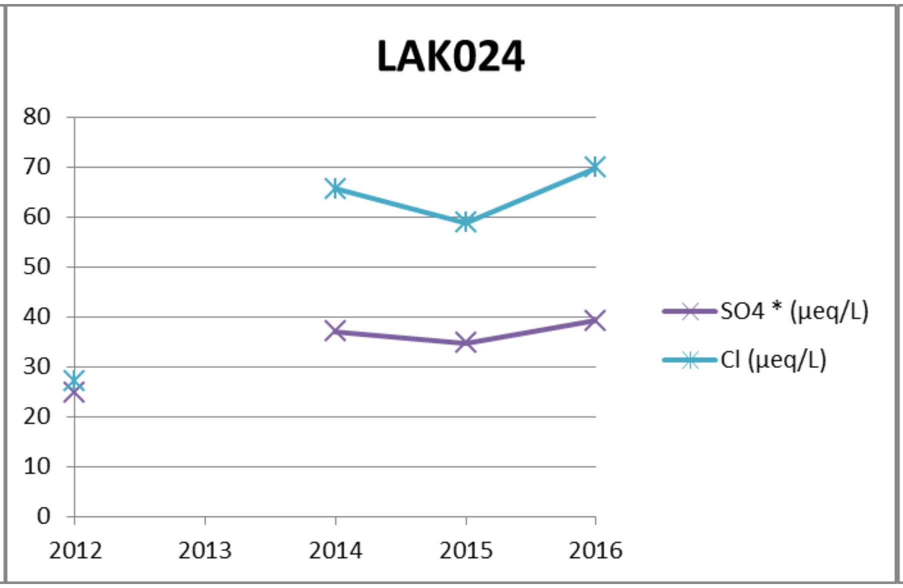


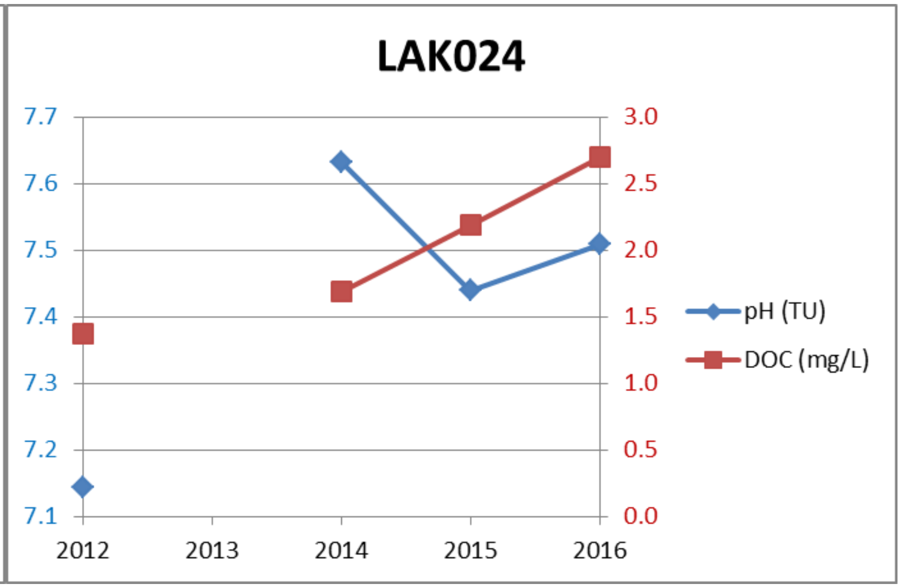


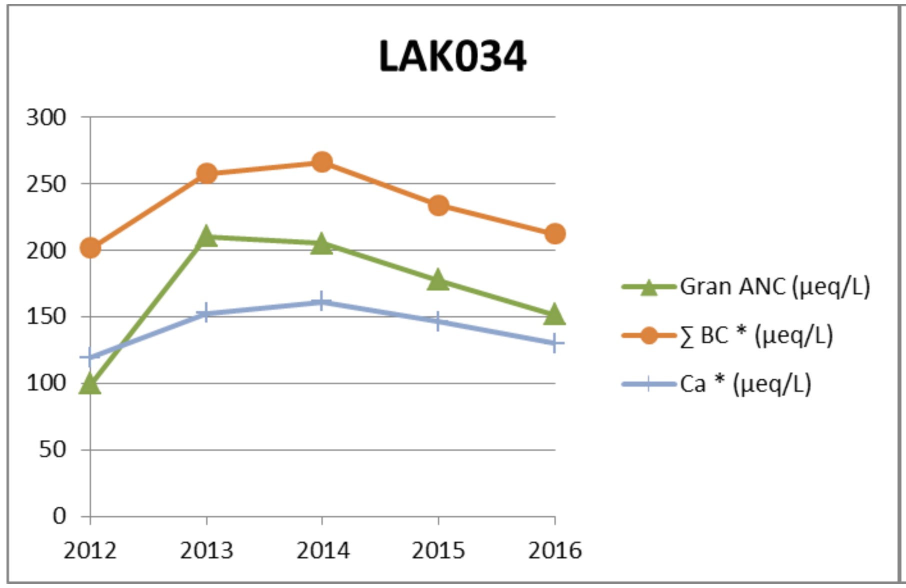


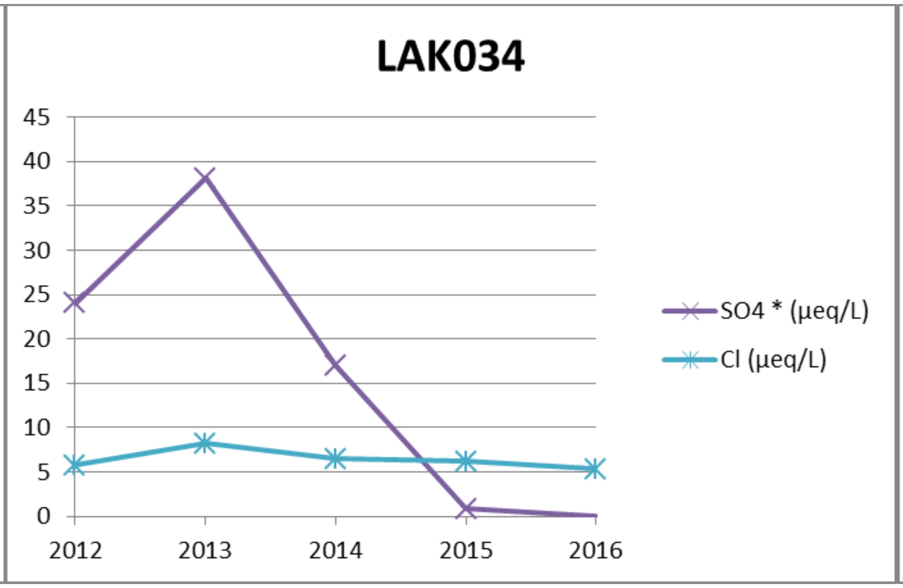


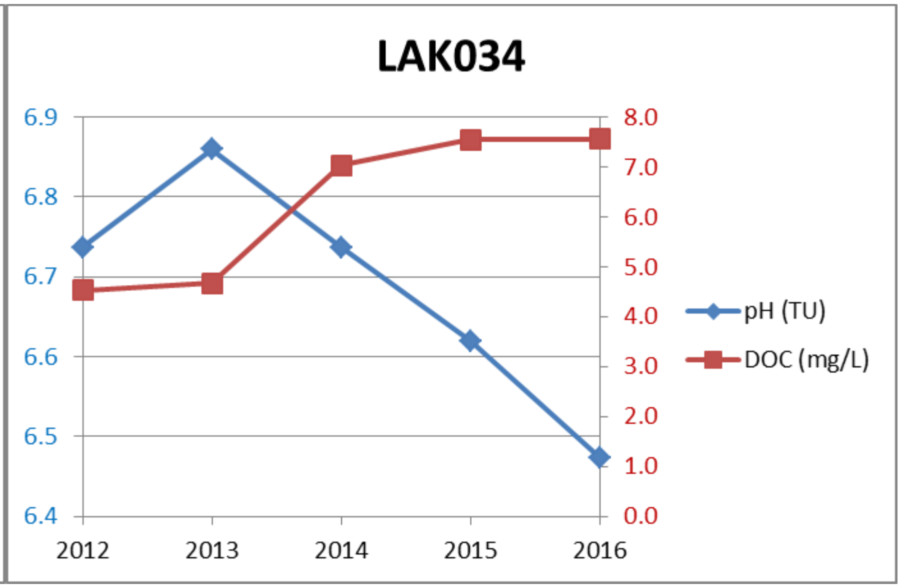

LAK024
600
500
400
300
200
100
0
2012
2013
2014
2015
2016
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)


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

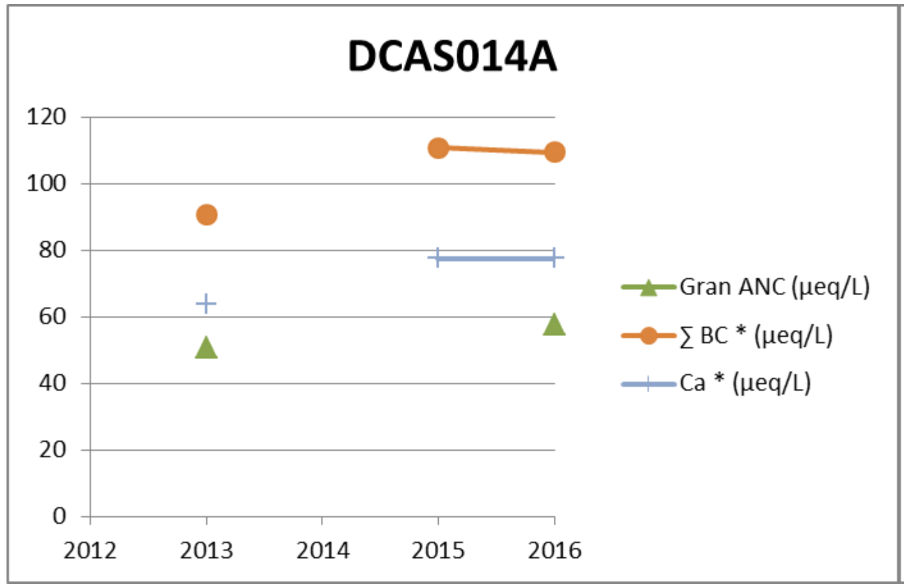

LAK024
7.7
7.6
7.5
7.4
7.3
7.2
7.1
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2012
2013
2014
2015
2016
pH (TU)
DOC (mg/L)

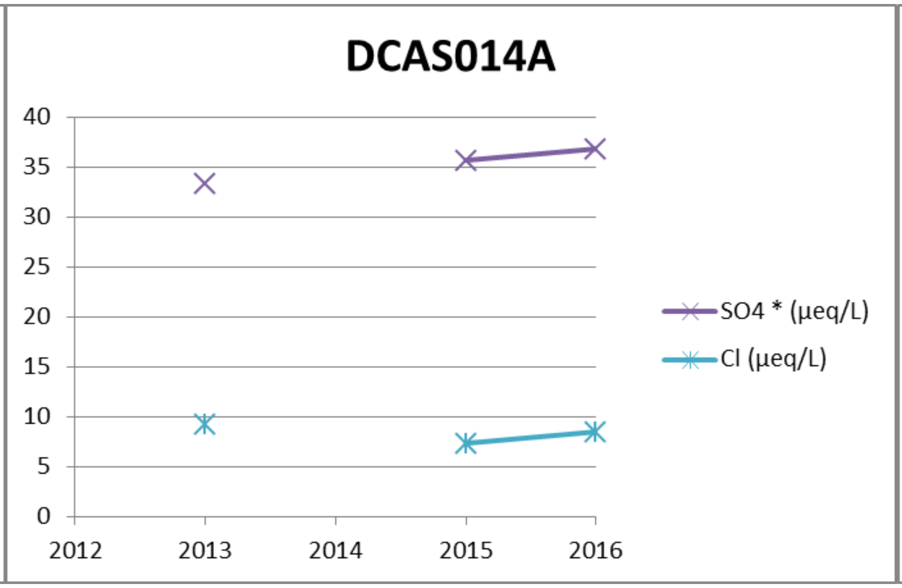

LAK034
300
250
200
150
100
50
0
2012
2013
2014
2015
2016
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)

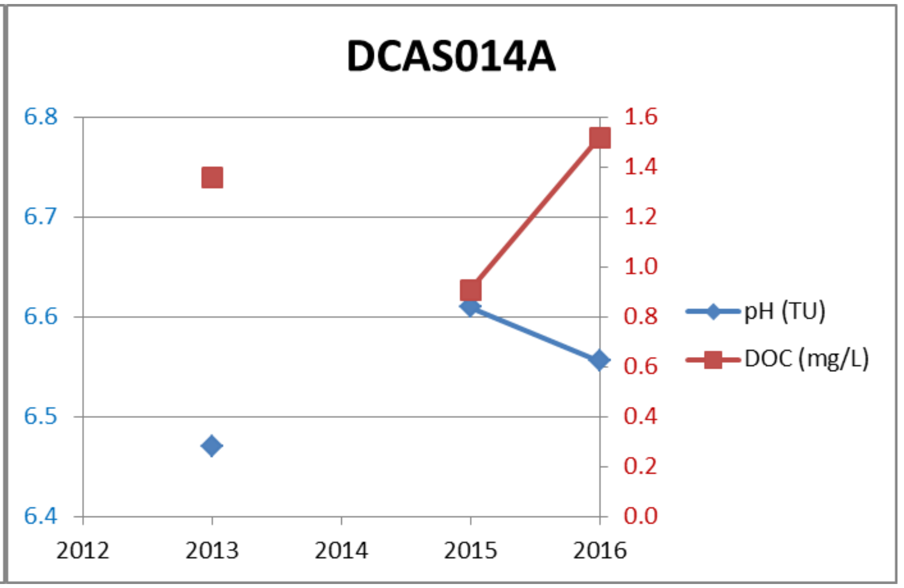

LAK034
45
40
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
SO4 * (µeq/L)
Cl (µeq/L)

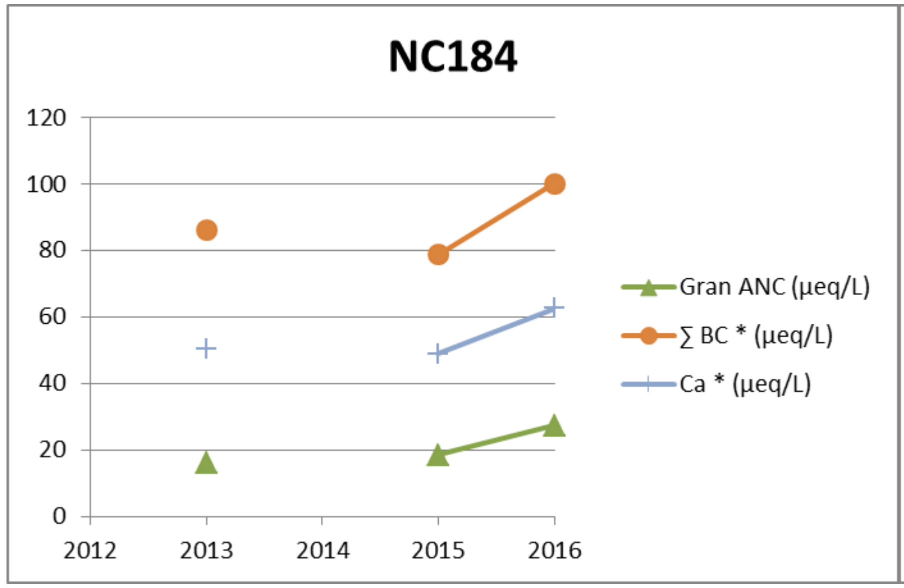

LAK034
6.9
6.8
6.7
6.6
6.5
6.4
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
pH (TU)
DOC (mg/L)

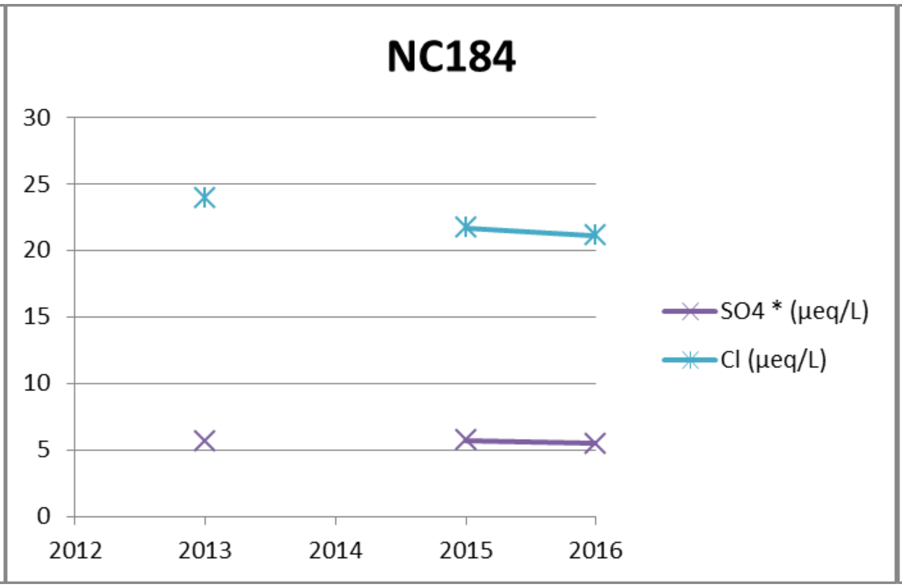
Control Lakes

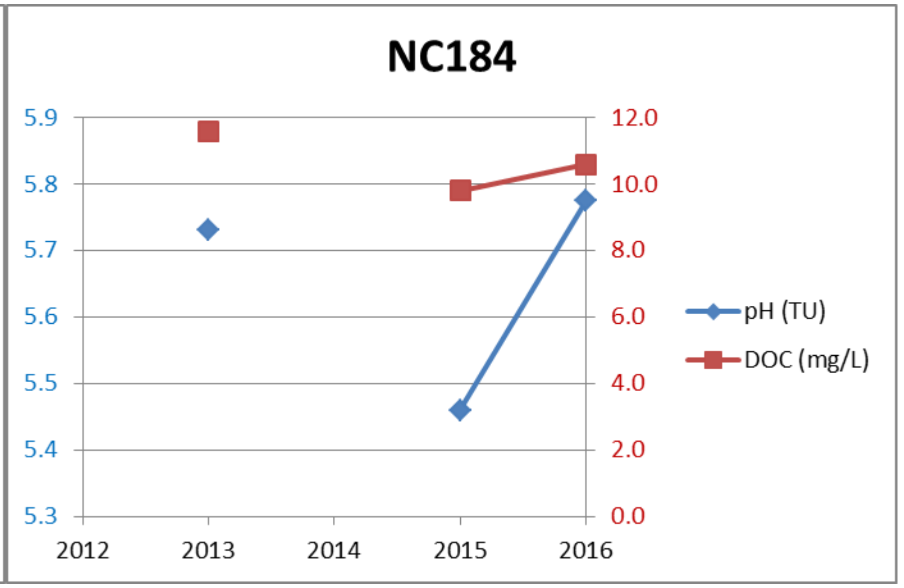


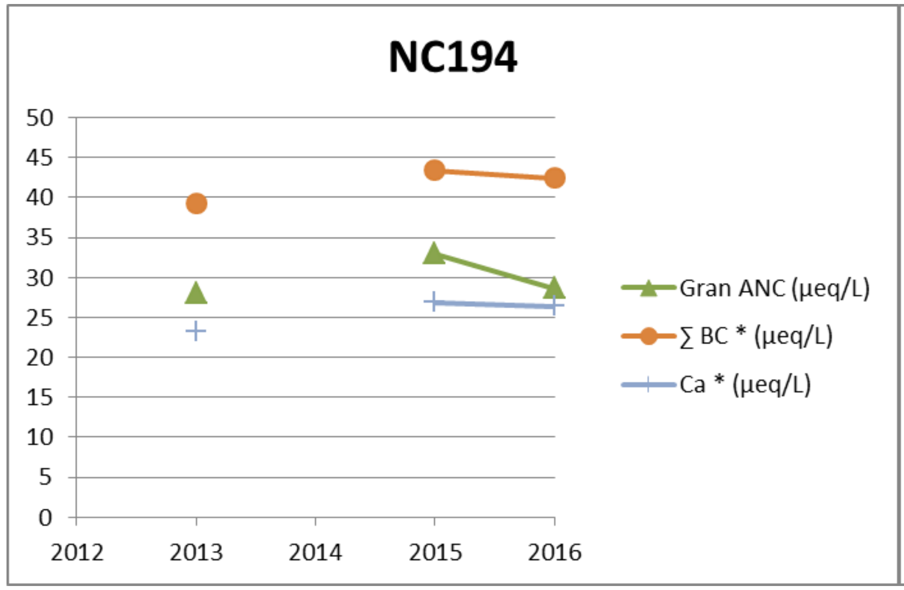


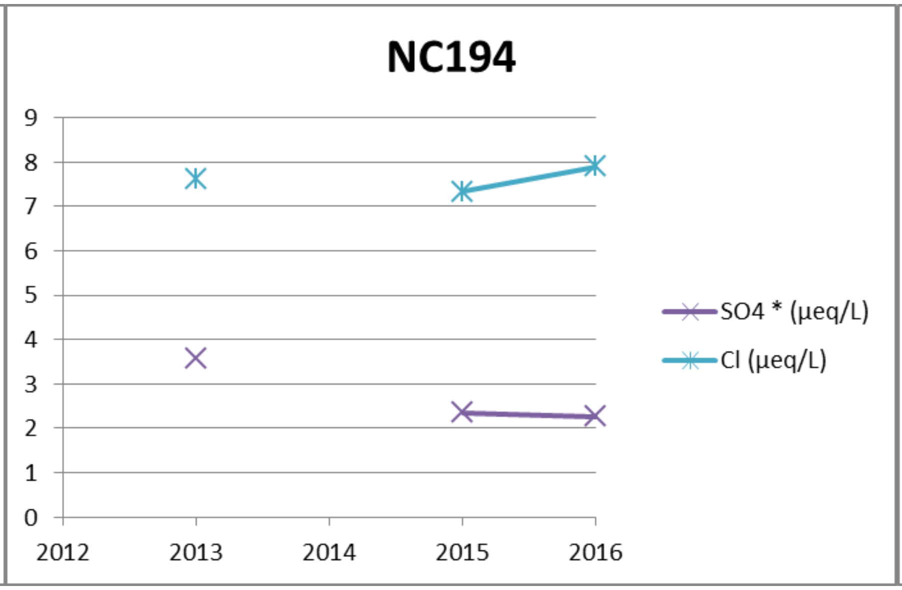


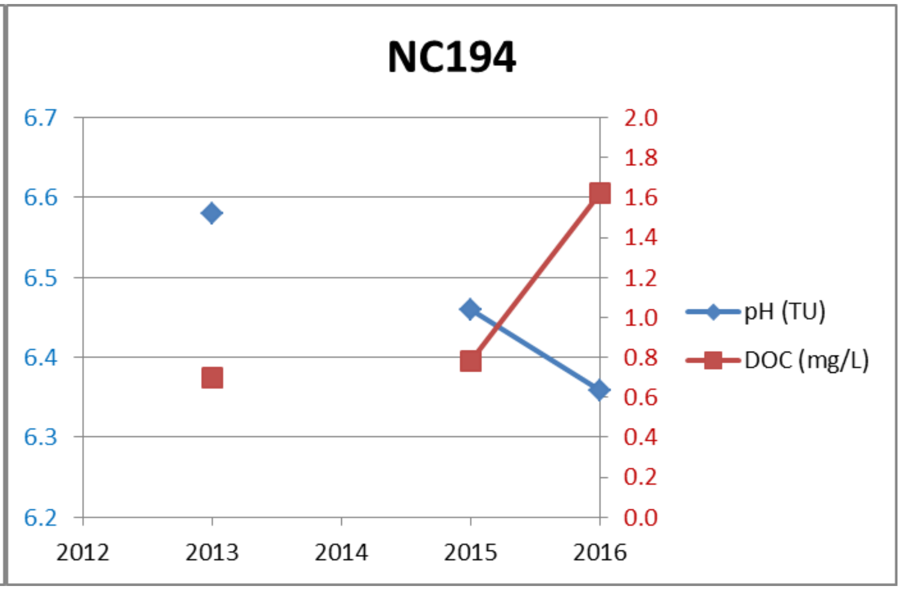







NC194
50
45
40
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)


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


NC194
6.7
6.6
6.5
6.4
6.3
6.2
2.0
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
pH (TU)
DOC (mg/L)

Rio Tinto

KMP SO_2 EEM Program – Technical Memo W07

Aquatic Ecosystems Actions and Analyses

April 3, 2018

DRAFT

Prepared for:

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

Prepared by:

ESSA Technologies Ltd.
Suite 600 – 2695 Granville St.
Vancouver, BC, Canada V6H 3H4
(Using data provided by Rio Tinto BC Works)

Table of Contents

DRAFT

Table of Figures

Table of Tables

DRAFT

DRAFT

1 Introduction

This Technical Memo provides extended information on the data and analyses in support of the 2017 requirements for the Aquatic Ecosystems component of the KMP SO_2 Environmental Effects Monitoring (EEM) program (ESSA et al. 2014b). These data and analyses thus provide the foundation for Section 3.5 in the 2017 Annual Report (ESSA et al. 2018).

Table 1-1. Aquatic analyses as specified in the EEM Plan. Extracted from Table 16, Section 6.2.5, "Summary of Lakes, Streams and Aquatic Biota Actions, 2013-2018". The numeric symbols (e.g., ①②③) are used to link sections of the present technical memo with the EEM requirements, and appear throughout this document.

Topic	2017
Steady state water modelling	*No work planned for 2017 on this task*
Chemistry: water body sampling	① Annual water sampling, laboratory analysis, and data evaluation. ② Continuation of intensive sampling to determine natural variability.
[SO4]0; F-factor	*No work planned for 2017 on this task*
Fish presence / absence sampling	③ Resample if lake pH change reaches threshold.
Episodic acidification	④ *No work planned for 2017 on this task*
Amphibians	⑤ Conduct a literature review of potential effects of acidification on amphibians in the Kitimat Valley[1].

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) and the Kitimat Airshed Assessment (KAA) (ESSA et al. 2014a). 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; Bennett and Perrin 2018). Wherever possible, the description of methods in this technical report refers to these reports instead of repeating information that is already well-documented elsewhere.

The following three documents (as described above) are listed here because they are referenced extensively throughout this technical memo, often without their full citation:

- The STAR (ESSA *et al*. 2013)
- The KAA (ESSA *et al.* 2014a)
- The EEM Plan (ESSA *et al.* 2014b)

2 Methods

2.1 Annual Monitoring Samples ①

2016 Annual Sampling

In 2017, Limnotek sampled 14 lakes as part of the EEM long-term sampling plan. These lakes included the seven sensitive lakes and three less sensitive lakes identified in the EEM Plan, the

---

[1] Revised commitment developed based on recommendations from KPAC and discussions with Rio Tinto.

high recreational value LAK024 (Lakelse Lake; added to the EEM in 2014), and three additional control lakes added to the EEM in 2015. The three control lakes (NC184, NC194 and DCAS14A) are all located outside of the KMP-influenced airshed and have baseline data for 2013 from sampling as part of the KAA (ESSA et al., 2014a). The sampling methodology is described in detail in Limnotek's technical report on the water quality monitoring (Bennett and Perrin 2018). Table 2-1 summarizes all of the EEM sites sampled during 2012-2017. Figure 2-1 shows a map of the lakes sampled in 2017.

Table 2-1. Summary of sites sampled within the EEM Program.

Sample Site	Year of Sampling						Rationale for sampling
	2012	2013	2014	2015	2016	2017	
	STAR	EEM	EEM	EEM	EEM	EEM	
Lake 006	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 012	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 022	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 023	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 028	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 042	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 044	✓	✓	✓	✓	✓	✓	EEM sensitive lake
Lake 007	✓	✓	✓	✓	✓	✓	EEM less sensitive lake
Lake 016	✓	✓	✓	✓	✓	✓	EEM less sensitive lake
Lake 034	✓	✓	✓	✓	✓	✓	EEM less sensitive lake
Lake 024	✓		✓	✓	✓	✓	Added to the EEM long-term monitoring lake set due to public importance
MOE3		✓					Potentially sensitive lakes / streams not previously sampled
Cecil Creek 1		✓					
Cecil Creek 2		✓					
Cecil Creek 3		✓					
MOE6			✓				
Goose Creek 1			✓				
Goose Creek 2			✓				
Goose Creek 4			✓				
Goose Creek 5			✓				
Goose Creek 6			✓				
Goose Creek 7			✓				
GNT1 (Goose Creek)				✓			
GNT2 (Goose Creek)				✓			
NC184		✓[2]		✓	✓	✓	Control lakes added to EEM in 2015
NC194		✓[1]		✓	✓	✓	
DCAS14A		✓[1]		✓	✓	✓	

DRAFT

---

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

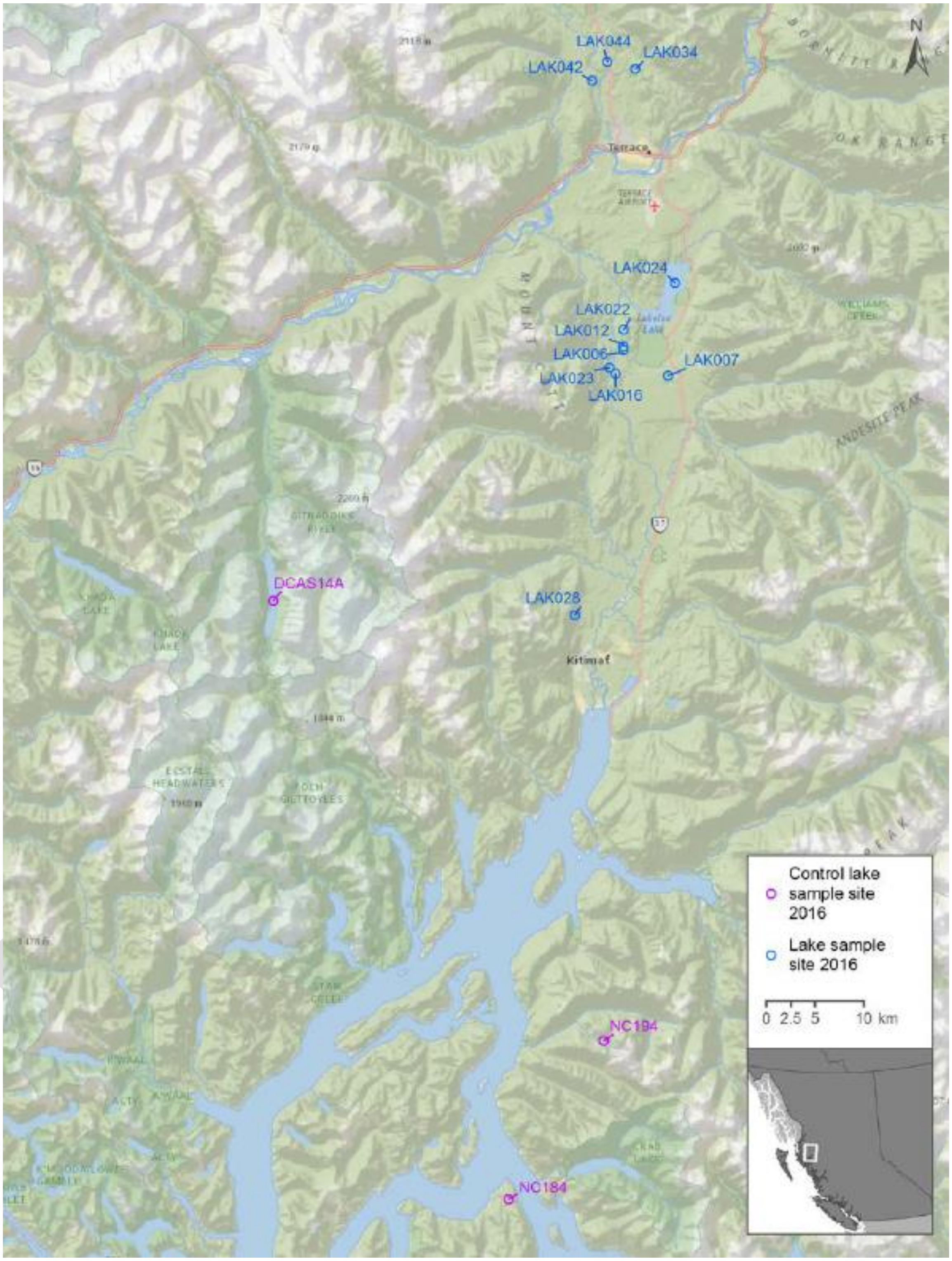


Figure 2-1. Location of the lakes that were sampled in 2017. The three control lakes are labelled with purple text (Source: Bennett and Perrin 2018).

2.2 Intensive Monitoring of Three Lakes ②

Starting in 2014, intensive monitoring was implemented in three of the EEM lakes – End Lake (LAK006), Little End Lake (LAK012) and West Lake (LAK023). These three lakes were selected based on being accessible by road, thus making repeated visits much more feasible than for remote lakes requiring access by helicopter or hiking. During the fall of 2014, the intensive monitoring included continuous pH monitors and multiple site visits to collect intra-season water samples for additional lab analyses and pH measurements. In 2015, the continuous pH monitors were deployed from mid-April until mid-November. During October 2015, three additional within-season water chemistry samples were taken at these three lakes, subsequent to annual sampling across all of the lakes (i.e., four samples in total for each of the intensively monitored lakes in 2015). In October 2016, this was repeated for the same three lakes (LAK006, LAK012 and LAK023) as well as being expanded to LAK028, LAK042 and LAK044. The three additional lakes were added in 2016 based on the recommendation in the 2015 EEM Annual Report to explore the feasibility of increasing the number of samples for lakes with low power to correctly detect whether the EEM KPI thresholds have been exceeded. This recommendation was based on the findings of the power analyses (reported in the 2015 EEM Annual Report), which demonstrated that the existing monitoring plan (i.e., annual samples only for these lakes) would have low power to detect changes in some of the primary metrics for water chemistry in LAK028 (for ANC, SO_4^{2-}), LAK042 (for pH, ANC), or LAK044 (for ANC, SO_4^{2-}). Finally, lake level monitoring was added in 2016 in End Lake, Little End Lake, and West Lake to provide an accurate, local measure of the timing of storm events, so as to better explain observed variation in pH (monitored continuously) and other water quality parameters of interest monitored during October (particularly sulphate, nitrate, DOC, ANC, and base cations). The lake level monitoring was continued in 2017.

This work was planned, implemented and documented by Limnotek. The methods and results for 2017 are reported in Bennett and Perrin (2018).

For the lakes with more than multiple samples during the fall season, the data from the multiple within-season samples have been used to determine mean annual values. In the 2013/2014 and 2015 Annual Reports, only the sample taken on the first day of the monitoring season (i.e., the day(s) of sampling all lakes) was designated as the “annual sampling” value. Starting with last year’s Annual Report, the mean annual values are used for all years in which additional within-season samples were taken.

2.3 Quality of Water Chemistry Data ①②

Sampling and laboratory quality control and quality assurance

The collection, handling, transport, and analyses of water quality samples were conducted with numerous quality checks, to ensure the highest quality data possible. Details on the methods for quality control and quality assurance for the water samples are described in Bennett and Perrin (2018).

Analyses of Charge Balance and Estimated vs. Measured Conductivity

In addition to the data quality control and assurance procedures applied during the sampling and subsequent laboratory analyses, we applied two additional methods to confirm the quality of the

DRAFT

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

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

pH measurements

Water quality samples taken in 2017 have multiple measures of pH, including a field measurement and two lab measurements (Trent University and ALS). As described above in Section 2.2, three lakes also have additional measurements of pH from continuous meters. In addition, samples taken during the bi-weekly visits to calibrate the continuous pH meters were sent to the two labs to measure pH and ANC. As described in the STAR, lab measurements of pH, rather than field measurements, have been used for the analyses of lake chemistry; lab pH measurements have lower variability, and therefore are more relevant to the detection of long term trends.

The 2012 data collected during the STAR included laboratory measurements of pH only from Trent University. Inter-annual comparisons of trends in pH have therefore been conducted using the pH measurements from Trent University. Limnotek (Bennett and Perrin 2018) analyzed differences among the different methods of measuring pH for quality assurance purposes, repeating similar comparisons conducted in previous years (Perrin and Bennett 2015, Limnotek 2016, Bennett and Perrin 2017).

2.4 Inter-annual Changes

Observed Changes

The EEM Program now has six consecutive years of monitoring data with which to examine inter-annual changes in water chemistry parameters. The monitoring data from 2017 represent the second year of true post-KMP sampling. The years 2012 to 2014 were prior to the implementation of KMP and 2015 was a transition year that included decreases in production in preparation for the transition then ramping up production as KMP was phased in during the year.

We calculated the changes in major water chemistry attributes between subsequent years and across the entire period for 2012-2017[3]. Year to year changes should be interpreted cautiously. The power analyses conducted and reported in the 2015 EEM Annual Report demonstrated that

---

[3] As noted in the 2013/2014 EEM Annual Report (ESSA Technologies 2015), because sampling in 2012 was performed in August and the sampling in subsequent years was performed in October, the observed differences between 2012 and 2013 represent a mixed effect of both changes due to year and changes due to season. For this reason, the observed changes between 2012 and 2013 are harder to interpret than the changes between other sequential years. However, to better understand this potential seasonal effect, we analyzed pH data from 2015 and 2016 for the 3 intensively monitored lakes to test if there were any consistent differences in mean August pH vs mean October pH.

DRAFT

the power to detect annual changes in pH, Gran ANC and SO_4 is very low due to high within-year and between-year variability, as well as measurement error. Of these three metrics, Gran ANC provided the most reliable indication of long term changes in acid-base chemistry (i.e., highest statistical power to detect changes of biological significance), but required ≥ 3 years of annual measurements to obtain acceptable statistical power in five of the sensitive lakes. Two of the seven sensitive lakes (LAK028 and LAK042) showed low statistical power to detect biologically significant changes in Gran ANC even after 10 years of annual measurements, due to high natural variability.

Expected Changes and Application of the Evidentiary Framework

The EEM Evidentiary Framework (Section 7.0 and Appendix H of the EEM Plan) provides a weight-of-evidence approach for assessing causality associated with observed changes in water chemistry. The principles of the framework are considered and applied in Section 4. More years of data will be required to achieve statistically reliable comparisons of pre-KMP and post-KMP conditions, as demonstrated by the statistical power analyses conducted in 2015.

2.5 Fish Sampling ③

Fish sampling was conducted in LAK028 in 2017 to determine if fish were present or absent. Details of the fish sampling methodology are described in Limnotek's technical report (Bennett and Perrin 2018).

Limnotek also conducted fish sampling in LAK006, LAK012, LAK023, and LAK044 in 2013 to measure the presence/absence of fish in four of the seven sensitive lakes within the EEM Program. Under the EEM Plan, the fish populations in some of these lakes could potentially be resampled if there were convincing evidence that a lake's pH had declined by more than 0.3 pH units. In 2015, fish sampling was completed in the three less sensitive lakes: LAK007, LAK016, and LAK034. Details of the fish sampling methodologies for the two years are described in Limnotek's previous technical reports (Perrin et al. 2013, Section 2.9; Limnotek 2016, Section 2.8).

2.6 Episodic Acidification Studies ④

Three studies are directly relevant to the episodic acidification sub-component of the aquatic ecosystems component of the EEM Program. First, the three intensively monitored lakes include continuous monitoring of pH during the ice free season. Second, there have been substantial efforts to establish a continuous pH monitoring station on Anderson Creek. In 2015, there was a Manta monitor installed by Limnotek, but the data collected suggested that the instrument may not have been functioning properly. Due to such concerns, the monitor was removed and set up alongside the Manta monitor in West Lake in 2016 to test for instrument issues (Limnotek 2016). Independently, Rio Tinto had a continuous pH monitor in place in Anderson Creek during 2016; however, the instrument was not properly re-calibrated through the season and therefore the data were unusable due to measurement drift. In 2017, a Manta monitor was installed in Anderson creek for 4 weeks in 2017 to validate the Rio Tinto data from their Foxboro instrument which was installed in Anderson Creek in July 2017. Third, Dr. Paul Weidman (School of Resource and Environmental Management & Department of Biology, Simon Fraser University) has been conducting a research project on episodic acidification and climate change. Dr. Weidman's research is highly relevant to the work of the EEM program although it is not a formal component

DRAFT

of the EEM program. Rio Tinto will provide an update on Dr. Weidman's research once his report is publicly available.

2.7 Amphibian Monitoring ⑤

In 2017, Rio Tinto commissioned a literature review of acidification impacts on amphibians and potential pathways of effects in support of the EEM (ESSA Technologies Ltd. 2017). This work was predominantly completed in 2017 and is currently in the final stages of review.

2.8 Water Column Chemistry of LAK028

During the last two sampling visits to LAK028 (October 18 and 26) additional samples were taken at depths of 11 m and 16 m. On October 26, a profile of the water chemistry was conducted at a deep location near the centre of the lake to gain a more comprehensive understanding of the lake chemistry of LAK028. Samples were taken every 1 m for temperature, pH, conductivity, total dissolved solids concentration, turbidity, dissolved oxygen concentration.

2.9 Kitimat River Water Quality

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

3 Results

3.1 Quality of Water Chemistry Data ①②

Sampling and laboratory quality control and quality assurance

The results of the sampling and laboratory quality control and quality assurance methods are presented in the associated technical report by Limnotek (Bennet and Perrin 2018). The laboratory data show high precision and accuracy, with no apparent problems. Measurements of pH from ALS were statistically significantly different from pH measurements in the field, and from pH measurements in the laboratory at Trent University, but these differences were still within the specified limits of ± 0.3 pH units for the equipment used by ALS.

Charge Balance Check

The charge balance has been examined for each year of sampling, based on the data from the annual sampling event. Table 3-1 shows four diagnostic metrics of the charge balance for the annual sample sets from 2012 to 2017. The charge balance for the 2017 data is better than almost all previous years.

The charge balance for the lakes in the EEM Program (sensitive and less sensitive), as sampled during the annual sampling event in 2017, is shown graphically in Figure 3-1. The linear trend line shown on the graph is heavily influenced by Lake 007 (not shown on the graph), which has cation and anion levels of an order of magnitude greater than the other lakes.

DRAFT

Table 3-1. Measures of the charge balance check for 2012 (STAR lakes), 2013 (EEM lakes, MOE3, Cecil Creek), 2014 (EEM lakes, MOE6), 2015 to 17 (EEM lakes, control lakes[4]). Negative (red) values for "Average %Diff" and "Average Difference" indicate less total charge from cations than from anions.

Year	Number of Samples †	Average %Diff	Average Abs (%Diff)	Average Difference (µeq/L)	Average Abs(Diff) (µeq/L)
2012	61	-0.7	2.6	-6.5	12.2
2013	14	-8.5	10.1	-28.2	42.8
2014	12	-5.0	5.2	-12.9	14.5
2015	13 [4]	-2.9	3.1	-16.6	17.3
2016	14	-1.7	2.3	1.7	12.6
2017	14	0.5	3.3	-2.1	7.9

† These data represent the "annual samples" from each lake.

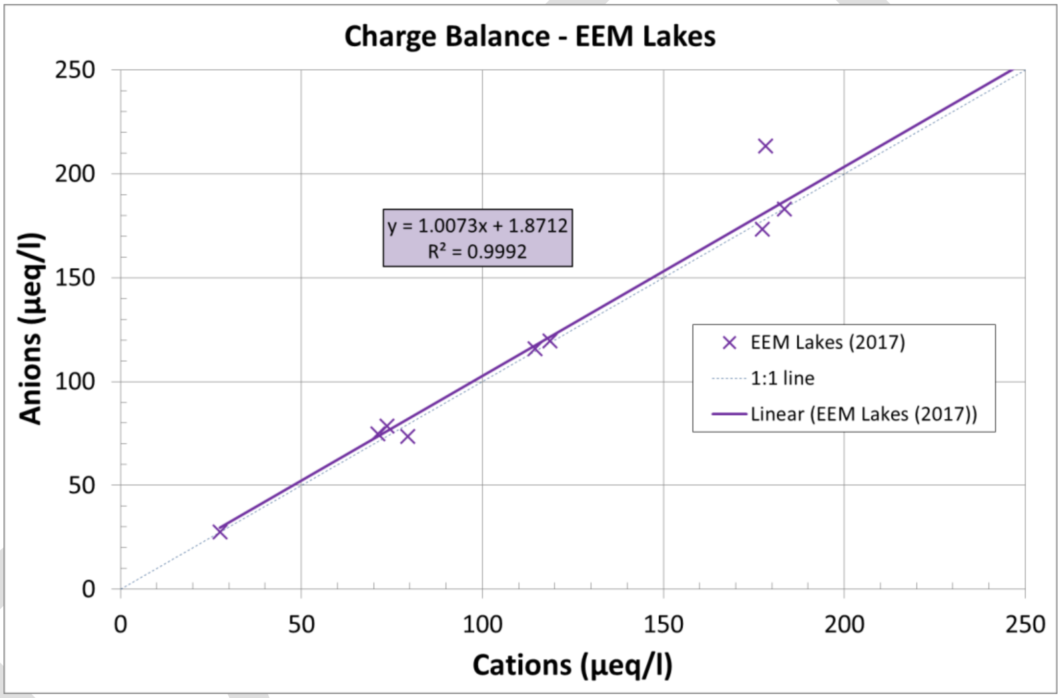


Figure 3-1. Analysis of charge balance for the EEM lakes in 2017. The Y-axis is the sum of all major anions (negatively charged ions); the X-axis the sum of all major cations (positively charged ions).

For each of the lakes with multiple within-season samples, Table 3-2 shows the measures of the charge balance check. In 2017, the average charge balance discrepancy was greater for this data set than for the single annual samples across all of the lakes, but still less than most previous years.

---

[4] For 2015, only NC184 and NC194 are included. DCAS14A has been excluded from this summary because of issues with its measured value for total alkalinity.

Table 3-2. Measures of the charge balance check for lakes with multiple within-season samples. In 2014 and 2015, these included (LAK06, LAK12 and LAK023). In 2016 and 2017, these included those same three lakes plus LAK028, LAK042 and LAK044. Negative (red) values for "Average % Diff" and "Average Difference" indicate less total charge from cations than from anions.

Year	# Lakes	Number of Samples	Average %Diff	Average Abs (%Diff)	Average Difference (µeq/L)	Average Abs(Diff) (µeq/L)
2014	3	15	-5.6	5.6	-11.1	11.1
2015	3	12	-3.5	3.5	-6.8	6.8
2016	6	24	-4.3	4.9	-10.4	11.6
2017	6	24	-1.3	3.5	-5.4	9.0

Measured versus Estimated Conductivity

Measured and estimated conductivity were compared for each year of sampling, based on the data from the annual sampling event. Table 3-3 shows two diagnostic metrics of the conductivity check for the annual sample sets from 2012 to 2017. The data for 2017 demonstrate an acceptable relationship between measured and estimated conductivity.

The conductivity check for the lakes in the EEM Program (sensitive and less sensitive), as sampled in 2017, is shown graphically in Figure 3-2. The linear trend line shown on the graph is heavily influenced by Lake 007 (not shown on the graph), which has conductivity values of an order of magnitude greater than most of the other lakes.

Table 3-3. Measures of the conductivity check for 2012 (STAR lakes), 2013 (EEM lakes, MOE3, Cecil Creek), 2014 (EEM lakes, MOE6), 2015 to 2017 (EEM lakes, control lakes[5]). Positive values of "Average %Diff" indicate that the estimated conductivity was higher than the measured conductivity. Negative values (shown in red) indicate that the estimated conductivity was lower than the measured conductivity.

Year	Number of Samples	Average %Diff	Average Abs (%Diff)
2012	61	4.9	6.0
2013	14	6.8	10.5
2014	12	-5.1	6.4
2015	13 [5]	-3.0	6.1
2016	14	-7.5	9.1
2017	14	-4.1	7.2

DRAFT

---

[5] As per Table 3-1, only NC184 and NC194 are included. DCAS14A is excluded due to data concerns that are being currently explored.

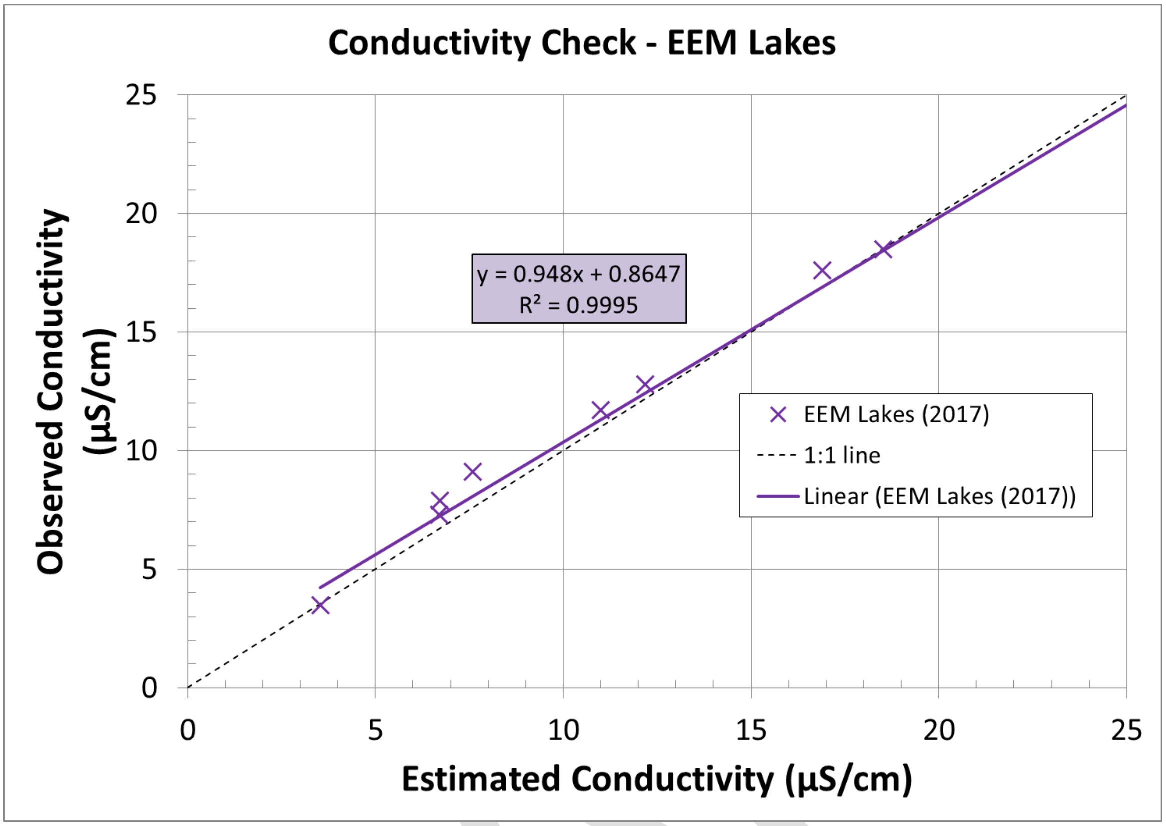


Figure 3-2. Conductivity check for the EEM lakes in 2017. Estimated conductivity is based on laboratory measurements of the concentrations of all ions and literature values for the conductivity of each ion, which is compared to the conductivity observed in field measurements.

DRAFT

For each of the lakes with multiple within-season samples, Table 3-4 shows the measures of the charge balance check. In 2017, the average conductivity difference was greater for this data set than for the single annual samples across all of the lakes, but still within acceptable limits for data quality. As explained in the footnote to Table 3-4, it appears that in 2015 the measured conductivity was erroneous for the three additional within-season samples taken at all three lakes, but that the ion measurements still showed acceptable charge balance (Table 3-2).

Table 3-4. Measures of the conductivity check for lakes with multiple within-season samples. In 2014 and 2015, these included (LAK06, LAK12 and LAK023). In 2016 and 2017, these lakes included those same three lakes plus LAK028, LAK042 and LAK044. Positive values of "Average %Diff" indicate that the estimated conductivity was higher than the measured conductivity.

Year	Lakes	Number of Samples	Average %Diff	Average Abs (%Diff)
2014	3	15	-3.2	6.2
2015	3	12	43.4 [6]	46.3
2016	6	24	-6.5	11.9
2017	6	24	-8.9	11.9

pH measurements

Lab measurements of pH were made at two different labs in 2013 to 2017. Limnotek examined the differences in pH measurements for 2017 among the two labs and the field measurement and concluded that the differences were within the expected ranges (i.e., factory/lab specified measurement error associated with each instrument; Bennett and Perrin 2017). In 2017, the values measured by ALS were higher than those measured by Trent University in all but one of the samples and the mean difference between the labs was similar to the previous 3 years. However, both labs apply substantial quality control, quality assurance and equipment calibration procedures; therefore, it is not possible to conclude which lab's measurements are closer to the true pH value. For the analyses presented in this technical memo, we used the Trent University measurements to be consistent with the data from the STAR – the 2012 samples were only analyzed by Trent University and not ALS.

3.2 Annual Water Chemistry Sampling Results ①

Appendix 1 reports the results of the annual water chemistry sampling for the EEM lakes and control lakes from the sampling conducted in 2017 (with the data from 2012-2016 included for reference), for major water chemistry metrics (pH, DOC, Gran ANC, base cations, and major anions).

3.3 Intensive Monitoring of Three Lakes ②

Results from the continuous monitoring of pH in West Lake (LAK023), End Lake (LAK006), and Little End Lake (LAK012) are reported in the associated Technical Memo by Limnotek (Bennett and Perrin 2018). The Limnotek results for pH monitoring are summarized below in Table 3-5 and

DRAFT

---

[6] It appears that for all 3 lakes the measured conductivity values for samples taken October 13, 20, and 27 are in error. Based on the first sample taken at each lake (October 4), the average % difference in conductivity was only -5.8%, which is within the range of other years and within the range of acceptable limits. Measured conductivity dropped substantially after the first sample, while the estimated conductivity remained relatively similar. Further examination confirmed that estimated conductivity was calculated correctly and there were no suspect data in the ion concentrations. The ion measurements are the most important data for the EEM Program – the ion measurements for these samples appear to be consistent with the data from the first sample, and the charge balances for all of the samples are within the range of acceptable limits. These errors appear to be limited only to the conductivity measurements for these three dates.

Table 3-7. Depending on the lake and pH sensor, pH varied by about 0.9 to 1.4 pH units over the period of continuous monitoring from April to November 2017. For sensor pH3 in End Lake, the range was 1.9 pH units but this reflects some extremely high readings that are suspected to be instrument errors. The mean pH values from all the sensors in End Lake and West Lake were the same in 2017 as they were in 2016, and therefore remained above pH 6.0, the level used as a biological threshold for analyses of critical loads (see STAR and KAA reports). The mean pH values for each of the sensors in Little End lake declined by 0.2 pH units, dropping below pH 6.0. Table 3-6 shows the results for mean pH for these three lakes for 2014 to 2017, which indicate that these lakes have decreased in pH but only by an average of 0.1 pH units across lakes and sensors.

The results from these lakes further confirm the results from previous of continuous monitoring – i.e., that these data show a high degree of variation in the half-hourly pH within each year, substantially higher than originally expected, but not in the mean annual pH. Understanding that natural intra-annual variation is very high was one of the primary reasons for conducting the power analyses as part of the 2015 EEM Annual Report (ESSA Technologies Ltd 2016) and the resultant recommendation that changes in primary lake chemistry metrics will need to be assessed within a probabilistic analytical framework rather than simple deterministic comparisons between years. The power analyses showed that continuous monitoring will increase the power of the monitoring program to be able to correctly detect changes in pH that exceed the EEM KPI threshold of 0.3 pH units (i.e., when the comprehensive review of the monitoring data is conducted in 2019).

As described in the power analysis completed in 2015, there is a high degree of variability in pH (the KPI) within most of the sensitive lakes and for Gran ANC and SO_4^{2-} (the informative indicators) within some of the sensitive lakes. In 2019, as part of the comprehensive evaluation of EEM monitoring data, we will generate a probability distribution for the change in each primary metric (pH, ANC, $SO_4^{2-)}$, based on the 2012-2018 monitoring data, explicitly accounting for natural variability and measurement error. We will then compare those distributions to the evaluation thresholds for each indicator within each lake. The results will be expressed as the *probability that a particular lake has exceeded a particular threshold*.

The Limnotek technical report (Bennet and Perrin 2018) describes notable patterns observed in the continuous pH data:

> *In Little End Lake, there was an upwards shift in pH of 0.5 pH units that occurred between Aug 12 and Aug 14 (Figure 9 [in Limnotek report]). The timing of this shift did not correspond with field maintenance visits which occurred on Aug 8 and Aug 21. The shift did correspond to a change in weather pattern from 12 hot, dry days (maximum air temperatures ranging from 27.9 to 33.7 degrees Celsius and no precipitation (Environment Canada "Terrace A" weather station, http://climate.weather.gc.ca/climate_data/daily_data_e.html?StationID=51037)) to cooler air temperatures (<20°C) and several mm of rainfall (4mm on Aug 12 and 13). Daily average water temperature at 2 m below the surface peaked at 20.5°C on August 13 (Manta data). There were upward shifts in pH in End Lake and West Lake around the same time, but not of the same magnitude as in Little End Lake. An hypothesis is the change in pH in Little End Lake was due to an episodic increase in photosynthetic rate that would shift pH upwards but cause of a change in photosynthetic rate is unknown.*

DRAFT

Bennet and Perrin (2018, p.29)

> *Similar to the pattern observed in 2016, a sharp drop in pH was observed among the Manta sensors in Little End Lake and West Lake in late October (Figure 9, Figure 10). This change started on the 20th of October, after five days of rain that began on the 15th of October (115mm of rainfall at the Terrace Airport). Another large storm event followed (154mm of rainfall) on the 21st to 24th of October and the pH in the lakes continued to decline. In End Lake, the decline in pH following the storm was not as abrupt, indicating hydrologic and biogeochemical differences between the End Lakes (Figure 8).*

Bennet and Perrin (2018, p.29)

Table 3-5. Minimum, maximum, average and range of pH measurements taken every 30 minutes in each of End, Little End and West lakes in April to November 2017. Source: Table 10 in Bennett and Perrin (2018)

Lake	Sensor	Number of observations	Minimum pH	Maximum pH	Range of pH	Mean pH ± SD
End	pH1	8815	5.6	6.6	1.0	6.3 ± 0.1
End	pH2	8815	5.6	6.5	0.9	6.2 ± 0.1
End	pH3	8815	5.6	7.5*	1.9*	6.3 ± 0.2
Little End	pH1	8862	5.0	6.4	1.4	5.9 ± 0.2
Little End	pH2	8862	5.3	6.3	1.0	5.8 ± 0.2
Little End	pH3	8862	5.1	6.4	1.3	5.9 ± 0.2
West	pH1	8010	5.7	6.9	1.2	6.3 ± 0.2
West	pH2	8010	5.6	6.8	1.2	6.2 ± 0.2
West	pH3	8010	5.7	6.9	1.3	6.2 ± 0.2

* Extreme values on sensor pH3 in End Lake were possibly due to instrument error (Bennett and Perrin 2018).

DRAFT

Table 3-6. Mean pH results from the continuous monitors in End, Little End and West lakes for 2014, 2015, 2016 and 2017. Measurements in 2014 were for a shorter period of time (late August to late November) than in other years (April to November), and had roughly half as many observations.

Lake	Sensor	2014 Mean pH ± SD	2015 Mean pH ± SD	2016 Mean pH ± SD	2017 Mean pH ± SD	Change in mean pH from 2014 to 2017
End	pH1	6.3 ± 0.2	6.3 ± 0.2	6.3 ± 0.1	6.3 ± 0.1	0.0
End	pH2	6.3 ± 0.2	6.3 ± 0.2	6.2 ± 0.1	6.2 ± 0.1	-0.1
End	pH3	6.4 ± 0.2	6.4 ± 0.2	6.3 ± 0.1	6.3 ± 0.2	-0.1
Little End	pH1	6.1 ± 0.2	6.0 ± 0.2	6.1 ± 0.2	5.9 ± 0.2	-0.2
Little End	pH2	6.0 ± 0.2	5.9 ± 0.2	6.0 ± 0.2	5.8 ± 0.2	-0.2
Little End	pH3	6.1 ± 0.2	6.0 ± 0.2	6.1 ± 0.2	5.9 ± 0.2	-0.2
West	pH1	6.4 ± 0.2	6.4 ± 0.2	6.3 ± 0.2	6.3 ± 0.2	-0.1
West	pH2	6.2 ± 0.2	6.3 ± 0.1	6.2 ± 0.2	6.2 ± 0.2	-0.0
West	pH3	6.4 ± 0.1	6.3 ± 0.1	6.2 ± 0.2	6.2 ± 0.2	-0.2

Table 3-7. Variation in mean pH (± standard deviation) between instruments, by lake, during sampling in May to October 2017. Source: Table 11 in Bennett and Perrin (2018).

Instrument or lab	Mean pH ± sd in May to October, 2017 (n=15)		
	End Lake	Little End Lake	West Lake
WTW field pH meter	6.0 ± 0.2	5.9 ± 0.3	6.1 ± 0.2
Trent University	6.0 ± 0.1	6.0 ± 0.2	5.8 ± 0.1
ALS	6.3 ± 0.2	6.4 ± 0.2	6.2 ± 0.1
Manta sensors	6.3 ± 0.1	5.9 ± 0.3	6.3 ± 0.3
Instrument/lab effect (*P*)	<0.001	<0.001	<0.001

Analyses of data for 2015, 2016 and 2017 from the 3 intensively monitored lakes with continuous monitoring of pH show that the difference in mean August pH and mean October pH varies across years within lakes, and across lakes within years (Table 3-8). Across all lakes and years, the mean August pH was 0.02 pH units higher than the mean October pH, but there does not appear to be any consistent pattern. The results in Table 3-8 provide an indication that samples taken in August are not biased relative to samples taken in October in a particular year and therefore it appears reasonable to use data from August 2012 (without any bias correction) with sampling data collected in October of subsequent years. The results from 2017 confirm the preliminary finding in the 2016 EEM Annual Report (based only on 2015 and 2016 data). However, this analysis is still only based on three years and should be repeated in subsequent years for further confirmation of this finding.

DRAFT

DRAFT

Table 3-8. Mean pH in August vs. mean pH in October, for each of the three intensively monitored lakes with continuous pH monitoring. These values represent an averaging of all measurements from the three Manta probes within each lake during each monthly period. None of the differences are greater than the measurement error (+/- 0.2 pH units for Manta instrument). Note: the monthly averages and differences reported in this table appear not to match in some places due to rounding errors (pH values are reported to nearest 0.1 pH units, but the calculations were conducted with more significant digits).

Year	Month	Metric	Lake		
			West Lake (LAK023)	End Lake (LAK006)	Little End (LAK012)
2015	Aug	COUNT	4455	4458	4101
		MEAN pH	6.2	6.4	6.2
		SD	0.1	0.1	0.2
	Oct	COUNT	4455	4455	4458
		MEAN pH	6.3	6.2	5.9
		SD	0.1	0.1	0.1
		DIFF (Aug-Oct pH)	-0.0	0.1	0.2
2016	Aug	COUNT	4452	4449	4452
		MEAN pH	6.2	6.3	6.0
		SD	0.1	0.1	0.2
	Oct	COUNT	4455	4455	4245
		MEAN pH	6.1	6.3	6.2
		SD	0.1	0.1	0.0
		DIFF (Aug-Oct pH)	0.1	-0.0	-0.2
2017	Aug	COUNT	4455	4314	4458
		MEAN pH	6.1	6.3	5.9
		SD	0.1	0.1	0.3
	Oct	COUNT	3945	3948	3942
		MEAN pH	6.1	6.3	6.0
		SD	0.2	0.1	0.1
		DIFF (Aug-Oct pH)	0.0	-0.1	-0.1
AVG. DIFF (Aug-Oct pH)			0.02		

3.4 Inter-annual Changes

Inter-annual changes in pH, Gran ANC, SO_4^{2-}, DOC, sum of base cations, chloride, and calcium are shown in terms of absolute change in Table 3-9, Table 3-10, and Table 3-11 and in terms of relative change in Table 3-12, Table 3-13, and Table 3-14. Changes are shown for six time periods of comparison: 2012-2013, 2013-2014, 2014-2015, 2015-2016, 2016-2017, and 2012-2017. 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 taken for a given lake in a given year[7].

---

[7] This represents a change in practice from the 2013/2014 and 2015 Annual Reports, in which annual sampling values (and therefore intra-annual changes) were based only on the single samples taken on the day(s) in which sampling was conducted across all of the lakes. When the monitoring plan was expanded to include additional intra-annual sampling for some lakes in October (and sometimes November), these data were used to better understand intra-annual variability and help provide context for the inter-annual patterns observed.

Figure 3-3 and Figure 3-4 show the changes in the same water chemistry parameters graphically. These figures allow better visualization of the distribution and variability in the observed changes between 2016 and 2017. Although the tables show changes for other periods as well, these figures have only been included for the changes from 2016 to 2017. Changes from 2016 to 2017 in particular are examined in more detail, in the context of expected changes based on the Evidentiary Framework, in the Discussion (Section 4).

Appendix 2 provides a detailed set of figures showing the inter-annual changes in major water chemistry metrics (Gran ANC, base cations, calcium, SO_4^{2-}, chloride, pH and DOC) for each of the EEM lakes across the six years of annual monitoring (2012-2017). Similar figures are also included for the three control lakes based on their four years of annual monitoring (2013 and 2015-2017).

However, as stated in Section 2.4, annual changes should be interpreted with substantial caution due to the combination of large natural variation (both within and between years) and limitations on measurement precision. The power analyses conducted and reported in the 2015 EEM Annual Report illustrated that *multiple* years of observations are required to reliably detect changes in mean pH, Gran ANC and SO_4; it is risky to draw conclusions based only on annual changes. We provide further discussion of these results in section 4.

DRAFT

Table 3-9. Inter-annual changes in pH, Gran ANC and SO_4^{2-} for EEM lakes, 2012-2017. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	pH (TU)						Gran ANC (µeq/L)						SO4* (µeq/L)					
From	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012
To	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017
LAK006	0.4	-0.1	-0.1	0.0	0.0	0.2	3.3	9.9	-6.5	-5.5	1.1	2.3	3.0	-2.3	-0.7	0.4	2.5	2.9
LAK012	0.6	-0.3	-0.1	0.3	-0.1	0.4	6.5	5.2	-2.9	-0.1	-7.6	1.2	5.2	4.5	1.7	-8.0	5.0	8.4
LAK022	0.2	0.1	-0.1	-0.1	0.0	0.1	8.5	10.5	-11.3	-1.1	-0.3	6.3	16.9	-9.3	-5.3	1.7	4.9	8.8
LAK023	0.2	0.0	0.0	0.0	-0.1	0.2	4.0	8.3	-2.1	-2.1	0.6	8.7	5.0	-5.1	-3.8	-2.4	-2.6	-8.9
LAK028	0.2	0.1	-0.2	-0.2	-0.2	-0.2	8.8	17.8	-11.8	-15.7	-5.0	-5.9	71.2	-33.7	-23.3	56.7	22.2	93.1
LAK042	0.8	-0.4	0.3	0.0	-0.2	0.5	41.4	-8.5	1.3	0.2	-11.7	22.7	-0.5	-1.8	-0.2	-0.5	3.5	0.6
LAK044	0.3	0.1	0.0	-0.2	0.1	0.2	7.3	-2.7	0.3	-2.1	3.0	5.8	0.0	-1.6	-0.9	0.4	0.4	-1.7
Total Lakes with Increase	**7**	**3**	**3**	**1**	**1**	**6**	**7**	**5**	**2**	**1**	**3**	**6**	**5**	**1**	**1**	**4**	**6**	**5**
Total Lakes with Decrease	**0**	**4**	**4**	**6**	**6**	**1**	**0**	**2**	**5**	**6**	**4**	**1**	**2**	**6**	**6**	**3**	**1**	**2**

LAK007	0.0	0.1	-0.1	0.0	0.0	0.0	24.5	-16.4	119.9	-197.0	13.0	-56.0	15.1	-35.8	14.9	1.1	0.4	-4.3
LAK016	0.4	0.0	0.0	-0.2	0.1	0.3	28.3	8.8	7.4	-19.2	-11.1	14.1	17.9	-8.7	-7.2	4.0	-1.8	4.1
LAK024	[1]	[1]	-0.2	0.1	-0.1	0.3	[1]	[1]	-29.1	20.1	-46.5	117.2	[1]	[1]	-2.4	4.5	-4.3	10.0
LAK034	0.1	-0.1	-0.1	-0.1	-0.1	-0.3	111.0	-5.4	-27.1	-26.2	-15.2	37.1	14.0	-21.1	-16.1	-0.9	0.1	-24.0
Total Lakes with Increase	**2**	**2**	**1**	**1**	**2**	**3**	**3**	**1**	**2**	**1**	**1**	**3**	**3**	**0**	**1**	**3**	**2**	**2**
Total Lakes with Decrease	**1**	**1**	**3**	**3**	**2**	**1**	**0**	**2**	**2**	**3**	**3**	**1**	**0**	**3**	**3**	**1**	**2**	**2**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-10. Inter-annual changes in DOC, base cations, and chloride for EEM lakes, 2012-2016. The differences between subsequent years and across the full record of sampling are shown. DOC = dissolved organic carbon, ΣBC = sum of base cations (i.e., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	DOC (mg/L)						∑ BC* (µeq/L)						Cl (µeq/L)					
From	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012
To	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017
LAK006	-0.4	0.6	0.1	0.3	-0.4	0.3	-3.0	8.0	1.2	2.1	3.7	11.9	2.9	-0.6	-1.5	-1.1	-0.1	-0.3
LAK012	-0.4	2.0	1.2	-2.4	0.1	0.6	-11.8	7.3	8.1	-11.2	3.2	-4.4	10.5	-4.4	0.8	-5.4	1.3	2.8
LAK022	0.9	-0.6	0.6	0.4	-0.8	0.6	11.0	4.9	-6.2	6.7	-5.0	11.4	5.4	-3.3	-1.1	0.0	-0.8	0.1
LAK023	-0.1	1.6	-0.3	0.5	-0.4	1.3	-2.1	15.2	-5.5	-1.2	-1.8	4.6	3.0	-1.3	0.1	-1.3	-0.7	-0.3
LAK028	2.2	-1.1	2.2	0.0	-0.8	2.4	48.4	4.4	-15.9	31.8	10.8	79.5	11.7	-6.7	-2.0	1.0	-1.3	2.7
LAK042	-3.5	0.9	-2.3	1.5	1.7	-1.6	7.6	-5.3	3.7	8.1	2.6	16.6	1.6	4.1	-5.4	0.7	-0.5	0.6
LAK044	-0.2	0.3	-0.2	0.4	-0.5	-0.2	1.0	2.1	2.9	-2.1	0.2	4.2	3.3	-2.9	0.0	0.2	-0.2	0.3
Total Lakes with Increase	**2**	**5**	**4**	**6**	**2**	**5**	**4**	**6**	**4**	**4**	**5**	**6**	**7**	**1**	**2**	**3**	**1**	**5**
Total Lakes with Decrease	**5**	**2**	**3**	**1**	**5**	**2**	**3**	**1**	**3**	**3**	**2**	**1**	**0**	**6**	**4**	**3**	**6**	**2**
LAK007	-0.5	0.6	-0.5	0.5	-0.5	-0.4	-51.9	63.5	-7.8	35.1	-93.5	-54.6	11.7	-17.1	4.8	1.4	0.6	1.4
LAK016	0.5	-0.2	0.3	0.8	-1.0	0.5	0.8	13.7	7.8	-2.1	-17.9	2.3	6.0	-3.0	-0.6	-0.3	-1.1	1.0
LAK024	[1]	[1]	0.5	0.5	-0.7	0.7	[1]	[1]	-2.8	57.7	-50.9	174.4	[1]	[1]	-6.8	11.0	-12.4	30.3
LAK034	0.1	2.4	0.5	0.0	-1.5	1.5	56.0	8.6	-32.3	-21.8	-34.5	-23.9	2.5	-1.8	-0.3	-0.8	-0.8	-1.3
Total Lakes with Increase	**2**	**2**	**3**	**4**	**0**	**3**	**2**	**3**	**1**	**2**	**0**	**2**	**3**	**0**	**1**	**2**	**1**	**3**
Total Lakes with Decrease	**1**	**1**	**1**	**0**	**4**	**1**	**1**	**0**	**3**	**2**	**4**	**2**	**0**	**3**	**3**	**2**	**3**	**1**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-11. Inter-annual changes in calcium for EEM lakes, 2012-2017. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	Ca* (μeq/L)					
From	2012	2013	2014	2015	2016	2012
To	2013	2014	2015	2016	2017	2017
LAK006	-3.2	4.6	0.6	0.3	2.2	4.5
LAK012	-9.7	4.5	5.5	-10.2	0.7	-9.2
LAK022	7.0	3.4	-4.4	4.0	-4.0	6.0
LAK023	-2.3	12.2	-3.2	-3.6	0.6	3.8
LAK028	37.6	0.8	-9.4	18.2	7.8	54.9
LAK042	8.7	-5.5	0.2	5.9	0.5	9.8
LAK044	0.9	0.0	2.0	-1.6	-0.4	1.0
Total Lakes with Increase	**4**	**5**	**4**	**4**	**5**	**6**
Total Lakes with Decrease	**3**	**2**	**3**	**3**	**2**	**1**

LAK007	-46.2	50.8	-10.2	34.9	-99.8	-70.5
LAK016	-3.2	8.0	8.5	-3.5	-13.4	-3.6
LAK024			-1.7	46.0	-46.9	126.4
LAK034	33.4	8.7	-15.0	-16.4	-24.4	-13.7
Total Lakes with Increase	**1**	**3**	**1**	**2**	**0**	**1**
Total Lakes with Decrease	**2**	**0**	**3**	**2**	**4**	**3**

DRAFT

Table 3-12. Inter-annual changes (%) in pH, Gran ANC and SO_4^{2-} for EEM lakes, 2012-2016. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	pH (TU)						Gran ANC (mg/L)						SO4* (µeq/L)					
From	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012
To	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017
LAK006	6%	-1%	-1%	0%	0%	3%	13%	34%	-17%	-17%	4%	9%	26%	-16%	-5%	3%	22%	26%
LAK012	12%	-5%	-1%	5%	-2%	8%	11%	8%	-4%	0%	-12%	2%	84%	40%	11%	-46%	53%	137%
LAK022	4%	2%	-2%	-1%	0%	2%	31%	29%	-24%	-3%	-1%	23%	56%	-20%	-14%	5%	14%	29%
LAK023	4%	-1%	0%	0%	-1%	3%	20%	35%	-7%	-7%	2%	44%	26%	-21%	-20%	-16%	-21%	-47%
LAK028	5%	2%	-4%	-3%	-4%	-4%	[1]	372%	-52%	-146%	[1]	[1]	125%	-26%	-25%	80%	17%	164%
LAK042	17%	-6%	6%	0%	-4%	11%	[1]	-40%	10%	1%	-84%	[1]	-7%	-31%	-5%	-13%	106%	9%
LAK044	5%	2%	0%	-4%	1%	4%	576%	-32%	6%	-34%	73%	454%	0%	-26%	-19%	11%	10%	-27%
Total Lakes with Increase	**7**	**3**	**3**	**1**	**1**	**6**	**5**	**5**	**2**	**1**	**3**	**5**	**5**	**1**	**1**	**4**	**6**	**5**
Total Lakes with Decrease	**0**	**4**	**4**	**6**	**6**	**1**	**0**	**2**	**5**	**6**	**3**	**0**	**2**	**6**	**6**	**3**	**1**	**2**

LAK007	-1%	2%	-1%	0%	0%	0%	2%	-1%	8%	-13%	1%	-4%	29%	-54%	49%	2%	1%	-8%
LAK016	6%	1%	0%	-3%	1%	6%	41%	9%	7%	-17%	-12%	21%	46%	-15%	-15%	10%	-4%	11%
LAK024	[2]	[2]	-3%	1%	-1%	4%	[2]	[2]	-6%	5%	-10%	39%	[2]	[2]	-7%	13%	-11%	40%
LAK034	2%	-2%	-2%	-2%	-1%	-5%	112%	-3%	-13%	-15%	-10%	37%	58%	-55%	-95%	-100%[3]	[3]	-100%
Total Lakes with Increase	**2**	**2**	**1**	**1**	**2**	**3**	**3**	**1**	**2**	**1**	**1**	**3**	**3**	**0**	**1**	**3**	**1**	**2**
Total Lakes with Decrease	**1**	**1**	**3**	**3**	**2**	**1**	**0**	**2**	**2**	**3**	**3**	**1**	**0**	**3**	**3**	**1**	**3**	**2**

[1] LAK028 and LAK042 had negative ANC values in 2012 and therefore the percentage change could not be properly calculated. LAK028 also had negative ANC values in 2016 and 2017.

[2] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

[3] The resulting SO_4^{2-} concentration for LAK034 for 2016 after correcting for marine influence was calculated as less than zero. Therefore the relative change from 2015 to 2016 was calculated as -104%. This value has been adjusted to -100%. The percent change from 2016 to 2017 could not be calculated due to the negative value in 2016.

Table 3-13. Inter-annual changes (%) in DOC, base cations and chloride for EEM lakes, 2012-2017. The differences between subsequent years and across the full record of sampling are shown. DOC = dissolved organic carbon, ΣBC = sum of base cations (e.g., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	DOC (mg/L)						∑ BC* (µeq/L)						Cl (µeq/L)					
From	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012	2012	2013	2014	2015	2016	2012
To	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017	2013	2014	2015	2016	2017	2017
LAK006	-10%	19%	3%	8%	-9%	8%	-5%	14%	2%	3%	5%	20%	51%	-7%	-18%	-16%	-3%	-6%
LAK012	-9%	47%	20%	-32%	3%	12%	-10%	7%	7%	-9%	3%	-4%	254%	-30%	8%	-49%	24%	68%
LAK022	17%	-9%	11%	6%	-12%	10%	11%	5%	-5%	6%	-4%	12%	78%	-27%	-13%	0%	-11%	2%
LAK023	-3%	40%	-5%	9%	-7%	30%	-3%	24%	-7%	-2%	-3%	7%	67%	-18%	1%	-20%	-14%	-6%
LAK028	45%	-16%	36%	0%	-10%	50%	66%	4%	-13%	29%	8%	109%	193%	-38%	-18%	11%	-13%	44%
LAK042	-26%	9%	-21%	18%	18%	-12%	14%	-9%	7%	14%	4%	31%	26%	53%	-45%	11%	-7%	9%
LAK044	-12%	17%	-11%	27%	-23%	-9%	7%	14%	17%	-10%	1%	30%	59%	-33%	0%	4%	-3%	6%
Total Lakes with Increase	**2**	**5**	**4**	**6**	**2**	**5**	**4**	**6**	**4**	**4**	**5**	**6**	**7**	**1**	**2**	**3**	**1**	**5**
Total Lakes with Decrease	**5**	**2**	**3**	**1**	**5**	**2**	**3**	**1**	**3**	**3**	**2**	**1**	**0**	**6**	**4**	**3**	**6**	**2**
LAK007	-84%	610%	-65%	208%	-68%	-59%	-3%	4%	-1%	2%	-6%	-4%	48%	-47%	25%	6%	2%	6%
LAK016	14%	-4%	8%	19%	-20%	13%	0%	8%	4%	-1%	-10%	1%	95%	-24%	-6%	-3%	-13%	16%
LAK024	[1]	[1]	30%	23%	-25%	48%	[1]	[1]	-1%	11%	-9%	51%	[1]	[1]	-10%	19%	-18%	111%
LAK034	3%	51%	7%	0%	-20%	33%	28%	3%	-12%	-9%	-16%	-12%	42%	-21%	-4%	-14%	-16%	-22%
Total Lakes with Increase	**2**	**2**	**3**	**4**	**0**	**3**	**2**	**3**	**1**	**2**	**0**	**2**	**3**	**0**	**1**	**2**	**1**	**3**
Total Lakes with Decrease	**1**	**1**	**1**	**0**	**4**	**1**	**1**	**0**	**3**	**2**	**4**	**2**	**0**	**3**	**3**	**2**	**3**	**1**

[1] LAK024 was not sampled in 2013, therefore change for 2012-13 and 2013-14 cannot be calculated.

Table 3-14. Inter-annual changes (%) calcium for EEM lakes, 2012-2017. The differences between subsequent years and across the full record of sampling are shown. The * indicates that the ionic concentrations have been corrected for marine influence. Numbers shown are the value in the later year minus the value in the earlier year.

	Ca* (μeq/L)					
From	2012	2013	2014	2015	2016	2012
To	2013	2014	2015	2016	2017	2017
LAK006	-11%	17%	2%	1%	7%	15%
LAK012	-13%	7%	8%	-14%	1%	-12%
LAK022	12%	5%	-6%	6%	-6%	10%
LAK023	-6%	33%	-6%	-8%	1%	10%
LAK028	79%	1%	-11%	24%	8%	116%
LAK042	118%	-35%	2%	55%	3%	133%
LAK044	14%	0%	26%	-16%	-4%	15%
Total Lakes with Increase	**4**	**5**	**4**	**4**	**5**	**6**
Total Lakes with Decrease	**3**	**2**	**3**	**3**	**2**	**1**

LAK007	-4%	4%	-1%	3%	-8%	-6%
LAK016	-3%	7%	7%	-3%	-11%	-3%
LAK024			0%	11%	-11%	46%
LAK034	28%	6%	-9%	-11%	-19%	-11%
Total Lakes with Increase	**1**	**3**	**1**	**2**	**0**	**1**
Total Lakes with Decrease	**2**	**0**	**3**	**2**	**4**	**3**

DRAFT

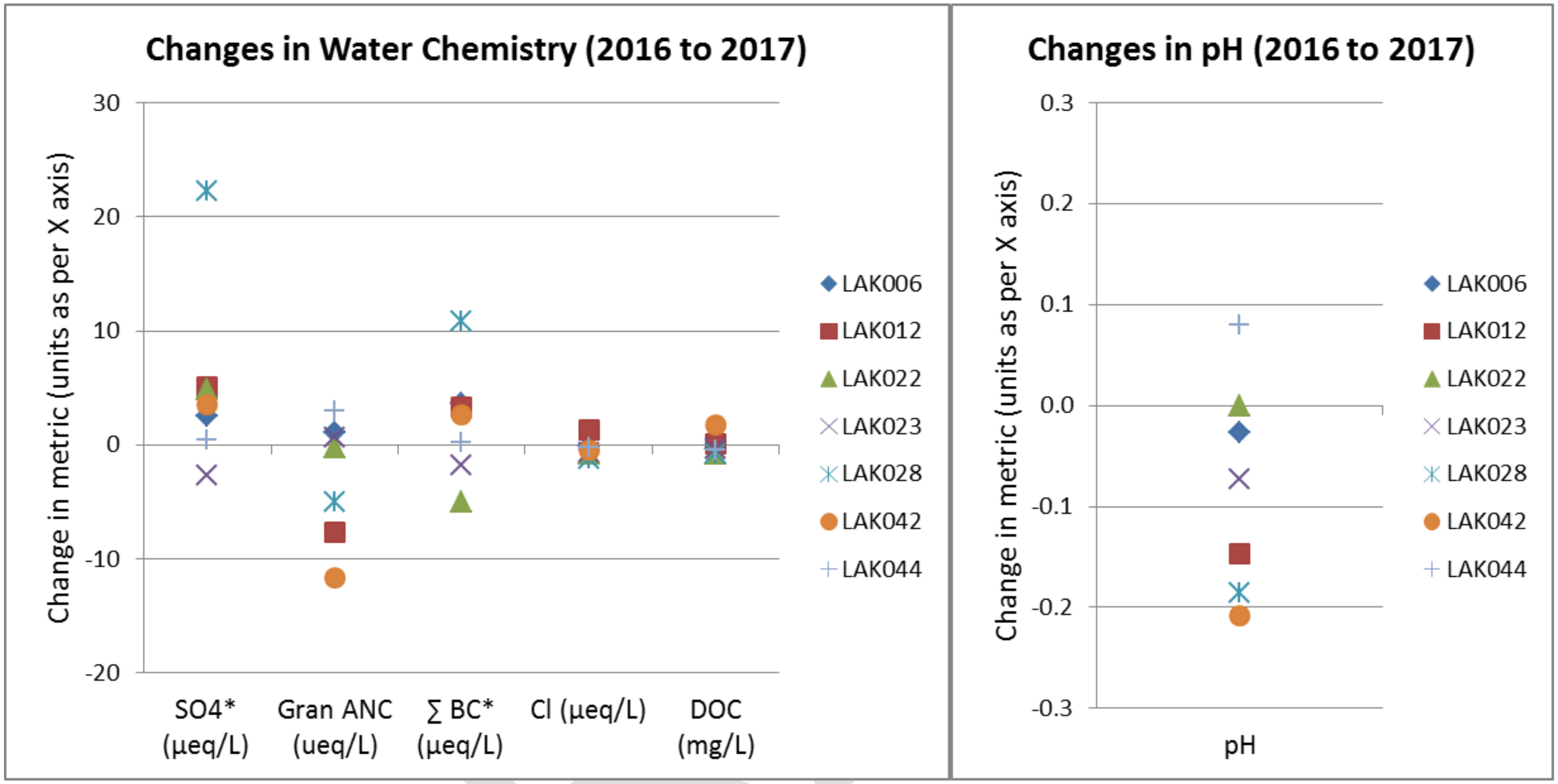


Figure 3-3. Changes in water chemistry metrics (left panel) and pH (right panel) across all of the sensitive EEM lakes, from 2016 to 2017. Values shown are the mean 2017 value minus the mean 2016 value.

DRAFT

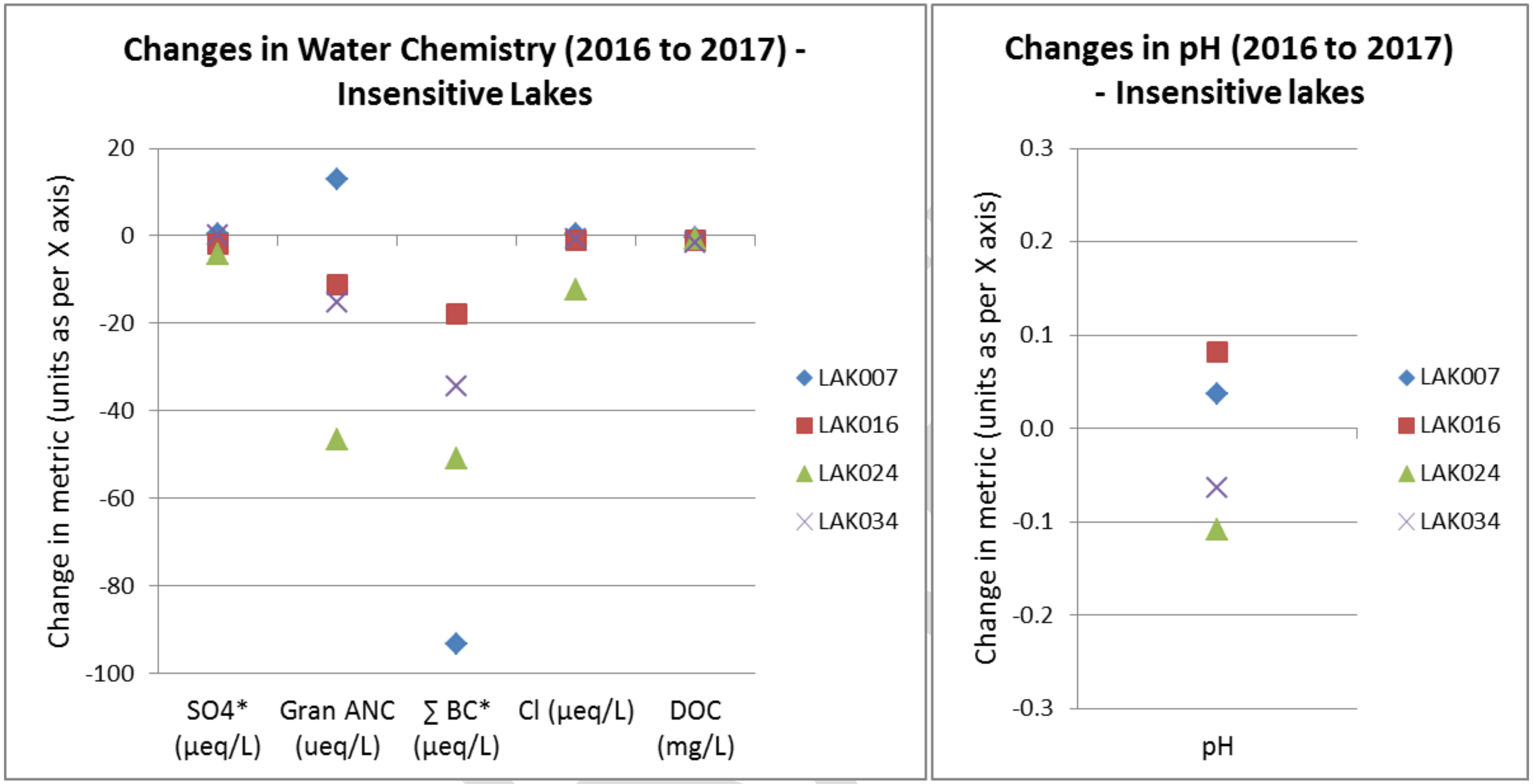


Figure 3-4. Changes in water chemistry metrics (left panel) and pH (right panel) across all of the less sensitive EEM lakes, from 2016 to 2017. Values shown are the mean 2017 value minus the mean 2016 value.

DRAFT

3.5 Episodic Acidification Studies ④

Research Project by Dr. Paul Weidman

As this project is being conducted by an external organization, the results from this work will be communicated separately as they become available.

Results from Intensive Monitoring of End Lake, Little End Lake and West Lake

The intensive monitoring of End Lake, Little End Lake and West Lake showed limited evidence of acidic episodes. As a simple screen, we reviewed the data from the continuous pH monitors for episodes in which the pH decreased by ≥ 0.3 pH units over a period ≤10 days. All three intensively monitored lakes showed a decline of 0.4 to 0.5 pH units over mid-October to the end of the sampling record in late October. This period closely aligns with the occurrence of fall storm events, as previously discussed in Section 3.3 and further described in the Limnotek report (Bennett and Perrin 2018, p.38-39):

> *The highest amount of precipitation fell in October, with a series of larger rain events starting Oct 15 and with the largest storm occurring on Oct 23 and 24 when 118mm of rain fell, accounting for 38% of the rainfall that month. Water surface elevation began to rise sharply on Oct 15 in all lakes (Figure 15 [in Limnotek report]) with levels peaking on October 24.*

As expected, lake levels of these three lakes increased in response to these storm events. The total change in surface water elevation was 36 cm in End Lake, 37 cm in Little End Lake and 46 cm in West Lake (Bennett and Perrin 2018). This pattern of a marked decrease in pH at the end of the field monitoring season corresponding with the onset of fall storms with high precipitation and corresponding increases in lake level aligns with observations from previous years.

End Lake (LAK006). The pH decreased by up to 0.3 pH units (at lowest 30-min value) over June 24 to July 1 (7 days). The pH decreased by approximately 0.4 pH units over October 18 to 28 (10 days), although this level was still almost 0.4 pH units higher than the values measured at the beginning of the sampling period in late April. Weekly chemical sampling between October 16 and 13 showed a 0.2 unit decline in pH, but no significant changes in cations or anions (i.e., concentrations of sulphate, base cations and DOC were all more or less constant). However, there was a decline in Gran ANC of about 10 µeq/L between October 16 and 23, suggesting that dilution of bicarbonate is the most likely explanation for the pH decline during this rainy week.

Little End Lake (LAK012). The pH decreased by 0.4-0.5 pH units over October 16 to 27 (11 days). However, LAK012 had also increased in pH by 0.5 pH units over 1 day in mid-August. Weekly chemical sampling between October 16 and 13 showed that sulphate, chloride and DOC all increased (by 9 µeq/L, 4 µeq/L and 2 mg/L respectively), suggesting that the large rainstorm which began on October 15 flushed these ions and associated hydrogen ions from the watershed, lowering Gran ANC (by 12 µeq/L) and pH by 0.2 units. Base cations increased by 20 µeq/L between October 16 and October 23, apparently also flushed from the watershed; base cation dilution was therefore not responsible for this acidic episode.

DRAFT

West Lake (LAK023). The pH decreased by approximately 0.3 pH units over September 9 to 11 (2 days); however, this occurred only shortly after the pH had increased by 0.4 pH units over September 2 to 5. The pH decreased by approximately 0.5 pH units October 14 to 27 (13 days). Surprisingly, the weekly chemical sampling between October 16 and 13 showed *no change* in pH (stayed at 5.9) and an *increase* in Gran ANC (by 6 µeq/L). During this week, sulphate concentrations increased by by 6 µeq/L and base cations by 7 µeq/L, roughly balancing each other. The two sources of information (Manta sensors and weekly chemistry samples) are inconsistent, unlike in the other two intensively monitored lakes. Hence it isn't clear what pattern needs to be explained.

Anderson Creek. The pH of Anderson Creek was continuously monitored over the period from May to November by Rio Tinto using a Foxboro pH meter, and during a 6-week period in July and August by Limnotek using a Manta sensor, to provide comparative data, as described in Bennett and Perrin (2018). The Manta-measured pH varied between 7.2 and 7.8 during July and August, and showed no acidic episodes. Initially the Manta showed a higher pH value than the Foxboro, but pH measurements by the two instruments converged by early August. The Foxboro measurements in May are less reliable due to lack of proper calibration (S. Zettler, Rio Tinto, pers. comm.), and there were some unexplainable fluctuations in measured flow on November 8, a day with no measured precipitation (and only 7 mm on the previous two days). We therefore focus our attention on the period from August through October (Figure 3-6).

Over the period from August through October 2017, there were a number of storms that were associated with pH declines in Anderson Creek (Figure 3-6). A major storm on September 10 (108 mm at the rain gauge which is maintained at the main entrance to the smelter site) was associated with a pH decline from 7.4 to 6.3 (Figure 3-6). After the September 10 storm there was a generally dry period, and the pH of Anderson Creek recovered back to 7.2, before declining again to 6.7 (Figure 3-6) in association with a storm on September 23-25 (which deposited a total of 35 mm of rain, 21 mm on Sept. 24). By September 29 (the date on which all EEM lakes were sampled), the pH in Anderson Creek had increased to 6.9, but not back to its 'dry-weather' level of 7.2 to 7.3.

October 2017 was a very rainy month. Storms on October 5-9 brought 69 mm of rain and storms between October 14 and 24 brought 400 mm of rain. The October 5-9 storm was associated with a decline in pH in Anderson Creek, from a maximum of 7.2 on October 5 to a minimum of 6.6 on October 9. The October 14-24 storms led to a 20-35 cm increase in lake elevations in the intensively monitored lakes (Figure 15 in Bennett and Perrin 2018), and were associated with pH declines from 7.0 to 5.7 in Anderson Creek (Figure 3-6). The pH values in Anderson Creek dropped below 6 on two occasions - October 20 and October 23 (Figure 3-6). Without full chemistry measurements we can't assess which ionic changes were most closely associated with these acidic episodes.

DRAFT

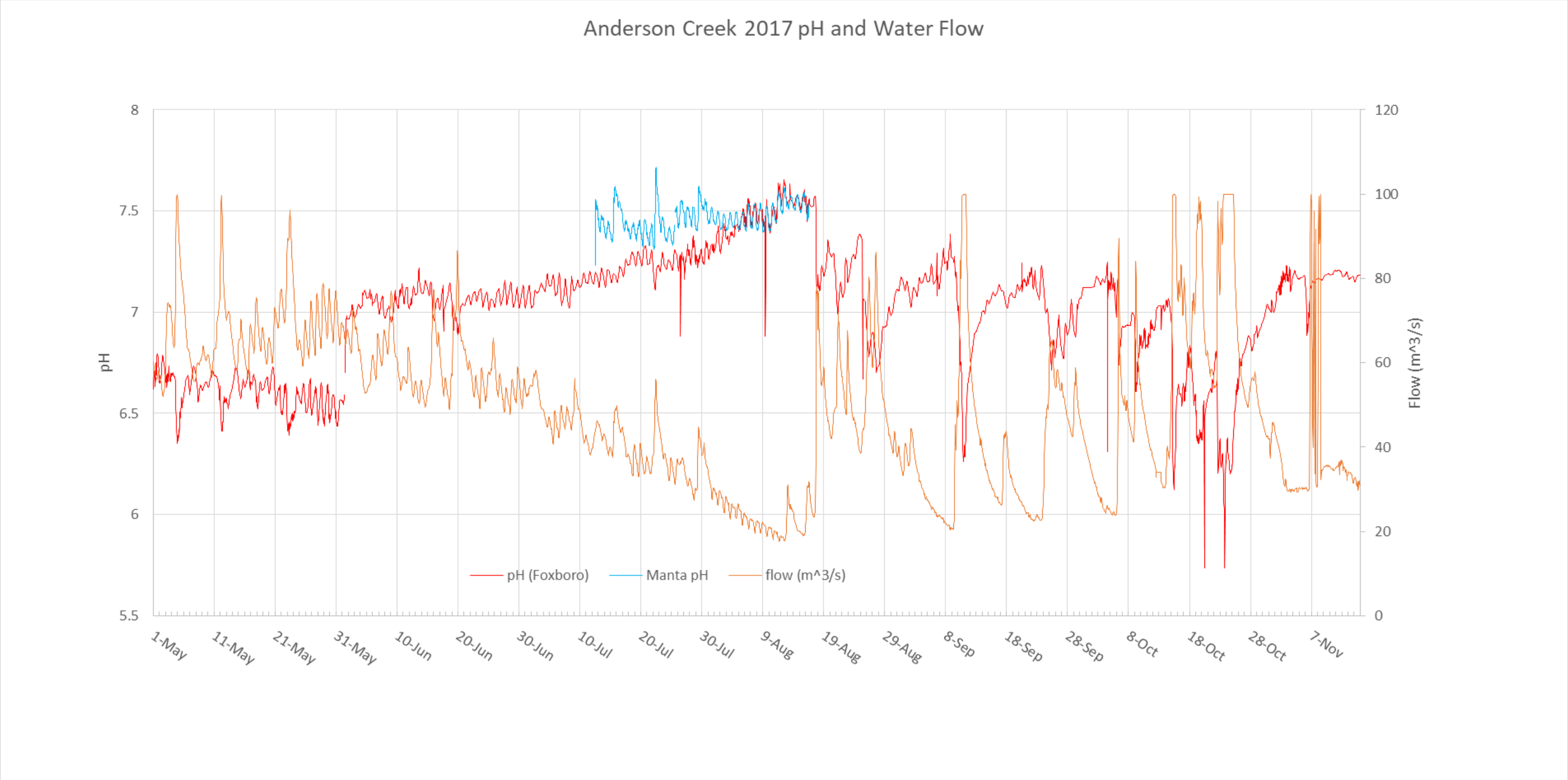


Figure 3-5. Measurements of pH (Foxboro – red line; Manta – blue line) and stream flow (orange line) in Anderson Creek from May to November. Some drift in pH measurements occurred during May due to a lack of calibration, as evidenced by the jump in pH on June 1. Appropriate calibration procedures occurred subsequent to August 1, but there was one missed calibration in June, and one missed calibration in July.

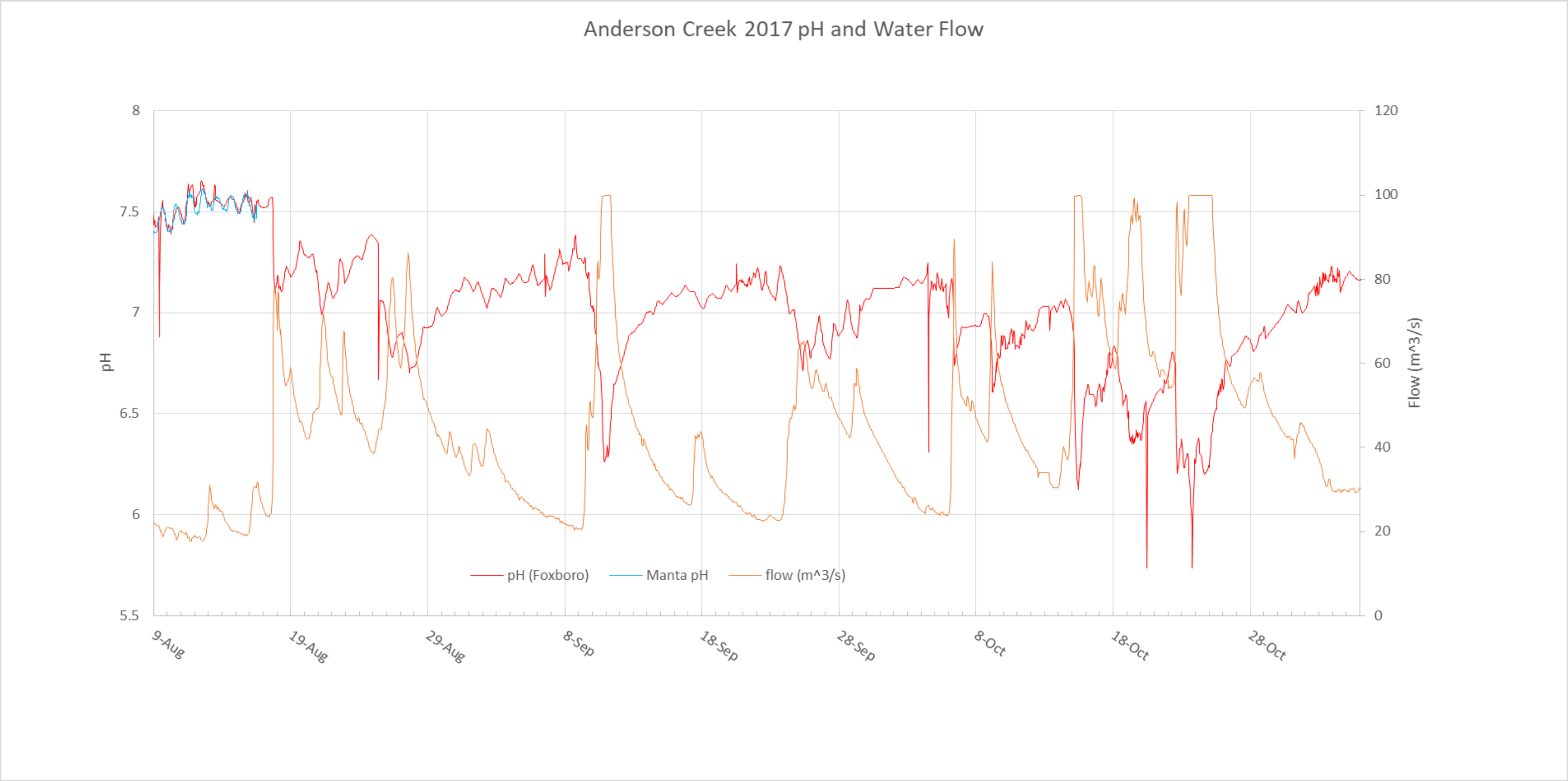


Figure 3-6. Measurements of pH (Foxboro – red line; Manta – blue line) and stream flow (orange line) in Anderson Creek during September and October.

DRAFT

3.6 Fish Sampling ③

No fish were captured in LAK028. One salamander was caught in one of the minnow traps. Additionally, no fish have been observed by the field crew during field visits to LAK028 in either 2016 or 2017.

From Bennet and Perrin (2018, p.46): "No fish were found in LAK028. The debris jam that formed a drop in the outlet stream likely produced a barrier for upstream fish movement. Further downstream, the channel was mostly a steep cascade that also would be expected to inhibit upstream fish migration. These two physical features alone may explain the lack of fish in LAK028."

3.7 Water Column Chemistry of LAK028

Water column sampling from LAK028 strongly suggests the presence of meromixis (surface and bottom waters do not mix), which was also implied by the small surface area relative to lake depth. The results of the water column sampling (see Bennett and Perrin 2018) show that thermal and chemical conditions change significantly at depths >9 m. The surface mixed layer (<9 m) had water temperature typical of north coast lakes in the fall, high dissolved oxygen that could support fish, conductivity and inorganic nitrogen concentrations typical of nutrient deficient lakes, and a surface pH (~ 5) at the low end of tolerances for aquatic organisms. The bottom water layer was anoxic and would not support fish, with higher pH, higher conductivity, a warming thermocline, an odour of H_2S, and other evidence of sulphur-reducing green and/or purple bacteria. See Bennett and Perrin (2018) for the sampling results, depth profiles of different chemistry metrics, and further interpretation of the observed patterns.

3.8 Kitimat River Water Quality

The results of the water quality sampling at the Rio Tinto intake on the Kitimat River are shown in Appendix 3. None of the results showed exceedances of the BC water quality objectives. The maximum measured sulphate concentration was less than 1% of the BC Drinking Water Guideline. Rio Tinto plans to improve the consistency in this sampling in 2018 (e.g., parameters sampled and timing of samples).

4 Discussion

4.1 Application of the Evidentiary Framework

The principles of the evidentiary framework are applied in the interpretation of the results in the subsequent two sections. The evidentiary framework suggests that sulphate concentrations should increase if there are either increased emissions of SO_2[8] or changing meteorological

DRAFT

---

[8] Mean daily SO_2 emissions increased moderately from 27.8 tons per day in 2016 to 29.7 tons per day in 2017 (a 6.8% increase).

patterns which result in increased sulphate deposition from the same SO_2 emissions. If changes in sulphate are driving acidification, then ANC and pH levels should correspondingly decrease, if all other constituents and hydrologic conditions remained unchanged. As noted in the EEM Evidentiary Framework, changes in base cations, nitrate or DOC can also help to explain observed changes in ANC and pH.

4.2 Inter-annual Changes in Lake Chemistry, 2016-2017

Some of the main patterns observed in the changes in lake chemistry between 2016 and 2017 are reported in this section. These patterns are reported in two ways:

- By water chemistry metric across lakes (i.e., how do the general patterns for sulphate, ANC and pH align with changes that would be expected if acidification were occurring), and
- By lake across metrics (i.e., how do the patterns observed in each lake align with changes that would be expected if acidification driven by smelter emissions were occurring).

As emphasized in Sections 2.4 and 3.4, annual changes should be interpreted with great caution due to the high degree of natural variation (both within and between years) and measurement precision, which result in a low power to accurately detect annual changes in lake chemistry, particularly in lake pH due its high variability.

Lake chemistry in 2017 could potentially have been affected by some of the large storm events in September and October (reflected in the flow of Anderson Creek in Figure 3-6, and in the lake levels of the intensively monitored lakes - Figure 15 in Bennett and Perrin 2018). The pH fluctuations in Anderson Creek, and in the three intensively monitored lakes, provide a general indication of the potential impacts of storm events on pH levels, though pH changes are not translatable across lakes (due to differences in neutralizing capacity and current pH levels). The sensitive lakes have lower pH levels than Anderson Creek, and therefore would be expected to have smaller pH declines due to the logarithmic nature of the pH scale.

All EEM lakes were sampled on September 29, so we examined the prior weather patterns to see if there might have been an influence on observed water chemistry. The pH fluctuations in Anderson Creek (discussed in section 3.5) indicate that the stream pH dropped from 7.2 to 6.7 in association with a storm on September 23 to 25 (which deposited 35 mm of rain). Therefore the EEM lake pH measurements on September 29th might have been a bit lower than they would have been if the preceding week had been dry weather. However, as noted above, pH declines are not translatable across lakes at different levels of acidity. The pH drop from 7.2 to 6.7 in Anderson Creek (equivalent to an increase in $[H^+]$ of 0.136 μeq/L), would only have lowered the pH of a lake at pH 5.00 (e.g., LAK028) to 4.99. It therefore seems unlikely that the rains preceding the September 29 sampling date had a significant effect on the pH measured in LAK028 on that day (5.0).

Some of the lake sampling in October overlapped with the major storms discussed above in section 3.5. An important question is whether these rainstorms created a “wet weather bias” in the apparent annual trends from 2016 to 2017, and from 2012 to 2017. As discussed above in section 3.5, there were inconsistent chemical responses to the late October storms in the three

DRAFT

intensively monitored lakes (End Lake – LAK006, Little End Lake – LAK012 and West Lake – LAK023). Sampling occurred on September 29, October 11, 17 and 24 in LAK042 and LAK044; on September 29, October 10, 18 and 26 in LAK028; and on September 29, October 9, 16 and 23 in LAK006, LAK012, and LAK023 (intensively studied lakes, discussed in section 3.5). However, as illustrated in Appendix 4, there was also no consistent pattern amongst these lakes in their chemical responses to the late October storms. In LAK028, pH declined by 0.3 pH units (from 5.0 to 4.7) between September 29 and October 10 (coinciding with the 69 mm rains of October 5-9), but didn’t change much between the October 18 and 26 sampling dates, despite the much larger 400 mm rains during this period. Between October 18 and 26 there were significant declines in sulphate, Gran ANC, Ca and total base cations, but little change in pH (less than a 0.05 pH unit decrease; see Appendix 4). The lack of consistent patterns may reflect the fact these lakes were sampled weekly, which is too infrequent a sampling interval to confidently infer the effects of rainstorms on water chemistry. Detailed studies of storm events (e.g., Wiggington et al. 1996) have sampled water chemistry on much finer time scales (e.g., hourly during rapid changes in flow).

An alternate way to explore the issue of “wet weather bias” in 2017 is to examine the Manta pH data from the intensively monitored lakes. Table 3-8 shows that there has been little change across years and lakes in the differences between August and October mean pH values in the three intensively monitored lakes. If the rainstorms in October of 2017 had exerted an unusual effect on pH readings relative to other years, we would have expected 2017 to show a larger difference between August and October pH values than has been seen in other years, but this is not the case. It is however still possible that the particular sampling dates in October, or October as a whole, had a wet weather bias. Table 4-1 shows the effects of different averaging intervals on the lake pH measured by the Manta instruments in End Lake, Little End Lake and West Lake. For these three lakes, there is no evidence that the October sampling dates for full water chemistry had significantly lower mean pH values than either the mean pH values for October 2017, or the mean pH values for the May-October period in 2017. So, at least in the intensively monitored lakes, there doesn’t appear to be a wet weather bias.

Table 4-1 Changes in lake pH over different averaging intervals in the intensively monitored lakes.

Lake	Mean pH ± SD on lake chemistry on 4 sampling dates in October 2017 [n]	Mean pH ± SD in October 2017 [n]	Mean pH ± SD over May-October 2017 [n]
End	6.3 ± 0.1 [n=570]	6.3 ± 0.1 [n=3,948]	6.3 ± 0.2 [n=26,445]
Little End	6.0 ± 0.1 [n=567]	6.0 ± 0.1 [n=3,942]	5.9 ± 0.2 [n=26,583]
West	6.1 ± 0.1 [n=561]	6.1 ± 0.2 [n=2,945]	6.2 ± 0.2 [n=24,030]

The following recommendation was put forth in the 2015 EEM Annual Report (based on the results of the power analyses):

- Wait until having collected 5 years of post-KMP monitoring data before drawing conclusions about potential changes to lake chemistry, due to the predicted low power and higher false positives (for some scenarios) in the first few years of post-KMP monitoring. At a minimum, wait until the end of the initial phase of the EEM program (3 years of post-KMP monitoring data).

DRAFT

In accordance with this recommendation and previously emphasized cautions about interpreting the annual changes in measured values, the observed changes discussed in the following two sections should be considered as preliminary indicators of potential changes that may be occurring rather than definitive patterns of change. We are reporting on the annual changes that have been measured thus far but have not yet conducted analyses on the long-term trends. The comprehensive review in 2019 will rigorously analyses the multi-year, pre-/post-KMP trends and patterns in the data.

4.2.1 Observed Changes by Metric, 2016-2017

DRAFT

Sulphate

- Sulphate would be expected to increase in lakes (if they are responsive on an annual time scale) due to increases in SO_2 emissions from KMP, or changes in wind patterns which caused changes in the amount of sulphate deposited to a given watershed (relative to past years) from the same emissions
- 6 of 7 sensitive lakes and 2 of 4 less sensitive lakes showed increases in SO_4^{2-} (corrected for influence of marine ions)
  - LAK028 had the largest increase (+22.2 µeq/L, representing an increase of 17%); this is less than a third of the magnitude of the increase from the previous year
  - The other 5 sensitive lakes with increases in SO_4^{2-} had smaller increases of 0.4 to 5.0 µeq/L (10-53%), which is a similar range to the previous year.
  - LAK042 showed an increase in SO_4^{2-} of 3.5 µeq/L, after four consecutive years of decreases, suggesting that if the lake is in fact responsive to changes in smelter emissions, the response has a lag of over 1 year, or that changes in wind patterns in 2017 brought more sulphate deposition to LAK042 compared to past years
  - The 2 less sensitive lakes with increases in SO_4^{2-} had increases of just 0.1 and 0.4 µeq/L
  - For LAK034, although SO_4^{2-} increased, the concentration is still near zero (0.06 µeq/L) after decreases in the previous three years
- Despite the moderately increase in emissions, 1 sensitive lake and 2 less sensitive lakes showed decreases in SO_4^{2-}
  - LAK023 (West Lake) decreased by 2.6 µeq/L, which is surprising given that the nearby LAK006 and LAK012 (End Lake and Little End Lake) showed increases of 2.5 and 5.0 µeq/L (respectively)
  - LAK016 and LAK024 decreased by 1.8 (-4%) and 4.3 (-11%) µeq/L, respectively
  - For LAK023, 2017 marked the 4th consecutive year of decreases, suggesting that if this lake is in fact responsive to changes in smelter emissions, the response has a lag of greater than 2 year, or that the path of SO_2 movement from the smelter, including the influence of topography and wind patterns, results in less sulphate deposition LAK023 than to LAK006 and LAK012

ANC

For the sensitive lakes, decreases in ANC would be expected (based on the evidentiary framework) to accompany increases in SO_4^{2-} concentrations

- 4 of the 7 sensitive lakes showed decreased ANC and increased SO_4^{2-}, consistent with the evidentiary framework
  - LAK012, LAK022, and LAK028 showed decreases of 0.3 to 7.6 µeq/L

    - LAK042 showed a more prominent decrease 11.7 µeq/L (-84%), which cannot be explained by the increase in sulphate (3.5 µeq/L) alone; there remains a further decrease of 8.2 µeq/L in ANC (i.e., 11.7 µeq/L – 3.5 µeq/L) which is due to some other factor. The most likely explanation for the additional decrease in ANC is the increase in DOC of 1.7 mg/l, which would contribute about 10.5 µeq/l of acidity, mediated by the addition of base cations (2.6 µeq/L). The cause of the increase in DOC is unknown, but could reflect changes in wetlands or vegetation along the shoreline and watershed of LAK042.
- 3 of the 7 sensitive lakes showed an increase in ANC
    - LAK006 and LAK023 demonstrated only very small increases in ANC (1.1 and 0.6 µeq/L or +4% and +2%, respectively)
    - In LAK044, ANC increased by 73% (3.0 µeq/L),
    - For all 3 lakes, the increase in ANC could possibly be related to decreases in DOC
    - For 2 of the lakes, the increase in ANC could also be associated with the increase in base cations
- LAK042 and LAK044 showed the largest decrease and largest increase, respectively, despite their proximate locations to each other
- Base cations are expected to increase ANC, whereas sulphate is expected to decrease ANC.
    - 4 of the 5 sensitive lakes with a negative value for {[Δ base cations] – [Δ sulphate]} also showed a decrease in ANC, which is what would be expected (LAK012, LAK022, LAK028 and LAK042). LAK012 and LAK028 also showed this pattern last year.
    - LAK006 and LAK023 showed positive values for both {[Δ base cations] – [Δ sulphate]} and ΔANC, which would also be expected (although the increases in ANC were very small). Neither of these lakes showed this pattern last year.
    - However, LAK044 had a negative value for {[Δ sum of base cations] – [Δ sulphate]} but showed an increase in ANC, which would not be expected. The increase in ANC is most likely associated with the decrease in DOC of 0.5 mg/L from 2016 to 2017 (equivalent to a decrease in organic acidity of 3.0 µeq/L). Last year this lake showed a pattern consistent with expectations (positive increases in both metrics). However, although the pattern in 2017 is inconsistent with expectations, the changes in base cations (+0.2 µeq/L) and sulphate (+0.4 µeq/L) were both very small, so one should not over-interpret this result.

For the less sensitive lakes, changes in ANC would be expected to be independent of changes in SO_4^{2-} as well as being relatively small

- ANC and SO_4^{2-} changed in the same direction for 3 of the less sensitive lakes (contrary to the evidentiary framework) and in opposite directions for the other less sensitive lake (consistent with the evidentiary framework, although that alone does not mean that ANC is being influenced by SO_4^{2-}, as discussed below
- 3 lakes showed decreases in ANC and 1 lake showed an increase (LAK007)
- Of the 3 lakes that showed decreases in ANC, all of them also showed decreased in total base cations (Table 3-9, Table 3-10), and the magnitudes of change were comparable for 2 of the lakes (LAK016 and LAK024). If sulphate were responsible for decreased ANC, one would expect to see increases in base cations due to cation exchange in the soils. The most likely explanation for the decreased ANC is a reduction in base cation supply from the watershed, due to changes in either weathering rates or transport of base cations

DRAFT

from the watershed to the lake (reflecting year to year variation in soil temperature and/or hydrology).
- Decreases in ANC were within the range of 10-12% (approximately 3-5% smaller than the previous year); LAK007 increased in ANC by 1%

pH

- For all of the lakes, changes in pH would be expected to be in the same direction as changes in ANC, as per the relationship defined by the pH-alkalinity titration curve (though the magnitude of the pH change would depend on the specific location along the curve)
    - 2 of 7 sensitive lakes have decreases of <0.05 pH units, which therefore round to zero; one of those lakes has an increase in ANC and one has a decrease
    - Of the 5 sensitive lakes with changes of >0.05 pH units, 4 of them demonstrate this expected pattern; 3 lakes show decreases in the two metrics and 1 shows increases
    - Only 2 of 4 less sensitive lakes demonstrate this expected pattern, with decreases in the two metrics
- pH decreased for 4 of 7 sensitive lakes and 2 of 4 less sensitive lakes; all of these decreases were within the accuracy of the pH meter used at Trent University (± 0.2 pH units)

Other metrics

- 9 of 11 EEM lakes decreased in DOC, which is a reversal of the dominant pattern in the previous year
    - LAK034 decreased by 1.5 mg/L
    - LAK042 increased by 1.7 mg/L (similar to last year's increase of 1.5 mg/L)
    - All other lakes changed by ≤ ±1.0 mg/L
- Base cations
    - 5 of 7 sensitive lakes increased in total base cations (all changes ≤ ±8%)
    - LAK028 increased by 10.8 µeq/L and all other lakes changed by ≤ 5.0 µeq/L
    - All 4 less sensitive lakes decreased in total base cations (-17.9 to -93.5 µeq/L or -6 to -16%)
- 9 of 11 EEM lakes decreased in chloride
    - One possible explanation for this pattern could be the very dry summer in 2017, which would have decreased the supply of chloride from the ocean
    - The magnitude of change for 10 of 11 lakes varied from -1.3 to +1.3 µeq/L
    - For LAK024, chloride decreased by 12.4 µeq/L (-18%), effectively reversing the substantial increase observed the previous year
- Calcium
    - 5 of 7 sensitive lakes increased in calcium
        - LAK028 increased by 7.8 µeq/L (+8%), but the changes in all other lakes (increases and decreases) were ≤ 4.0 µeq/L (see discussion of LAK028 below)
    - All 4 less sensitive lakes decreased in calcium (-8% to -19%)

DRAFT

4.2.2 Observed Changes by EEM Lake, 2016-2017

The observed changes for 2016 to 2017 for each lake in major lake chemistry metrics are summarized here. We then consider whether these changes are consistent with the expectations of a potential KMP-driven acidification impact (as per the patterns of changed outlined in the evidentiary framework).

After a 9-year trend in generally declining SO_2 emissions, 2016 represented a substantial increase in emissions and therefore a strong reversal of this longer term trend. Emissions in 2016 provided a very strong contrast with previous years. Mean daily SO_2 emissions in 2017 (29.7 tons per day) showed a 6.8% increase over 2016 (27.8 tons per day).

The 2016 sampling data provided the opportunity to see where lakes are responsive on annual timescale to changes in emissions. As discussed in the 2016 Annual Report, some of the lake chemistry metrics in some of the lakes appeared to be responsive to the 2016 increase in SO_2 emissions but others did not respond in 2016. Lakes that did not show an increase in sulphate concentrations in 2016 may simply be responsive on a longer timescale or are not particularly responsive to changes in emissions (due to the spatial distribution of sulphate deposition, or other factors). In previous years of the EEM program it was not possible to assess whether the generally observed decreases in sulphate were due to decreases in emission in the same year (i.e., highly responsive, little lag in effect) or a result of the many previous years of continuing decreases in emissions (i.e., less responsive, multi-year lag in effect).

However, as emphasized throughout this report, changes between individual years should be interpreted with a very high degree of caution given high natural variation and measurement error. Definitive conclusions should therefore not be drawn based on these simple inter-annual comparisons. The observed changes between 2016 and 2017, as with annual changes in previous years, should be considered preliminary indications of the patterns that may be occurring, but it will not be possible to draw stronger conclusions about these patterns and potential mechanisms until more data are collected and analyzed in the comprehensive EEM review in 2019.

Control Lakes

Monitoring results for the three control lakes (DCAS14A, NC184, NC194; see Appendices 1 and 2) show changes in sulphate concentrations between 2016 and 2017 of -5.7 µeq/L (-16%), -0.8 µeq/L (-14%), and +0.2 µeq/L (+10%), respectively, which provides additional evidence that they are not being influenced by the smelter emissions. The control lakes have not been extensively analyzed at this point but will be an invaluable component of the comprehensive statistical analyses that will be conducted in 2019. Including reference samples from beyond the predicted SO_2 plume is an important component of the monitoring design for determining whether or not observed effects are related to smelter emissions. The control lakes will increase the statistical power to accurately detect changes in the EEM lakes and will help advance our understanding of natural inter-annual variability in lake chemistry.

It should be noted that although NC184 shows a decrease in pH of 0.4 units from 2016 to 2017, that this does not mean that the KPI has been exceeded (which only apply to the EEM sensitive lakes) or that it is less suitable as a control. In fact the observations from 2017 reinforce its suitability as a control lake because the results demonstrate that NC184 is a sensitive lake outside

DRAFT

of the deposition zone of the smelter. The pH of NC184 has previously shown both an increase of 0.3 pH units and another decrease of 0.3 pH units. The change in pH from 2016 to 2017 corresponds with a large decrease in ANC that appears to be associated with a decrease in base cations of comparable magnitude, possibly related to the dry conditions in the summer of 2017 (although only one of the other two control lakes displays a comparable pattern). One of the objectives of the control lakes is to gain a better understanding of other regional patterns in lake chemistry beyond increased sulfur emissions in the plume that may be influencing lake chemistry. As discussed above, the control lakes are not being further analyzed at this point.

Sensitive EEM Lakes

LAK006. SO_4^{2-} increased by 2.5 µeq/L, but ANC increased by 1.1 µeq/L and pH remained unchanged (i.e., by < ± 0.05 pH units, well within the ± 0.2 pH units accuracy of laboratory pH measurements). The increase in ANC could be driven by the increase in base cations. The increase in ANC is approximately equal to the difference between Δ BC and Δ SO_4.

- INCONSISTENT with expectations from evidentiary framework

LAK012. SO_4^{2-} increased by 5.0 µeq/L, with a decrease in ANC (-7.6 µeq/L) and a decrease in pH (by 0.1 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), as expected with increased sulphate. Base cations also increased, but by a smaller magnitude than the increase in sulphate.

- CONSISTENT with expectations from evidentiary framework

LAK022. SO_4^{2-} increased by 4.9 µeq/L, ANC decreased by a very small margin (-0.3 µeq/L) and pH remained unchanged (i.e., by < ± 0.05 pH units, well within the ± 0.2 pH units accuracy of laboratory pH measurements). The limited change in ANC may partly reflect decreases of 0.8 mg/l in DOC (which would contribute about 5.4 µeq/L[9] of ANC and decreases of 0.8 µeq/L in chloride), which likely counterbalanced the decrease in base cations and the increase in SO_4^{2-}.

- INCONSISTENT with expectations from evidentiary framework

LAK023. Decrease in SO_4^{2-} (-2.6 µeq/L; -21%) for the fourth consecutive year, which is not expected if the lake is responsive on a 1-2 year time scale to increased sulphate emissions. ANC increased by a small amount (0.6 µeq/L; +2%) and pH decreased (by 0.1 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements). DOC decreased by 0.8 mg/L, which could remove about 4.4 µeq/L of acidity; this decrease in organic acids was supplemented by both the decrease in mineral acidity from sulphate, and the decrease in acidity associated with chloride (decreased by 1.3 µeq/L).

- INCONSISTENT with expectations from evidentiary framework

LAK028. Large increase in SO_4^{2-} (22.2 µeq/L, 17% increase) as expected with increased sulphur emissions (though larger than the 6.8% increase in emissions from 2016 to 2017) and indicating that the lake is responsive on an annual scale to such emissions. Among the acid-sensitive lakes, LAK028 demonstrated the most substantial changes between 2016 and 2017 in absolute terms, including a 22.2 µeq/L increase in sulphate concentrations and a 10.8 µeq/L increase in base cations. ANC decreased (-5.0 µeq/L) and pH decreased (by 0.2 pH units, within the ± 0.2 pH units

---

[9] Organic anions calculated based DOC using the methodology of Oliver et al. (1983), as applied throughout the STAR, EEM and the rest of this report.

DRAFT

accuracy of laboratory pH measurements), as expected for sensitive lakes with increased sulphate concentration. The increase in base cations appears to be mitigating the magnitude of the decrease in ANC. These changes appear to be a continuation of similar patterns observed in the previous year, albeit with reduced magnitudes of change.

- CONSISTENT with expectations from evidentiary framework

LAK042. SO_4^{2-} increased by 3.5 µeq/L, ANC decreased (-11.7 µeq/L) and pH decreased (by 0.2 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), as expected with increased sulphate In 2016, LAK042 had decreased in sulphate and it was hypothesized that as one of the most distant lakes from the smelter LAK042 may have a limited and/or lagged response in sulphate concentrations to increases in emissions, or may in fact not have received increased deposition between 2015 and 2016 due to variations in wind patterns. However, the observations from 2017 are consistent with the expectations based on increase emissions.

Despite having the largest absolute decrease in ANC of any of the sensitive lakes from 2016 to 2017, LAK042 still has the largest increase in ANC over the period of record from 2012 to 2017 (22.7 µeq/L; Table 3-9), which was associated with the second largest increase in base cations (16.6 µeq/L, and a decrease in DOC of 1.7 mg/L (equivalent to a decrease in organic anions of 10.5 µeq/L); Table 3-10. Given that sulphate increased by 0.6 µeq/L over this period (Table 3-9), it appears that the increase in ANC was mostly related to an increase in base cations and a decrease in organic anions.

- CONSISTENT with expectations from evidentiary framework with respect to annual changes in 2017, but INCONSISTENT with respect to changes over the period of record

LAK044. SO_4^{2-} increased by 0.4 µeq/L, ANC increased by 3.0 µeq/L and pH increased by 0.1 pH units (within the ± 0.2 pH units accuracy of laboratory pH measurements). The changes in ANC and pH are consistent with each other but not with the increase in SO_4^{2-}, albeit that SO_4^{2-} increased by only a very small margin. LAK044 is also one of the most distant lakes from the smelter and therefore may have a limited and/or lagged response in SO_4^{2-} concentrations to increases in emissions. ANC does not appear to be responding to changes in SO_4^{2-}, but could be responding to the decrease in DOC (small change but equivalent to a decrease in organic ions of a greater magnitude than the increase in ANC).

- INCONSISTENT with expectations from evidentiary framework

Less Sensitive EEM Lakes

The evidentiary framework is intended to identify patterns of change associated with the potential for an acidification effect driven by the increased sulphate emissions. The less sensitive lakes in the zone of increased sulphate deposition are expected to show an increase in sulphate concentrations, but are not expected to experience any acidification effect (i.e., declines in ANC and pH). Changes in ANC are expected to be relatively small and independent of changes in sulphate concentration and therefore our expectation is that the less sensitive lakes *should* be inconsistent with the evidentiary framework.

LAK007. SO_4^{2-} increased by a very small margin (0.4 µeq/L) but ANC also increased (by 13.0 µeq/L). The direction and magnitude of the change in base cations is inconsistent with the observed change in ANC. Although ANC increased, the pH remained unchanged (i.e., by < ± 0.05 pH units, well within the ± 0.2 pH units accuracy of laboratory pH measurements), which is consistent with

DRAFT

the lake being very high on the pH-ANC curve (i.e., changes in ANC are not expected to result in much change in pH). LAK007 has an ANC of about 1400 µeq/L so it is highly insensitive to acidification.

- ➢ CONSISTENT with expectations for an insensitive lake

LAK016. SO_4^{2-} decreased (-1.8 µeq/L), which is not expected with increased sulphate emissions. ANC decreased (-11.1 µeq/L), which is not consistent with a decrease in SO_4^{2-}. The decrease in ANC could be associated with the larger decrease in base cations (-17.9 µeq/L). The increase in pH (by 0.1 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements) is inconsistent with a decrease in ANC. For a less sensitive lake, pH is not expected to change much in association with changes in ANC. However, LAK016 has an ANC of about 80 µeq/L so it is moderately sensitive to acidification.

- ➢ CONSISTENT with expectations for a moderately sensitive lake

LAK024. SO_4^{2-} decreased (-4.3 µeq/L), which is not expected with increased sulphate emissions. ANC decreased (-46.5 µeq/L), which is not consistent with a decrease in SO_4^{2-}. The decrease in ANC is very likely associated with the decrease in base cations (-50.9 µeq/L), which is of very similar magnitude. The decrease in pH (by 0.1 pH units, within ± 0.2 pH units accuracy of laboratory pH measurements) is consistent with the change in ANC but the change in ANC is clearly not being driven by sulphate. LAK024 has an ANC of about 500 µeq/L so it is insensitive to acidification.

- ➢ CONSISTENT with expectations for an insensitive lake

LAK034. SO_4^{2-} increased but only from 0.0 to 0.1 µeq/L. The ultra-low levels of SO_4^{2-} in 2016 and 2017 suggest that LAK034 is not being influenced by the sulphate emissions. However, LAK034 is one of the most distant lakes from the smelter and therefore it is possible that it may simply have a limited/lagged response in sulphate concentrations to increases in emissions. ANC decreased (-15.2 µeq/L) and pH decreased (by 0.1 pH units, within the ± 0.2 pH units accuracy of laboratory pH measurements), but given lack of sulphate, the decrease in ANC could not be driven by sulphate. The decrease in ANC is likely associated with the corresponding decrease in base cations (-34.5 µeq/L). LAK034 has an ANC of about 135 µeq/L, so it can be considered relatively insensitive to acidification (compared to the seven acid-sensitive lakes).

- ➢ CONSISTENT with expectations for a relatively insensitive lake distant from the smelter

DRAFT

4.2.3 Observed Changes in LAK028

The data and analyses from the STAR and EEM program have thus far suggested that LAK028 has the highest potential risk of acidification due to KMP. The data indicate that both Gran ANC and pH increased over the period from 2012 to 2014 (as the old smelter was decommissioned, and SO_2 emissions declined), but that sulphate concentrations increased (contrary to expectations). Since 2015, sulphate has increased, and both pH and GranANC have declined. These changes are are consistent with a hypothesis of sulphate-driven acidification, though pH (the primary KPI) has not declined significantly below levels observed in 2012, given the measurement error of pH (± 0.2 pH units). With only two years of post-KMP observations, high natural variability and measurement error, it is not possible to make any conclusions about trends at this point. We have provided some further exploration of LAK028 in the current annual report. Table 4-2 and Figure 4-1 show the monitoring data for LAK028 for pH, ANC, and SO_4^{2-} over the period of record.

Table 4-2. pH, Gran ANC and SO_4^{2-}* for LAK028 compared to pre-KMP baseline (2012-14) and EEM thresholds.

								EEM thresholds	
	2012	2013	2014	2015	2016	2017	2012 to 2017	Value	Δ
pH	5.0	5.2	5.3	5.1	5.0	4.8	-0.2	4.7 [1]	-0.3 [1]
Gran ANC (μeq/L)	-4.0	4.8	22.6	10.8	-4.9	-9.9	-5.9	*n/a* [2]	*n/a* [2]
SO_4^{2-}* (μeq/L)	57.5	129.9	95.6	72.0	128.8	150.9	93.4	*n/a* [3]	*n/a* [3]

[1] pH is the Key Performance Indicator (KPI) in the EEM

[2] Thresholds for the EEM informative indicator of Gran ANC are under development. We are using the titration data from the laboratory methods for determining Gran ANC to determine lake-specific pH-ANC relationships, from which we can calculate the change in ANC associated with a pH decrease of 0.3 units. This work is in progress and will be ready for the comprehensive review in 2019.

[3] The appropriate thresholds for the EEM informative indicator of SO_4^{2-} will be calculated based on the Gran ANC thresholds (using the ESSA-DFO model) once we have developed the Gran ANC thresholds (as described in the previous footnote).

DRAFT

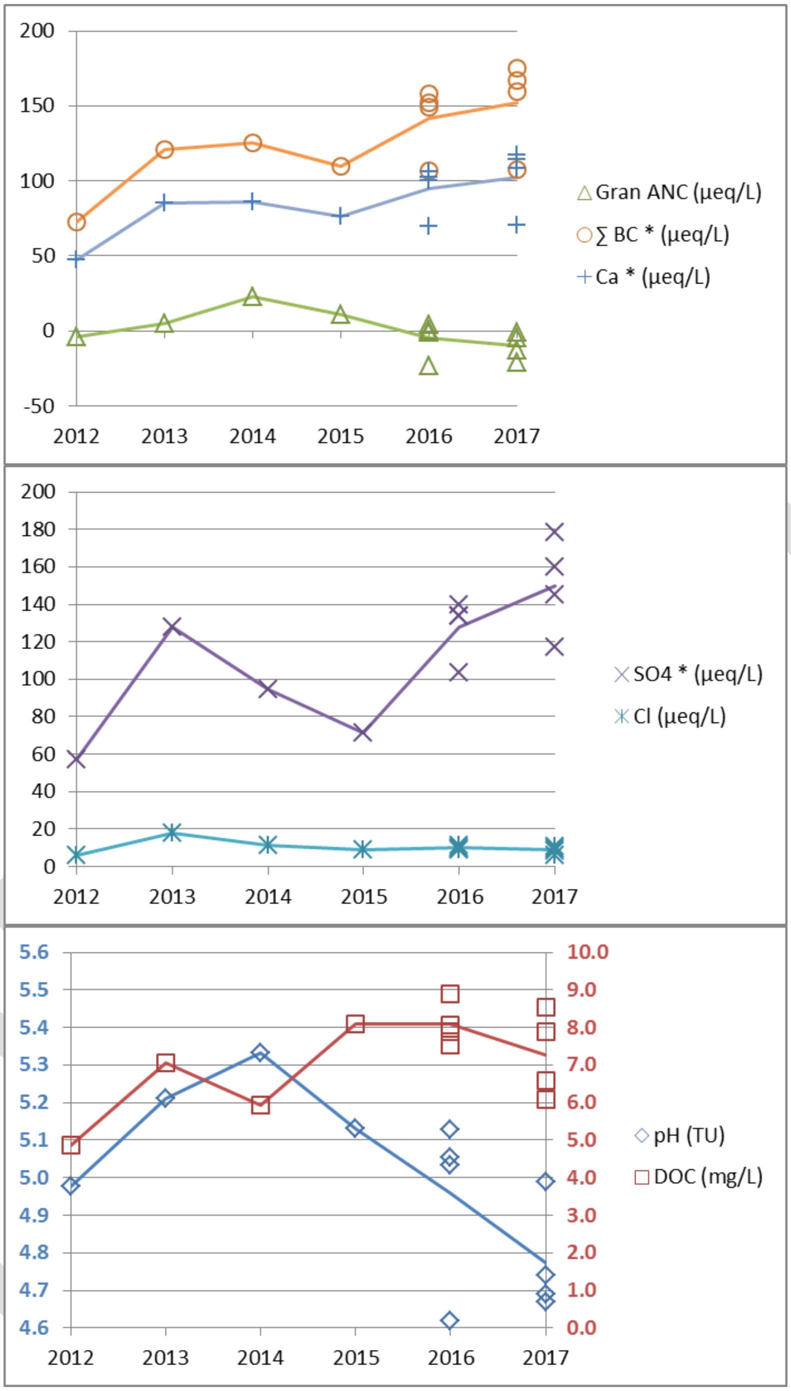


Figure 4-1. Changes in lake chemistry for LAK028 from 2012 to 2017. The solid lines represent the annual trend – i.e., based on the single annual sample in 2012-2015 and based on the mean of all within-season samples in 2016 and 2017. The points represent the values from individual sampling events in each year.

As part of the STAR, the results of the Steady State Water Chemistry model showed that LAK028 had the highest predicted exceedance of critical loads of acidity for all the STAR lakes, and was one of only 5 lakes with a predicted steady state pH that represents a decrease in pH of greater than 0.3 pH units. Geographically, it is located much closer to the smelter than any of the other sensitive lakes. The data collected in 2012 suggested that the chemistry of LAK028 had already been influenced by exposure to emissions of the pre-KMP smelter, with high sulphate and fluoride concentrations (see section 9.4.1.2.3 of STAR report, ESSA et al. 2013).

We compared LAK028 to acid-sensitive lakes from the northeast U.S., as analyzed by Sullivan et al. (1988). Figure 4-2 shows that the sulphate and ANC levels for LAK028 are comparable to those acid-sensitive lakes, except that LAK028 has slightly lower ANC due to organic acids. One indicator of acidification is the ratio of SO_4^{2-} * to total base cations (a ratio > 1 is indicative of acidification), as described in Sullivan et al. (1988). In LAK028, this ratio was < 1 in all years except for 2013 (Table 4-3), but it has been increasing in recent years, up to 0.98 in 2017, meaning it is at the threshold for indicating acidification. The monitoring data shows that base cations are increasing as sulphate increases, neutralizing some of the H+ associated with the SO_4^{2-} *.

There are two ways of estimating the proportion of deposited acidity that was neutralized between 2016 and 2017. First, one can compute the F-factor (Δ Base $\text{Cations}_{2016\text{-}2017}$ / Δ $\text{Sulphate}_{2016\text{-}2017}$). From the data in Table 4-3, $F_{2016\text{-}2017}$ is estimated at 0.49 [10]. From this method, one can infer that 49% of the acidity deposited between 2016 and 2017 was neutralized through increases in base cations. This is marginally higher than the F-factor that was assumed for the STAR (0.44), indicating a slightly higher level of acid neutralization by cation exchange, but lower than the F-factor calculated last year for 2015-2016 (0.56); however these values are still very similar. Looking over the time period from 2015 to 2017 generates an estimated F-factor of 0.54, very similar to that computed for 2015-2016 (0.56).[11]

The second way of estimating the proportion of deposited acidity that was neutralized between 2016 and 2017 is to compare the decrease in Gran ANC (4.97 µeq/L) to the increase in SO_4^{2-} (22.20 µeq/L). If there were no mechanisms of acid neutralization, and no other changes in water chemistry, the decrease in Gran ANC would equal the increase in SO_4^{2-}. This comparison implies that 78%[12] (74% when using the change from 2015 to 2017) of the deposited acidity was neutralized (through one neutralizing process or another). One possible explanation for the difference between the two methods described above is that some of the deposited sulphate was neutralized by sulphate reduction, which has been described by Baker et al. (1986) and Kelly et al. (1987), and used in acidification modelling by Marmorek et al. (1990). The water column sampling conducted in LAK028 in 2017 (Section 3.7) provides indirect evidence that sulphur reduction is occurring in the lake (i.e., sampling from depths below 9 m indicate presence sulphur reducing bacteria, odour of H_2S, and very low measurements of sulphate). Sulphate reduction could also be occurring in wetlands within the watershed of LAK028, but we have no way of confirming that this has or has not occurred. Another mechanism of acid neutralization is through conversion of hydrogen to aluminum in either watershed soils or in the lake. Between 2015 and 2016, the

---

[10] $\text{F-factor}_{2016\text{-}2017} = [\Delta \text{ Base Cations}_{2016\text{-}2017}] / [\Delta \text{ Sulphate}_{2016\text{-}2017}] = [10.82\ \mu eq/L] / [22.20\ \mu eq/L] = 0.49$

[11] $\text{F-factor}_{2015\text{-}2017} = [\Delta \text{ Base Cations}_{2015\text{-}2017}] / [\Delta \text{ Sulphate}_{2015\text{-}2017}] = [42.58\ \mu eq/L] / [78.88\ \mu eq/L] = 0.54$

[12] $(\Delta SO_4^{2-\,*} - \Delta \text{Gran ANC}) / \Delta SO_4^{2-\,*} = (22.20\ \mu eq/L - 4.97\ \mu eq/L) / 22.20\ \mu eq/L = 0.78$

DRAFT

concentration of total aluminum increased by 9 µeq/l (from 67 to 76 µeq/L) and by 2 µeq/L between 2016 and 2017.

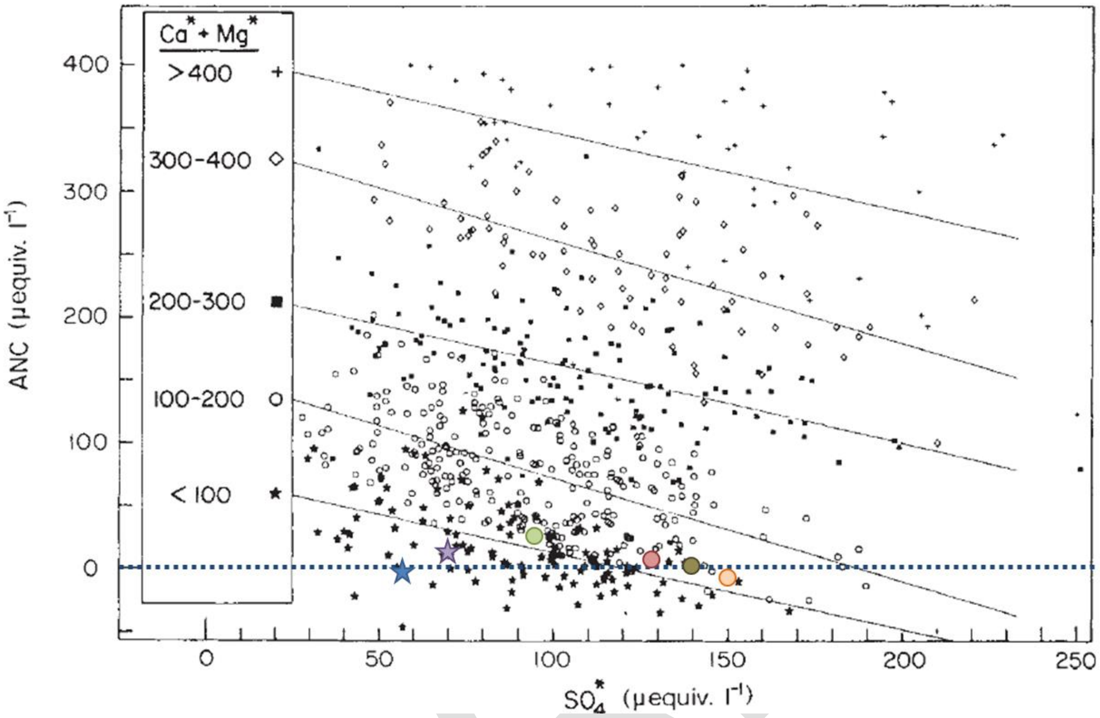


Figure 4-2. ANC and SO_4^{2-} * for LAK028 compared to acid sensitive lakes in the northeast U.S. The underlying figure is from Sullivan et al. (1988), showing the relationship between ANC and SO_4^{2-} * as stratified by the sum of marine-adjusted Ca and Mg cations. The stars represent the data for LAK028 from each of the annual sampling events (blue = 2012, red = 2013, green = 2014, purple = 2015, brown = 2016, orange = 2017). The * (e.g., Ca*, Mg*) signifies that concentrations have been adjusted to account for marine influence.

Table 4-3. Sulphate and base cation concentrations for LAK028. Values in 2016 and 2017 are mean annual values; previous years only had annual samples.

Year	SO4 * (µeq/L)	Ca * (µeq/L)	Mg * (µeq/L)	Ca*+Mg*	∑ BC * (µeq/L)	Gran ANC	SO4 * / ∑ BC *	pH
2012	56.90	47.54	9.50	57.05	72.91	-3.98	0.78	4.98
2013	128.12	85.11	18.27	103.38	121.31	4.80	1.06	5.21
2014	94.43	85.92	17.74	103.66	125.71	22.64	0.75	5.33
2015	71.11	76.52	15.66	92.17	109.83	10.79	0.65	5.13
2016	127.79	94.69	23.75	118.45	141.59	-4.93	0.90	4.96
2017	149.99	102.48	26.49	128.97	152.41	-9.89	0.98	4.77

Changes over 2012-2017. LAK028 showed a 93.1 µeq/L increase in the SO_4^{2-} * anion over 2012-2017 (Table 3-9), which was mostly balanced by a 79.5 µeq/L increase in total base cations (Table 3-10). The increase in base cations over 2012-2017 likely reflects more than just cation exchange (possibly greater weathering rates or less dilution of base cations with reduced runoff), since much of the increase occurred between 2012 and 2013 (Table 4-3). Though DOC increased by 2.4

mg/L between 2012 and 2017 (Table 3-10), with an increase of 11.4 µeq/L in organic anions[13], there has been only a smaller decrease over 2012-2017 in Gran ANC (-5.9 µeq/L, Table 3-9). Our preliminary conclusion in 2016 was that the acidity contributed by increases in SO_4^{2-} over 2012-2016 appeared to have been balanced by increases in base cations (as well as possibly other mechanisms discussed above, such as sulphate reduction), and increases in DOC did not appear to have resulted in any further acidification.

Potential Neutralization of Acidity by Sulphate Reduction

Equation 6 in Marmorek et al. (2000) estimates F_L, the fraction of acidity neutralized by sulphate reduction, as follows:

$$F_L = \frac{S_S}{R \times (r+1) + S_S} \qquad [1],$$

where:

S_S = the sulphate mass transfer coefficient (the height of the water column from which sulphate is removed each year, e.g. 0.5 m);
R = runoff in m/yr;
r = the ratio of the area of the watershed to the area of the lake

As discussed in Marmorek et al. (2000), F_L will be largest in watersheds with low runoff and a small watershed to lake area ratio, which together generate a long water residence time, giving the bacteria more time for sulphate reduction.

Table 25 of the EEM Program plan (ESSA et al. 2014) has the necessary information to apply equation [1]. Calculations indicate that the fraction of acidity neutralized by this mechanism (last column of Table 4-4) is likely quite small for all of the lakes, and only 2.4% for LAK028. Therefore despite the interesting confirmation of sulphate reduction in LAK028 by Bennett and Perrin (2018), in-lake neutralization by sulphate reduction is likely only responsible for a small fraction of the acid neutralization occurring in the watershed of LAK028. Much of the deposited acidity will flow through LAK028 without being neutralized, due to the large watershed-to-lake area ratio (10.8), and high runoff (1.58 m), which together make a large denominator in equation [1]. LAK044, which has the longest residence time of all of the lakes, is the only lake where the fraction of acidity neutralized exceeds 0.1.

DRAFT

---

[13] Based on the annual calculation of organic anions based on the methodology of Oliver et al (1983), as applied throughout the STAR and EEM.

Table 4-4. Fraction of acidity neutralized by sulphate reduction within each of the sensitive EEM lakes, based on equation 6 in Marmorek et al. (1990). Data on lake area, watershed area and runoff are from Table 25 in the EEM Program Plan (ESSA et al. 2014). Calculations for LAK028 are highlighted.

SITE_ID	Lake Area (ha)	Depth at sampling point (m)	Watershed Area (ha)	Runoff (m)	F_L (acid neutralization by SO4 reduction)
LAK006	10.25	5.7	91.2	0.88	0.054
LAK012	2.30	3.5	90.1	0.86	0.014
LAK022	5.74	10.1	39.9	0.83	0.070
LAK023	6.77	2.7	40.3	0.90	0.074
LAK028	1.02	15.5	11.9	1.58	0.024
LAK042	1.46	12.0	37.2	0.60	0.031
LAK044	2.01	15.0	9.9	0.64	0.116
LAK047	1.61	0.5	42.9	2.41	0.007
LAK054	1.52	5.1	125.3	1.61	0.004
LAK056	1.77	6.6	27.3	1.60	0.019

5 Recommendations

The 2018 sampling plan for water chemistry should follow the 2017 sampling plan. No additional changes are recommended at this time. Additional information on within-season variability in lake chemistry for LAK028, LAK042 and LAK044 (included in 2016 and 2017) will be valuable for analyzing trends over time, as will continued sampling of the control lakes, and the intensively monitored lakes.

The trends in LAK028 are of particular interest. The 2018 sampling of LAK028 will provide important additional information for assessing long term trends. LAK028 has very high year-to-year variability in both Gran ANC and pH. So far we only have two years with 4 samples during the fall index period (prior years had only one sample per year). We will have greater confidence in the apparent changes in water chemistry after collecting additional data in 2018 (i.e., another year with four samples in the fall index period), and thoroughly assessing all the data in the comprehensive 2019 report.

We recommend completing an analysis of the bathymetry of LAK028, as was done previously for End Lake, Little End Lake and West Lake. This will provide a more precise estimate of the volume of LAK028, from which we can derive more accurate estimates of the water residence time in LAK028, which will be helpful for modelling changes in its water chemistry over time.

We also recommend resampling the eight tributaries collectively called Goose Creek, six of which were sampled in 2014, and two of which were sampled in 2015. These tributaries of the Kitimat River are below the steep hill on which LAK028 is found, and are reportedly used for spawning by cutthroat trout. Resampling these tributaries will provide an indication if there have been any significant changes in the water chemistry of these streams since 2014-2015. One of these streams is acid sensitive (Goose Ck 4, Gran ANC < 50 µeq/L), two are moderately acid-sensitive

DRAFT

(Goose Creek 1 and 2, Gran ANC < 100 µeq/L), and five are insensitive to acidification (Gran ANC > 200 µeq/L), as described in ESSA (2015, 2016).

An option worthy of consideration in 2018 is to sample the benthic organisms in the Goose Creek tributaries, and compare their community composition to that expected from other streams in the region with similar attributes, using the Reference Condition Approach (RCA). RCA has been used across many parts of the province by the Ministry of Environment. The streams would be sampled at the end of summer during the period with the lowest flow.

Another option that we have considered is to sample the littoral benthos in LAK028, but we (ESSA and Limnotek) believe that sampling the Goose Creek tributaries would provide information of much greater value due to the potential use of these streams by cutthroat trout. LAK028 is inaccessible to fish due to high stream gradients, and the 2017 sampling found no fish there.

The primary future analyses of interest will be the 6-year comprehensive assessment in 2019. The EEM report (ESSA et al. 2014b, pg. 32) recommended that laboratory Gran ANC titrations be used to estimate lake-specific ANC thresholds that correspond to a pH decline of 0.3, thereby taking into account the unique mix of organic anions found in each lake. Recent work by ESSA has demonstrated how past lab reports of Gran ANC titrations can be used to derive ANC thresholds. We have acquired the lab reports from all past lake samples from Trent University, and are in the process of estimating a lake-specific mean ANC threshold (and its variation) for each EEM lake. We will complete these analyses in 2018, and use these thresholds in the comprehensive 2019 report.

6 References Cited

Baker, L. A., P.L. Brezonik, and C.D. Pollman. 1986. Model of internal alkalinity generation: sulfate retention component. Water Air Soil Pollut. 31: 89-94

Bennett, S. and C.J. Perrin. 2017. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lakes in 2016. Report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 40pp. plus appendices.

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

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Rio Tinto Alcan, Trent University, Trinity Consultants and University of Illinois. 2013. Sulphur Dioxide Technical Assessment Report in Support of the 2013 Application to Amend the P2-00001 Multimedia Permit for the Kitimat Modernization Project. Vol.2: Final Technical Report. Prepared for RTA, Kitimat, BC. 450 pp.

ESSA Technologies, J. Laurence, Risk Sciences International, Trent University, and Trinity Consultants. 2014a. Kitimat Airshed Emissions Effects Assessment. Report prepared for BC Ministry of Environment, Smithers, BC. 205 pp. + appendices.

DRAFT

ESSA Technologies, J. Laurence, Limnotek, Risk Sciences International, Trent University, and Trinity Consultants. 2014b. Sulphur Dioxide Environmental Effects Monitoring Program for the Kitimat Modernization Project. Program Plan for 2013 to 2018. Prepared for Rio Tinto Alcan, Kitimat, B.C. 99 pp.

ESSA Technologies. 2015. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project – 2013 and 2014 Annual Reports. Prepared for Rio Tinto Alcan, Kitimat, B.C. 27 pp.

ESSA Technologies Ltd. 2016. Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project – 2015 Annual Report. Prepared for Rio Tinto Alcan, Kitimat, B.C.

ESSA Technologies Ltd. 2017. Literature Review on Acidification Risk to Amphibians. Draft prepared for Rio Tinto, BC Works B.C. 43 pp. (*being finalized presently*)

Kelly, C.A., J.W.M. Rudd, R.H. Hesslein, D.W. Schindler, P.J. Dillon, C.T. Driscoll, S.A. Gherini and R.E. Hecky. 1987. Prediction of biological acid neutralization in acid-sensitive lakes. Biogeochemistry 3: 129-140.

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

Marmorek, D.R., M.L. Jones, C.K. Minns, and F.C. Elder. 1990. Assessing the potential extent of damage to inland lakes in eastern Canada due to acidic deposition. I. Development and evaluation of a simple "site" model. Can. J. Fish. Aquat. Sci. 47: 55-66.

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

Perrin, C.J and S. Bennett 2015. Rio Tinto Alcan Kitimat Modernization Project: Environmental effects monitoring of lake water quality in 2014. Data report prepared by Limnotek Research and Development Inc. for Rio Tinto Alcan Ltd. 20p.

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

Sullivan, T.J., J.M. Eilers, M.R. Church, D.J. Blick, K.N. Eshleman, D.H. Landers, and M.S. DeHann. 1988. Atmospheric wet sulphate deposition and lakewater chemistry. Nature 331:607-609.

Wigington Jr., P.J., D.R. DeWalle, P.S. Murdoch, W.A. Kretser, H.A. Simonin, J. Van Sickle, J.P. Baker. 1996. Episodic Acidification of Small Streams in the Northeastern United States: Ionic Controls of Episodes. Ecological Applications 6(2):389-407

DRAFT

DRAFT

Appendix 1: Water Chemistry Data from Annual Sampling, 2012-2016

The two tables below shows the sample results for each of the EEM lakes and control lakes from annual monitoring conducted from 2012 to 2017, including pH, dissolved organic carbon (DOC), Gran ANC, and the concentration of major anions and cations, as well as the sum of all base cations (BC). In 2013-2017, the pH of the water samples was measured by two different laboratories (Trent University and ALS).

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

Lake	Year	pH		pH		DOC		Gran ANC		SO4*		Cl		F		Ca*		Mg*		K*		Na*		∑ BC*
		TU	*SD*[1]	ALS	*SD*	mg/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L
LAK006	2012	5.8				3.6		25.7		11.4		5.8		4.5		30.3		12.5		2.9		14.9		60.6
LAK007	2012	8.0				0.6		1437.6		51.4		24.6		2.8		1272.2		157.0		19.3		55.4		1503.9
LAK012	2012	5.6				4.6		57.0		6.1		4.2		5.0		74.5		20.8		5.2		20.0		120.6
LAK016	2012	6.3				3.7		68.7		39.0		6.3		7.8		117.7		20.5		7.3		20.8		166.3
LAK022	2012	5.9				5.3		27.8		30.2		6.9		6.1		58.1		16.0		3.2		20.8		98.1
LAK023	2012	5.7				4.2		19.8		19.0		4.5		5.6		39.4		12.0		3.7		10.8		65.9
LAK024	2012	7.1				1.4		299.5		24.8		27.3		1.6		273.2		33.0		4.2		29.6		340.0
LAK028	2012	5.0				4.9		-4.0		56.9		6.1		20.7		47.5		9.5		3.1		12.8		72.9
LAK034	2012	6.7				4.5		99.4		24.1		5.8		5.8		119.3		31.6		5.8		44.9		201.7
LAK042	2012	4.7				13.2		-20.4		6.2		6.1		3.2		7.4		22.7		3.1		20.3		53.4
LAK044	2012	5.4				1.7		1.3		6.2		5.6		2.9		6.8		3.2		4.1		0.0		14.2
LAK006	2013	6.2		6.1		3.2		29.0		14.4		8.7		5.6		27.1		13.0		5.3		12.2		57.6
LAK007	2013	7.9		8.1		0.1		1462.1		66.5		36.3		3.7		1226.0		156.5		21.9		47.6		1452.0
LAK012	2013	6.3		6.1		4.2		63.5		11.3		14.7		8.2		64.8		20.3		9.2		14.6		108.9
LAK016	2013	6.7		7.2		4.2		96.9		56.9		12.3		11.5		114.4		23.9		11.2		17.6		167.1
LAK022	2013	6.2		6.1		6.2		36.4		47.1		12.4		8.7		65.1		19.2		6.0		18.8		109.1
LAK023	2013	6.0		6.0		4.0		23.8		24.1		7.5		7.4		37.1		13.3		5.1		8.3		63.9
LAK024	2013																							
LAK028	2013	5.2		5.5		7.1		4.8		128.1		17.7		32.0		85.1		18.3		5.0		13.0		121.3
LAK034	2013	6.9		7.4		4.7		210.4		38.1		8.2		10.0		152.7		41.7		9.2		54.1		257.7
LAK042	2013	5.5		5.4		9.7		21.0		5.7		7.7		3.2		16.0		22.3		3.4		19.3		61.0

DRAFT

Lake	Year	pH		pH		DOC		Gran ANC		SO4*		Cl		F		Ca*		Mg*		K*		Na*		∑ BC*
		TU	*SD*[1]	ALS	*SD*	mg/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L	*SD*	µeq/L
LAK044	2013	5.7		6.0		1.5		8.6		6.2		8.9		3.8		7.8		3.6		5.9		-2.0		15.3
Lak006	2014	6.1	*0.1*	6.6	*0.6*	3.8	*1.0*	38.8	*2.5*	12.1	*2.2*	8.1	*0.6*	4.8	*0.5*	31.7	*8.7*	14.6	*0.8*	4.7	*0.2*	14.5	*0.6*	65.5
LAK007	2014	8.1		8.0		0.7		1445.7		30.7		19.2		1.9		1276.8		156.7		20.2		61.8		1515.5
LAK012	2014	6.0	*0.2*	6.7	*0.4*	6.3	*2.2*	68.8	*15.2*	15.8	*11.6*	10.3	*4.9*	5.2	*0.5*	69.3	*3.5*	21.3	*1.3*	7.3	*1.1*	18.3	*3.6*	116.1
LAK016	2014	6.7		6.7		4.0		105.7		48.2		9.3		9.5		122.4		25.0		10.1		23.3		180.8
LAK022	2014	6.3		6.4		5.7		46.9		37.8		9.0		6.9		68.5		18.9		5.2		21.4		114.0
LAK023	2014	5.9	*0.1*	6.7	*0.6*	5.7	*1.0*	32.1	*2.5*	18.9	*2.2*	6.1	*0.6*	6.2	*0.5*	49.3	*8.7*	14.9	*0.8*	4.0	*0.2*	10.8	*0.6*	79.0
LAK024	2014	7.6		7.5		1.7		472.1		37.2		65.7		2.3		402.3		50.1		7.8		50.2		510.4
LAK028	2014	5.3		5.7		5.9		22.6		94.4		11.0		23.3		85.9		17.7		4.4		17.6		125.7
LAK034	2014	6.7		7.0		7.0		205.0		17.0		6.5		7.7		161.4		43.6		9.4		51.9		266.3
LAK042	2014	5.1		5.4		10.6		12.5		4.0		11.8		2.6		10.5		23.6		3.7		17.9		55.7
LAK044	2014	5.8		5.6		1.8		5.9		4.6		5.9		2.8		7.8		3.9		5.3		0.4		17.3
Lak006	2015	6.0	*0.1*	6.4	*0.6*	3.9	*0.3*	32.4	*0.7*	11.5	*0.7*	6.6	*0.6*	4.4	*0.2*	32.3	*0.6*	14.8	*0.3*	3.9	*0.1*	15.7	*0.6*	66.7
Lak007	2015	8.0		7.9		0.3		1565.6		45.6		24.0		2.6		1266.6		161.5		21.0		58.6		1507.7
LAK012	2015	6.0	*0.2*	6.3	*0.3*	7.5	*2.1*	65.9	*4.2*	17.6	*6.1*	11.1	*3.3*	4.7	*0.3*	74.8	*7.8*	23.2	*1.8*	8.1	*1.6*	18.0	*1.6*	124.2
LAK016	2015	6.8		6.9		4.3		113.1		40.9		8.7		8.6		130.9		25.0		9.8		22.9		188.6
LAK022	2015	6.1		6.2		6.3		35.6		32.5		7.9		5.9		64.1		18.1		4.4		21.2		107.8
LAK023	2015	5.9	*0.1*	6.2	*0.1*	5.4	*0.7*	30.0	*2.0*	15.1	*1.5*	6.2	*0.6*	5.2	*0.3*	46.1	*3.0*	13.9	*0.6*	3.8	*0.1*	9.7	*0.2*	73.5
Lak024	2015	7.4		7.5		2.2		443.0		34.7		59.0		2.1		400.5		49.3		8.7		49.0		507.6
LAK028	2015	5.1		5.3		8.1		10.8		71.1		9.0		20.5		76.5		15.7		3.2		14.4		109.8
LAK034	2015	6.6		6.7		7.6		177.8		0.9		6.2		4.7		146.5		37.1		5.3		45.1		234.0
LAK042	2015	5.4		5.5		8.3		13.8		3.8		6.5		2.3		10.7		23.1		2.5		23.0		59.3
LAK044	2015	5.8		5.8		1.6		6.2		3.7		5.9		2.7		9.8		4.4		5.5		0.5		20.3
Lak006	2016	6.0	*0.1*	6.3	*0.2*	4.2	*0.2*	26.9	*2.0*	11.8	*0.3*	5.6	*0.4*	4.2	*0.2*	32.6	*1.0*	14.8	*1.3*	4.2	*1.2*	17.2	*1.8*	68.8
Lak007	2016	8.0		8.1		0.8		1368.6		46.7		25.4		2.6		1301.5		162.8		20.2		58.3		1542.8
LAK012	2016	6.2	*0.0*	6.5	*0.2*	5.1	*0.5*	65.8	*2.3*	9.5	*1.1*	5.6	*0.3*	4.6	*0.2*	64.7	*1.7*	20.8	*1.2*	6.0	*1.2*	21.6	*1.6*	113.0
LAK016	2016	6.6		6.9		5.2		93.9		44.9		8.5		8.2		127.4		26.4		8.9		23.7		186.5
LAK022	2016	6.1		6.4		6.7		34.4		34.2		7.9		5.8		68.1		19.2		4.2		23.1		114.6
LAK023	2016	5.9	*0.0*	6.2	*0.1*	5.8	*0.2*	27.9	*3.8*	12.7	*0.4*	4.9	*0.4*	5.1	*0.2*	42.5	*1.8*	14.1	*0.9*	4.7	*1.1*	11.0	*1.5*	72.3
LAK024	2016	7.5		7.6		2.7		463.1		39.2		70.0		2.3		446.5		55.3		9.5		53.9		565.3
LAK028	2016	5.0	*0.2*	5.1	*0.2*	8.1	*0.6*	-4.9	*12.5*	127.8	*16.3*	10.0	*1.1*	26.8	*1.7*	94.7	*16.7*	23.8	*3.5*	3.7	*0.4*	19.5	*3.2*	141.6
LAK034	2016	6.5		7.1		7.6		151.6		0.0		5.4		4.4		130.0		34.3		3.8		44.1		212.3
LAK042	2016	5.4	*0.0*	5.7	*0.1*	9.8	*0.4*	14.0	*3.1*	3.3	*0.5*	7.2	*0.5*	2.2	*0.2*	16.7	*3.4*	24.7	*0.7*	2.7	*0.4*	23.3	*0.4*	67.4
LAK044	2016	5.5	*0.0*	6.0	*0.3*	2.0	*0.2*	4.1	*2.6*	4.1	*0.2*	6.1	*0.3*	2.3	*0.1*	8.2	*0.8*	4.1	*0.1*	5.5	*0.2*	0.3	*0.4*	18.2
Lak006	2017	6.0	*0.1*	6.4	*0.2*	3.8	*0.2*	27.9	*5.3*	14.4	*0.6*	5.4	*0.5*	4.2	*0.1*	34.8	*0.9*	15.6	*0.5*	4.1	*0.2*	18.0	*0.8*	72.5
LAK007	2017	8.0		8.0		0.3		1381.6		47.1		25.9		2.4		1201.7		165.2		19.9		62.6		1449.4
LAK012	2017	6.1	*0.2*	6.5	*0.1*	5.2	*1.0*	58.2	*6.5*	14.6	*5.2*	7.0	*2.4*	4.4	*0.1*	65.4	*9.0*	21.7	*2.3*	7.7	*1.9*	21.5	*1.9*	116.3
LAK016	2017	6.7		6.8		4.1		82.7		43.2		7.3		7.7		114.0		24.7		6.9		22.9		168.6
LAK022	2017	6.1		6.3		5.9		34.2		39.0		7.1		5.4		64.1		19.5		3.8		22.2		109.6
LAK023	2017	5.9	*0.0*	6.2	*0.1*	5.4	*0.1*	28.5	*4.7*	10.1	*3.4*	4.2	*0.5*	4.6	*0.1*	43.2	*4.2*	13.8	*0.7*	2.3	*0.5*	11.2	*0.6*	70.5
LAK024	2017	7.4		7.6		2.0		416.6		34.9		57.5		2.0		399.6		52.2		8.5		54.2		514.4
LAK028	2017	4.8	*0.1*	5.1	*0.1*	7.3	*1.1*	-9.9	*9.0*	150.0	*25.9*	8.7	*1.9*	27.2	*3.4*	102.5	*21.9*	26.5	*5.0*	3.5	*0.7*	19.9	*3.1*	152.4
LAK034	2017	6.4		6.8		6.0		136.5		0.1		4.5		3.4		105.6		30.3		2.7		39.1		177.8

Lake	Year	pH		pH		DOC		Gran ANC		SO4*		Cl		F		Ca*		Mg*		K*		Na*		∑ BC*
		TU	SD[1]	ALS	SD	mg/L	SD	µeq/L	SD	µeq/L	SD	µeq/L	SD	µeq/L	SD	µeq/L	SD	µeq/L	SD	µeq/L	SD	µeq/L	SD	µeq/L
LAK042	2017	5.2	*0.1*	5.4	*0.3*	11.6	*2.3*	2.3	*4.2*	6.8	*1.9*	6.7	*0.9*	2.4	*0.1*	17.1	*5.5*	26.9	*2.3*	2.8	*0.5*	23.2	*0.9*	70.0
LAK044	2017	5.6	*0.1*	6.0	*0.2*	1.6	*0.1*	7.0	*4.4*	4.5	*0.4*	5.9	*0.2*	2.2	*0.0*	7.9	*0.3*	4.2	*0.2*	5.6	*0.2*	0.7	*0.4*	18.4
NC184	2013	5.7				11.6		16.2		5.7		24.0		0.3		50.5		17.5		4.4		13.8		86.2
NC194	2013	6.6				0.7		28.0		3.6		7.6		0.3		23.2		3.4		5.2		7.4		39.2
DCAS14A	2013	6.5				1.4		50.6		33.4		9.2		0.6		63.9		10.3		10.3		6.1		90.6
NC184	2015	5.5		5.6		9.8		18.4		5.7		21.7		0.5		48.8		16.1		2.9		10.8		78.7
NC194	2015	6.5		6.5		0.8		33.0		2.3		7.3		0.5		26.9		4.4		4.3		7.9		43.4
DCAS14A	2015	6.6		6.7		0.9				35.7		7.3		0.5		77.6		12.4		11.2		9.9		111.0
NC184	2016	5.8		6.2		10.6		27.3		5.5		21.2		0.5		62.6		19.3		2.7		15.5		100.1
NC194	2016	6.4		6.6		1.6		28.7		2.3		7.9		0.5		26.4		4.3		3.8		7.9		42.4
DCAS14A	2016	6.6		6.8		1.5		57.5		36.8		8.5		0.5		77.5		11.8		10.5		9.7		109.6
NC184	2017	5.4		6.0		13.3		9.8		4.7		14.7		0.5		45.2		17.4		2.5		15.9		81.0
NC194	2017	6.4		6.4		1.0		12.4		2.5		4.8		0.5		29.9		5.7		3.6		9.9		49.1
DCAS14A	2017	6.6		6.7		1.5		51.0		31.1		5.6		0.5		68.2		11.8		9.1		9.9		99.0

[1] SD = standard deviation

DRAFT

Sampling Data in "Raw" Units

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

Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (µS/s)	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**	5.8		3.6	1.3	6.7	0.6	0.2	0.1	0.1	3.0	0.6	0.2	0.1	0.5	0.0	0.1	0.0
Lak007	**2012**	8.0		0.6	71.9	148.9	2.6	0.9	0.1	4.7	1.8	25.5	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	**2012**	5.6		4.6	2.9	12.7	0.3	0.1	0.1	0.7	3.4	1.5	0.3	0.2	0.5	0.7	0.1	0.2
LAK016	**2012**	6.3		3.7	3.4	17.9	1.9	0.2	0.1	0.8	3.9	2.4	0.3	0.3	0.6	0.0	0.1	0.0
LAK022	**2012**	5.9		5.3	1.4	10.7	1.5	0.2	0.1	0.7	3.7	1.2	0.2	0.1	0.6	0.0	0.1	0.0
LAK023	**2012**	5.7		4.2	1.0	7.5	0.9	0.2	0.1	0.3	3.3	0.8	0.2	0.1	0.3	0.0	0.1	0.0
LAK024	**2012**	7.1		1.4	15.0	40.0	1.3	1.0	0.0	0.4	2.4	5.5	0.5	0.2	1.2	0.0	0.0	
LAK028	**2012**	5.0		4.9	-0.2	12.2	2.8	0.2	0.4	1.5	3.4	1.0	0.1	0.1	0.4	0.1	0.4	0.0
LAK034	**2012**	6.7		4.5	5.0	22.4	1.2	0.2	0.1	1.6	4.9	2.4	0.4	0.2	1.1	0.0	0.0	0.0
LAK042	**2012**	4.7		13.2	-1.0	11.9	0.3	0.2	0.1	0.7	8.5	0.2	0.3	0.1	0.6	0.6	0.4	0.0
LAK044	**2012**	5.4		1.7	0.1	3.1	0.3	0.2	0.1	0.4	3.0	0.1	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	**2013**	6.2	6.1	3.2	1.5	7.0	0.7	0.3	0.1	2.5	2.5	0.5	0.2	0.2	0.5	0.0	0.0	0.0
Lak007	**2013**	7.9	8.1	0.1	73.2	147.0	3.4	1.3	0.1	2.5	2.5	24.6	2.0	0.9	1.8	0.0	0.0	0.0
LAK012	**2013**	6.3	6.1	4.2	3.2	12.8	0.6	0.5	0.2	2.5	2.5	1.3	0.3	0.4	0.6	0.4	0.1	0.0
LAK016	**2013**	6.7	7.2	4.2	4.9	20.3	2.8	0.4	0.2	22.7	7.1	2.3	0.3	0.4	0.6	0.0	0.0	0.0
LAK022	**2013**	6.2	6.1	6.2	1.8	13.8	2.3	0.4	0.2	2.5	2.5	1.3	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	**2013**	6.0	6.0	4.0	1.2	9.6	1.2	0.3	0.1	30.1	2.5	0.7	0.2	0.2	0.3	0.0	0.1	0.0
LAK024	**2013**																	
LAK028	**2013**	5.2	5.5	7.1	0.2	20.3	6.2	0.6	0.6	20.4	2.5	1.7	0.3	0.2	0.6	0.2	0.6	0.0
LAK034	**2013**	6.9	7.4	4.7	10.5	28.3	1.9	0.3	0.2	2.5	2.5	3.1	0.5	0.4	1.4	0.0	0.0	0.0
LAK042	**2013**	5.5	5.4	9.7	1.1	8.0	0.3	0.3	0.1	2.5	2.5	0.3	0.3	0.1	0.6	0.3	0.3	0.0
LAK044	**2013**	5.7	6.0	1.5	0.4	3.3	0.3	0.3	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	**2014**	6.1	6.6	3.8	1.9	8.5	0.6	0.3	0.1	7.7	40.5	0.6	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	**2014**	8.1	8.0	0.7	72.4	154.2	1.6	0.7	0.0	2.5	2.5	25.6	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	**2014**	6.0	6.7	6.3	3.4	13.9	0.8	0.4	0.1	7.6	5.3	1.4	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	**2014**	6.7	6.7	4.0	5.3	21.5	2.4	0.3	0.2	2.5	6.7	2.5	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	**2014**	6.3	6.4	5.7	2.3	14.4	1.9	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	**2014**	5.9	6.7	5.7	1.6	9.3	0.9	0.2	0.1	10.9	5.3	1.0	0.2	0.2	0.4	0.0	0.1	0.0
LAK024	**2014**	7.6	7.5	1.7	23.6	63.1	2.1	2.3	0.0	5.1	2.5	8.1	0.8	0.4	2.5	0.0	0.0	0.0
LAK028	**2014**	5.3	5.7	5.9	1.1	20.2	4.6	0.4	0.4	2.5	2.5	1.7	0.2	0.2	0.6	0.1	0.5	0.0
LAK034	**2014**	6.7	7.0	7.0	10.3	27.5	0.9	0.2	0.1	2.5	2.5	3.2	0.5	0.4	1.3	0.1	0.0	0.0
LAK042	**2014**	5.1	5.4	10.6	0.6	10.8	0.3	0.4	0.1	2.5	2.5	0.2	0.3	0.2	0.6	0.4	0.3	0.0
LAK044	**2014**	5.8	5.6	1.8	0.3	3.6	0.3	0.2	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	**2015**	6.0	6.4	3.9	1.6	5.6	0.6	0.2	0.1	3.4	5.4	0.7	0.2	0.2	0.5	0.1	0.1	0.0
Lak007	**2015**	8.0	7.9	0.3	78.4	151.2	2.3	0.9	0.0	5.6	2.5	25.4	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	**2015**	6.0	6.3	7.5	3.3	10.1	0.9	0.4	0.1	8.3	8.0	1.5	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	**2015**	6.8	6.9	4.3	5.7	20.7	2.0	0.3	0.2	7.9	2.5	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	**2015**	6.1	6.2	6.3	1.8	12.8	1.6	0.3	0.1	2.5	2.5	1.3	0.2	0.2	0.6	0.1	0.1	0.0

DRAFT

Lake	Year	pH (TU)	pH (ALS)	DOC (mg/L)	Gran Alkalinity (mg/L)	Conduct-ivity (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)
LAK023	2015	5.9	6.2	5.4	1.5	5.9	0.8	0.2	0.1	6.3	2.5	0.9	0.2	0.2	0.3	0.0	0.1	0.0
LAK024	2015	7.4	7.5	2.2	22.2	58.7	2.0	2.1	0.0	8.1	2.5	8.1	0.7	0.4	2.3	0.1	0.0	0.0
LAK028	2015	5.1	5.3	8.1	0.5	17.8	3.5	0.3	0.4	2.5	2.5	1.5	0.2	0.1	0.5	0.2	0.6	0.0
LAK034	2015	6.6	6.7	7.6	8.9	22.3	0.1	0.2	0.1	2.5	2.5	2.9	0.5	0.2	1.2	0.1	0.0	0.0
LAK042	2015	5.4	5.5	8.3	0.7	8.1	0.2	0.2	0.0	2.5	2.5	0.2	0.3	0.1	0.7	0.2	0.3	0.0
LAK044	2015	5.8	5.8	1.6	0.3	3.5	0.2	0.2	0.1	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2016	6.0	6.3	4.2	1.3	7.8	0.6	0.2	0.1	2.5	2.5	0.7	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2016	8.0	8.1	0.8	68.5	153.7	2.4	0.9	0.1	6.5	2.5	26.1	2.0	0.8	1.8	0.0	0.0	0.0
LAK012	2016	6.2	6.5	5.1	3.3	12.4	0.5	0.2	0.1	5.0	4.7	1.3	0.3	0.2	0.6	0.3	0.1	0.0
LAK016	2016	6.6	6.9	5.2	4.7	20.8	2.2	0.3	0.2	10.9	2.5	2.6	0.3	0.4	0.7	0.0	0.1	0.0
LAK022	2016	6.1	6.4	6.7	1.7	13.7	1.7	0.3	0.1	2.5	2.5	1.4	0.3	0.2	0.7	0.1	0.1	0.0
LAK023	2016	5.9	6.2	5.8	1.4	9.1	0.6	0.2	0.1	2.5	5.1	0.9	0.2	0.2	0.4	0.0	0.1	0.0
LAK024	2016	7.5	7.6	2.7	23.2	66.3	2.2	2.5	0.0	20.7	2.5	9.0	0.8	0.4	2.6	0.1	0.0	0.0
LAK028	2016	5.0	5.1	8.1	-0.2	23.7	6.2	0.4	0.5	21.5	2.5	1.9	0.3	0.2	0.6	0.1	0.7	0.0
LAK034	2016	6.5	7.1	7.6	7.6	22.1	0.0	0.2	0.1	2.5	2.5	2.6	0.4	0.2	1.1	0.1	0.0	0.0
LAK042	2016	5.4	5.7	9.8	0.7	8.8	0.2	0.3	0.0	2.5	3.7	0.3	0.3	0.1	0.7	0.2	0.3	0.0
LAK044	2016	5.5	6.0	2.0	0.2	3.9	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
Lak006	2017	6.0	6.4	3.8	1.4	8.8	0.7	0.2	0.1	2.5	2.5	0.7	0.2	0.2	0.5	0.0	0.1	0.0
Lak007	2017	8.0	8.0	0.3	69.1	149.0	2.4	0.9	0.0	2.5	2.5	24.1	2.1	0.8	2.0	0.0	0.0	0.0
LAK012	2017	6.1	6.5	5.2	2.9	12.9	0.7	0.2	0.1	9.7	5.6	1.3	0.3	0.3	0.6	0.3	0.1	0.0
LAK016	2017	6.7	6.8	4.1	4.1	18.5	2.1	0.3	0.1	2.5	2.5	2.3	0.3	0.3	0.7	0.0	0.1	0.0
LAK022	2017	6.1	6.3	5.9	1.7	12.8	1.9	0.3	0.1	2.5	2.5	1.3	0.3	0.2	0.6	0.0	0.1	0.0
LAK023	2017	5.9	6.2	5.4	1.4	7.9	0.5	0.2	0.1	7.7	2.5	0.9	0.2	0.1	0.3	0.0	0.1	0.0
LAK024	2017	7.4	7.6	2.0	20.9	57.4	2.0	2.0	0.0	11.2	2.5	8.1	0.8	0.4	2.4	0.1	0.0	0.0
LAK028	2017	4.8	5.1	7.3	-0.5	26.9	7.2	0.3	0.5	25.3	3.3	2.1	0.3	0.1	0.6	0.1	0.7	0.0
LAK034	2017	6.4	6.8	6.0	6.8	17.6	0.0	0.2	0.1	2.5	2.5	2.1	0.4	0.1	1.0	0.1	0.0	0.0
LAK042	2017	5.2	5.4	11.6	0.1	9.8	0.4	0.2	0.0	2.5	5.4	0.3	0.3	0.1	0.7	0.3	0.4	0.0
LAK044	2017	5.6	6.0	1.6	0.4	4.4	0.2	0.2	0.0	2.5	2.5	0.2	0.1	0.2	0.1	0.0	0.0	0.0
NC184	2013	5.7		11.6	0.8	10.0	0.4	0.9	0.0	0.0	0.0	1.0	0.3	0.2	0.8			
NC194	2013	6.6		0.7	1.4	3.9	0.2	0.3	0.0	0.0	0.0	0.5	0.1	0.2	0.3			
DCAS14A	2013	6.5		1.4	2.5	10.6	1.7	0.3	0.0	52.6	2.5	1.3	0.1	0.4	0.3	0.0	0.0	0.0
NC184	2015	5.5	5.6	9.8	0.9	11.6	0.4	0.8	0.0	2.5	2.5	1.0	0.2	0.1	0.7	0.2	0.3	0.0
NC194	2015	6.5	6.5	0.8	1.7	5.4	0.1	0.3	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	2015	6.6	6.7	0.9		14.0	1.8	0.3	0.0	6.8	2.5	1.6	0.2	0.4	0.4	0.0	0.0	0.0
NC184	2016	5.8	6.2	10.6	1.4	12.8	0.4	0.8	0.0	2.5	2.5	1.3	0.3	0.1	0.8	0.1	0.3	0.0
NC194	2016	6.4	6.6	1.6	1.4	5.9	0.1	0.3	0.0	2.5	2.5	0.5	0.1	0.2	0.3	0.0	0.0	0.0
DCAS14A	2016	6.6	6.8	1.5	2.9	14.8	1.8	0.3	0.0	2.5	2.5	1.6	0.2	0.4	0.4	0.0	0.0	0.0
NC184	2017	5.4	6.0	13.3	0.5	11.4	0.3	0.5	0.0	2.5	2.5	0.9	0.2	0.1	0.7	0.2	0.3	0.0
NC194	2017	6.4	6.4	1.0	0.6	4.9	0.1	0.2	0.0	2.5	2.5	0.6	0.1	0.1	0.3	0.0	0.0	0.0
DCAS14A	2017	6.6	6.7	1.5	2.6	11.7	1.5	0.2	0.0	2.5	2.5	1.4	0.2	0.4	0.3	0.0	0.0	0.0

DRAFT

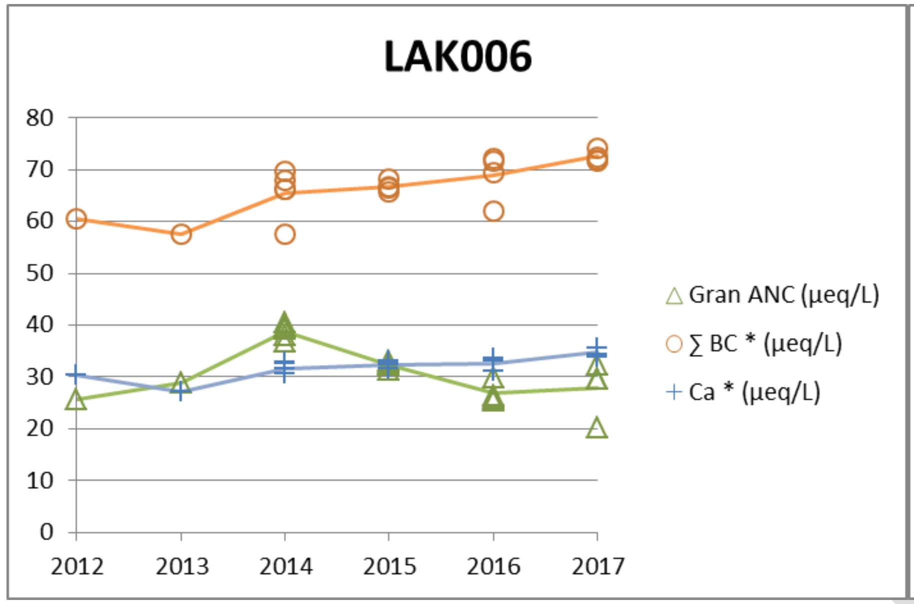
DRAFT

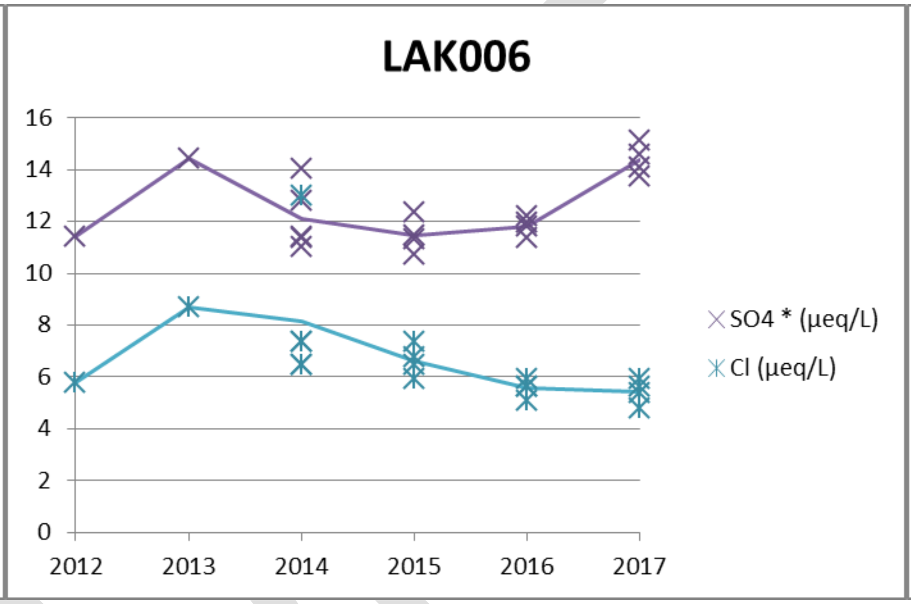
Appendix 2: Changes in Ion Concentrations from 2012 to 2017

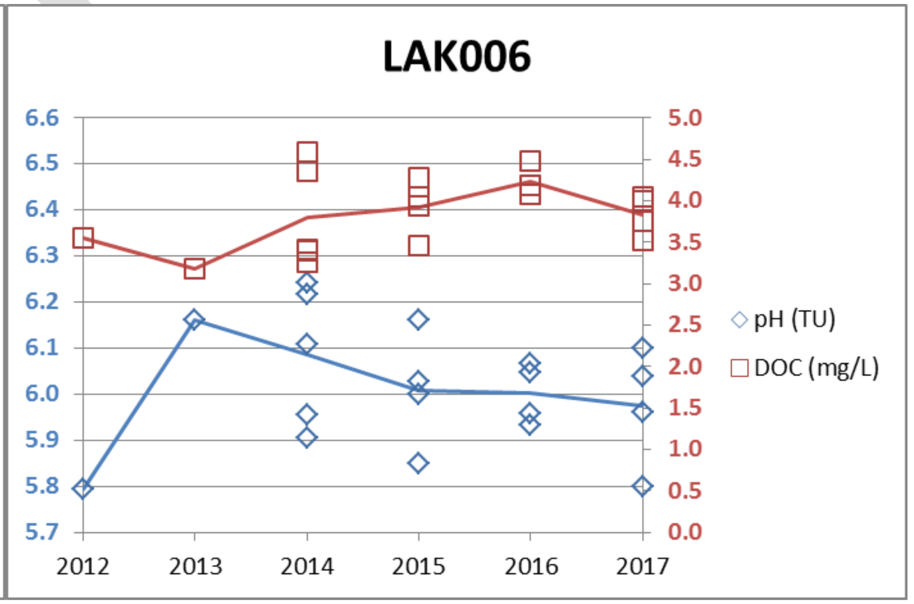
For each of the EEM lakes, the figures in this appendix show the inter-annual changes in six major water chemistry metrics from 2012 to 2017: Gran ANC, base cations and calcium (left panel), sulfate and chloride (centre panel), and pH and dissolved organic carbon (right panel). The selection of each pair of metrics is solely based on optimizing graphical representation across all metrics and lakes (i.e., metrics with somewhat similar numeric ranges are shown together). The right panel has two Y-axes. 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.

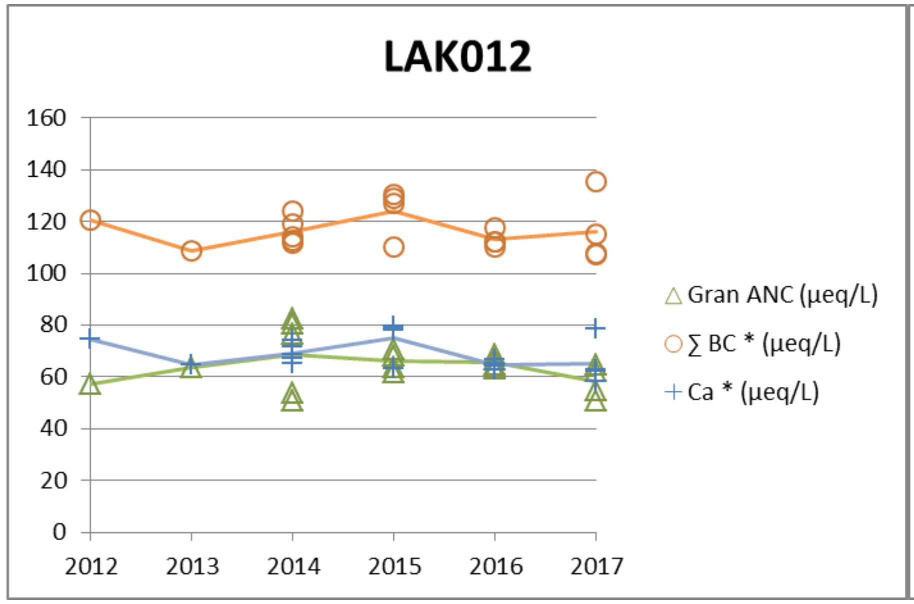
These figures show the results for all of the sampling events for each lake in each year, whether that included multiple within-season samples or only a single annual sample. The points represent the values for individual sampling events. The solid lines represent the annual trend, based on either the 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.

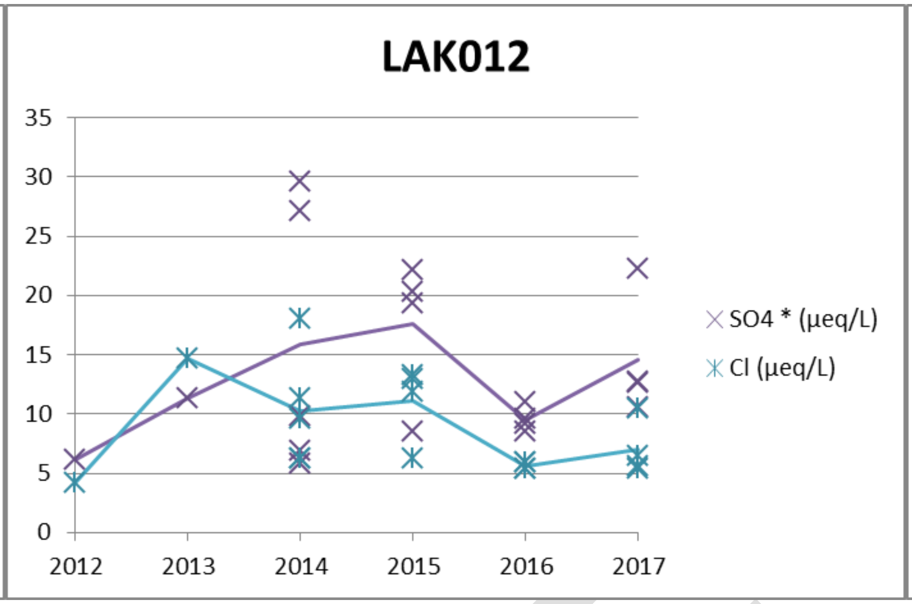
Sensitive Lakes

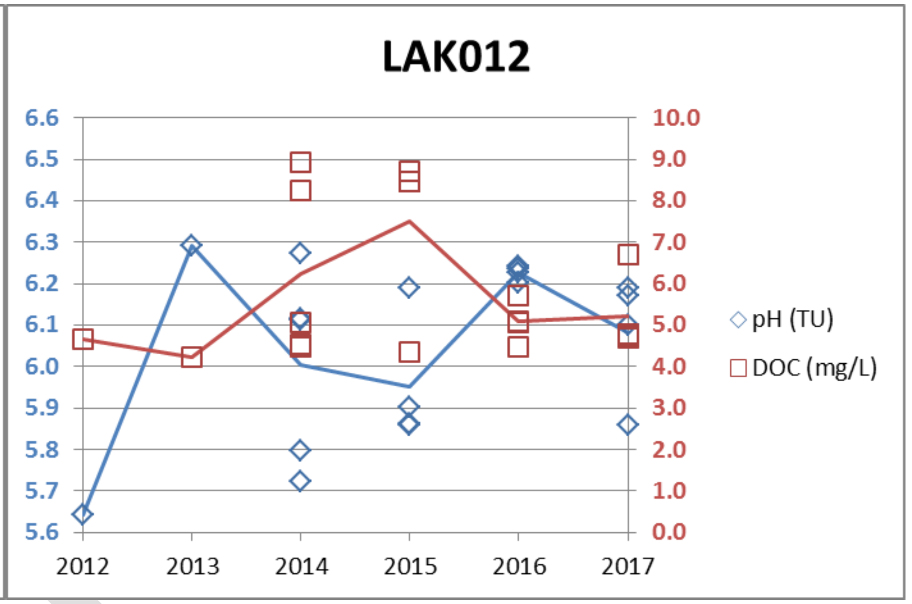


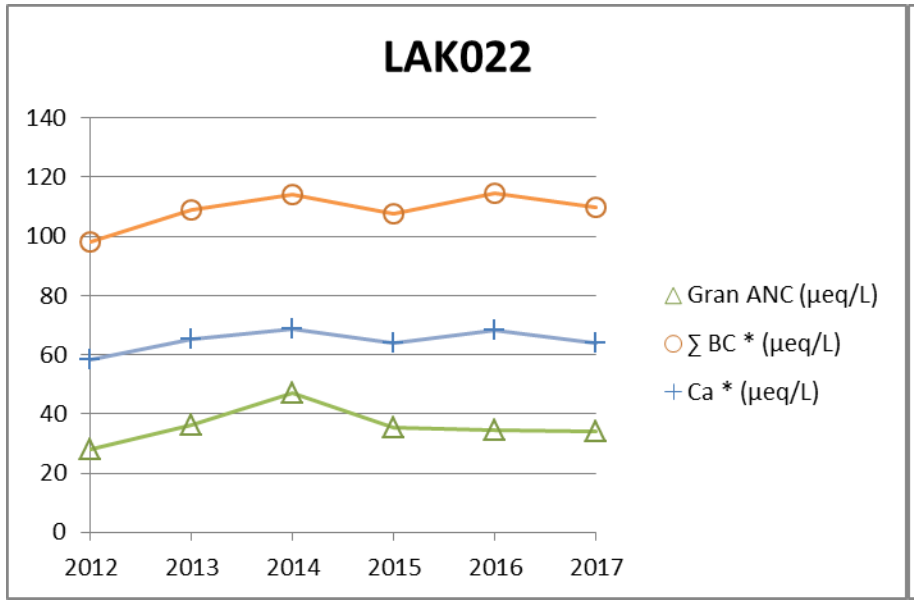


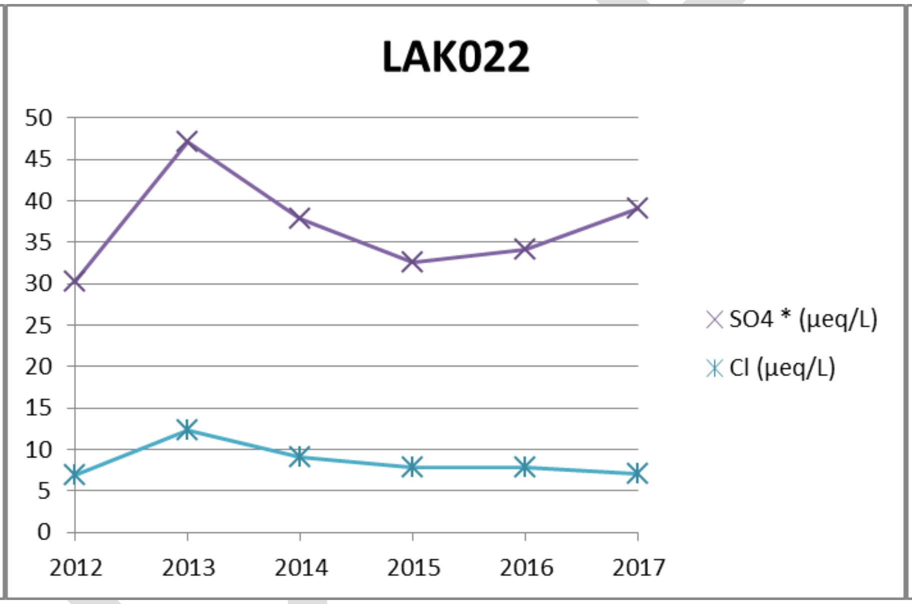


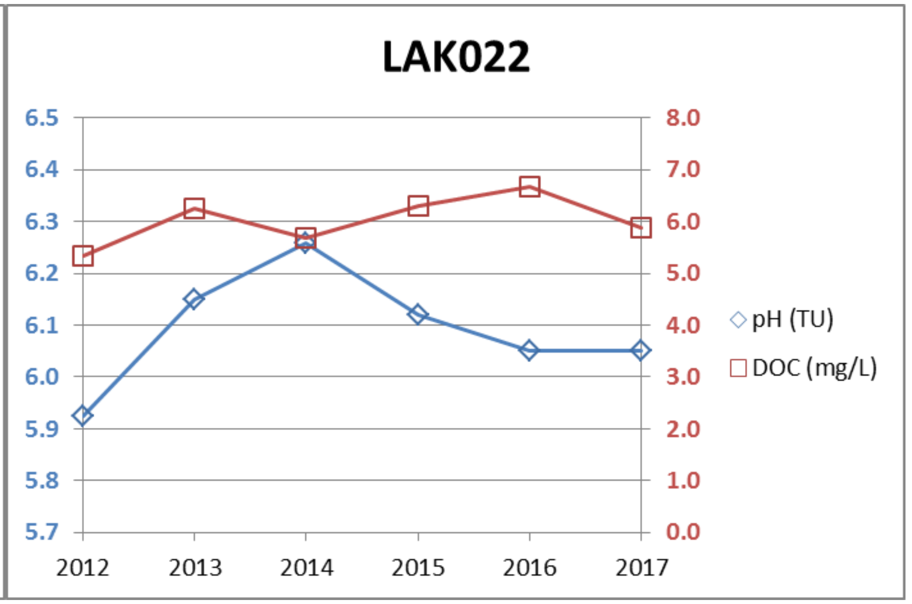

LAK012
160
140
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

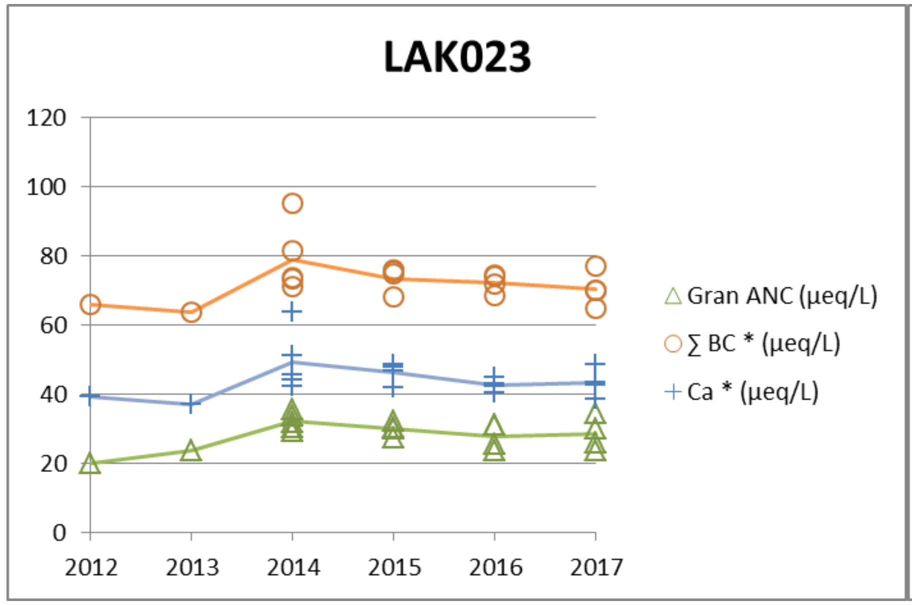

LAK012
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
× SO4 * (µeq/L)
⁎ Cl (µeq/L)

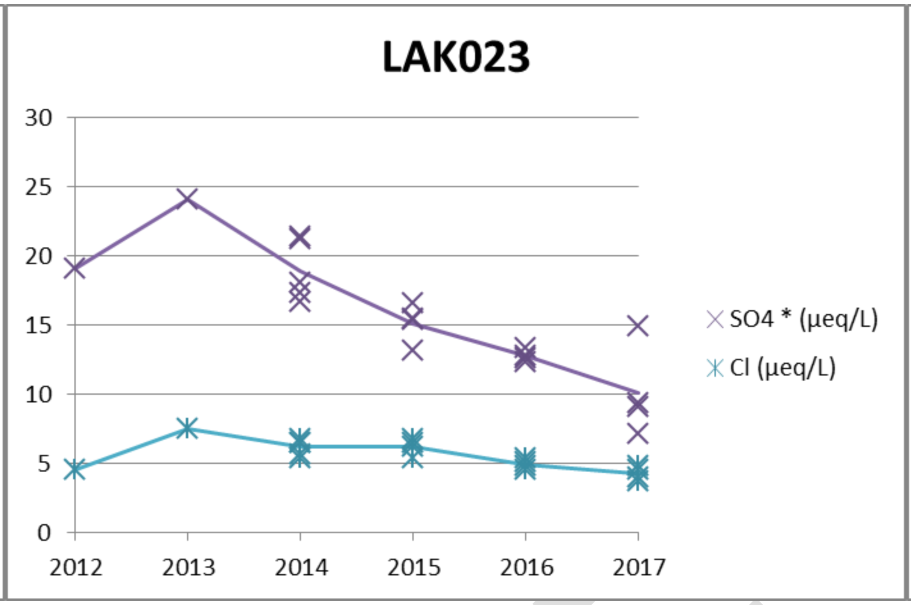

LAK012
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
◇ pH (TU)
□ DOC (mg/L)

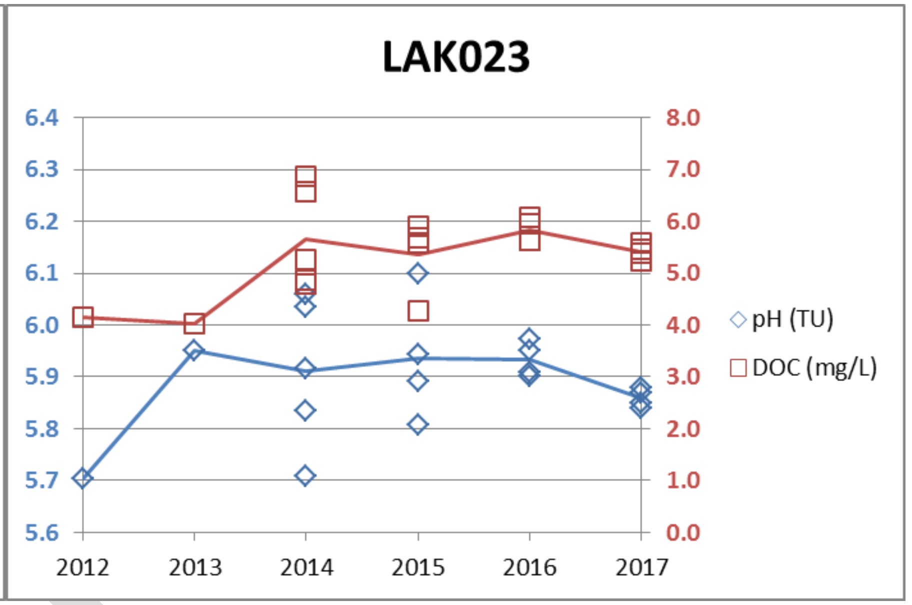

LAK022
140
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

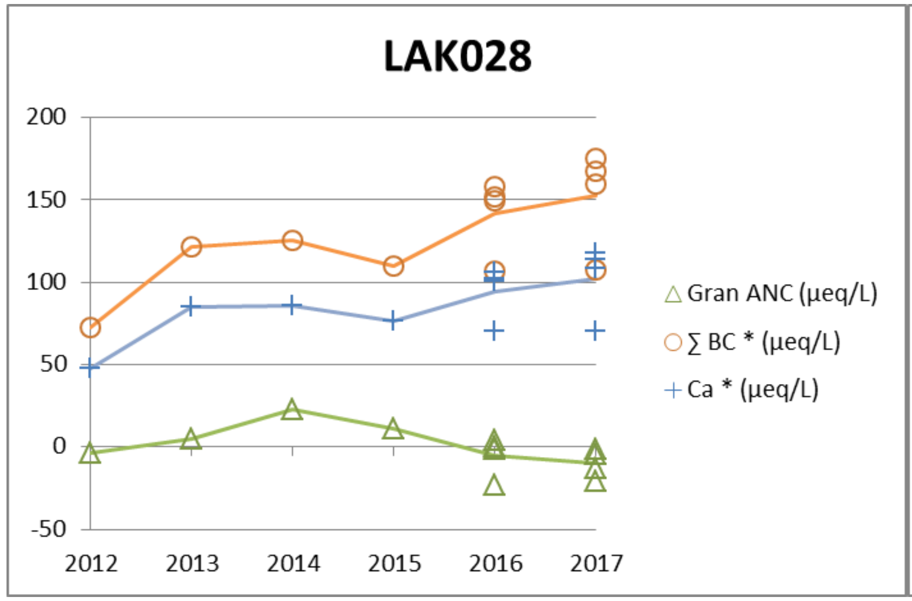

LAK022
50
45
40
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
× SO4 * (µeq/L)
⁎ Cl (µeq/L)

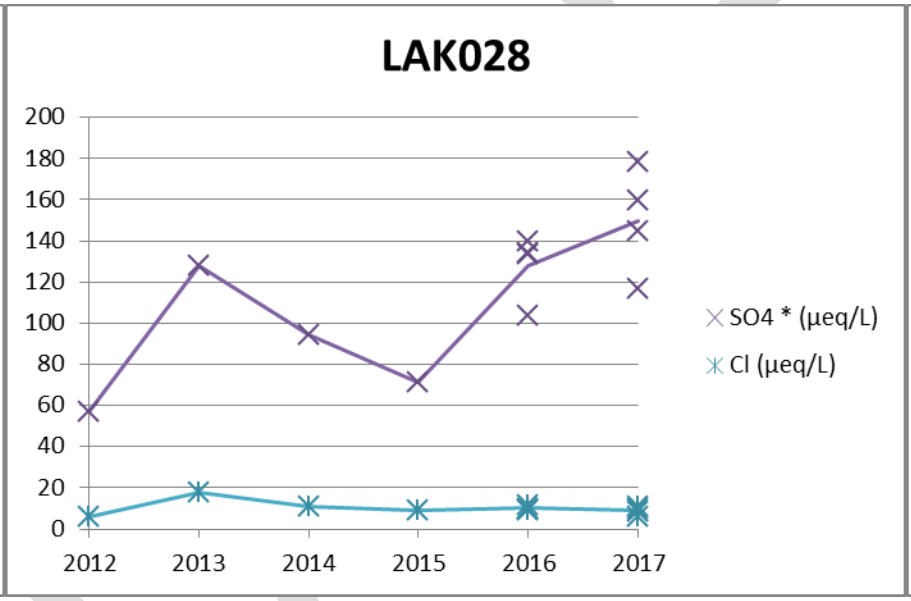

LAK022
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
◇ pH (TU)
□ DOC (mg/L)

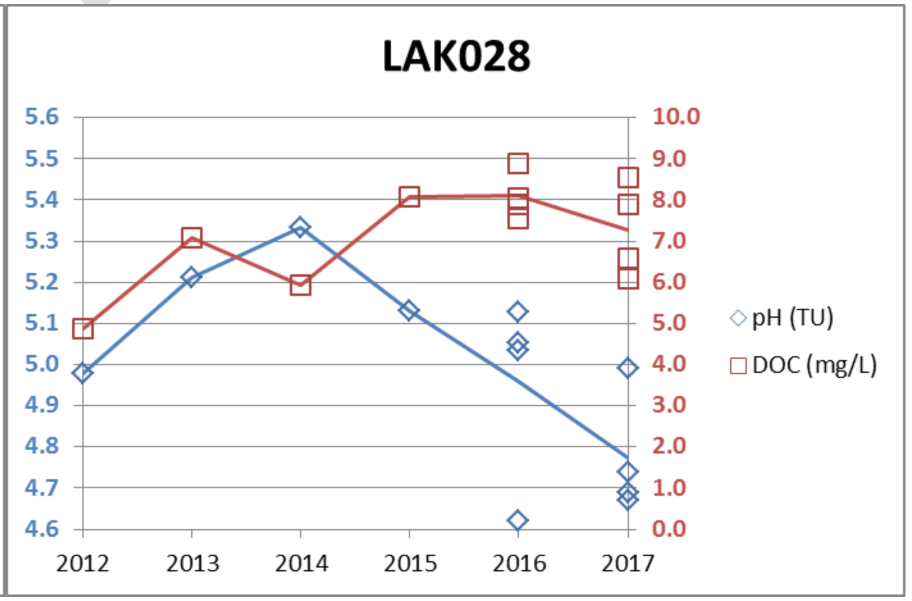

LAK023
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

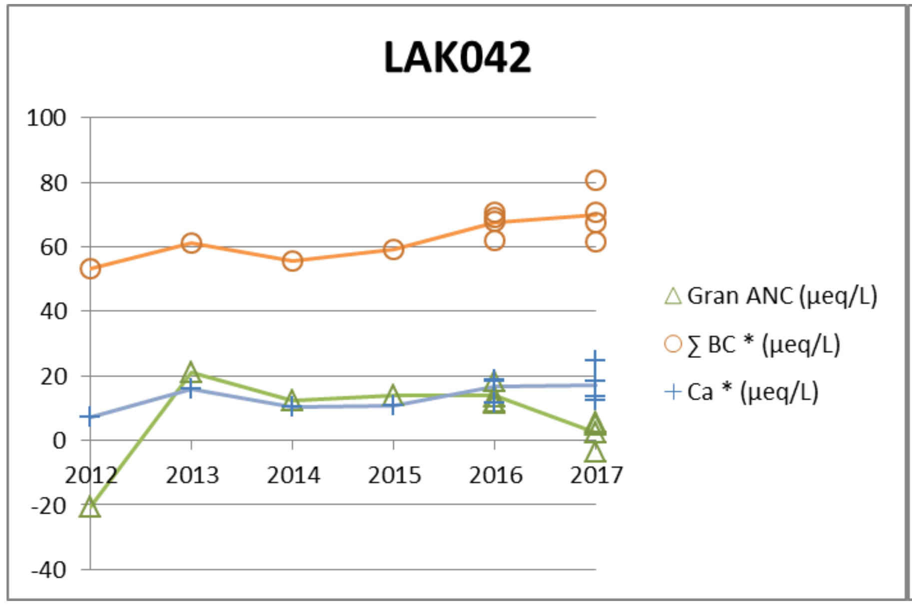

LAK023
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
× SO4 * (µeq/L)
✳ Cl (µeq/L)

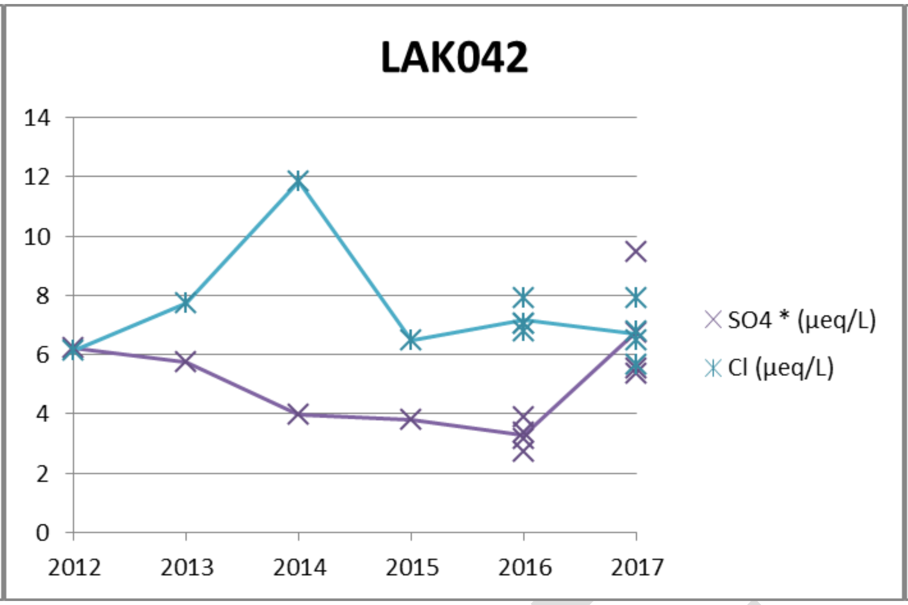

LAK023
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
◇ pH (TU)
□ DOC (mg/L)

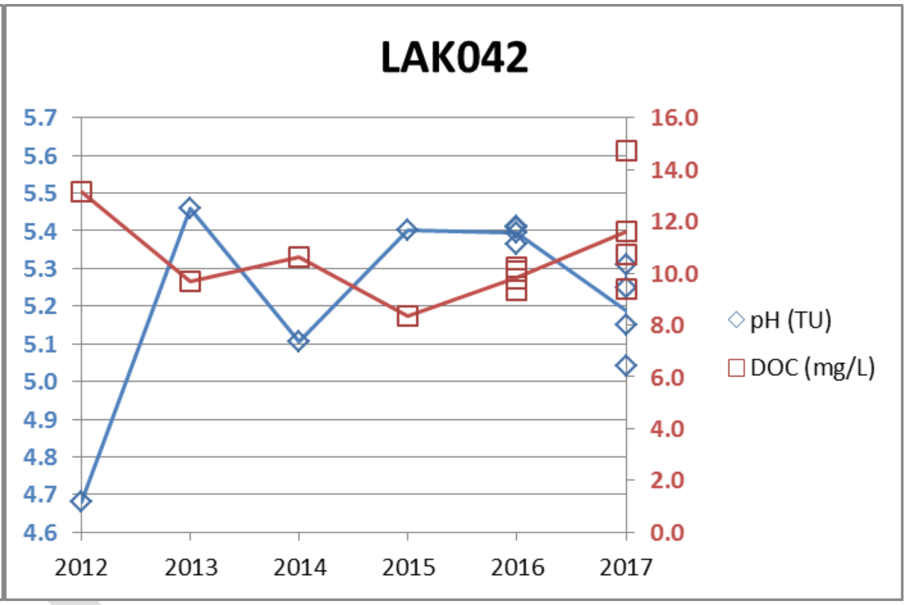

LAK028
200
150
100
50
0
-50
2012
2013
2014
2015
2016
2017
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

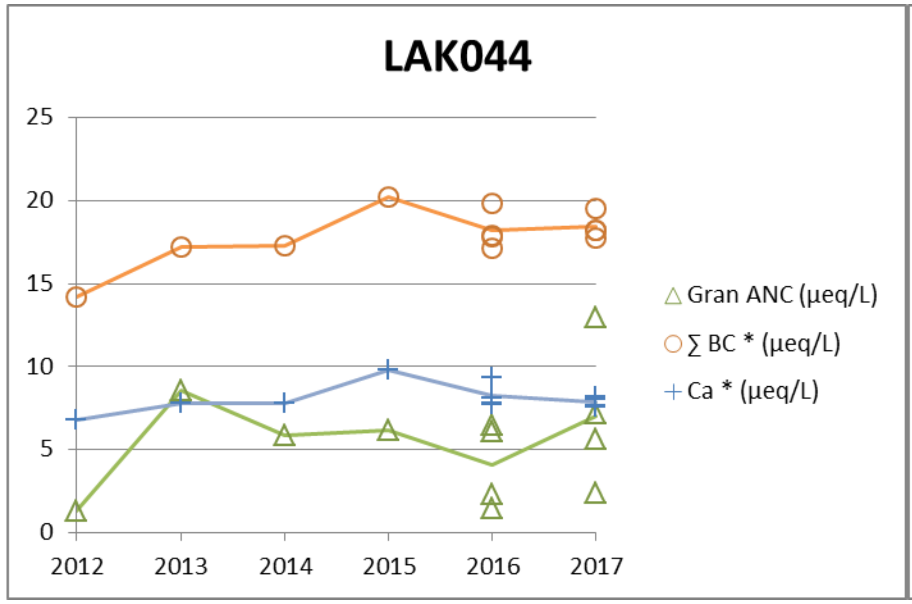

LAK028
200
180
160
140
120
100
80
60
40
20
0
2012
2013
2014
2015
2016
2017
× SO4 * (µeq/L)
✳ Cl (µeq/L)

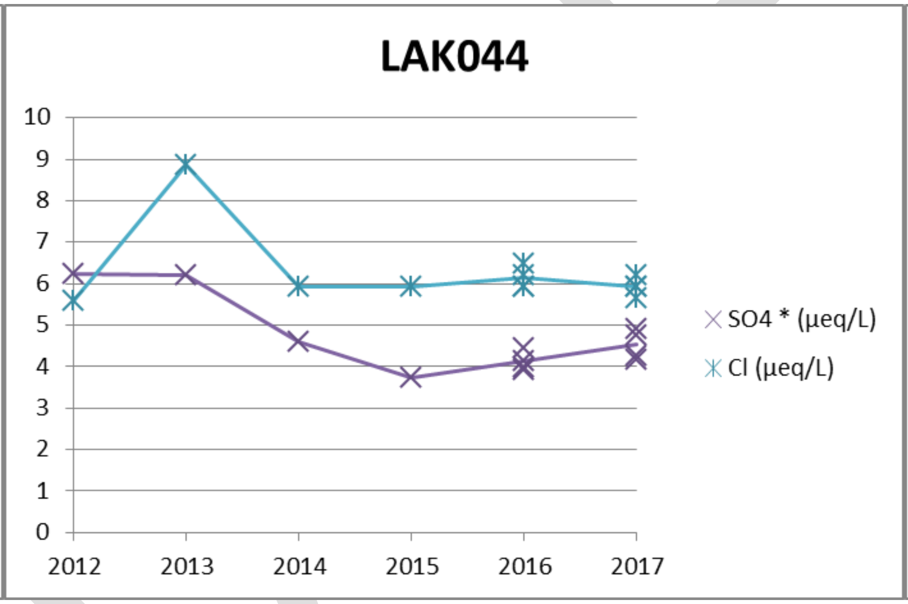

LAK028
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
◇ pH (TU)
□ DOC (mg/L)

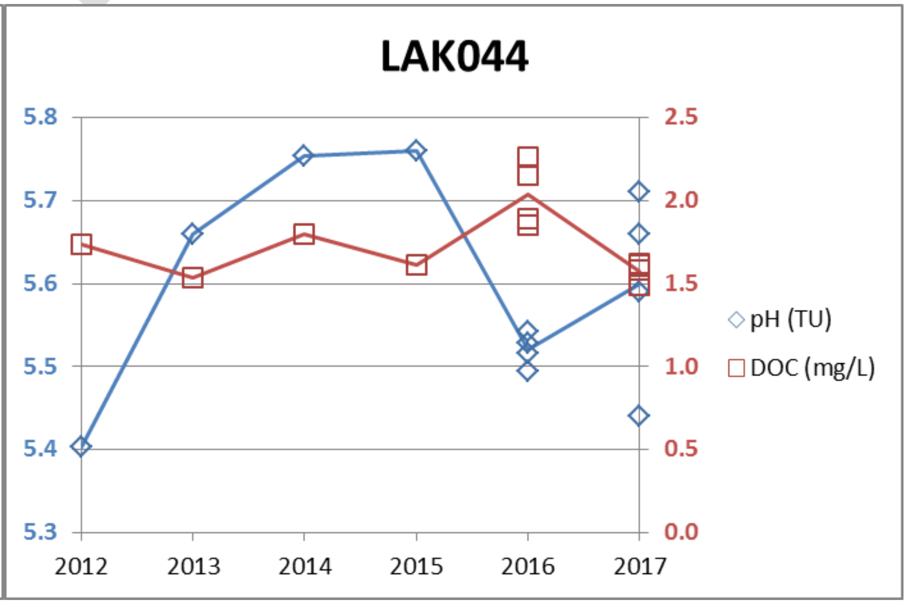

LAK042
100
80
60
40
20
0
-20
-40
2012
2013
2014
2015
2016
2017
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)


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

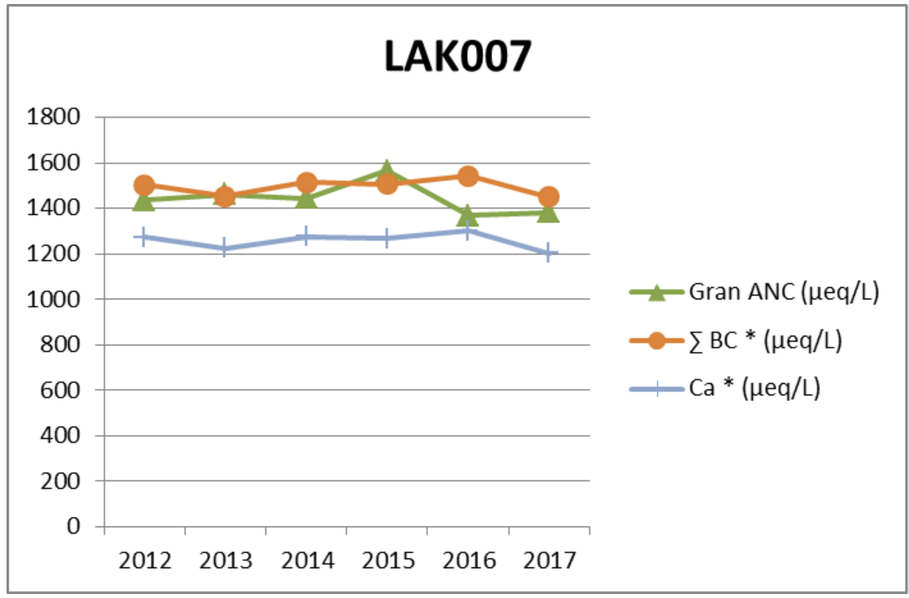

LAK042
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2012
2013
2014
2015
2016
2017
◇ pH (TU)
□ DOC (mg/L)

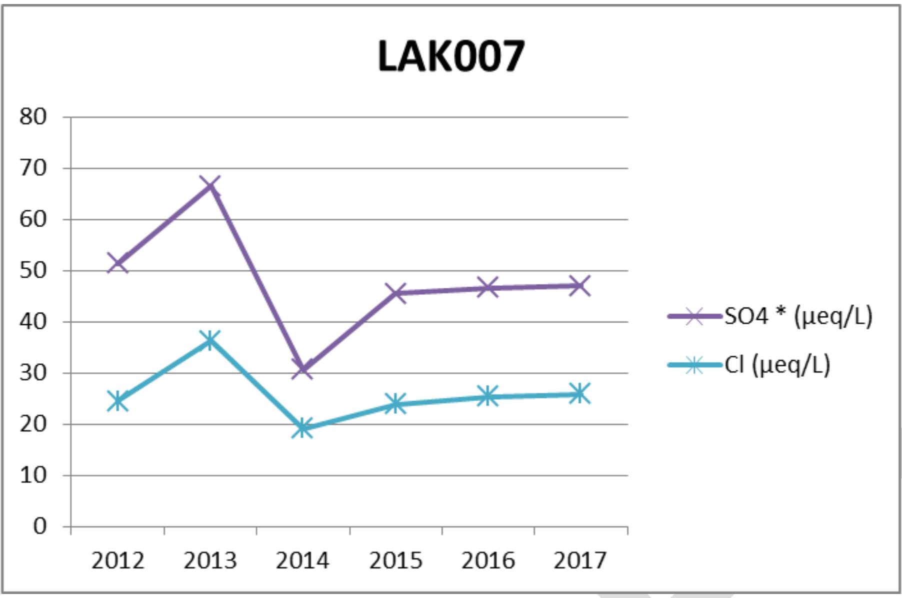

LAK044
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
△ Gran ANC (µeq/L)
○ ∑ BC * (µeq/L)
+ Ca * (µeq/L)

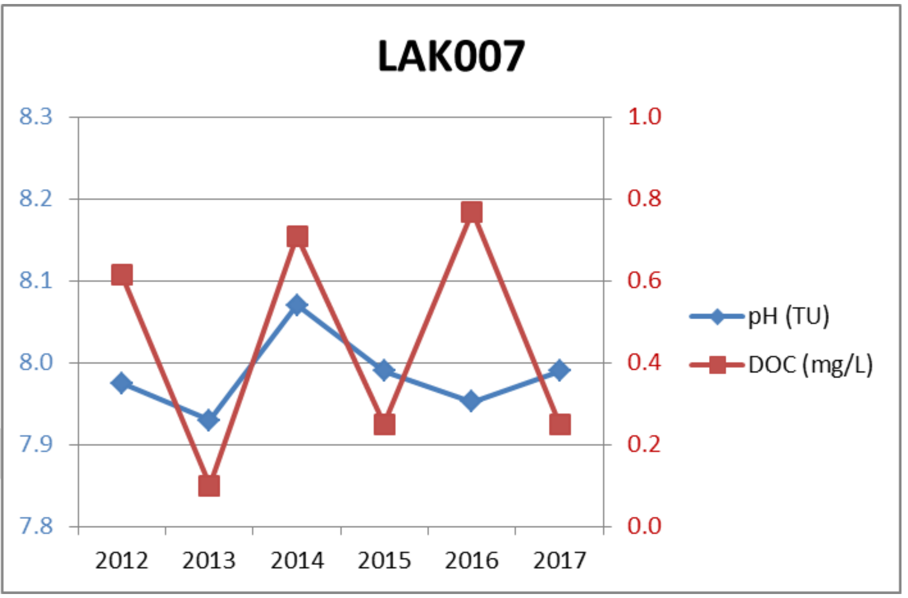

LAK044
10
9
8
7
6
5
4
3
2
1
0
2012
2013
2014
2015
2016
2017
× SO4 * (µeq/L)
⋇ Cl (µeq/L)

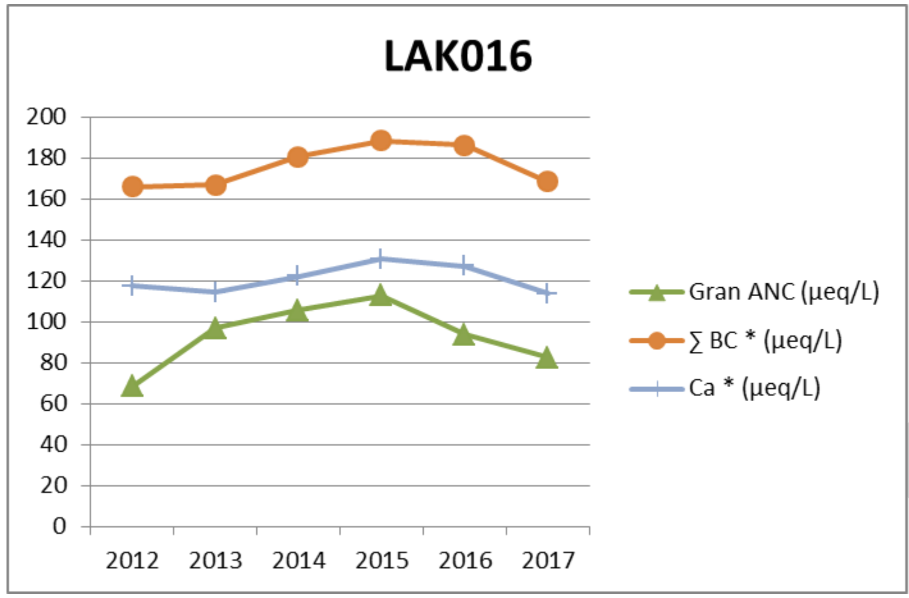

LAK044
5.8
5.7
5.6
5.5
5.4
5.3
2.5
2.0
1.5
1.0
0.5
0.0
2012
2013
2014
2015
2016
2017
◇ pH (TU)
□ DOC (mg/L)

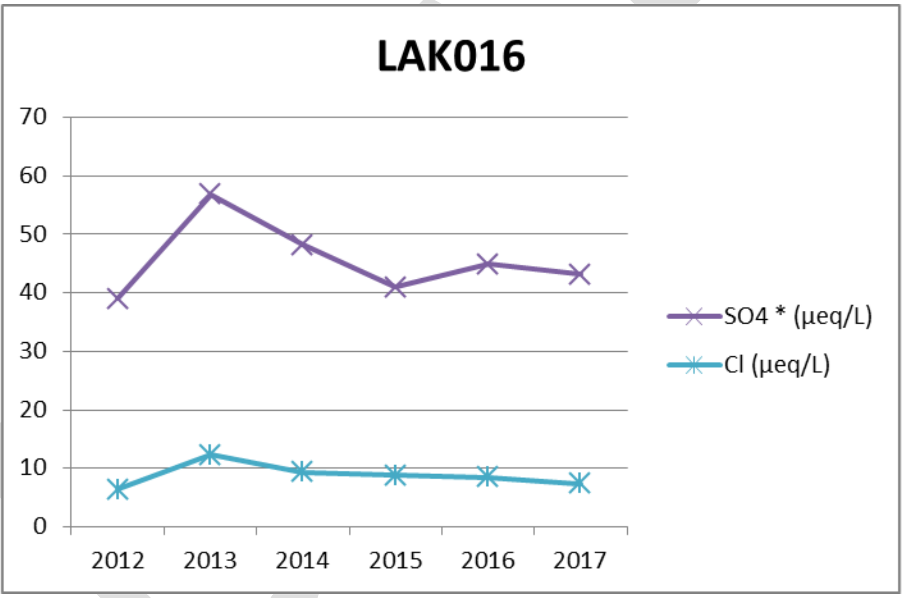
Less Sensitive Lakes

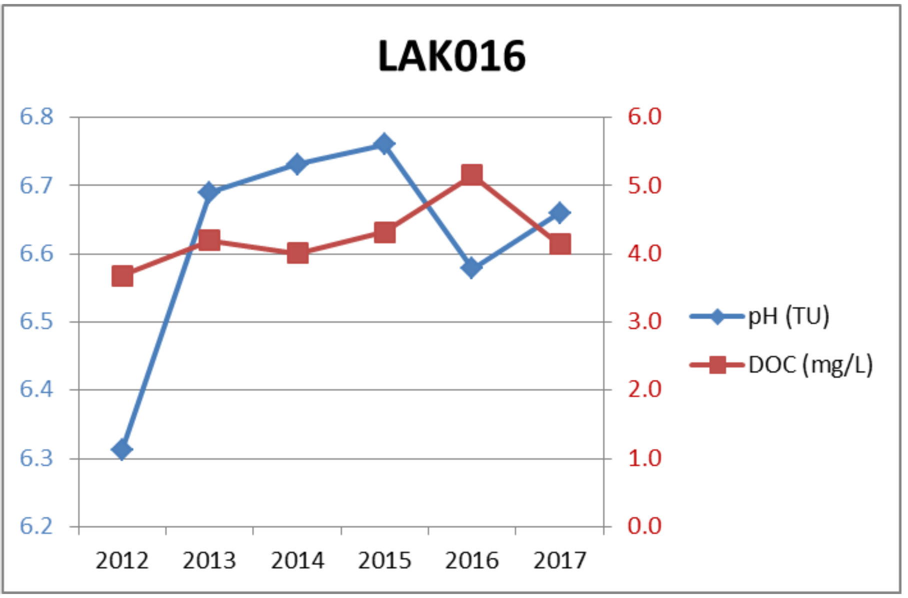


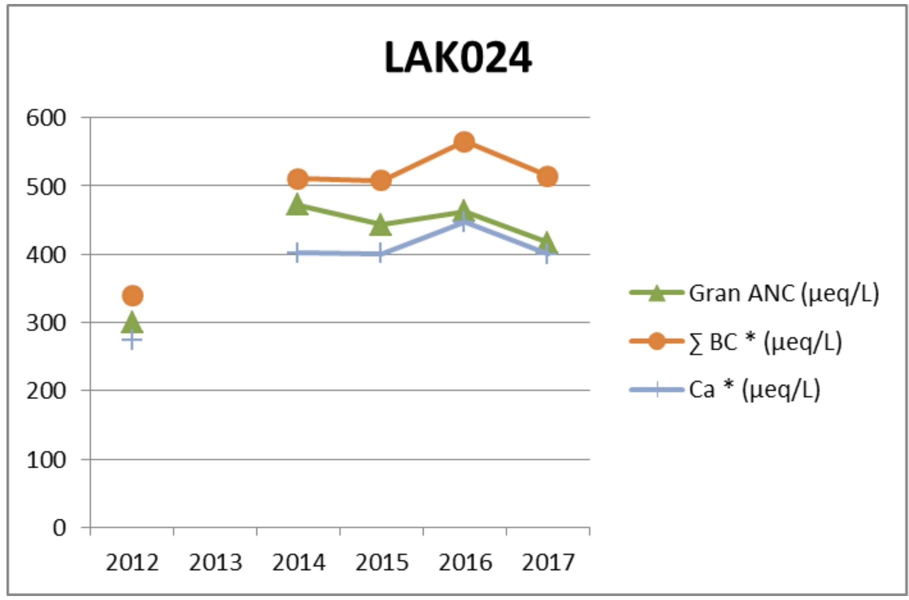


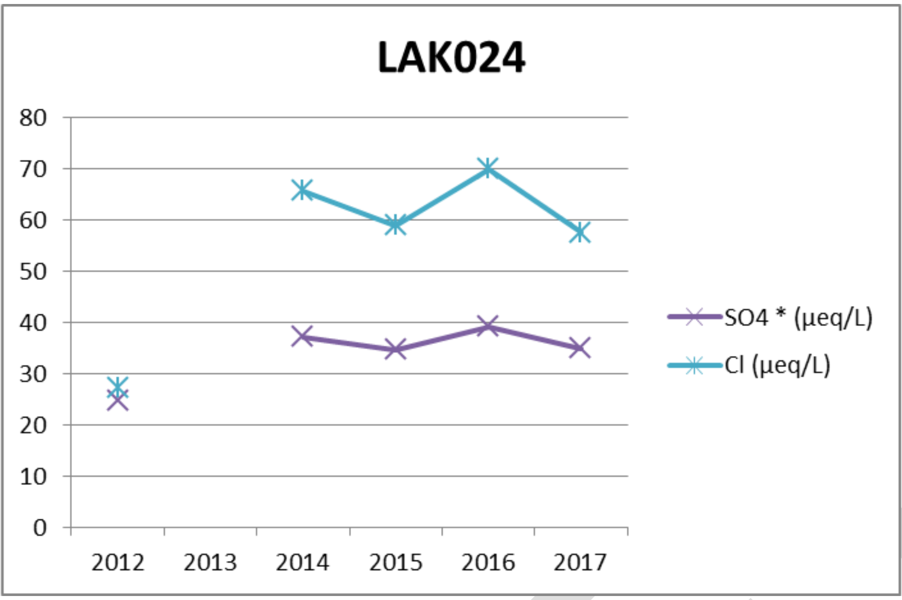


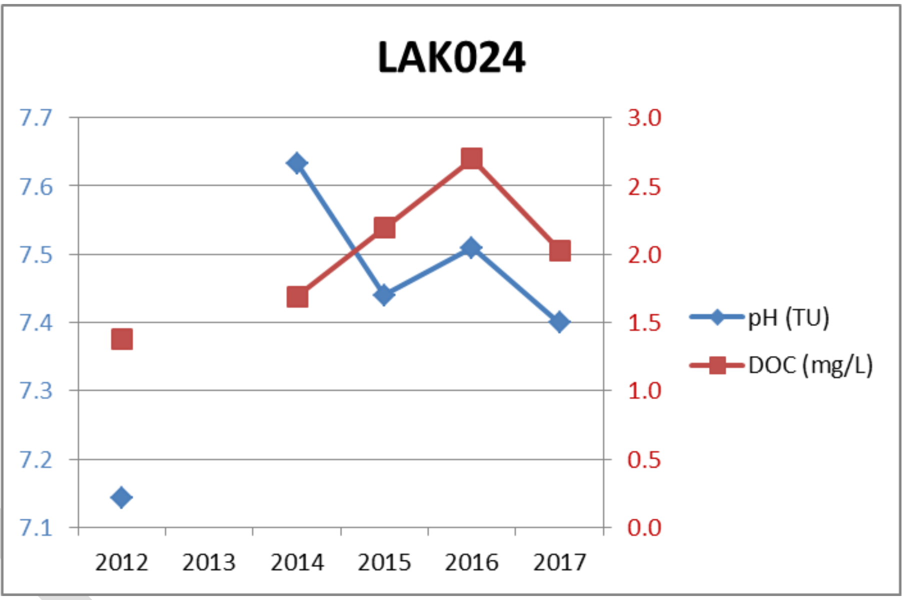


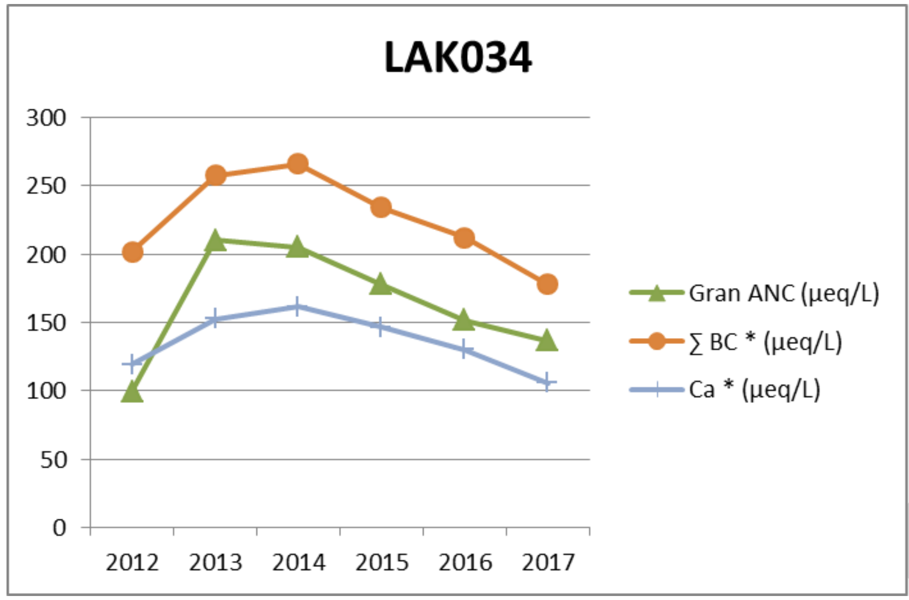


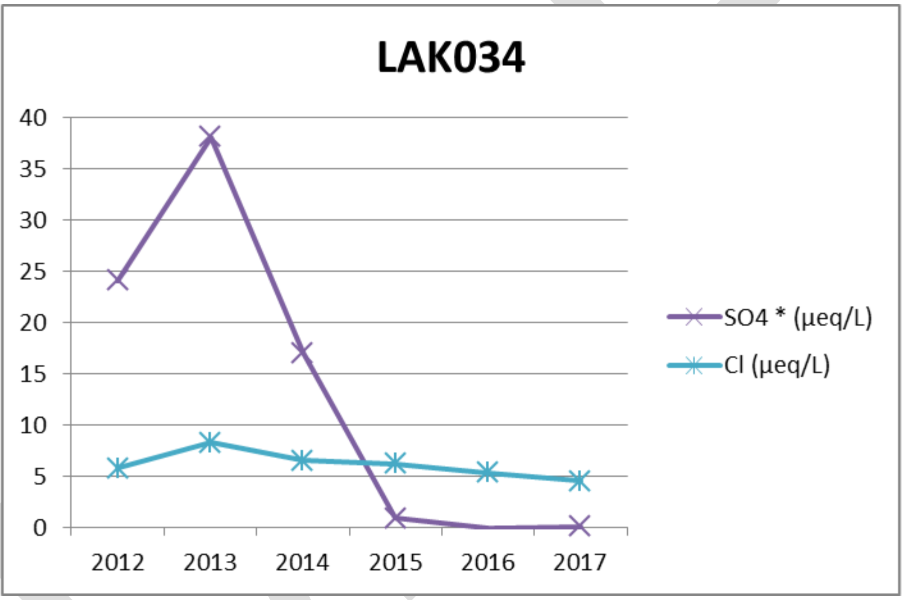


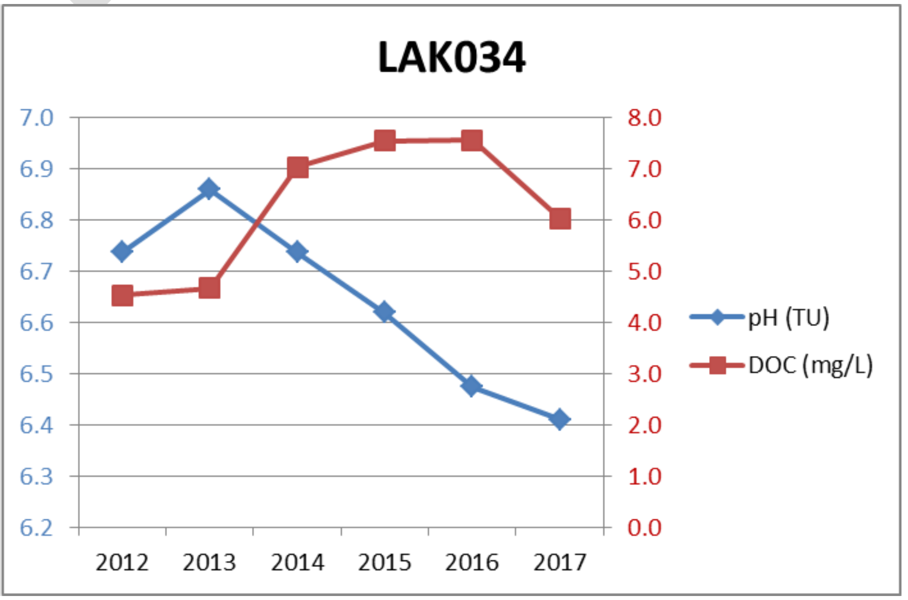

LAK024
600
500
400
300
200
100
0
2012
2013
2014
2015
2016
2017
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)


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

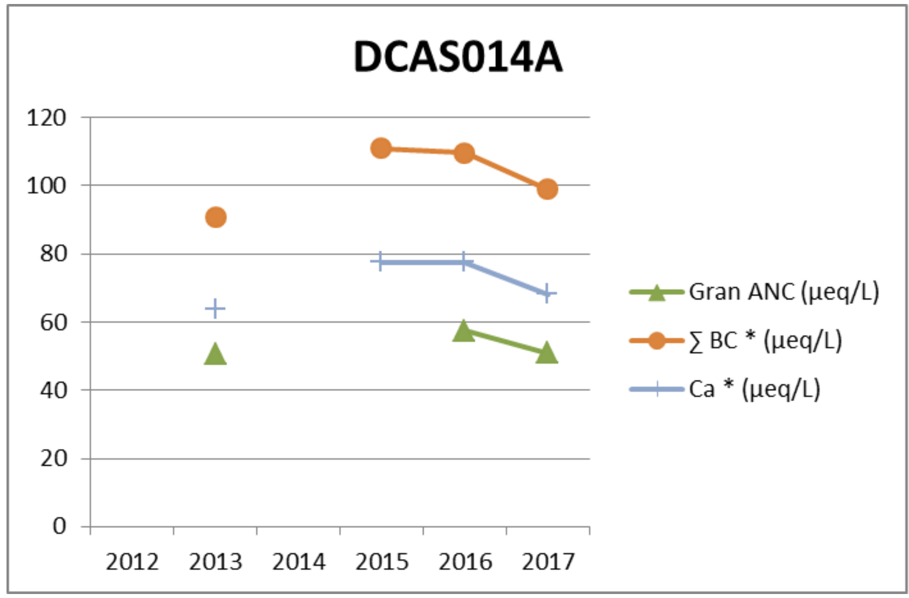

LAK024
7.7
7.6
7.5
7.4
7.3
7.2
7.1
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2012
2013
2014
2015
2016
2017
pH (TU)
DOC (mg/L)

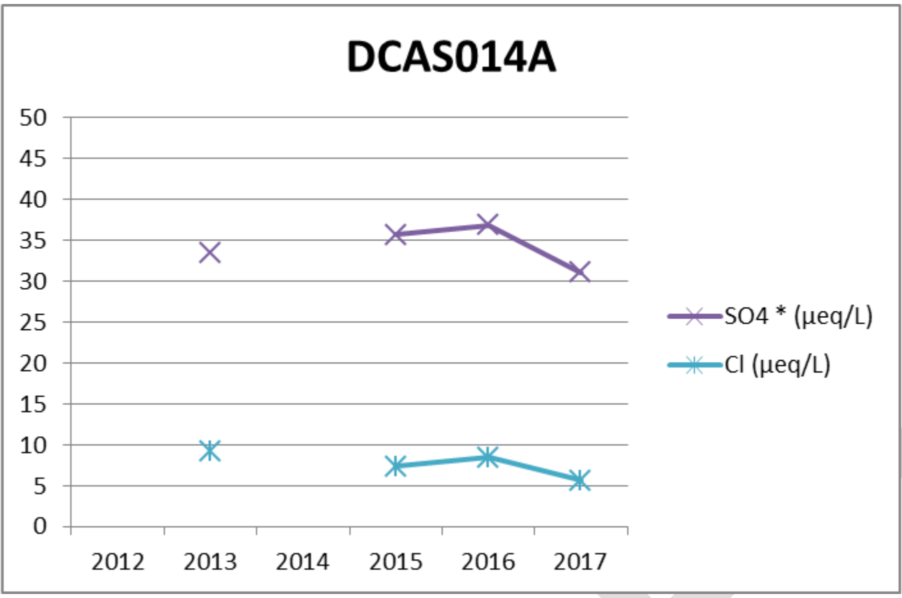

LAK034
300
250
200
150
100
50
0
2012
2013
2014
2015
2016
2017
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)

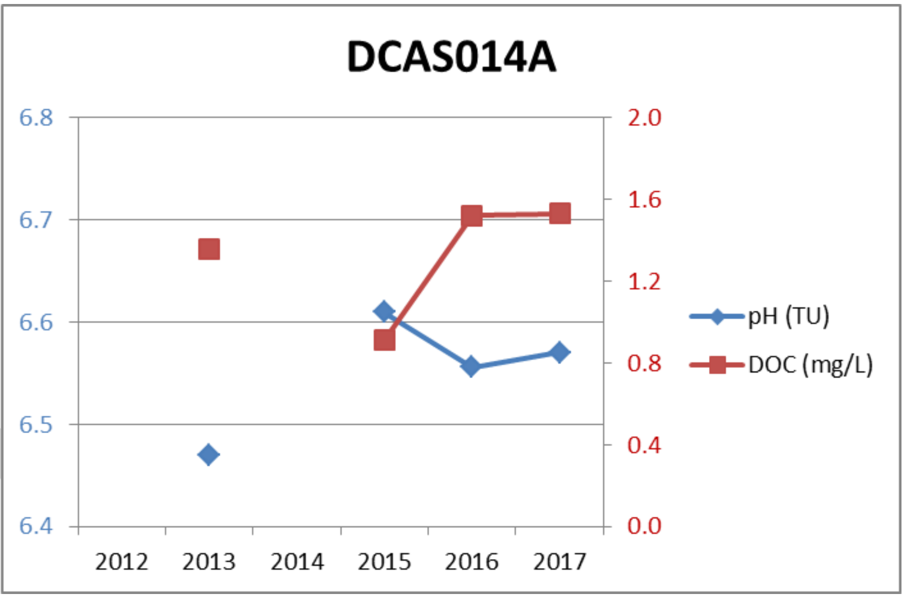

LAK034
40
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
SO4 * (μeq/L)
Cl (μeq/L)

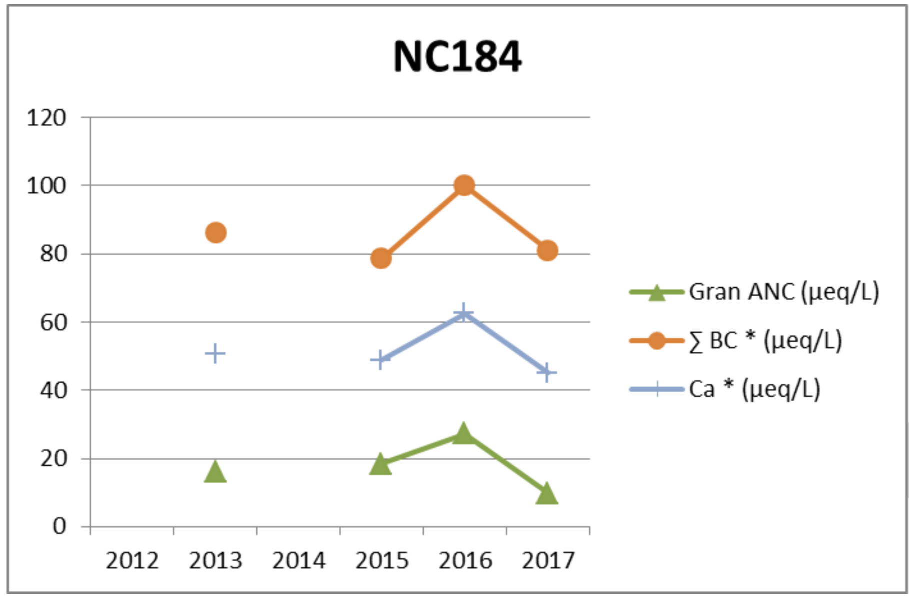

LAK034
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2012
2013
2014
2015
2016
2017
pH (TU)
DOC (mg/L)

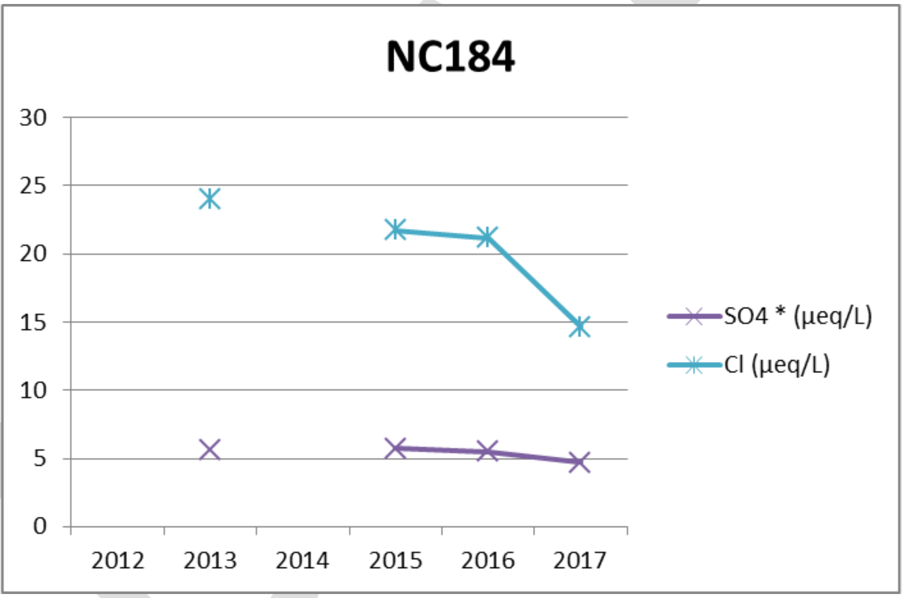
Control Lakes

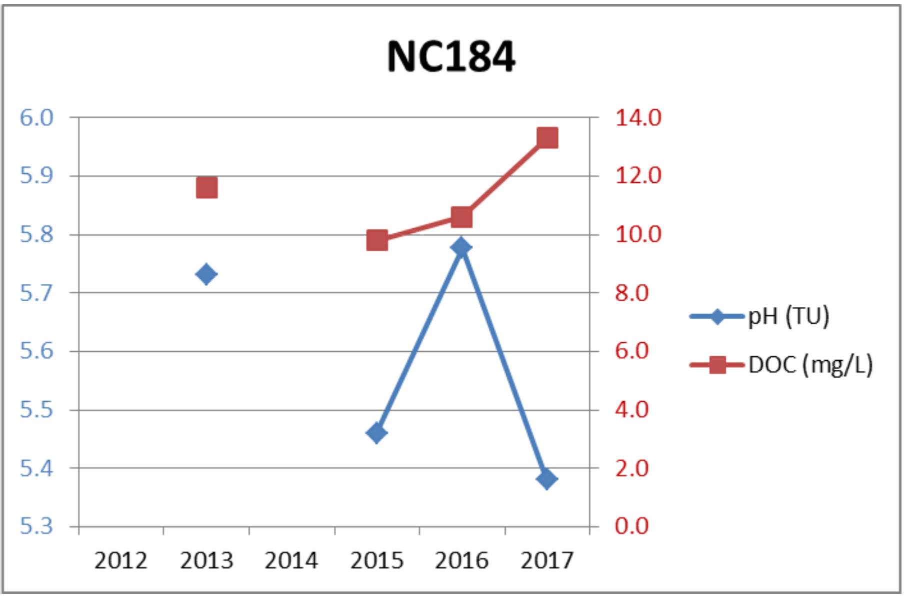


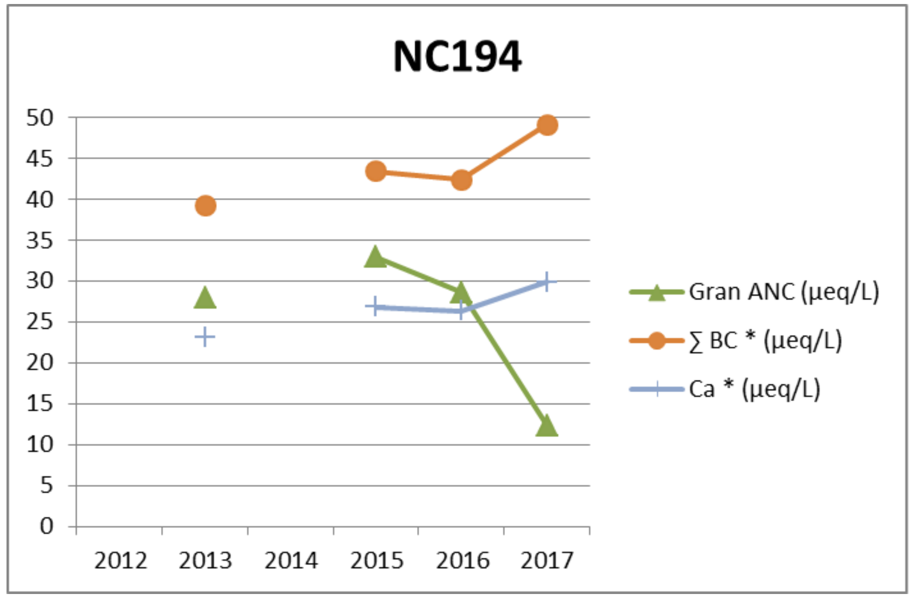


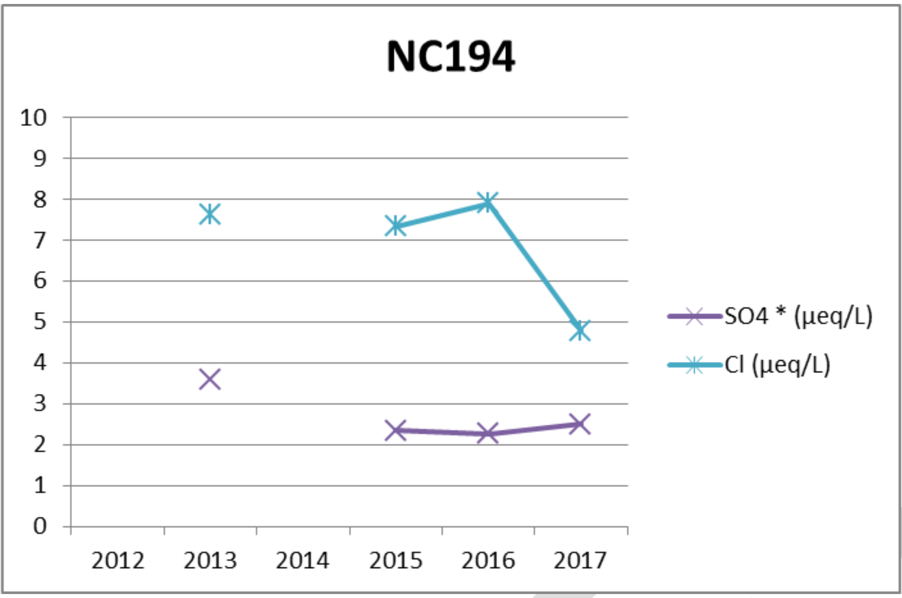


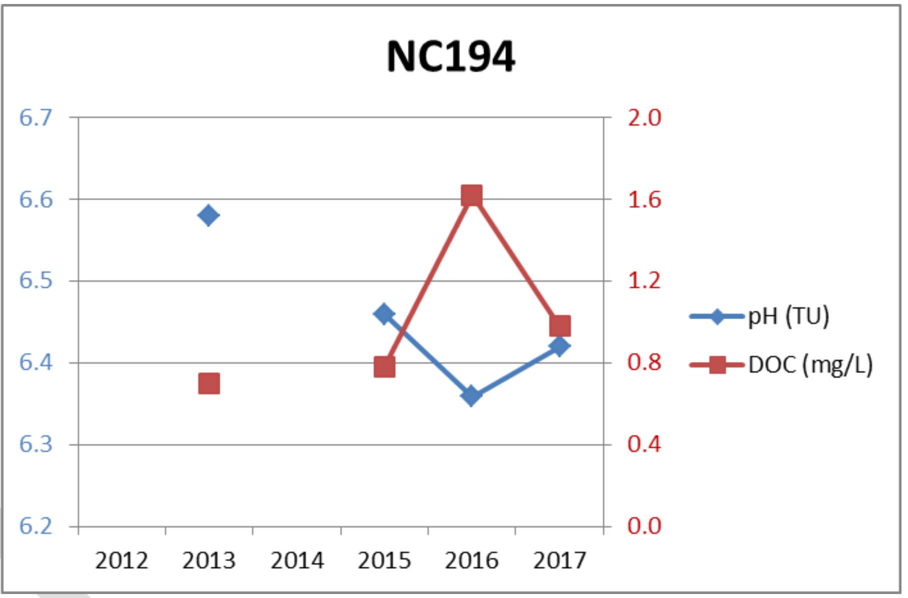







NC194
50
45
40
35
30
25
20
15
10
5
0
2012
2013
2014
2015
2016
2017
Gran ANC (µeq/L)
∑ BC * (µeq/L)
Ca * (µeq/L)


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


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

DRAFT

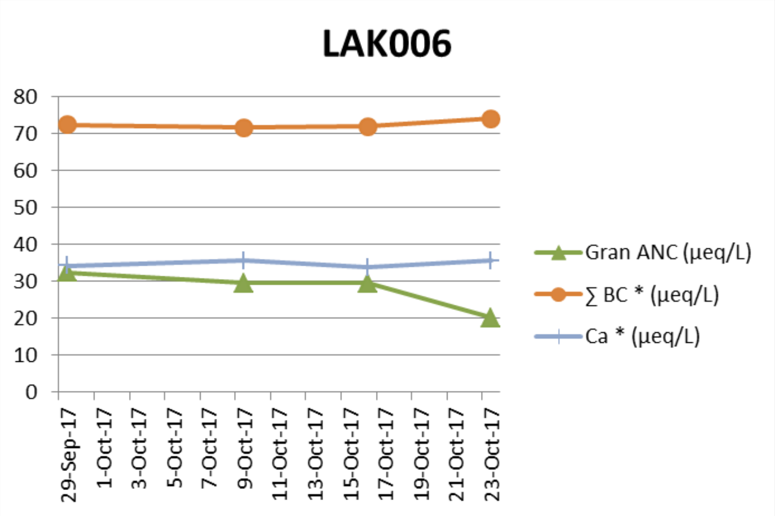
Appendix 3: Kitimat River Water Quality Sampling

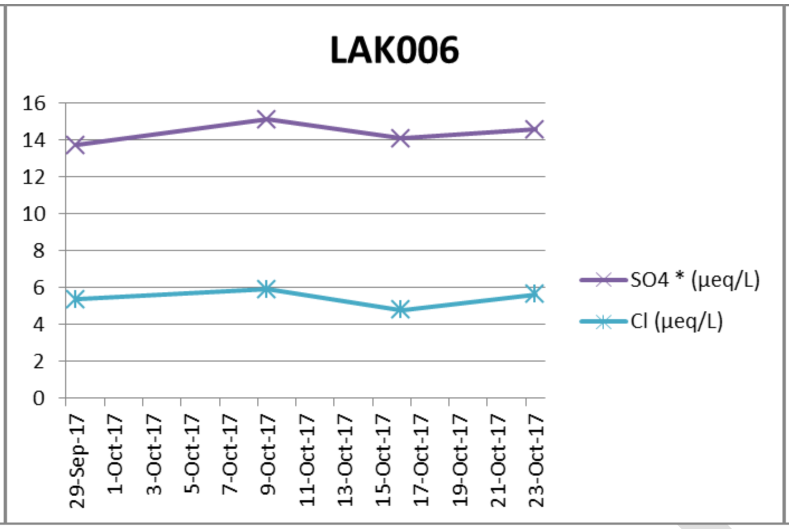
The following water quality sampling was conducted at the Rio Tinto intake from the Kitimat River (see Sections 2.9 and 3.8).

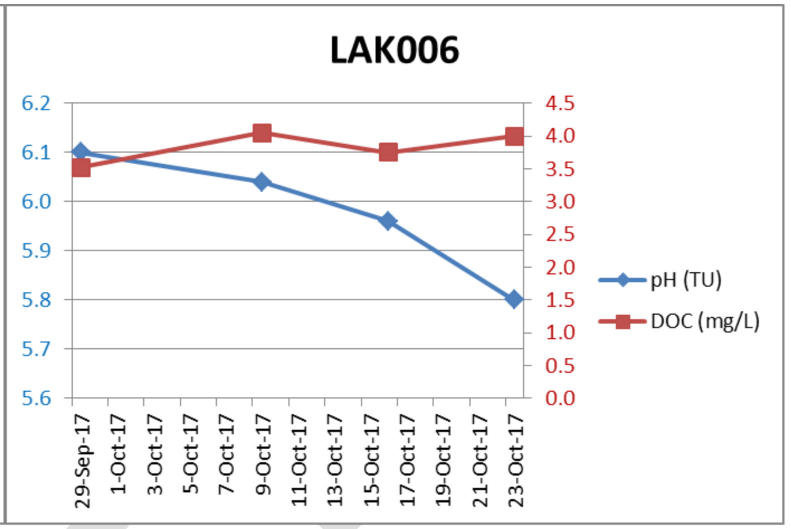
Parameter	Units	BC Drinking Water Quality Guidelines	Sampling Date					
			26-Jun-17	31-Aug-17	30-Sep-17	9-Oct-17	30-Nov-17	31-Dec-17
Dissolved Sulphate (SO_4)	mg/l	500		2.04	1.85	1.95		3.94
Fluoride (F)	mg/l	1.5	0.032	0.028	0.036	0.037	0.041	0.017
Nitrate plus Nitrite (N)	mg/l			0.04	0.049	0.049	0.085	0.11
Total Suspended Solids	mg/l		<4.0	<4.0	8.5	53.8	0	0
Dissolved Calcium (Ca)	mg/l		4.02	3.75	5.27	5.03	4.88	7.34
Dissolved Magnesium (Mg)	mg/l		0.384	0.398	0.588	0.598	0.579	0.883
Dissolved Hardness ($CaCO_3$)	mg/l			11	15.6	15	14.6	22
pH			7.33	7.45	7.56	7.32	7.28	7.41
Dissolved Aluminum (Al)	mg/l	9.5	0.0217	0.0225	0.0452	0.054	0.0931	0.0234
Dissolved Antimony (Sb)	mg/l		<0.00050		<0.00050	<0.00050	<0.00050	<0.00050
Dissolved Arsenic (As)	mg/l	0.01	<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Barium (Ba)	mg/l		0.0081		0.0113	0.0108	0.0108	0.0153
Dissolved Beryllium (Be)	mg/l		<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Bismuth (Bi)	mg/l		<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Boron (B)	mg/l		<0.050		<0.050	<0.050	<0.050	<0.050
Dissolved Cadmium (Cd)	mg/l	0.005	<0.000010		<0.000010	<0.000010	<0.000010	<0.000010
Dissolved Chromium (Cr)	mg/l		<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Cobalt (Co)	mg/l		<0.00020		<0.00020	<0.00020	<0.00020	<0.00020
Dissolved Copper (Cu)	mg/l	1	0.00312		0.0143	0.00727	0.0114	0.0042
Dissolved Iron (Fe)	mg/l	0.3	0.0427		0.0837	0.088	0.128	0.115
Dissolved Lead (Pb)	mg/l	0.01	<0.00020		<0.00020	<0.00020	<0.00020	<0.00020
Dissolved Lithium (Li)	mg/l		<0.0020		<0.0020	<0.0020	<0.0020	<0.0020
Dissolved Manganese (Mn)	mg/l	0.05	0.004		0.0068	0.0047	0.0148	0.0219
Dissolved Mercury (Hg)	mg/l	0.001	<0.000050					
Dissolved Molybdenum (Mo)	mg/l	0.25	<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Nickel (Ni)	mg/l		<0.0010		<0.0010	<0.0010	<0.0010	<0.0010
Dissolved Selenium (Se)	mg/l	0.01	<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Silicon (Si)	mg/l		1.58		2.39	2.01	2.55	3.2
Dissolved Silver (Ag)	mg/l		<0.000020		<0.000020	<0.000020	<0.000020	<0.000020
Dissolved Strontium (Sr)	mg/l		0.0235		0.0322	0.0312	0.0281	0.0425
Dissolved Thallium (Tl)	mg/l		<0.000010		<0.000010	<0.000010	<0.000010	<0.000010
Dissolved Tin (Sn)	mg/l		<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Titanium (Ti)	mg/l		<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Uranium (U)	mg/l		<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Vanadium (V)	mg/l		<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zinc (Zn)	mg/l	5	<0.0050		<0.0050	<0.0050	<0.0050	<0.0050
Dissolved Zirconium (Zr)	mg/l		<0.00010		<0.00010	<0.00010	<0.00010	<0.00010
Dissolved Potassium (K)	mg/l		0.354		0.605	0.548	0.429	0.658
Dissolved Sodium (Na)	mg/l		0.807		1.27	1.13	1.29	2.7
Dissolved Sulphur (S)	mg/l		<3.0		<3.0	<3.0	<3.0	<3.0

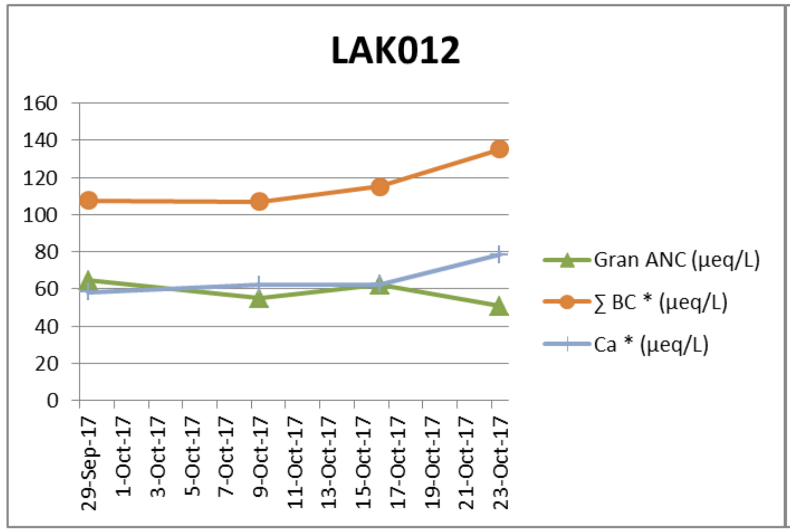
DRAFT

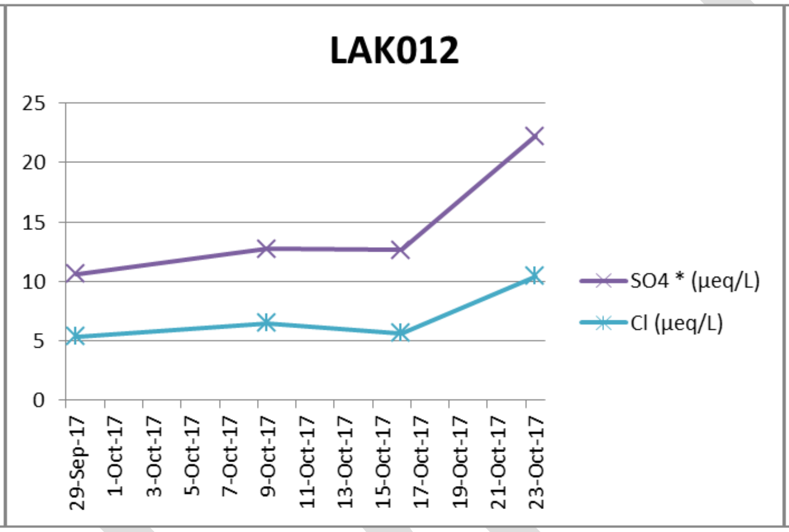
Appendix 4: Patterns of Water Chemistry Change During October 2017

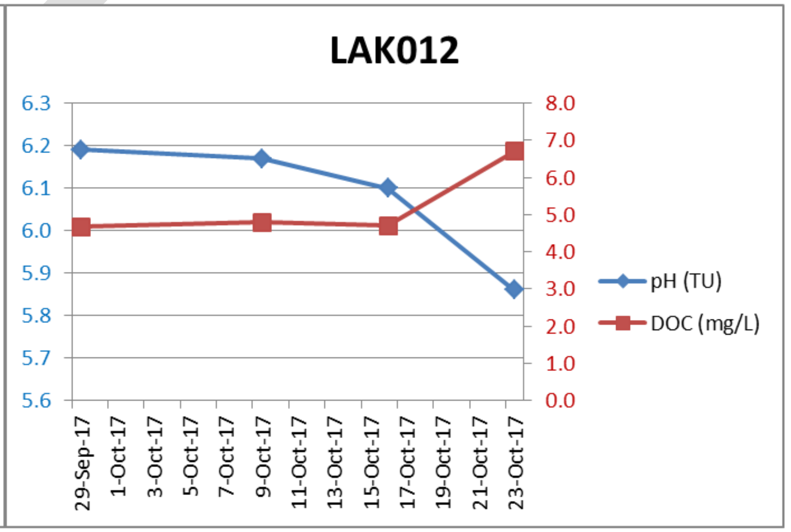


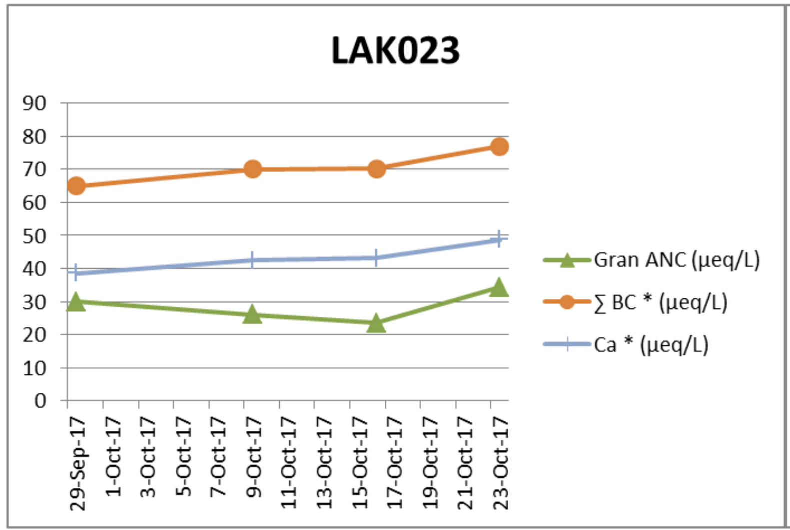


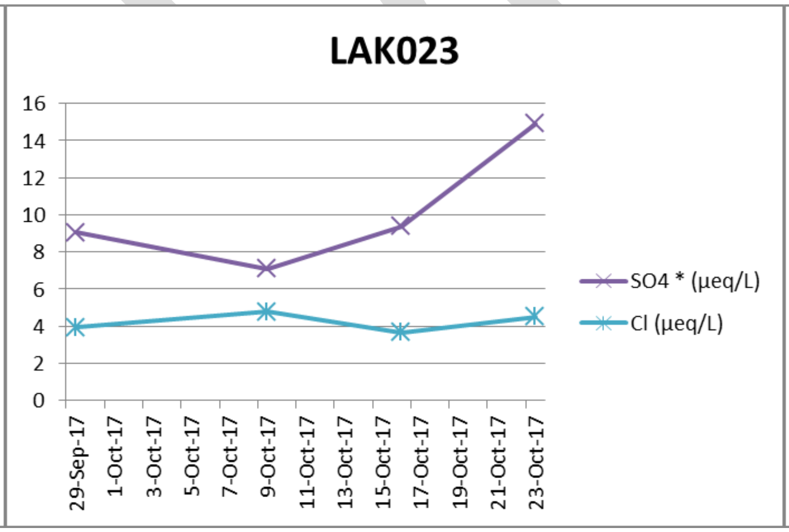


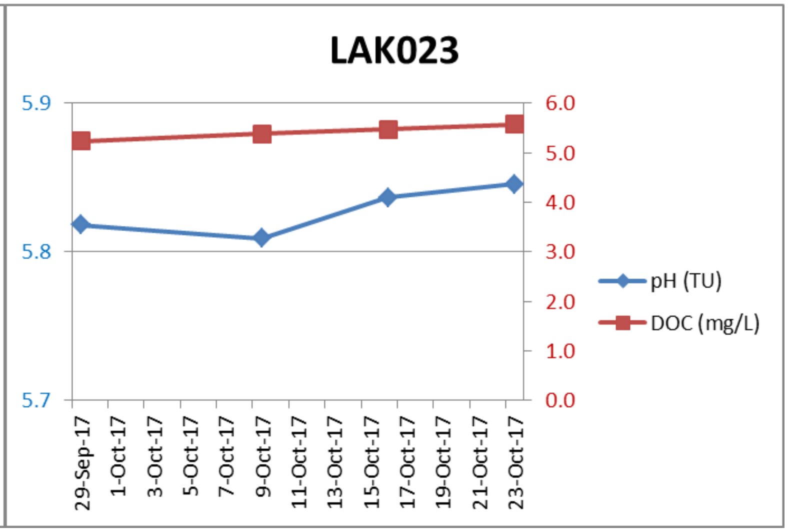


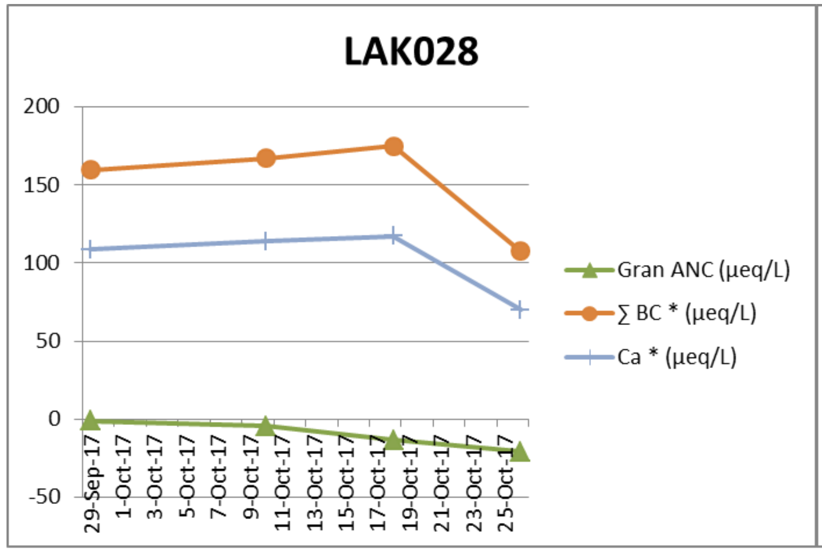


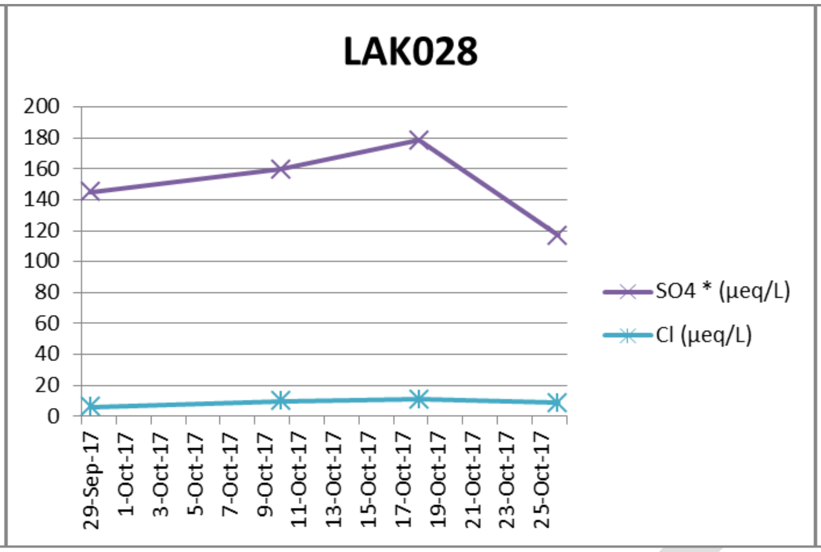


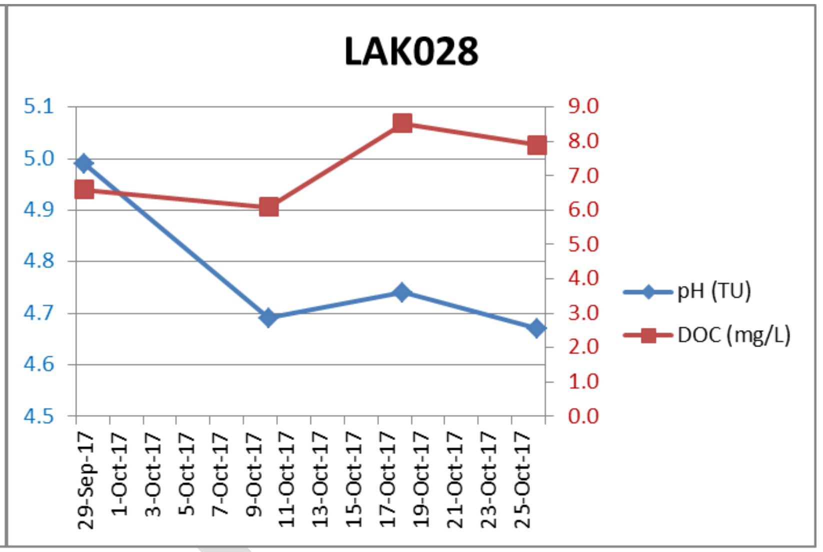


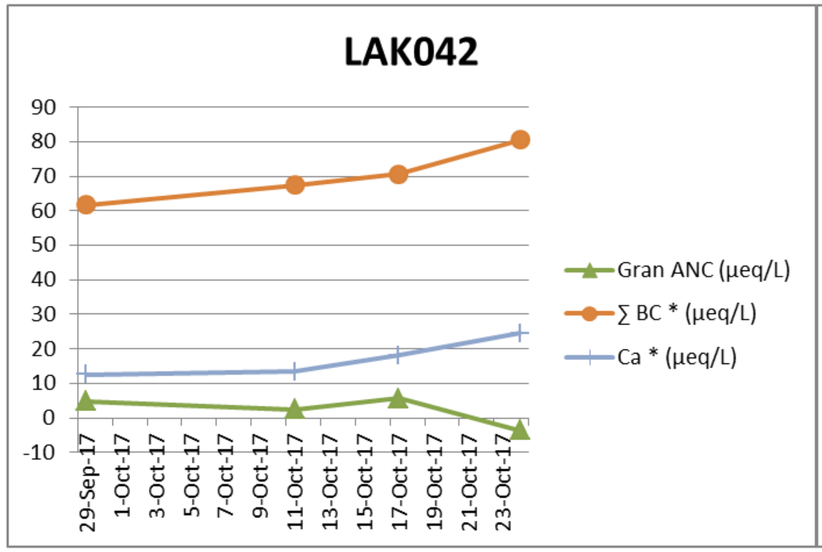


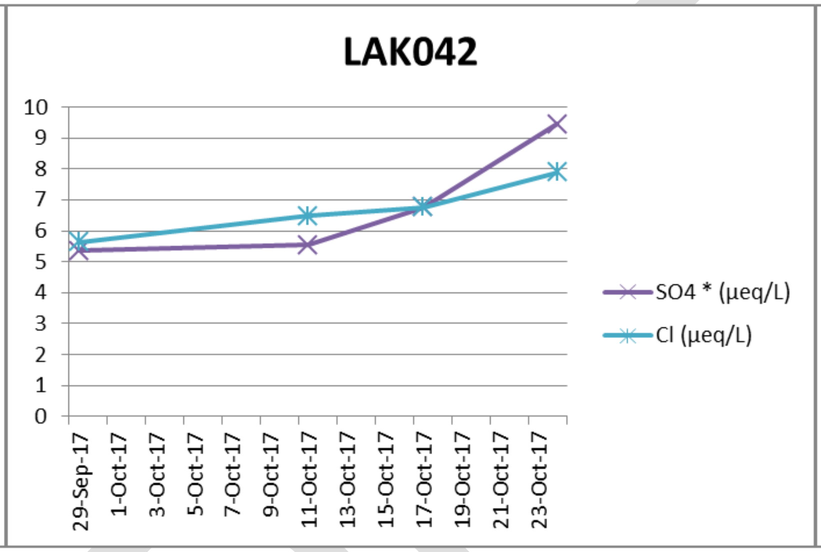


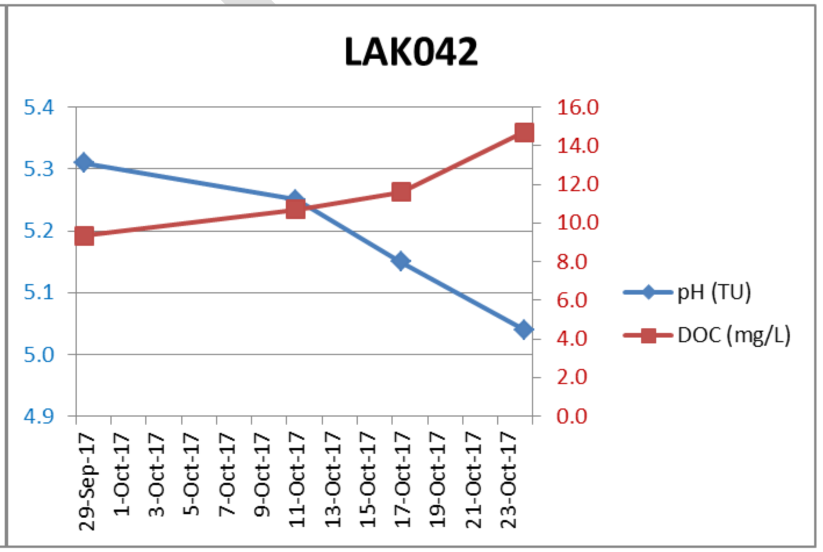

LAK028
200
150
100
50
0
-50
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
25-Oct-17
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)

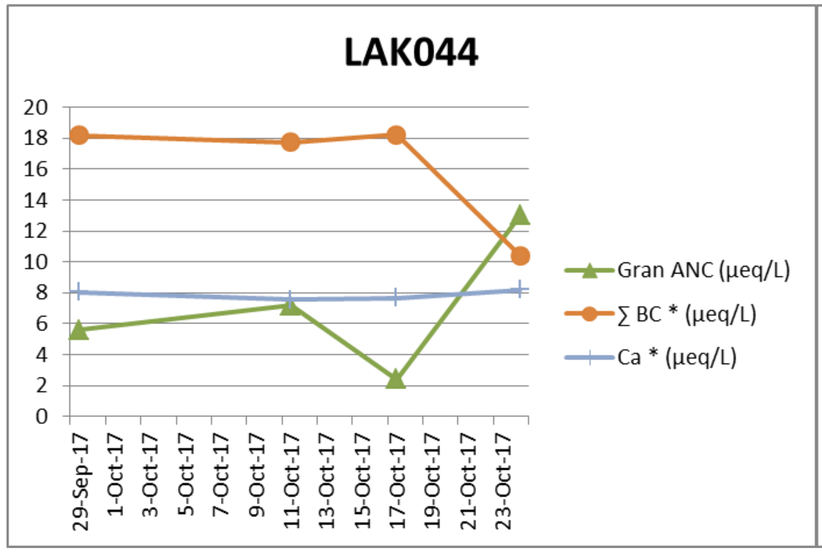

LAK028
200
180
160
140
120
100
80
60
40
20
0
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
25-Oct-17
SO4 * (μeq/L)
Cl (μeq/L)

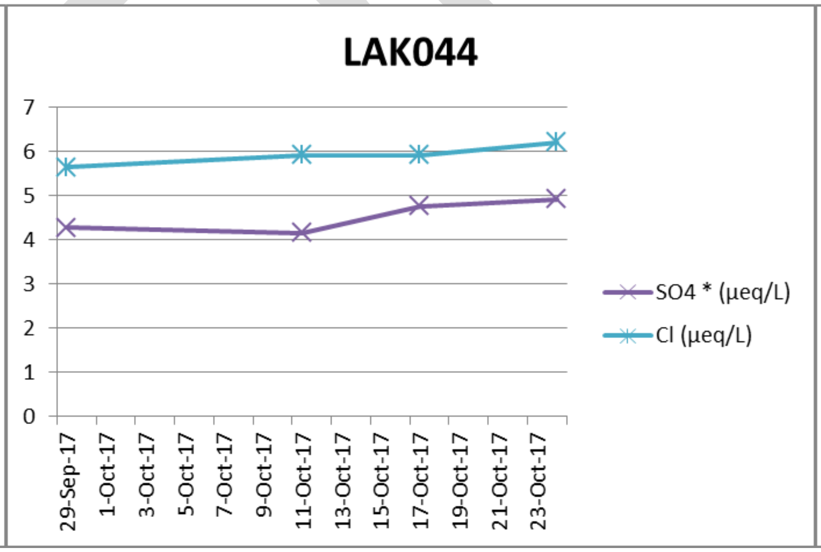

LAK028
5.1
5.0
4.9
4.8
4.7
4.6
4.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
25-Oct-17
pH (TU)
DOC (mg/L)

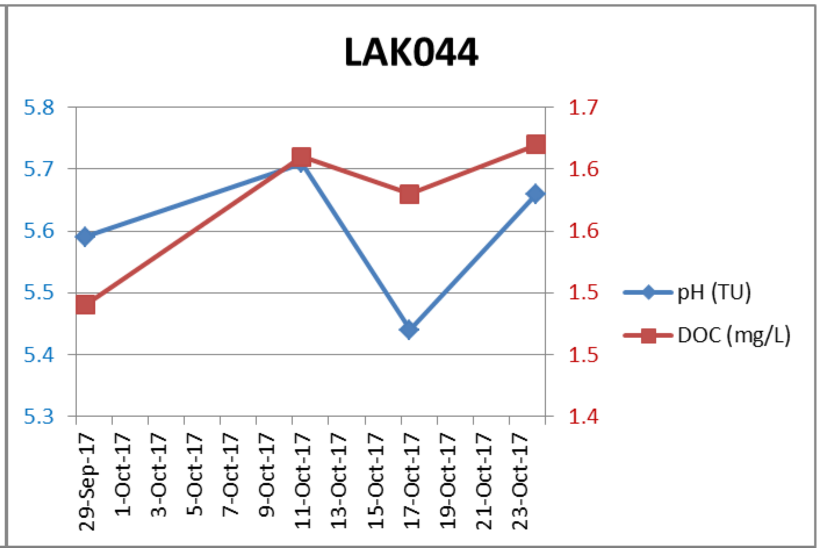

LAK042
90
80
70
60
50
40
30
20
10
0
-10
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)


LAK042
10
9
8
7
6
5
4
3
2
1
0
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
SO4 * (μeq/L)
Cl (μeq/L)


LAK042
5.4
5.3
5.2
5.1
5.0
4.9
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
pH (TU)
DOC (mg/L)


LAK044
20
18
16
14
12
10
8
6
4
2
0
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
Gran ANC (μeq/L)
∑ BC * (μeq/L)
Ca * (μeq/L)


LAK044
7
6
5
4
3
2
1
0
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
SO4 * (μeq/L)
Cl (μeq/L)


LAK044
5.8
5.7
5.6
5.5
5.4
5.3
1.7
1.6
1.6
1.5
1.5
1.4
29-Sep-17
1-Oct-17
3-Oct-17
5-Oct-17
7-Oct-17
9-Oct-17
11-Oct-17
13-Oct-17
15-Oct-17
17-Oct-17
19-Oct-17
21-Oct-17
23-Oct-17
pH (TU)
DOC (mg/L)