

Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project

2013 and 2014 Annual Reports

Package of Technical Memoranda

Compiled for:

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The following technical memoranda are cited in the **2013 and 2014 Annual Reports**, and are provided on the following pages in the order listed below:

Technical Memo P01. Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: 2011–2012 (March 2015, Trent University)

Technical Memo P02. Atmospheric Sulphur Dioxide – Passive Diffusive Sampler Network: Pilot Study (March 2015, Trent University)

Technical Memo V01. Vegetation Resource Inventory Metadata (December 2014, ESSA Technologies Ltd.)

Technical Memo V02. Sensitive Ecosystems (March 2015, ESSA Technologies Ltd.)

Technical Memo S01. Steady-State Soil Modelling – Revised Modelling and Mapping of Terrestrial Critical Loads (March 2015, Trent University)

Technical Memo S02. Steady-State Soil Modelling - Supplemental Soil Sampling (March 2015, Trent University)

Technical Memo W01. Freshwater Chemistry Analyses (March 2015, ESSA Technologies Ltd.)

Technical Memo W02. Continuous Monitoring of pH in West Lake, End Lake and Little End Lake in Fall, 2014. (January 2015, Limnotek Research and Development Inc.)

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KMP SO₂ EEM Program – Technical Memo P01

Atmospheric Sulphur Dioxide
Passive Diffusive Sampler Network: 2011–2012

March 2015

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1 Overview

A passive diffusive sampler is a device for measuring the gaseous atmospheric concentration of an analyte by diffusion through a static air layer onto an adsorbent membrane. They require no electricity, no pumps, have no moving parts, they are compact and portable, inexpensive, and simple to use.

Passive samplers should ideally provide reliable, cost-effective measurements of air concentrations at multiple locations to evaluate ‘hotspots’ or determine long-term trends. Observations represent time-integrated ‘average’ concentrations for the exposure period, typically one week to one month.

2 Kitimat Passive Diffusive Sampler Network

During 2011 and 2012, Rio Tinto Alcan operated a passive sampler network to provide empirical observations of atmospheric sulphur dioxide (SO₂) concentrations.

A comprehensive network review was carried out during 2012, with the goal to move towards a low maintenance, cost-effective reliable network of SO₂ passive samplers providing scientifically defensible data to support the Environmental Effects Monitoring Program.

This technical memo describes the monitoring results for the 2011 and 2012, and recommendations from the network review.

3 Network Overview

The network was established during 2011 with 19 sites, and expanded in 2012 with the addition of two sites (n = 21). The majority of the monitoring sites were located in and around Kitimat (see Figure 1 and Table 1). During 2011, the network was operated for 11 weeks (04 August–20 October), and 21 weeks during 2012 (17 May–18 October).

Passive samplers were deployed weekly at each site (one sampler per site), using Radellio samplers coated with triethanolamine (TEA). Weekly exposures are recommended (by the manufacturer) in regions where relative humidity is > 70%.

The limit of quantification for Radellio TEA samplers is 1 ppb (7 days). The analysis of sampler membranes was carried out by Maxxam Analytics.

To evaluate the performance of the passive samplers, they were co-located with four (five during 2011) continuous stations (see Figure 2).



Table 1. ID, name and location (latitude and longitude) of monitoring sites in the Kitimat Passive Diffusive Sampler Network. Note: Only the first 19 stations were operated during 2011.

ID	Site Name	Latitude	Longitude
1	Bish Road Lookout	53.9380	-128.727
2	Bish Site	53.9647	-128.704
3	Rifle Range	54.0170	-128.709
4	KMP	54.0195	-128.703
5	Bend	54.0282	-128.713
6	Haul Road	54.0293	-128.702
7	Sand Hill	54.0514	-128.710
8	PNG Station	54.0664	-128.691
9	Claque Mountain	54.0787	-128.695
10	Kitamaat Village	53.9734	-128.651
11	Low Spot	54.0246	-128.652
12	Low Channel	54.0469	-128.664
13	Kitimat Riverlodge	54.0540	-128.671
14	Kitimat City Centre MAML	54.0559	-128.654
15	Colghlin Park	54.0521	-128.628
16	High School	54.0602	-128.627
17	Whitesail	54.0669	-128.639
18	Cablecar	54.0996	-128.626
19	Williams Creek*	54.4276	-128.447
21	Power Line Corridor	54.0950	-128.668
22	Onion Lake Ski Trail	54.3035	-128.616

* Site 19 is located north of Kitimat close to Terrace Airport. Site 20 was not established.

Figure 1. Location of monitoring sites in the Kitimat Passive Diffusive Sampler Network. Note: the network was composed of 19 sites in 2011, and expanded to 21 during 2012. The site name and co-ordinates are given in Table 1.



Figure 2. Location of continuous sulphur dioxide monitoring stations (red and yellow squares) where passive diffusive samplers were co-deployment during 2011 and 2012.

4 Kitimat Passive SO₂ Network: 2011

During 2011, more than 60% of exposed samplers were reported by Maxxam as less than the MDL (method detection limit), i.e., they were recorded as non-valid observations.

This prompted questions on the appropriate period of sample exposure (1 week, 2 week, etc), sampler limit of detection, site locations, quality of analytical procedures, suitability of samplers under (regionally) high humidity, etc.

5 Kitimat Passive SO₂ Network: 2012

To address the issues identified during 2011, a comprehensive network review was carried out. The review included the following tasks:

1. Laboratory analytical procedures were reviewed and revised (method update);
2. The 2011 raw data were recaptured;
3. Site criteria were evaluated and sites relocated (where required);
4. The network was expanded (2 new sites);
5. Rotating triplicate sample exposure were implemented (replaced rotating duplicate);
6. A database was established for 2011 and 2012 results;
7. Data quality objectives were established to evaluate data, i.e., comparison to continuous stations, variability between replicate exposures;
8. A focused co-exposure trial was carried out.

During 2012, ~100% of exposures were greater than the analytical detection limit (compared with < 40% during 2011). There were several potential reasons for the increase in data:

1. Changes in meteorology and / or emissions during 2012 compared with 2011;
2. Changes (updates) to sites and field procedures;
3. Upgrades to analytical equipment (Maxxam);
4. Changes in laboratory methods (Maxxam);
5. Ongoing external review of Maxxam results

As a result, the 2012 monitoring season provided data to: [i] assess spatial variability of atmospheric SO₂, [ii] evaluate variation between replicate exposures, and [iii] assess performance against continuous samplers.

[i] Spatial variability in atmospheric SO₂: The data showed a strong gradient in atmospheric SO₂ across stations during 2012 based on the median of weekly observations during the period 07 June–11 October 2012 (n = 14–18; observations blank corrected).

Higher concentrations were observed along the ‘plume’ broadly consistent with modelled data (see Figure 3).

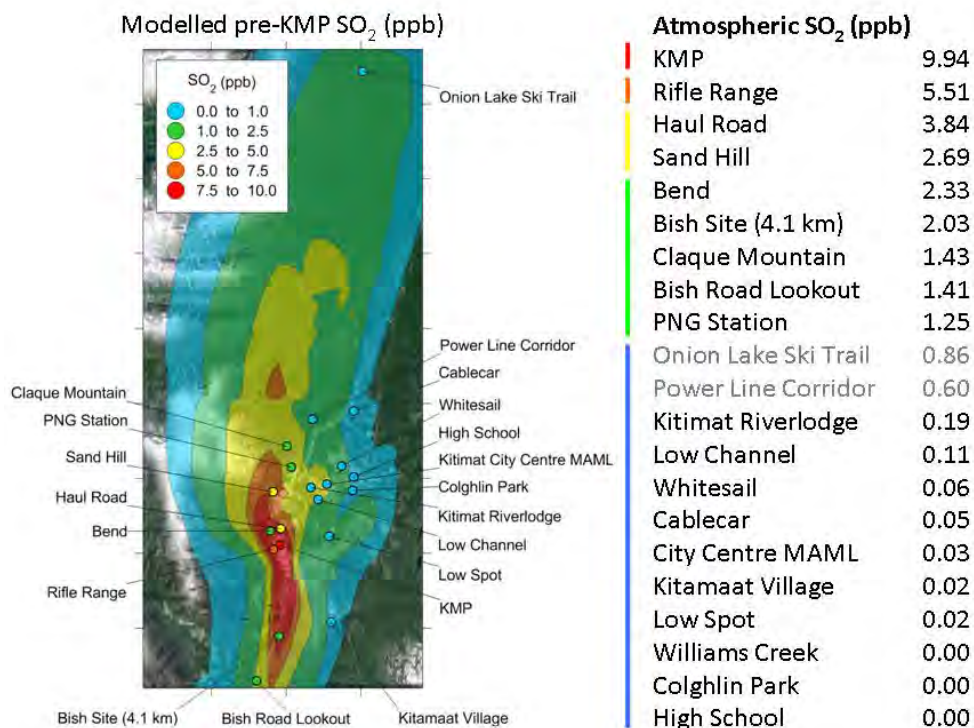


Figure 3. Median atmospheric sulphur dioxide (SO₂) concentrations observed during 2012 (07 June–11 October) at passive diffusive sampler monitoring sites. Modelled (pre-KMP) atmospheric SO₂ concentrations are also shown (left). Note: Onion Lake Ski Trail and Power Line Corridor are greyed as these sites were not in operation during the entire 2012 monitoring period.

[ii] Variability in replicate exposures: During 2012, there were 29 triplicate exposures (encompassing 7, 14 and 28 day exposures); the variability between replicates was evaluated using the coefficient of variation (COV, i.e., standard deviation / mean × 100).

The average COV between replicate samplers (n = 3) was 39.0%, the median was 31.6%. In general, high COV may be caused by low atmospheric concentrations. Limiting the analysis to sites with observations > 1 ppb (n = 7), the average COV between replicate samplers (n = 3) was similarly 38.6%, and the median COV was 30.6%.

The high variability between replicate exposures is a concern.

[iii] Comparison with continuous samplers: During 2012, there were 46 one-week and 23 two-week exposures co-located with continuous SO₂ samplers; the correspondence between passive and continuous was assessed using linear regression (R²).

The coefficient of determination between continuous and passive atmospheric concentrations for one week exposures was R² = 0.449 (n = 46), and for two week exposures was R² = 0.590 (n = 23).

Limiting analysis to sites with observations > 1 ppb; the relationship between continuous and passive atmospheric concentrations for one week exposures was R² = 0.021 (n = 12), and for two week exposures was R² = 0.440 (n = 4).

The limited correspondence with continuous data is a concern.

6 Co-Exposure Study

During 2012, triplicate passive samplers for Ormantine tubes, Willems badges and Radiello were co-exposed at three sites with continuous SO₂ samplers (Haul road, Riverlodge and Kitamaat village; see Figure 2), for exposure periods of 1, 2 and 4 weeks during the period 16 August–27 September (7 exposures). Further two sets of Radiello were exposed and analysed at Illinois University (ILL) and Maxxam Analytics (MAX).

The objective of the study was to evaluate [A] variability in triplicate samplers, [B] the performance of Radiello compared with other samplers and continuous samplers, the influence of exposure length, and [C] Maxxam analytical procedures.

[A] Variability in triplicate exposures: The variability (COV) was evaluated as the average across all stations and all exposures, the average for the high concentration site, and with increasing exposure length.

Average Variability in triplicate samplers across all sites and exposures:

- Ormantine tubes: Not evaluated as > 59% returned < DL.
- Willems badges: 7.2% (range 1.0–15.5%).
- Radiello (ILL): Not presented as three exposures were ‘lost’.
- Radiello (MAX): 31.3% (range 5.8–93.7%).

Variability in triplicate samplers at the high concentration site (Haul road):

- Willems badges: 6.0% (range 2.7–9.6%)
- Radiello (MAX): 35.3% (range 5.8–93.7%)

Variability in triplicate samplers with exposure length (1, 2 and 4 weeks):

- Willems badges: 6.3%, 8.2% and 6.4%
- Radiello (MAX): 44.3%, 31.9% and 26.3%

[B] Passive against continuous SO₂ data: The amount measured on the passive membrane was compared (using linear regression) against cumulative SO₂ measured at the co-located continuous stations (see Figure 4). Note: continuous data for Haul road were not included as data were unavailable owing to equipment error. The loss of data for the high concentration site severely limited the assessment.

[C] Inter-laboratory comparison: Co-exposed sets of triplicate Radiello samplers were sent to Illinois and Maxxam (3 sites × 4 exposures). In addition, WMO standard QC solutions were supplied to both laboratories.

Comparison of measured concentrations between laboratories was good ($R^2 = 0.95$) owing to the gradient in atmospheric concentration; however, there was considerable scatter in the data at lower concentrations. Further, maxxam had higher absolute difference for target WMO solutions compared with Illinois (9.0% compared with 0.6%).

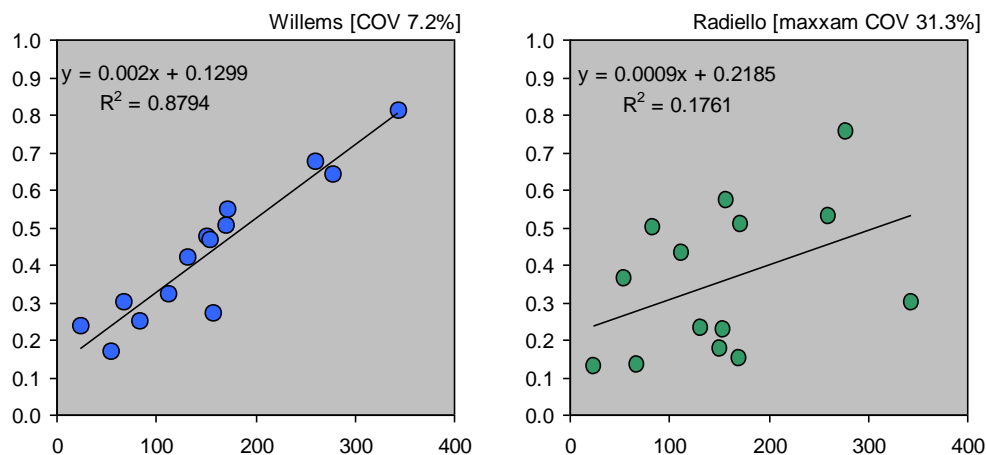


Figure 4. Comparison of cumulative continuous SO₂ (ppb [x-axis]) against amount on passive samplers (mg L⁻¹) for Willems badge and Radiello samplers.

7 Conclusions

There was a significant improvement in the number of data observations during 2012 (virtually no data flagged as <DL by Maxxam); however, variability in replicate exposures and the limited correspondence with continuous measurement is a concern (may be related to field and / or laboratory procedures, or regional suitability of TEA-based samplers).

Nonetheless, the data showed a consistent gradient in air concentrations associated with the plume, i.e., the 2012 summary statistics provides a 'reasonable' spatial ranking of atmospheric SO₂.

8 Recommendations

1. The network was heavily weighted to low concentration regions (related to previous human health focus); it is recommended that many of the 'urban' sites be moved to regions predicted to experience increases in air concentration (consistent with modelled plume);
2. Two week exposures show no loss in measurement accuracy; it is recommended that exposure duration is increased to two weeks (or greater), and replication is increased at sites;
3. Supplemental sampler exposure evaluation should be carried out to evaluate variability and sampler performance at high air concentrations;
4. As per manufacturer specifications, TEA-based Radiello samplers appear to be sensitive to high humidity and have a detection limit of < 1 ppb (weekly exposure). An alternative (commercial) sampler is recommended for future monitoring, e.g., potassium or sodium carbonate (e.g., IVL or AGAT PAQS) or possibly Nylasorb based (e.g., Willems) samplers.

RioTintoAlcan

KMP SO₂ EEM Program – Technical Memo P02

Atmospheric Sulphur Dioxide
Passive Diffusive Sampler Network: Pilot Study

March 2015

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1 Overview

Passive samplers can be used to provide empirical observations of atmospheric SO₂ concentrations to (a) assess spatial and temporal changes, (b) evaluate modelled concentration fields, and (c) estimate dry deposition of SO₂. They provide time-integrated air concentrations which support the assessment of ecosystems impacts under the EEM program.

Ideally a passive sampler network should be cost-effective, low maintenance and provide reliable, scientifically defensible data. However, the 2011–2012 RTA Passive Monitoring Program, which used Radiello triethanolamine (TEA) coated samplers, did not produce consistent reliable data (see Technical Memo: Passive Diffusive Sampler Network 2011–2012, March 2015).

The EEM program proposed a pilot study to evaluate the performance of SO₂ passive samplers prior to re-establishment of a network. Future network deployments depended upon the performance of samplers during the pilot study.

2 Passive Sampler Pilot Study

The goal of the pilot study is to evaluate the performance of passive SO₂ samplers against continuous SO₂ monitors across a gradient in air concentrations. It is proposed that passive samplers are deployed across three active monitoring stations during summer 2015 (May to September).

Passive samplers will be deemed effective, i.e., reliable for network deployment, if they exhibit: (a) a high correlation with continuous SO₂ monitors (e.g., $r \geq 0.8$), and (b) low variability between replicate exposures.

3 Passive Samplers

Passive samplers: SO₂ passive samplers with a carbonate-based coating have been shown to have a high degree of reliability (Cruz et al. 2005, Swaans et al. 2007) compared to TEA coated samplers. The 2011–2012 network employed TEA coated samplers which showed high variability between replicates, limited correlation with continuous observations, and poor levels of detection.

It is proposed that two carbonate-based samplers are evaluated in the pilot study: IVL diffusive sampler and AGAT Laboratories Passive Air Quality Sampler (PAQS).

The IVL samplers may be viewed as the ‘industry standard’; IVL have > 25 years experience with diffusive samplers, their SO₂ samplers have been widely used around the globe (Carmichael et al. 2003, Ferm and Rodhe 1997), they are well represented in the peer-review literature and shown to have good correspondence with continuous samplers (Ferm and Rodhe 1997, Swaans et al. 2007).

The PAQS provide a potential ‘local’ option for a carbonate-based sampler; though notably their reported lower detection limit is 2.5 times higher than the IVL samplers. However, AGAT Laboratories have agreed to provide discounted sampler pricing during the pilot study.

Lower detection limit (30 day exposure): 0.04 ppb IVL samplers compared with 0.1 ppb for PAQS

4 Monitoring Stations

It is proposed that three continuous monitoring stations (KMP, Haul Road and Riverlodge: Figure 1) are included in the pilot study to capture a range in atmospheric SO₂ concentrations (Table 1).

Passive samplers should be similarly deployed (consistent sampler housing, setting, exposure period) across all three stations during the pilot study. It is essential that continuous SO₂ monitors are in operation during the study to allow evaluation of the samplers.

Table 1. Average monthly atmospheric concentration (ppb) of sulphur dioxide (SO₂) during summer 2014 at KMP, Haul Road and Riverlodge continuous monitoring stations (see Figure 1 for station location).

Month	Average Atmospheric Concentration of Sulphur Dioxide (ppb)		
	KMP	Haul Road	Riverlodge
May 2014	4.54	2.67	0.65
June 2014	4.64	3.08	0.17
July 2014	5.34	2.93	0.30
August 2014	4.71	3.14	0.56



Figure 1. Location of continuous sulphur dioxide monitoring stations for co-deployment of passive samplers during the 2015 pilot study.

5 Sampler Deployment

Pilot study duration: A four month period between May and August is proposed to allow adequate capture of data for the statistical evaluation of sampler performance against continuous SO₂ observations.

Sampler deployment: A combination of two and four week deployments is proposed, with rotating replicate exposures to evaluate variability between samplers.

While both IVL and AGAT Laboratories recommend one month exposures, two weeks deployments provide greater resolution in temporal concentrations. Further, passive sampler performance may be reduced under long(er) exposure periods.

Similarly both IVL and AGAT Laboratories indicate that one sampler per exposures is adequate but note that replicate exposures provide greater confidence in sampler results.

Passive sampler numbers: A total of 60 passive samplers are required from both IVL and AGAT Laboratories. In addition, sampler-specific housing will need to be obtained from each supplier.

Sampler analysis: Individual sampler pricing includes the cost of analysis carried out by the supplier; IVL 50.00 US\$ (420 SEK) per sampler, and PQAS 52.50 C\$ per sampler (note AGAT will provide discounted pricing of 26.25 C\$ during the pilot study).

IVL: www.diffusivesampling.ivl.se

AGAT Laboratories: www.agatlabs.com/energy/air-quality-monitoring/passive-monitoring.cfm

6 Literature Cited

Carmichael, G.R., Ferm, M. and 28 others. 2003. Measurements of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America using passive samplers. *Atmospheric Environment* 37, 1293–1308.

Cruz, L.P.S., Campos, V.P., Novaes, J.A.P. and Tavares, T.M. 2005. Laboratory validation of a passive sampler for SO₂ atmospheric monitoring. *Journal of the Brazilian Chemical Society*, 16:1, 50–57.

Ferm, M. and Rodhe, H. 1997. Measurements of air concentrations of SO₂, NO₂ and NH₃ at rural and remote sites in Asia. *Journal of Atmospheric Chemistry* 27, 17–29.

Swaans, W., Goelen, E., De Fré, R., Damen, E., Van Avermaet, P., Roekens, E. and Keppens, V. 2007. Laboratory and field validation of a combined NO₂–SO₂ Radiello passive sampler. *Journal of Environmental Monitoring* 9, 1231–1240.

Technical Memo: 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.



KMP SO₂ EEM Program – Technical Memo V01

Vegetation Resource Inventory Metadata

December 2014

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(Using data provided by Rio Tinto Alcan)

1 Overview

The Vegetation Resource Inventory (VRI) data obtained cover the majority (approximately 90%) of the KMP SO₂ technical assessment study area, with a small section missing at the southern portion. These are standard VRI data¹, mapped to a scale of 1:20,000. This study area VRI map contains 8,031 polygons, each with up to 185 attributes. The attributes are of several different types:

- Identification: e.g., opening_id, original unit information, polygon_ID, labels
- Site: e.g., bec zone, subzone, variant, phase, age
- Stand composition: e.g., species and their percentage of the top six, live and dead volume by the first three species at two different utilization levels (12.5 and 17.5 cm)
- Stand-level variables: e.g., basal area, branch biomass, crown closure, soil moisture, density
- Data sources: e.g., for calculation of age, volume, or basal area

Most records have few of the columns populated, but all have information about the BEC and the top species on the site.

The complete listing of all the data columns is given below (in alphabetical order)². More recent versions of the VRI data have more columns.

¹ Data were downloaded from DataBC <https://apps.gov.bc.ca/pub/dwds/home.so>, and clipped to the original study area.

² A full description of the data columns can be found in the VRI Relational Data Dictionary: http://www.for.gov.bc.ca/hts/vridata/standards/datadictionary/vegcomp_poly_rank1_data_dictionary_draft4.0.pdf.

2 List of VRI Data Columns

ADJST_IND	DVLTOT_125	LVLSP1_125	PROJ_AGE_1
AGE_DTA_CD	DVLTOT_175	LVLSP1_175	PROJ_AGE_2
ALPN_DESIG	DVLTOT_225	LVLSP1_225	PROJ_DATE
ATRI_B_DATE	ECO_SRC_CD	LVLSP2_125	PROJ_HT_1
AV_LBL_HT	EST_SI	LVLSP2_175	PROJ_HT_2
AV_LBL_WD	EST_SI_SPC	LVLSP2_225	PROJECT_ID
B_A_DTA_CD	FEAT_SKEY	LVLSP3_125	Q_DIAM_125
BARK_BIOM	FEATURE_ID	LVLSP3_175	Q_DIAM_175
BASAL_AREA	FIZ_CD	LVLSP3_225	Q_DIAM_225
BCLCS_LV_1	FMLB	LVLSP4_125	RANK_CD
BCLCS_LV_2	FOLG_BIOM	LVLSP4_175	REF_DATE
BCLCS_LV_3	FTG_IND	LVLSP4_225	REF_YR_ID
BCLCS_LV_4	FULL_LABEL	LVLSP5_125	SHRB_CC
BCLCS_LV_5	HERB_COVER	LVLSP5_175	SHRB_HT
BEC_PHSE	HERB_PCT	LVLSP5_225	SHRB_PATT
BEC_SZONE	HERB_TYPE	LVLSP6_125	SI_DATA_CD
BEC_VAR	HRVSTDT	LVLSP6_175	SITE_INDEX
BEC_ZONE	HT_DATA_CD	LVLSP6_225	SITE_MESO
BRNCH_BIOM	INPUT_DATE	LVLTOT_125	SM_LABEL
BRYOID_PCT	INTERP_CD	LVLTOT_175	SOIL_MST_1
C_I_CODE	INTERPRETR	LVLTOT_225	SOIL_MST_2
CC_CLASS	INTRP_DATE	MAP_ID	SOIL_MST_3
COMP_LET	INV_REGION	MOD_PROCES	SOIL_NUTR
COMPARTMNT	INV_STD_CD	N_LOG_DATE	SPEC_CD_1
COV_PCT_1	LAND_CD_1	N_LOG_DIST	SPEC_CD_2
COV_PCT_2	LAND_CD_2	NFOR_DESC	SPEC_CD_3
COV_PCT_3	LAND_CD_3	NP_CODE	SPEC_CD_4
CR_CLOSURE	LAYER_ID	NP_DESC	SPEC_CD_5
CRUISE_CD	LBL_CLS_IN	NVEG_COV_1	SPEC_CD_6
CRUISE_NO	LBL_CTR_X	NVEG_COV_2	SPEC_PCT_1
DBH_LIMIT	LBL_CTR_Y	NVEG_COV_3	SPEC_PCT_2
DEAD_PCT	LBL_DISTUR	NVEG_PCT_1	SPEC_PCT_3
DEAD_STEMS	LBL_HIS_SY	NVEG_PCT_2	SPEC_PCT_4
DVLSP1_125	LBL_HIST	NVEG_PCT_3	SPEC_PCT_5
DVLSP1_175	LBL_HT	NVEG_TYP_1	SPEC_PCT_6
DVLSP1_225	LBL_OPN_CD	NVEG_TYP_2	STEM_HA_CD
DVLSP2_125	LBL_OPN_NO	NVEG_TYP_3	SURF_EXP
DVLSP2_175	LBL_PLANT	P_AGE_CS_1	TREE_PATRN
DVLSP2_225	LBL_POLYID	P_AGE_CS_2	VERT_COMPL
DVLSP3_125	LBL_SPECIS	P_HT_CAS_1	wkt_geom
DVLSP3_175	LBL_TEND	P_HT_CAS_2	WSTEM_BIOM
DVLSP3_225	LBL_VEGCOV	POLY_AREA	
DVLSP4_125	LBL_WIDTH	POLY_ID	
DVLSP4_175	LIVE_STEMS	PRINTABLE	
DVLSP4_225			
DVLSP5_125			
DVLSP5_175			
DVLSP5_225			
DVLSP6_125			
DVLSP6_175			
DVLSP6_225			



KMP SO₂ EEM Program – Technical Memo V02

Sensitive Ecosystems

April 2015

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1 Sensitive Ecosystems

One of the actions under the EEM Plan called for investigation into whether there are sensitive ecosystems in the SO₂ assessment study area, and if so, whether they occur in areas already covered by the existing EEM sampling network for vegetation, soil and water.

Two sensitive ecosystems occur in the study area, according to the BC Conservation Data Centre (CDC): black cottonwood-red alder/salmonberry, and wet subarctic Sitka spruce/salmonberry. Both are located along the Skeena River (the thick green line shown in Figure 1). None of the lake or stream sampling sites under the EEM Plan are located near these ecosystems, although one vegetation sampling site is located nearby (map on the left in Figure 1).

Some EEM sampling sites do overlap polygons from the VRI that contain Sitka spruce, cottonwood or alder, but these polygons are along other waterways near Kitimat, not in the areas explicitly identified as sensitive ecosystems (map on the right in Figure 1). Alder Cottonwood represents almost one quarter of the VRI polygons in the study area, which is not unexpected since these tend to be the first species on a site. This is likely to be an overestimation of potentially sensitive systems because the polygons only show where the species occur, without analysis of species dominance or suitable soils. Further investigation would be needed to determine if some of these sites might be adequate surrogates for the CDC-listed ecosystems, or whether EEM sampling locations might need to be added in those known sensitive ecosystems.

A recent assessment carried out for the proposed LNG site outside of Kitimat identified 12 sensitive ecological communities in that area. Four of these (identified by an asterisk *) were dominant.

Blue-listed

- amabilis fir – Sitka spruce / devil's club
- western redcedar – Sitka spruce / skunk cabbage
- Sitka spruce / Pacific crab apple *
- Lyngbye's sedge / Douglas water hemlock estuary *
- cattail marsh
- Sitka sedge / hemlock / parsley marsh

Red-listed

- Sitka spruce / salmonberry *
- tufted hairgrass / meadow barley estuary
- tufted hairgrass / Douglas aster estuary
- Lyngbye's sedge estuary
- sweet gale / Sitka sedge fen
- Sitka willow / Pacific willow / skunk cabbage swamp *

All of these areas are found in the CWHvm1 area in the southern section of the study area (Figure 2). Since this area is more heavily sampled, it is likely that some of the sampling sites overlap these systems (Figure 2), but actually overlaying the two maps would be necessary to know which systems are being sampled. The maps we have do not contain sufficient information to identify which are the appropriate sensitive ecosystems.

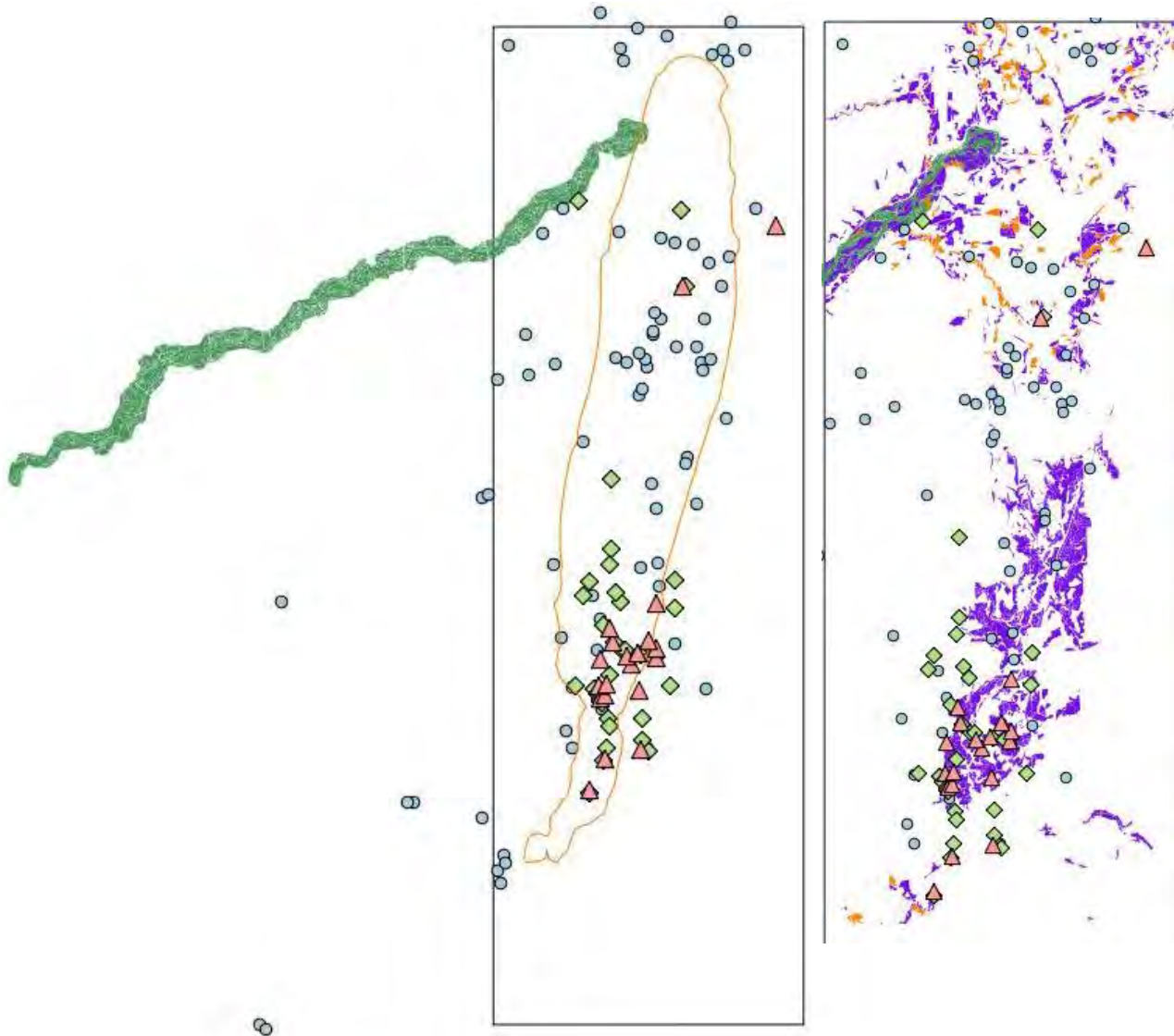


Figure 1: Map of the sensitive ecosystems and EEM sampling locations. The map on the left shows the location of the two sensitive ecosystems identified by the CDC (the thick green line). The map on the right shows the location of the presence of Sitka Spruce (orange) or Alder/Cottonwood (purple) in the study area, from VRI data. Colour legend for EEM sampling: pink triangles = atmospheric sampling stations, green diamonds = vegetation survey locations, and blue circles = water sampling locations. The orange line denotes the predicted 10 kg/ha/yr deposition isopleth. The thick green line = the location of the sensitive ecosystems. Note that only a subset of the air and water sampling locations will be sampled under the EEM plan, and soil sampling sites have not yet been determined.

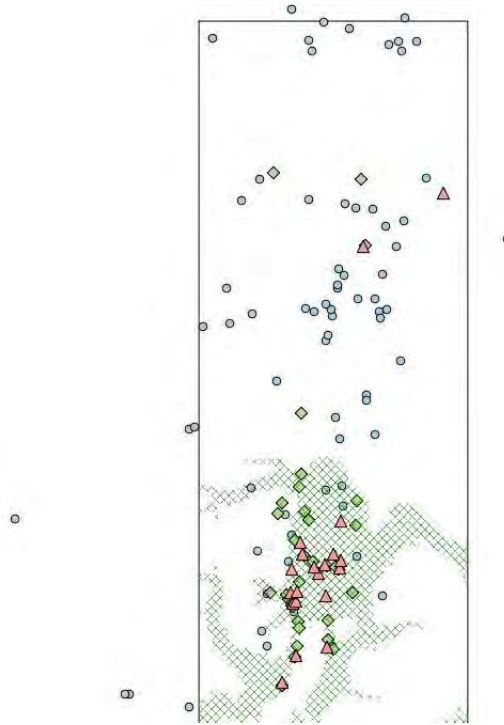


Figure 2: Map of the areas that might contain sensitive ecosystems and EEM sampling locations. The cross-hatched area shows the BEC variant (CWHvm1) in which all the sensitive ecosystems identified by the LNG study were found. Colour legend for EEM sampling: pink triangles = atmospheric sampling stations, green diamonds = vegetation survey locations, and blue circles = water sampling locations. Note that only a subset of the air and water sampling locations will be sampled under the EEM plan, and no soil sampling sets have yet been determined.

2 Sensitive Organisms

The CDC also identifies ten species at risk in the study area, which are listed in Table 1 and mapped in Figure 3. Only three of these species have been seen in the past 15 years. (That does not necessarily mean the others no longer occur in the area; just that they have not been seen.) The coastal tailed frog is the sole vertebrate on the CDC list, and it is present in many sites throughout the study area (isolated small red dots on the map in Figure 3). The moose moonwort is the only red-listed species, with 8 plants observed in 2006. The cryptic paw, found just south of Kitimat, is a recent listing for the CDC.

Table 1: CDC-listed species within the study area. Species in bold are those that have been observed within the last 15 years. (Source: BC CDC)

Vascular Plants	Fungi	Vertebrates
bog rush	cryptic paw	coastal tailed frog
bog adder's-mouth orchid	oldgrowth specklebelly	
white adder's-mouth orchid		
eminent bluegrass		
lance-fruited draba		
moose moonwort <i>red-listed</i>		
stalked moonwort		

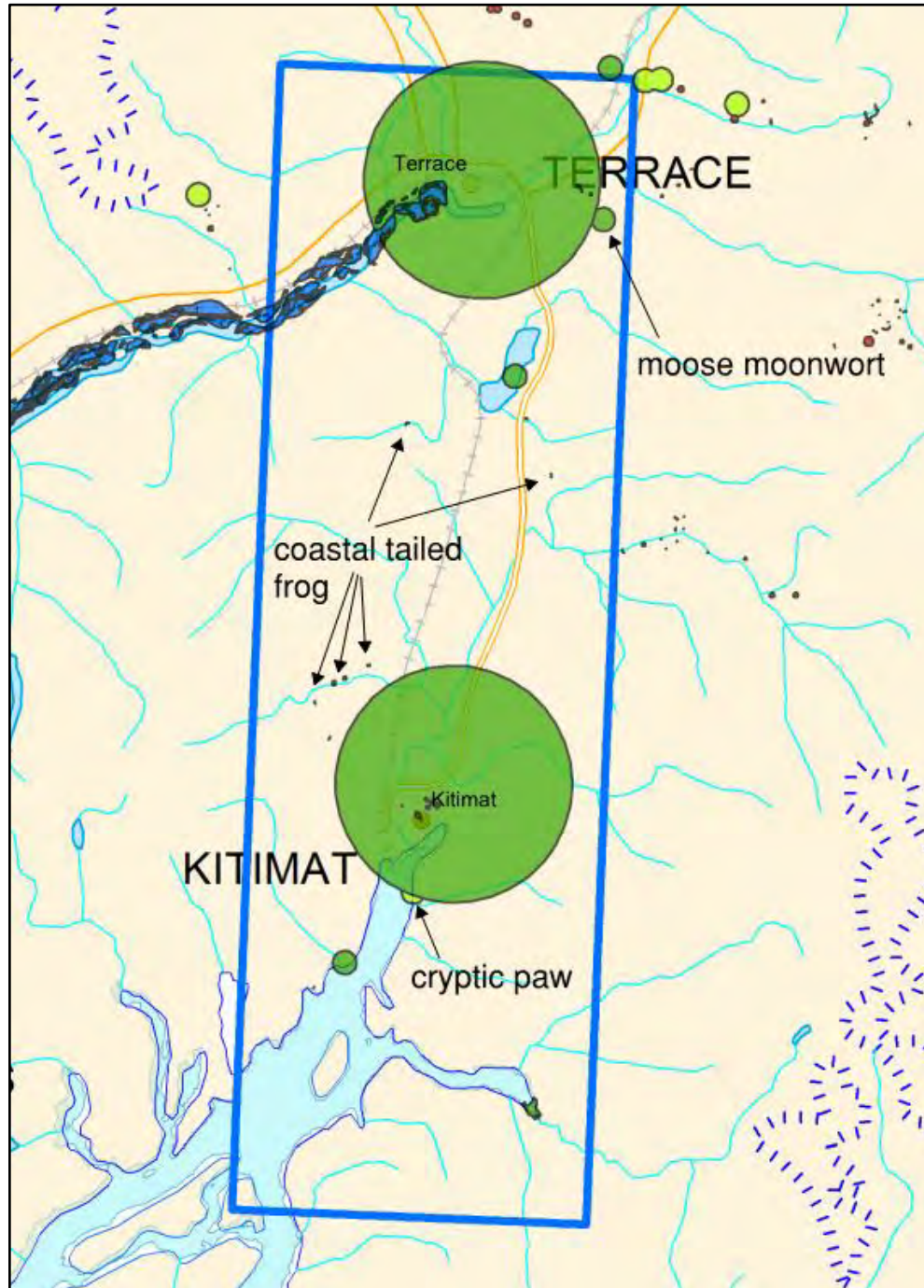


Figure 3: Map of the sensitive ecosystems and organisms in and near the study area. The blue rectangle indicates the study area. The dark blue polygons along the Skeena River represent the two sensitive ecosystems. The small red dots / specs are locations of coastal tailed frog (only a subset of these are noted on the map). Dark green circles are plants; lighter green circles are fungi. (Source: Maija Finvers, Terrain Information Specialist, Terrestrial Unit Head, Ecosystem Information Section, Knowledge Management Branch, MOE www.env.gov.bc.ca/tei/)

3 Data Sources

We searched the following sites and sources for data for this analysis:

- Sensitive Ecosystem Initiative: we looked at the spatial coverage of work done thus far under this initiative, but most is concentrated on the areas in the southern interior and the south coastal systems, and there was no information that overlapped with the study area.
- GeoBC: we requested TEM and PEM data for the study area, but no data were available for this study area.
- iMapBC: we spent some time looking at different layers to see what might have appropriate information that would cover this study area.
- EcoCat: we searched the report catalogue (both keyword search and location search) for reports that might contain maps of the area. Most reports available within the study area reported on stream or fish conditions in order to get fishing permits. Few reports contained information that was directly relevant to this task, or maps were not available. One report, for example, described TEM work that had been done in the South Kalum area, but all data and the information in the report was completely non-spatial and, when spatial data were requested from the contact, they were not available. Another report on the EcoCat (EcoCat Report 10991) had a map of sensitive ecosystems that extended into the study area (those along the Skeena River corridor shown in Figure 1).
- BC MOE, Knowledge Information Branch: we contacted them directly, requesting any data that may be applicable for this task. They were able to send us complete PEM coverage, and partial TSM, and older TIM and NEM data (more on these data layers below). After searching through these files, it was clear that almost all the data in these files were soils and terrain data, and contained no explicit information about sensitive ecosystems. The staff at the Knowledge Branch also pointed us to the Ecocat reports that we had already seen, and recommended the Conservation Data Center (CDC) as a good source of information.
- Conservation Data Centre: This website allows users to view and search relevant areas for different species and ecosystems, but does not allow the download of such shapefiles that can then be overlaid with our sampling locations. The CDC map shown in Figure 3 was kindly provided by the MOE Knowledge Information Branch.

Data Sources that were used:

- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 33798. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 24052. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 77863. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 88523. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 43828 B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>

- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 3534. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 3640. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 3630. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 3716. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 1880. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 73835. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 70597. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>
- B.C. Conservation Data Centre. 2014. Occurrence Report Summary: 70598. B.C. Ministry of Environment. Available: <https://www.maps.gov.bc.ca/eess/cdc>

2014: LNG Canada Export Terminal Environmental Assessment Certificate Application: Section 5 Assessment of Potential Environmental Effects.

Map Layers:

<http://a100.gov.bc.ca/pub/acat/public/viewReport.do?reportId=10991>

Vegetation Resource Inventory (VRI) data

Maps of sampling locations within the study area.

Predictive Ecosystem Mapping (PEM) and Terrestrial Ecosystem Mapping (TEM) are different levels of mapping characteristics of the ecosystem. TEM mapping is generally done at a broader scale, from air or other remote sensed information. PEM is usually done at a smaller scale, and usually uses some form of modelling to relate known ecosystem attributes with other predicted site attributes. The basic PEM maps usually contain site series information, while some other PEM maps contain extra attributes that have been inferred or estimate. There were no TEM maps available for this area. We had complete coverage from a PEM map, but only giving site series information, and we had some coverage from TIM and TSM (two different terrain and soils maps).

The PEM map in this area had the three general categories of fields:

- those related to the identity of the project or polygon,
- those giving current Biogeoclimate information
- variables related to the site series of different components. Information about up to three different components can be recorded: the decile, site series, modifiers to the assumed site series, and map code.

TIM and TSM maps have many more fields, mostly related to the terrain and surface material. Like the PEM maps, there are all the fields related to the identity of the project or polygon. Also like the PEM, up to three different terrain components can be defined. Each component then has the following information that can be defined: decile, texture, surficial material, surficial qualifier, three different surface expressions, bedrock type, subterrain texture (up to three for each component), subsurficial material, subsurficial qualifier, subsurficial subtype, subsurface expression (up to three for each component). As well as these terrain components, there are also up

to three geomorphological process classes. Each of these classes also has a qualifier, subtype, process, and process subtype.

Actual Variable Names:

PEM Maps

Fields related to the identity of the project or polygon TEIS_ID, PROJPOLYID, BAPID, FCODE, PROJ_TYPE, PROJ_SCALE, PROJ_ID, MAPSH_NBR, POLY_NBR, ECO_SEC, Shape, Area
Current Biogeoclimate information: BGC_ZONE, BGC_SUBZON, BGC_VRT, BGC_PHASE

Variables related to the site series of different components.

SDEC_1, SDEC_2, SDEC_3 = ecosystem decile, component 1, 2, or 3

SITE_S1, SITE_S2, SITE_S3 = site series number, component 1, 2, or 3

SITEAM_S1A, SITEAM_S2A, SITEAM_S3A = assumed site series, modifier 1, component 1, 2, or 3

SITEAM_S1B, SITEAM_S2B, SITEAM_S3B = assumed site series, modifier 2, component 1, 2, or 3

SITEMC_S1, SITEMC_S2, SITEMC_S3 = site series map code, component 1, 2, or 3

MC_ID1, MC_ID2, MC_ID3 = map code id, component 1, 2, or 3

TIM and TSM Data

TDEC_1, TDEC_2, TDEC_3 = decile of terrain, component 1, 2, 3

TTEX_1A, TTEX_1B, TTEX_1C, TTEX_2A, TTEX_2B, TTEX_2C, TTEX_3A, TTEX_3B, TTEX_3C = terrain texture 1 (A), 2 (B), or 3 (C) for component 1, 2, 3

SURFM_1, SURFM_2, SURFM_3 = surficial material for component 1, 2, 3

SURFM_Q1, SURFM_Q2, SURFM_Q3 = surficial material qualifier for component 1, 2, 3

SURFM_ST1, SURFM_ST2, SURFM_ST3 = surficial material subtype for component 1, 2, 3

SURF_E1A, SURF_E1B, SURF_E1C, SURF_E2A, SURF_E2B, SURF_E2C, SURF_E3A, SURF_E3B, SURF_E3C = surface expression 1 (A), 2 (B), or 3 (C) for component 1, 2, 3

BEDROCK_1, BEDROCK_2, BEDROCK_3 = bedrock type, component 1, 2, 3

STTEX_1A, STTEX_1B, STTEX_1C, STTEX_2A, STTEX_2B, STTEX_2C, STTEX_3A, STTEX_3B, STTEX_3C = subterrain texture 1 (A), 2 (B), or 3 (C) for component 1, 2, 3

SSURFM_1, SSURFM_2, SSURFM_3 = subsurficial material for component 1, 2, 3

SSURFM_Q1, SSURFM_Q2, SSURFM_Q3 = subsurficial material qualifier for component 1, 2, 3

SSURFM_ST1, SSURFM_ST2, SSURFM_ST3 = subsurficial material subtype for component 1, 2, 3

SSURF_E1A, SSURF_E1B, SSURF_E1C, SSURF_E2A, SSURF_E2B, SSURF_E2C, SSURF_E3A, SSURF_E3B, SSURF_E3C = subsurface expression 1 (A), 2 (B), or 3 (C) for component 1, 2, 3

TTTEX_1C, TTTEX_1B, TTTEX_1A, TTTEX_2C, TTTEX_2B, TTTEX_2A, TTTEX_3C, TTTEX_3B, TTTEX_3A

TSURFM_1, TSURFM_2, TSURFM_3

TSURFM_Q1, TSURFM_Q2, TSURFM_Q3

TSURFM_ST1, TSURFM_ST2, TSURFM_ST3

TSURF_E1A, TSURF_E1B, TSURF_E1C, TSURF_E2A, TSURF_E2B, TSURF_E2C, TSURF_E3A, TSURF_E3B, TSURF_E3C

COMREL1_2, COMREL2_3

GEOP_1, GEOP_2, GEOP_3 = Geomorphological process class: first, second, third

GEOP_Q1, GEOP_Q2, GEOP_Q3 = qualifier: first, second, third

GEOP_ST1, GEOP_ST2, GEOP_ST3 = subtype: first, second, third

GEOP_INZ1, GEOP_INZ2

GEOP_INZ1A, GEOP_INZ1B, GEOP_INZ1C

GEOP_SCM1 = first process

GEOP_SCM1A, GEOP_SCM1B, GEOP_SCM1C, GEOP_SCM2A, GEOP_SCM2B, GEOP_SCM2C, GEOP_SCM3A, GEOP_SCM3B, GEOP_SCM3C = first process, subtype 1 (A), 2 (B), 3 (C) for component 1, 2, 3



KMP SO₂ EEM Program – Technical Memo S01

Steady-State Soil Modelling

Revised Modelling and Mapping of Terrestrial Critical Loads

March 2015

Prepared for:

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1 Overview

To support the Key Performance Indicator ‘critical load exceedance risk’ under the Environmental Effects Monitoring (EEM) program, critical loads of acidity for (upland) forest soils will be revised during 2017.

Revised modelling and mapping of terrestrial critical loads will incorporate additional (new) observational data, improved regionalisation methods and updated model parameters as recommended under the STAR (ESSA et al., 2013) or following the Kitimat Airshed Emissions Effect Assessment (KAEEA; ESSA et al., 2014).

2 Critical Loads: 2017 Updates

The mapping and modelling of critical loads during 2017 under the EEM will follow the methodology described in the STAR (ESSA et al., 2013) incorporating seven principal revisions (labelled A to G).

A. Soil data. Under the STAR, 51 soil plots were sampled and analysed for bulk density, organic matter content, particle size distribution and total element content. These data were used to estimate soil base cation weather rates, which were subsequently regionalised across the study domain.

Since 2013, additional soil sampling has been carried out in the STAR study domain (see Figure 1) under several external projects (KAEEA [n = 8], BC Ministry of Forest Experimental Plots [EP0712; n = 3] and the LNG Canada Project [URL: lngcanada.ca; n = 22]). Further, as recommended in the STAR, supplemental soil sampling will be carried out during the EEM Program to address critical uncertainties and data gaps in the regionalisation of soil base cation weathering rates (see Technical Memo: Supplemental Soil Sampling, March 2015).

Task A. All new soil data will be captured and incorporated into the STAR soils database. Base cation weathering rates will be estimated for all additional soil sampling plots with total element content data following the methodology used in the STAR.

B. Soil mapping. Under the STAR, the regionalisation of soil weathering rates was carried out by allocating the statistical summaries from 4–6 sampling plots to mapped bedrock classes across the region. The approach did not accommodate the variability in weathering rates within each class and provided limited or no integration of surficial geology.

The KAEEA used a regression-kriging approach (Hengl et al. 2004), which is a well-established geostatistical mapping technique (McBratley et al., 2003), to regionalise soil parameters, e.g., weathering rates. The approach provided a better representation of the spatial variability in weathering rates, removing the dependency on bedrock classes.

Task B. Spatial prediction or regionalisation of soil input parameters for the determination of critical loads, e.g., weathering rates and soil organic matter will be carried out using regression-kriging. The approach will incorporate all available soil data in the study area (see revision A).

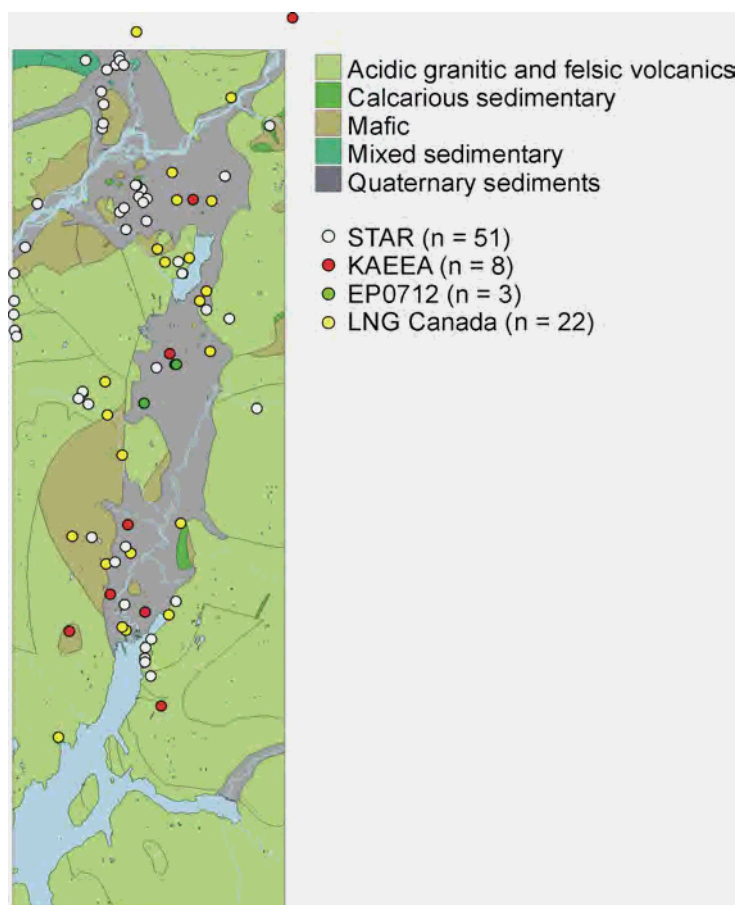


Figure 1. Location of soil sampling sites with total element analysis within (and outside) the STAR (ESSA et al., 2013) study domain. In addition to the 51 soil plots sampled under the STAR, soil plots have been sampled under the Kitimat Airshed Emissions Effect Assessment (KAEEA; n = 8), the BC Ministry of Forestry experimental growth plots (EP0712, n = 3) and the LNG Canada Project (n = 22). The map depicts major bedrock and surficial (glaciofluvial material indicated as ‘quaternary sediments’) geology in the study area.

C. Base cation deposition. Under the STAR, the determination of critical load did not include base cation deposition. This was recognised as a critical uncertainty.

The National Atmospheric Deposition Program (NADP) precipitation chemistry stations at Haul Road and at Lakelse Lake provide data to evaluate regional base cation deposition. In addition, data may be supplemented with observations from other precipitation stations in western North American, and regional maps of rainfall volume.

Task C. Base cation deposition will be mapped across the study domain and incorporated into the determination of critical loads of acidity for (upland) forest soils.

D. Background sulphur and nitrogen deposition. Under the STAR, modelled sulphur and nitrogen deposition estimates did not include background deposition estimates. The modelled deposition represented the contribution of stationary and mobile emissions sources to total deposition, rather than total anthropogenic deposition to the study domain. Transboundary

atmospheric sources can contribute a significant amount of anthropogenic sulphur and nitrogen deposition, as observed by monitoring stations in background regions.

The KAEEA (ESSA et al., 2014) incorporated a constant sulphur deposition of 10 meq m⁻² yr⁻¹ and nitrogen deposition of 5 meq m⁻² yr⁻¹ to represent background deposition. The selected values represented precautionary estimates of background deposition as actual background deposition will vary across a region.

Task D. Incorporation of background sulphur and nitrogen deposition in the determination of exceedance of critical loads following the KAEEA (ESSA et al., 2014).

E. Critical Bc:Al ratio. Under the STAR, a Bc:Al ratio equal to 1.0 was used as the critical chemical criterion or indicator of damage to receptor ecosystems, i.e., upland forest ecosystems on mineral soil. In contrast, the KAEEA (ESSA et al., 2014) incorporated broad vegetation-specific critical limits, i.e., Bc:Al = 1.0 for coniferous forests and Bc:Al = 6.0 for deciduous and mixed forests.

Following the KAEEA, the EEM will incorporate vegetation-specific Bc:Al limits into the revised critical loads of acidity. In collaboration with the BC MOE, regionally-relevant vegetation-specific Bc:Al ratios will be identified from available literature sources (e.g., Sverdrup and Warfvinge, 1993). A map overlay or decision tree approach will be used to delineate or map identified vegetation types from existing spatial databases (see Technical Memo: Vegetation Resource Inventory Metadata, December 2014).

Task E. Spatial delineation of unique vegetation types within the study domain and assignment of vegetation-specific Bc:Al ratios. Incorporation of vegetation-specific Bc:Al ratios into the determination of critical loads of acidity.

F. Multiple chemical criteria. Under the STAR, the exceedance of critical loads for acidity (and subsequent risk rating) was based on one chemical criterion, i.e., Bc:Al = 1.0 for forest ecosystems. In contrast, the KAEEA incorporated a multi-criteria approach to evaluate the influence of the chosen criterion on predicted exceedance. Four critical chemical criteria were selected (ESSA et al., 2014).

Following the KAEEA, the EEM will incorporate a sensitivity analysis on the influence of the chosen criterion on predicted exceedance. In consultation with the BC MOE, a range of critical chemical criteria will be identified from literature sources (e.g., UNECE 2004).

Task F. Determination of exceedance of critical load under multiple chemical criteria to assess the influence of the chosen criterion on predicted exceedance following the KAEEA (ESSA et al., 2014).

G. Effects domain. The Key Performance Indicator ‘critical load exceedance risk’ is estimated as the proportional areal exceedance of the receptor study domain. In the absence of provincially-established air zone boundaries, the STAR used a study domain along the Kitimat valley encompassing the modelled post-KMP 10 kg SO₄²⁻ ha⁻¹ yr⁻¹ deposition plume and potentially sensitive terrestrial and aquatic receptor ecosystems. This study domain was defined in agreement with BC MOE, and encompassed 1991 km² of forested ecosystems on mineral soil (69% of the study area). The proportional exceedance reported in the STAR was referenced to this domain area.

Under the KAEAA (ESSA et al. 2014), the BC MOE favoured an ‘effects domain’ based on the area under the modelled 7.5 kg SO₄²⁻ ha⁻¹ yr⁻¹ deposition plume.

The EEM will evaluate exceedance under both domains.

Task G. Determination of proportional areal exceedance using the original domain and an effects domain defined by the area under the 7.5 kg SO₄²⁻ ha⁻¹ yr⁻¹ deposition plume.

3 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.

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Technical Memo: Vegetation Resource Inventory Metadata, December 2014. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2013 and 2014 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

Technical Memo: Supplemental Soil Sampling, March 2015. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2013 and 2014 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

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: www.icpmapping.org].



KMP SO₂ EEM Program – Technical Memo S02

Steady-State Soil Modelling Supplemental Soil Sampling

March 2015

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1 Overview

This memo describes the selection of supplemental soil sampling sites to address critical uncertainties and data gaps identified under the STAR (ESSA et al., 2013).

A list of 17 potential plots is provided (Figure 1 and Table 1); it is recommended that at least 12 plots are sampled (Table 1). The STAR recommended a maximum of 10–15 sites, and the EEM program recommended a maximum of 12–18 sites.

2 Supplemental Soil Sampling Plots

The STAR (ESSA et al., 2013) identified spatial variability in estimated soil base cation weathering rate as a critical uncertainty. Weathering rates were estimated using a limited number of soil plots (4–6) assigned to each bedrock category, irrespective of overlying surficial geology. As such, the STAR noted that weathering rates may have been underestimated in certain regions.

The STAR and the EEM program identified several broad regions for supplemental soil sampling to expand weathering estimates. These regions were revised to accommodate additional soil sampling carried out in the STAR study domain under several external projects, and proposed revisions to the regionalisation methodology (see Technical Memo: Revised Modelling and Mapping of Terrestrial Critical Loads, March 2015). A list of 17 potential plots were selected from five regions (Figure 1 and Table 1), it is recommended that at least 12 plots are sampled (Table 1), and that field sampling procedures follow the STAR (see Appendix A).

1. Exceeded [E] area soil plots. The STAR identified areas with exceedance of critical loads close to the RTA smelter and areas with potential exceedance further north. Four E plots were identified, all accessible by road. It is recommended that at least two E plots area sampled (near and far from the smelter).

2. South-western [S] region soil plots. Under the STAR, soil plot selection and subsequent sampling were based on an initial study domain that incorporated limited area south of the RTA smelter. Following field sampling, the study domain was expanded to accommodate emissions plumes that moved south of the smelter. As such, there are few soil plots in the southern portion of the study domain.

Three S plots were identified in the southern portion of the study domain, located on primarily acid-sensitive bedrock geology and in regions with high predicted post-KMP modelled sulphur deposition. It is recommended that at least two S plots are sampled, all road accessible. The S plots could be further supplemented with an additional plot (further south) that requires air access.

3. Alpine [A] soil plots. Soil sampling under the STAR focused primarily on road accessible plots. As such, few alpine or high elevation soil plots were sampled. The BC MOE have raised concerns with respect to the representivity of alpine acid-sensitive ecosystems in regional soil base cation weathering estimates.

Four A plots were identified along the western portion of the Kitimat valley, within the modelled post-KMP 10 kg SO₄²⁻ ha⁻¹ yr⁻¹ deposition plume. In addition all proposed plots were co-located with soil chemistry plots sampled under the LNG Canada Project (URL: lngcanada.ca). It is recommended that all four A plots are sampled. All sites are only accessible by air; however, soil sub-samples may potentially be obtained from LNG Canada.

4. Acid-sensitive lake [L] catchment soil plots. The STAR noted potential spatial inconsistencies between estimated soil base cation weathering rates and study lakes with low base cation concentrations. As such, the STAR recommended that supplemental soil sampling be co-located within the catchments of acid sensitive lakes.

Five acid-sensitive lakes are routinely sampled under the EEM program, all lakes were identified as L plots. It is recommended that at least three L plots are sampled (Table 1), including one site that is only air accessible (L28; Figure 1).

5. Lodgepole Pine [P] stands. The BC MOE requested that supplemental soil sampling include plots with dominant Lodgepole pine (*Pinus contorta*) stands. One plot location, close to Terrace Airport, was provided by the BC MOE (Figure 1 and Table 1). It is recommended that this P plot be sampled and potentially be amended with additional road accessible P plots, as requested by the BC MOE.



Figure 1. Location of proposed supplemental soil sampling plots (n = 17) in the EEM study domain. The site IDs denote plots in the southern [S] portion of the study area, plots with predicted exceedance [E] of critical load, plots located within the catchments of acid sensitive lakes [L], plots in alpine [A] or upland regions and a lodgepole pine [P] plot. The co-ordinates for each plot are given in Table 1.

Table 1: Proposed supplemental soil sampling plots (n = 17). The easting and northern co-ordinates area referenced under UTM Zone 9, Datum WGS84. The location of each plot is shown in Figure 1.

#	ID	Easting	Northing	Notes
1	E01	519351	5986688	On RTA property
2	E02 ^{\$}	519521	5986396	On RTA property
3	E03	519231	5985660	On RTA property
4	E04 ^{\$}	521693	6001365	
5	S01 ^{\$}	514798	5973743	
6	S02	513671	5972936	
7	S03 ^{\$}	517099	5977208	
8	A01 ^{\$}	517869	6007327	LNG Canada soil chemistry plot. Air access
9	A02 ^{\$}	518176	6013397	LNG Canada soil chemistry plot. Air access
10	A03 ^{\$}	519367	6016711	LNG Canada soil chemistry plot. Air access
11	A04 ^{\$}	519771	6018828	LNG Canada soil chemistry plot. Air access
12	L06	524155	6020661	EEM monitored lake.
13	L12 ^{\$}	524145	6021028	EEM monitored lake.
14	L22	524185	6022796	EEM monitored lake. Air access
15	L23 ^{\$}	522750	6018850	EEM monitored lake.
16	L28 ^{\$}	519139	5993425	EEM monitored lake. Air access
17	P01 ^{\$}	528172	6036227	Lodgepole pine plot requested by BC MOE

^{\$} Recommended or preferential soil sampling plots

3 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.

Technical Memo: Revised Modelling and Mapping of Terrestrial Critical Loads, March 2015. In, Sulphur Dioxide Environmental Effects Monitoring for the Kitimat Modernization Project, 2013 and 2014 Annual Reports. ESSA Technologies Ltd, Vancouver, Canada.

Appendi A. STAR soil sampling procedures.

Soil survey field sheet: 2012 Kitimat RTA | ESSA | TRENTU

Site ID

On-site observations (centre auger pit)

Date: ☐ JUN ☐ JUL ☐ AUG 2012Time: 24 hour clock (Pacific)Coordinates: lat. lon.GPS elevation (m): Site photograph: ☐ Y ☐ NMineral soil depth (cm)⁵: Distance from road or trail (m): Forest floor depth (cm)⁵: Site gradient (slope): ☐ steep ☐ moderate ☐ flatSite position: ☐ crest ☐ upper slope ☐ middle slope ☐ lower slope ☐ depression ☐ levelDominant vegetation^{ss}: Outcropping rock (%): Recent rainfall ☐ Y ☐ N Snow on ground ☐ Y ☐ N

Moisture regime:

Dry [D] Moist [M] Wet [W]

Depth: 0-10 cm

☐ D ☐ M ☐ W

Depth 15-25 cm

☐ D ☐ M ☐ W

Depth 40-50 cm

☐ D ☐ M ☐ W

Roots present:

☐ Yes ☐ No☐ Yes ☐ No☐ Yes ☐ No

Size of stones:

☐ Small
☐ Medium
☐ Large☐ Small
☐ Medium
☐ Large☐ Small
☐ Medium
☐ Large

Volume of stones:

 % % %

Recorded by:

Comments and notes:

See overleaf for sampling protocol and description of required observations

⁵ Average depth of mineral soil and forest floor for all auger pits (in addition, list the depth of the centre auger pit for mineral and forest floor). ^{ss} List all tree dominant species (use comment box if needed)

Soil sampling protocol: 2012 Kitimat

Equipment: GPS, soil auger (AMS Dutch auger head with bayonet connector), soil core sampler (AMS 404.02 2" x 2" SCS complete), measuring tape, sharp knife, forest floor quadrat, Zip-lock bags, sharpie, digital camera, additional core liner (404.28 2" X 2" SST liner)...

Objective: Collection of mineral soil from 50 sites following rapid protocol using soil auger and corer. Mineral soil should be sampled at three (fixed) depths from five auger pits and composited by depth ('composite' samples), at one auger pit fixed volume soil cores should be sampled at the three (fixed) depths ('bulk density' samples), and a fixed area sample of forest floor should also be collected from one pit ('forest floor' sample). In total seven sample bags should be collected at each site (assuming mineral soil is > 50 cm).

1. Site location: Potential sampling sites represent the centre co-ordinates of a 500 m × 500 m grid with assumed 'homogenous' geological rock type, i.e., soil parent material. Only grids accessible from (or close to) trails are listed. If you are within 250 m of the co-ordinates, you are 'in the sampling grid'.

2. Site selection: The soil sampling location should reflect the general vegetated landscape, i.e., avoid the unique clearing in the sun. The site should be undisturbed (i.e., not recently harvested, > 50 m from trail, etc). If the landscape is irregular, give preference to upland locations between lower slope (or depression) and crest. If significant disturbance, do not sample (go to next site). Use digital camera to record sites.

3. Soil sampling: At each site, establish an ~ 20 m × 20 m grid; using a soil auger collect soils at each grid corner and the grid centre, giving a total of five auger points. Collect soils from three fixed depths (0-10 cm, 15-25 cm and 40-50 cm) at each of the five points. If forest floor is present, remove prior to collection of auger samples (i.e., the 0-10 cm depth starts at the bottom of the forest floor layer). The five samples from each common depth should be composited, giving three 'composite' samples per site, i.e., put all 0-10 cm samples into one Zip-lock, etc. Approximately 150-200 g of soil should be collected for each depth-composite. Collect samples using a Dutch-style auger (mark auger stem with coloured tape to delineate sampling depths). Label zip-lock bags for each depth-composite, i.e., Sxxxx-0-10, Sxxx-15-25 and Sxxx-40-50. Finally, record the average soil depth (average of the maximum depth at each pit, estimated using the soil auger).

4. Collect bulk density samples from the grid centre point using steel cylinders of fixed volume; use a dedicated ring holder (AMS soil corer) for core sampling after application of a soil auger to prepare a sampling platform at the predetermined depth (0-10 cm, 15-25 cm and 40-50 cm). If forest floor is present, remove prior to collection of bulk density samples. Carefully remove soil-filled cylinder from the ring holder and trim soil extending beyond both cylinder ends using a sharp knife. Resample cylinders with large stones, or large roots extending beyond the core. Store soils in zip-lock freezer bags and label for each bulk density depth, i.e., Sxxxx-0-10-DB, Sxxx-15-25-DB and Sxxx-40-50-DB.

5. A fixed area forest floor sample should be collected for bulk density. At the centre pit, use a small quadrat (e.g., 20 cm × 20 cm) to collect the forest floor layer, cut around the inner circumference of quadrat to remove material, and measure the average depth (average of four sides [record on field sheet]). Store forest floor in a zip-lock freezer bag and label, i.e., Sxxxx-DB-FF.

6. Complete field sheet (overleaf): Site ID, location and elevation are important. Observations are based on the centre auger pit or the site area. Use comments box for additional notes.

Soil depth: use auger to record the maximum depth of the mineral soil, or indicated '> 1 m'.

Dominant vegetation: record tree species (use comments box if additional space is required).

Outcropping rock: record the percent area of outcropping rock across the study location.

Moisture regime: is the soil wet at centre pit? Record for each sample (fixed) depth.

Roots present: are roots visible in auger soil (at each sample depth) at centre pit?

Size of stones: record size of stones encountered during auger use (at each sample depth for centre pit).

Volume of stones: based on the frequency of stones, estimated the fraction of the soil pit occupied by stones.

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RioTintoAlcan

KMP SO₂ EEM Program – Technical Memo W01

Freshwater Chemistry Analyses

March 2015

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1 Introduction

The following Technical Memo provides extended information on the data and analyses in support of the 2013 and 2014 requirements for the Aquatic Ecosystems component of the KMP SO₂ Environmental Effects Monitoring (EEM) program (ESSA et al. 2014b). These data and analyses thus provide the foundation for Section 3.5 in the 2013/2014 EEM Annual Report (ESSA et al. 2015).

Table 1-1. Aquatic analyses as specified in the EEM. Extracted from Table 16, Section 6.2.5, “Summary of Lakes, Streams and Aquatic Biota Actions, 2013-2018”. The numeric symbols (e.g., ③④⑤) are used to link sections of the present technical memo with the EEM requirements, and appear throughout this document.

Topic	2013	2014
Steady state water modelling	–	① Re-run acidification models to calculate CLs, to assess the effects of sampling in Aug (2012) versus Oct (2013). ¹
Chemistry: water body sampling	② Annual water sampling and laboratory analysis; ③ sample Cecil Creek.	④ Annual water sampling and laboratory analysis. ⑤ More intensive sampling of 3 lakes to determine natural variability. ⑥ Develop weight-of-evidence approach for assessing whether chemical change is causally related to KMP (Section 7 of this document).
[SO ₄] ₀ ; F-factor	–	–
Fish presence / absence sampling	⑦ Sampling of 4 vulnerable lakes.	⑧ Reconnaissance of habitat and water chemistry in Goose Creek – future sampling TBD based on results.

This technical memo applies many methods and approaches that have already been described in detail in other relevant documents. Most of the methods follow those employed in the SO₂ Technical Assessment Report (STAR, ESSA et al. 2013) and the Kitimat Airshed Assessment (KAA, ESSA et al. 2014a). Full details on the actual collection, processing and analysis of the water chemistry samples are reported in technical reports prepared by Limnotek for each year’s annual monitoring (Perrin et al. 2013, 2015). Wherever possible, the description of methods in the present 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/program (ESSA et al. 2014b)

¹ In addition to task ① in 2014 that involved re-running critical load models to assess the effects of August 2012 vs October 2013 sampling, critical loads and exceedances were also calculated for the lakes MOE 3 and MOE 6, to determine whether they need to be added to the long-term monitoring lake set

2 Methods

2.1 Annual Monitoring Samples ②③④

2013 Annual Sampling

In 2013, the 10 lakes identified in the EEM plan for long-term sampling were sampled. These lakes included 7 sensitive lakes and 3 less sensitive lakes. In addition to the EEM lakes, sampling was done for Lake MOE3 and for three sites along Cecil Creek, to assess whether those sites would be sensitive to increases in sulphur deposition. It was not feasible to sample Lake MOE6 in 2013 due to weather conditions which made it unsafe for the helicopter to fly there during the sampling period. Table 2-1 summarizes all of the sites sampled during the 2013 and 2014 annual sampling periods. Figure 2-1 shows a map of the locations of the sites sampled in 2013.

2014 Annual Sampling

In 2014, Limnotek sampled the 10 lakes identified in the EEM plan for long-term sampling. These lakes included 7 sensitive lakes and 3 less sensitive lakes. Lake 024 (Lakelse Lake) was added in 2014 to the set of lakes for the EEM long-term monitoring plan, due to its very high public and ecological importance. In addition to the EEM lakes, sampling was completed for Lake MOE6 and for six sites throughout the Goose Creek watershed, to assess whether those sites would be sensitive to increases in sulphur deposition. Table 2-1 summarizes all of the sites sampled during the 2013 and 2014 annual sampling periods. The locations of the EEM lakes sampled in 2014 are shown on the map in Figure 2-1.

The lakes and streams identified in Table 2-1 were sampled by Limnotek (Perrin et al. 2013, 2015). The sampling methodology is described in detail in Limnotek's technical reports on the water quality monitoring (Perrin et al. 2013, 2015).

Table 2-1. Summary of sites sampled during 2013 and 2014 annual sampling. Sites that are part of the EEM program are distinguished from additional sites sampled in each of the years.

Sample Site	Year of Sampling			Rationale for sampling in 2013 / 2014
	2012	2013	2014	
	During STAR	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			✓	

Measurement of Cation Concentrations – Total vs. Dissolved

As part of the STAR, water quality samples were analyzed for both the total and dissolved concentrations of base cations (e.g., Ca, Mg, Na, K). In 2013, the lab analyses of water quality samples only included total concentrations and not dissolved concentrations. The rationale to exclude analyses of dissolved concentrations of base cations was that there was almost no difference between the two measures for these lakes (C. Perrin, pers. comm.). In fact, because there is generally little difference between total and dissolved measures, the concentrations of major cations are rarely distinguished as being measures of total or dissolved concentration (J. Aherne, pers. comm.). However, because we had utilized dissolved concentrations as inputs to the Steady State Water Chemistry model in the STAR, we wanted to use dissolved measures for consistency. We fit a regression to the total and dissolved measures for each of the base cations in 2012 and used the equations to estimate the dissolved concentrations of the base cations in 2013 from the total concentrations measured in 2013. In 2014, the lab analyses of the water quality samples returned to analyzing both total and dissolved concentrations.

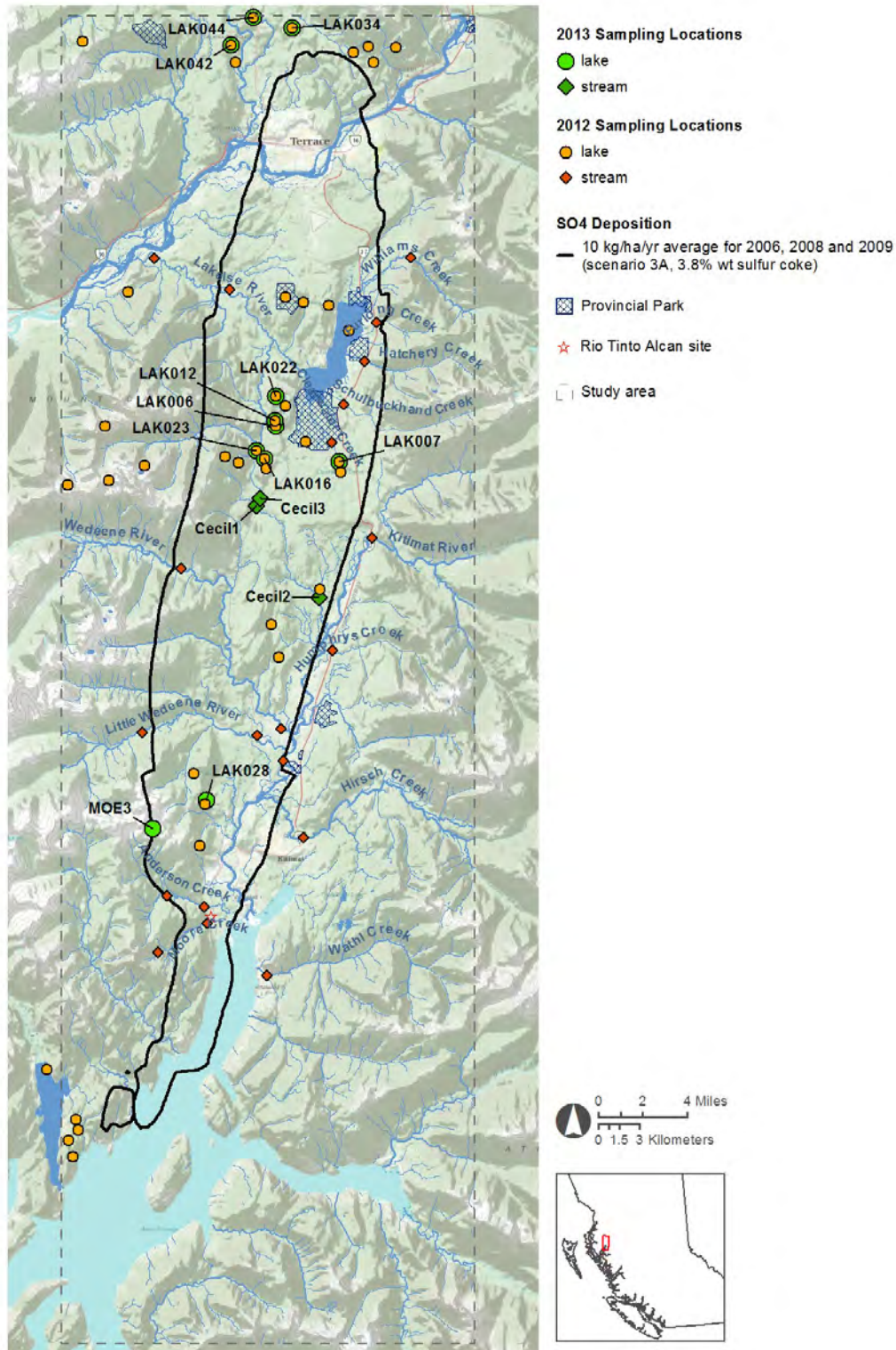


Figure 2-1. Location of lakes and stream sites that were sampled in 2013. The 2012 sampling sites are shown for reference. The area within the black line was predicted by ESSA et al. (2013) to receive more than 10 kg SO₄ per hectare per year under KMP. Note that LAK024 (Lakelse Lake) is not labelled because it was not added to the EEM lakes until 2014 (LAK024 is the large lake northeast of LAK022). (Source: Perrin et al. 2013)

2.2 Intensive Monitoring of Three Lakes ⑤

In 2014, pH was intensively monitored for Lakes 006, 012, and 023, including continuous pH monitors and multiple site visits to collect intra-season samples for additional lab and pH measurements. This work was planned, implemented and documented by Limnotek. The methods and results are reported in Bennett and Perrin (2015). The introduction of the Technical Memo is copied here:

“Early in 2014, a decision was made to begin continuous monitoring of pH and temperature in each of End Lake (LAK006), Little End Lake (LAK012) and West Lake (LAK023). These lakes were selected for the long term monitoring by Rio Tinto Alcan (RTA) with decision support from ESSA Technologies Ltd. (ESSA). The objective was to document variability in pH and related chemistry in each of the three lakes over the fall season. Limnotek set up and installed the instrumentation and conducted routine maintenance and calibration of the instruments during a period of deployment from August 29, 2014 through November 25, 2014. Results of pH measurement are reported in this memo.”

Bennett and Perrin (2015, p. 1)

2.3 Quality of Water Chemistry Data ①②③④⑧

Sampling and laboratory quality control and quality assurance

The collection, handling, transport, and analyses of water quality samples were conducted with numerous quality checks, to ensure the highest quality data possible. Details on the methods for quality control and quality assurance for the water samples are described in the Limnotek technical reports from each of the years of annual sampling (see Perrin et al. 2013, 2015).

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 (lake or stream), then examined the average charge balance across all sites within a particular data set. 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 2013 and 2014 have multiple measures of pH, including a field measurement and two lab measurements (Trent University and ALS). The three lakes described in 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, rather than field

measurements, of pH have been used for the analyses of lake chemistry, especially the modeling of critical loads, exceedances and predicted changes in pH.

The 2012 data collected during the STAR only had one laboratory measurement of pH (Trent University), therefore inter-annual comparisons have been conducted using the Trent pH results. However, we were able to compare the two labs' results for 2013 and 2014.

Repeat Analyses of 2013 Samples

When comparing the 2013 data with the 2012 data, we observed large changes in the concentrations of various ions between the two sampling periods, including both increases and decreases. We also observed that the charge balance was not as good for the 2013 data as it had been for the 2012 data. Given these observations, we requested Trent University to run repeat analyses on their stored samples to ensure the differences we were observing reflected true changes in lake chemistry (reflecting true natural variation by year and season) and not any issues with measurement errors due to sampling, shipping or laboratory procedures. These analyses were run as an additional, precautionary quality control measure. Analyses were repeated for the following water chemistry parameters: conductivity, pH, total alkalinity, Gran alkalinity, fluoride, chloride, sulphate, aluminum, calcium, magnesium, potassium, sodium, iron, and manganese.

2.4 Flow Data

We downloaded available stream flow data from Environment Canada's Water Survey of Canada (<http://wateroffice.ec.gc.ca>) for the available stations within the study area. The three stations in the study area are: Kitimat River below Hirsch Creek (08FF001), Hirsch Creek near the mouth (08FF002), and Little Wedeene River below Bowbyes Creek (08FF003). For each station, two types of data were available for download. The "historic" records provided data up to December 31, 2012, and the "real-time" records provided recent data starting August 11, 2013.

Our purpose for acquiring these stream flow data was to examine regional hydrologic conditions preceding the sampling periods to provide additional context for our interpretation of the observed patterns.

2.5 Critical Loads and Exceedances ①

Steady State Water Chemistry Model

We used the Steady State Water Chemistry Model (SSWC) to estimate critical loads of acidity and potential exceedances for sampled sites. The SSWC is described in detail by Henriksen and Posch (2001), Henriksen et al. (2002) and UNECE (2004).

Extensive details on how we have implemented the SSWC, including details on all of the data inputs required, are documented in the STAR (ESSA et al. 2013, Section 8.6.3.4) and the KAA (ESSA et al. 2014a, Section 6.1.2 and Appendix 15).

In the present work, critical loads and potential exceedances were calculated for all of the sites sampled in 2013 (EEM lakes, Cecil Creek, MOE3) and MOE6, which was sampled in 2014. Calculation of critical loads and potential exceedances for sites sampled in 2014 was not scheduled to be done for the present report. We were able to model Lake MOE6 in 2014 because the

necessary data inputs (i.e., watershed area, average basin runoff, average basin deposition) were already prepared (we had planned to sample MOE6 in 2013).

Spatial Definition of Watersheds

The methodology for defining the watershed area upstream of sampled lakes and streams was improved from the STAR to the KAA. The approach applied in the KAA (described below) is more accurate than the approach applied in the STAR, which was strictly based on the digital elevation model (DEM) and not informed by the Freshwater Atlas.

As defined in the KAA, watershed area is calculated using this approach:

We defined upstream watersheds for each sampled lake primarily using the 1:20K [Freshwater Atlas Fundamental Watersheds](#). The Freshwater Atlas watersheds do not use lake outflows as natural pour points to define the watershed boundaries, so watershed polygons often encompass lakes and result in an area of watershed downstream of the lake. We used flow direction calculated from the [Canadian Digital Elevation Data 1:50K digital elevation model \(DEM\)](#) to identify areas downstream of the lake and remove them from the Freshwater Atlas watershed polygons. The 1:20K [Freshwater Atlas stream network](#) was used to enforce drainage within the DEM, and ESRI's hydrology toolset was used within ArcMap to define the upstream/downstream areas around the lake outflow.

ESSA et al. (2014a, Appendix 15.1, p. 266)

The KAA approach is more accurate than the STAR approach and should be used going forward. However, it does result in some differences in watershed area (and therefore calculations of average runoff and deposition). To determine if switching methods would significantly affect the results of the STAR, we re-calculated the critical loads and exceedances from the STAR applying the new methodology for watershed definition, to compare with the original results.

August 2012 vs. October 2013 ①

One of the explicit actions for 2014 in the Lakes, Streams and Aquatic Biota component of the EEM plan was to, “re-run acidification models to calculate CLs, to assess the effects of sampling in Aug (2012) versus Oct (2013).”. As described above, we used the SSWC model to calculate critical loads based on the October 2013 sampling data in order to compare the results to those from the STAR, based on the August 2012 data. As per above, the original STAR critical loads were also recalculated using the improved method for watershed definition as applied in the KAA, in order to ensure consistent methods between the two sampling periods.

The purpose of this comparison was to determine the effect of changing sampling season. Although sampling lakes after fall mixing is considered to be the better season for sampling (Landers et al. 1987), logistical constraints during the STAR made it necessary to conduct sampling during August. Our expectations of potential differences in water chemistry based on the season of sampling have been informed by research by the US EPA (Environmental Protection Agency) on temporal variability in lakewater chemistry, conducted on lakes in the northeastern US as part of their National Surface Water Survey program (Herlihy et al. 1990). Based on the EPA's research, we would expect that pH, ANC and base cations would (on average, across many lakes) be higher during the fall than during the summer. However, EPA found substantial variability in seasonal patterns among individual lakes. In addition, the lakes studied by EPA in the northeastern U.S. are subjected to different weather patterns than those in the Kitimat Valley, in particular much drier weather in the fall in the northeastern U.S. compared to the the Kitimat Valley. Certain seasonal

patterns may be generally consistent across western and eastern North America, despite variation from site to site and year to year. In a study of 69 high elevation lakes in national parks in the Western U.S., Clow et al. (2003) found that solute concentrations generally increase in the fall as the relative importance of groundwater inputs to streams and lakes increase and uptake of nitrogen by vegetation declines.

In the present work, any potential seasonal effect is also conflated with a year effect as the two sampling periods occur in different seasons and different years, and it is not possible to rigorously disentangle these two effects.

Other methodological considerations

The same pre-KMP deposition values were used in the SSWC model to calculate critical loads and exceedances based on the 2013 monitoring data as had been used in the STAR. The emissions and deposition modeling necessary to provide an updated pre-KMP deposition layer specific to 2013 was not done as part of the EEM program. As sulphur emissions from KMP have generally been declining (ESSA et al. 2015, Figure 4), it is likely that our use of pre-KMP deposition values from the STAR overestimated actual sulphate deposition in 2013. In the SSWC model and the methods we used in the STAR to estimate original sulphate concentrations (STAR, pg. 243-244), an overestimate of sulphate deposition would lead to an underestimate of pre-industrial base cation concentrations, an underestimate of a lake's critical load, and an overestimate of exceedance. Therefore, use of pre-KMP deposition from 2012 with 2013 lake chemistry is precautionary, and may lead to a conclusion that a lake's critical load would be exceeded under KMP when it fact it would not be.

2.6 Predicted Changes in pH (Δ pH)

For sites sampled in 2013, we used the ESSA/DFO model (Marmorek et al. 1990) to calculate the predicted future pH and therefore Δ pH ([future pH] – [current pH]). Detailed documentation of our application of the ESSA/DFO model is provided in the STAR (Section 8.6.3.4) and the KAA (Appendix 16).

2.7 Weight-of-Evidence Approach for Assessing Causality ©

One of the tasks identified in the EEM plan was to develop a weight-of-evidence approach for assessing causality associated with observed changes in water chemistry. Such an approach was developed concurrent to the finalization of the EEM plan and was therefore incorporated into the EEM plan itself, where it is referred to as the Evidentiary Framework. Refer to Section 7.0 and Appendix H of the EEM plan.

As described in Sections 2.8 and 4.1, the Evidentiary Framework has been interpreted in the present technical memo in the context of decreasing emissions, in order to provide expectations for changes in water chemistry against which to compare the observed changes. The analysis of inter-annual changes during a period of declining emissions (next section) provides a test of the evidentiary framework.

2.8 Inter-annual Changes

Observed Changes

The EEM program now has three 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 for 2012-2013, 2013-2014, and 2012-2014. However, because sampling in 2012 was performed in August and the sampling in 2013 and 2014 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 from 2013 to 2014, which represents a change in year but with sampling during a consistent season.

Expected Patterns of Change

The observed changes between 2013 and 2014 were examined and compared with expected patterns of change based on the Evidentiary Framework (Section 7.0 and Appendix H of the EEM). We only compared the 2013-2014 patterns against expected patterns because the changes from 2012 were more convoluted to interpret because of the combined effect of year and sampling season.

2.9 Fish Sampling ⑦

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 EEM lakes. 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. The fish sampling methodology is described in Section 2.9 of Limnotek's technical report (Perrin et al. 2013).

2.10 Goose Creek ⑧

In 2014, six sites within the Goose Creek watershed were sampled to assess their potential sensitivity. Sampling of these sites was conducted by Limnotek. Refer to Bennett (2014) for a detailed description of the sampling approach and methods used.

Initial analyses of the water chemistry data from these samples were conducted in 2014 and are presented in this technical memo. However, the calculation of critical loads and potential exceedances has not been completed at this time and is scheduled to be performed in 2015.

3 Results

3.1 Quality of Water Chemistry Data ①②③④⑧

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 reports (Perrin et al. 2013, 2015).

Charge Balance Check

The charge balance was 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 and Goose Creek (2014). The charge balance was not as good in 2013 or 2014 as it was in 2012, but is still acceptable. 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 EEM lakes (sensitive and less sensitive) in each of the three sampling years is shown graphically in Figure 3-1. The figure shows that the charge balances for 2012 and 2014 show a markedly closer fit to the 1:1 line (i.e., cations = anions). 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), 2013 (EEM, MOE3, Cecil Creek), 2014 (EEM, MOE6), 2014-GS (Goose Creek). 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
2014-GC	6	-4.7	4.9	-30.4	32.6

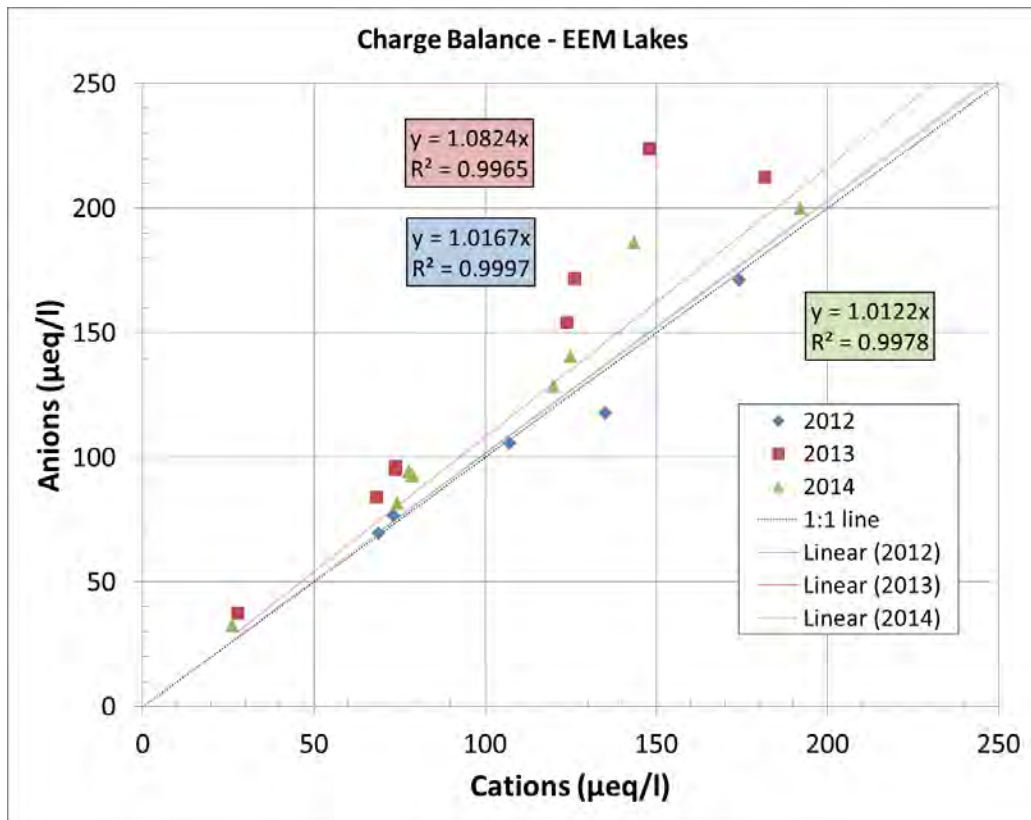


Figure 3-1. Analysis of charge balance for the EEM lakes, 2012-2014. The Y-axis is the sum of all major anions (negatively charged ions); the X-axis the sum of all major cations (positively charged ions).

Measured vs. 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 and Goose Creek (2014). The results show an acceptable relationship between measured and estimated conductivity for each of the data sets. On average estimated conductivity was higher than measured conductivity, except for the 2014 sample set.

The conductivity check for the EEM lakes (sensitive and less sensitive) in each of the three 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), 2013 (EEM, MOE3, Cecil Creek), 2014 (EEM, MOE6), 2014-GS (Goose Creek). 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
2014-GC	6	3.4	3.4

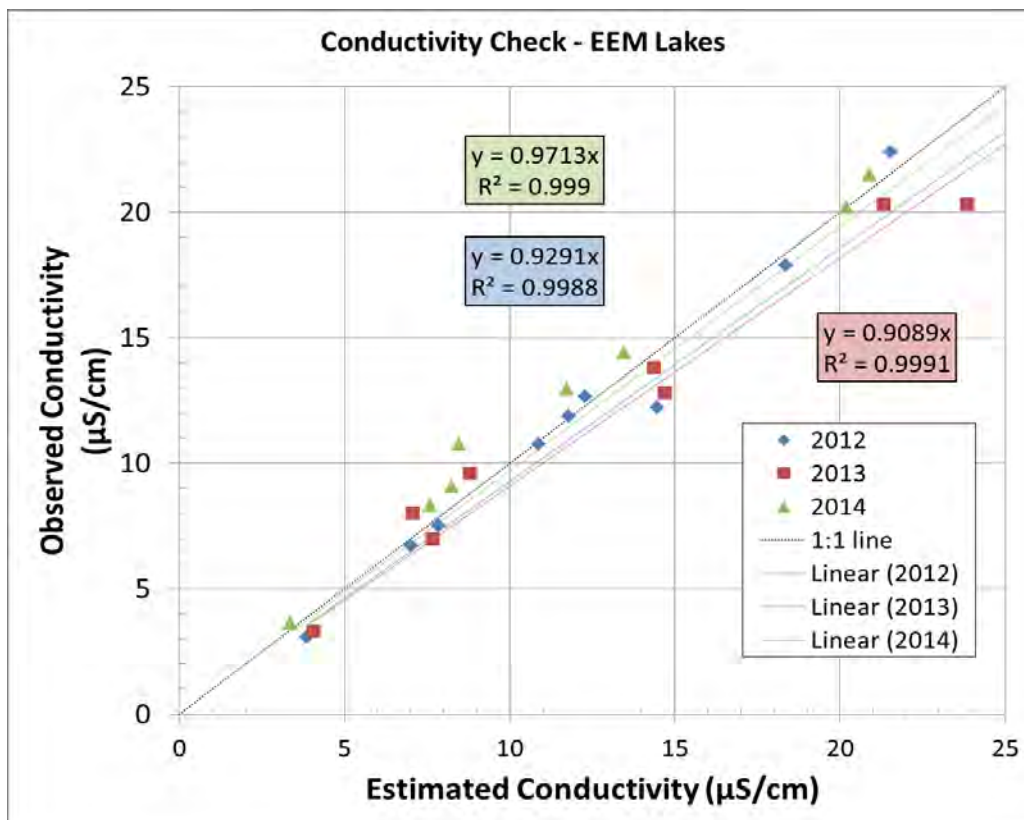


Figure 3-2. Conductivity check for the EEM lakes, 2012-2014. Estimated conductivity is based on laboratory measurements of the concentrations of all ions and literature values for the conductivity of each ion, which is compared to the conductivity observed in field measurements.

pH measurements

Lab measurements of pH were made at two different labs in both 2013 and 2014. Figure 3-3 and Figure 3-4 show comparisons for each sample year between pH measurements from the two labs. In both years, the values measured by ALS are 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.

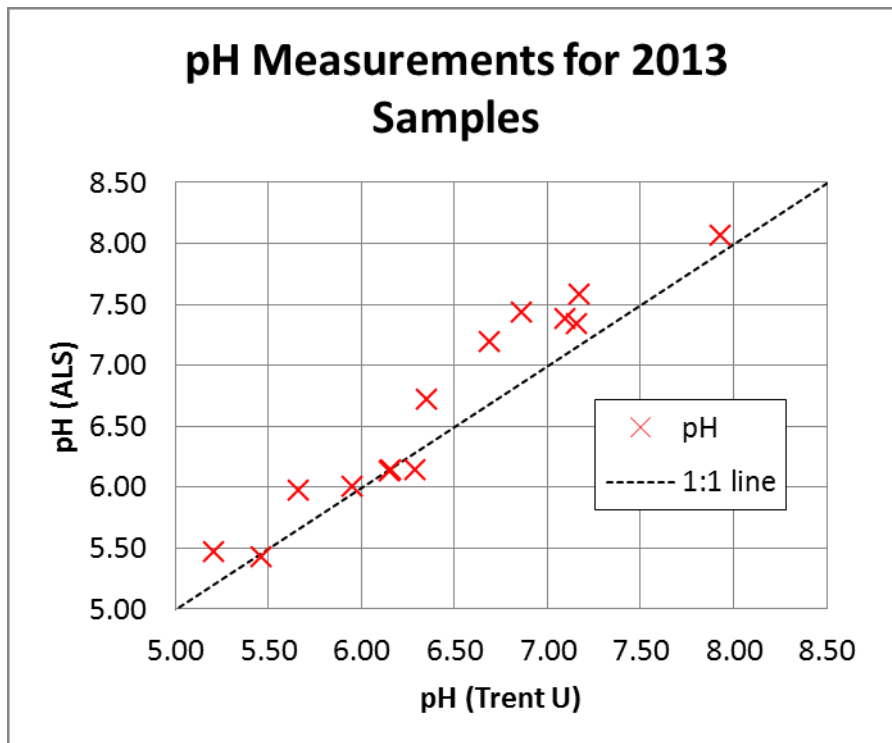


Figure 3-3. Comparison of lab pH measurements for 2013 samples. All 2013 samples are included (i.e., EEM lakes and non-EEM sites).

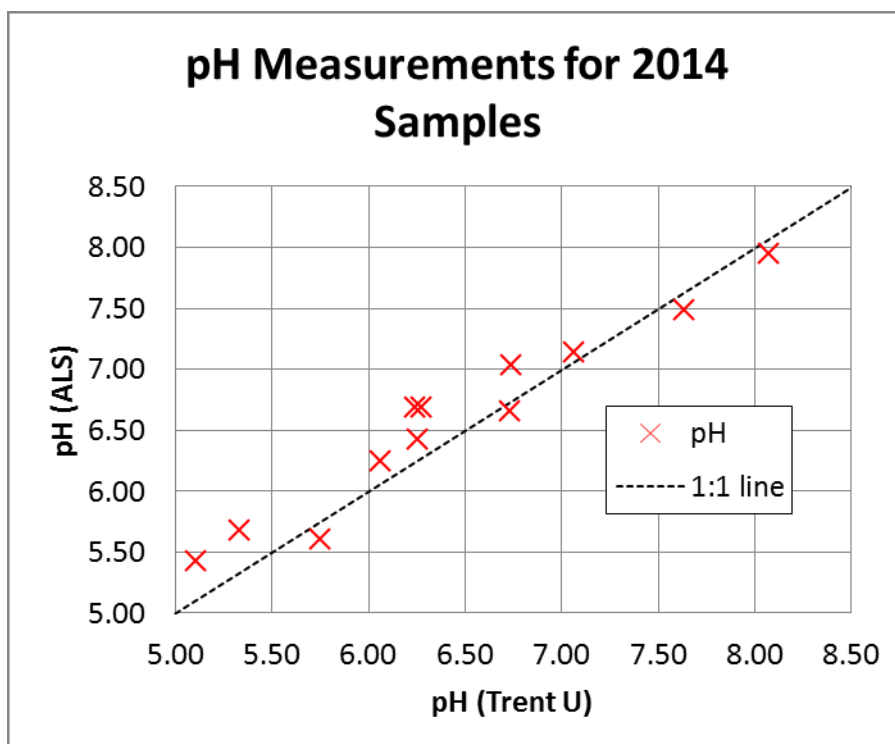


Figure 3-4. Comparison of lab pH measurements for 2013 samples. All 2013 samples are included (i.e., EEM lakes and non-EEM sites).

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.

Repeat Analyses of Chemical Concentrations of 2013 Samples

As described in Section 2.3, repeat analyses of chemical concentrations were performed on stored samples collected in 2013. The quantitative results are not included in this memo. The repeat analyses showed that for $\alpha = 0.05$, there were statistically significant differences between the values from the original analyses and the repeated analyses for roughly half of the attributes measured. However, the absolute differences were relatively small and within the plausible expectations for changes based on a year of storage (J. Aherne, pers. comm.). Additionally the magnitudes of the differences were not large enough to be meaningful in the context of assessing the chemical characteristics of the water. These repeat analyses did not provide any evidence that there were large and/or systemic issues in the original data. The overall conclusion was that original data values for the 2013 water chemistry data could be applied with confidence in their quality.

3.2 Water Chemistry Results

EEM Lakes – Annual Water Chemistry Data

Appendix 1 reports the results of the annual water chemistry sampling for the EEM lakes from the sampling conducted in 2013 and 2014 (with the 2012 STAR data included for reference), for major water chemistry metrics (pH, DOC, Gran ANC, base cations, and major anions).

EEM Lakes – Changes in Ion Concentrations from 2012 to 2013

The lake specific changes in ion concentrations from 2012 to 2013 are shown in Figure 3-5 for total cations and total anions, Figure 3-6 for major cations, and Figure 3-7 for major anions.

Appendix 2 provides a detailed set of figures showing the changes between 2012 and 2013 in each of the measured ions (cations and anions) for each of the EEM lakes. The analyses and figures presented in this section and Appendix 2 have not been extended to include 2014. In general, solute concentrations were higher in the fall of 2013 than in the summer of 2012, consistent with our expectations from other studies described above in section 2.5.3.

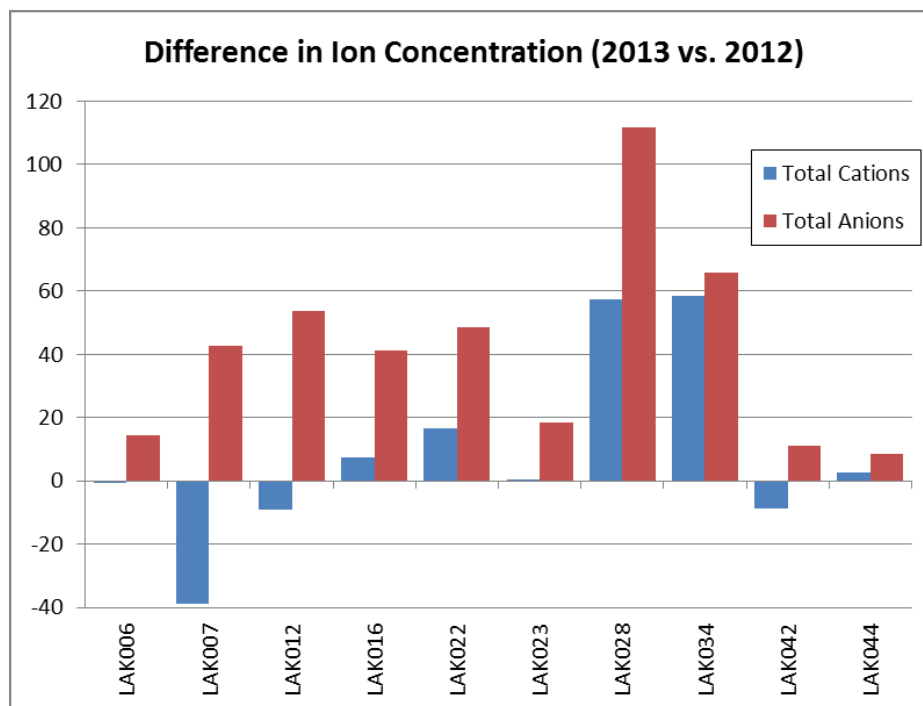


Figure 3-5. Lake-specific differences between 2012 and 2013 for both total cation concentration and total anion concentration. Note: These data have not been corrected for marine influence (applicable to SO₄ and base cations). Each bar represents 2013 concentrations minus 2012 concentrations.

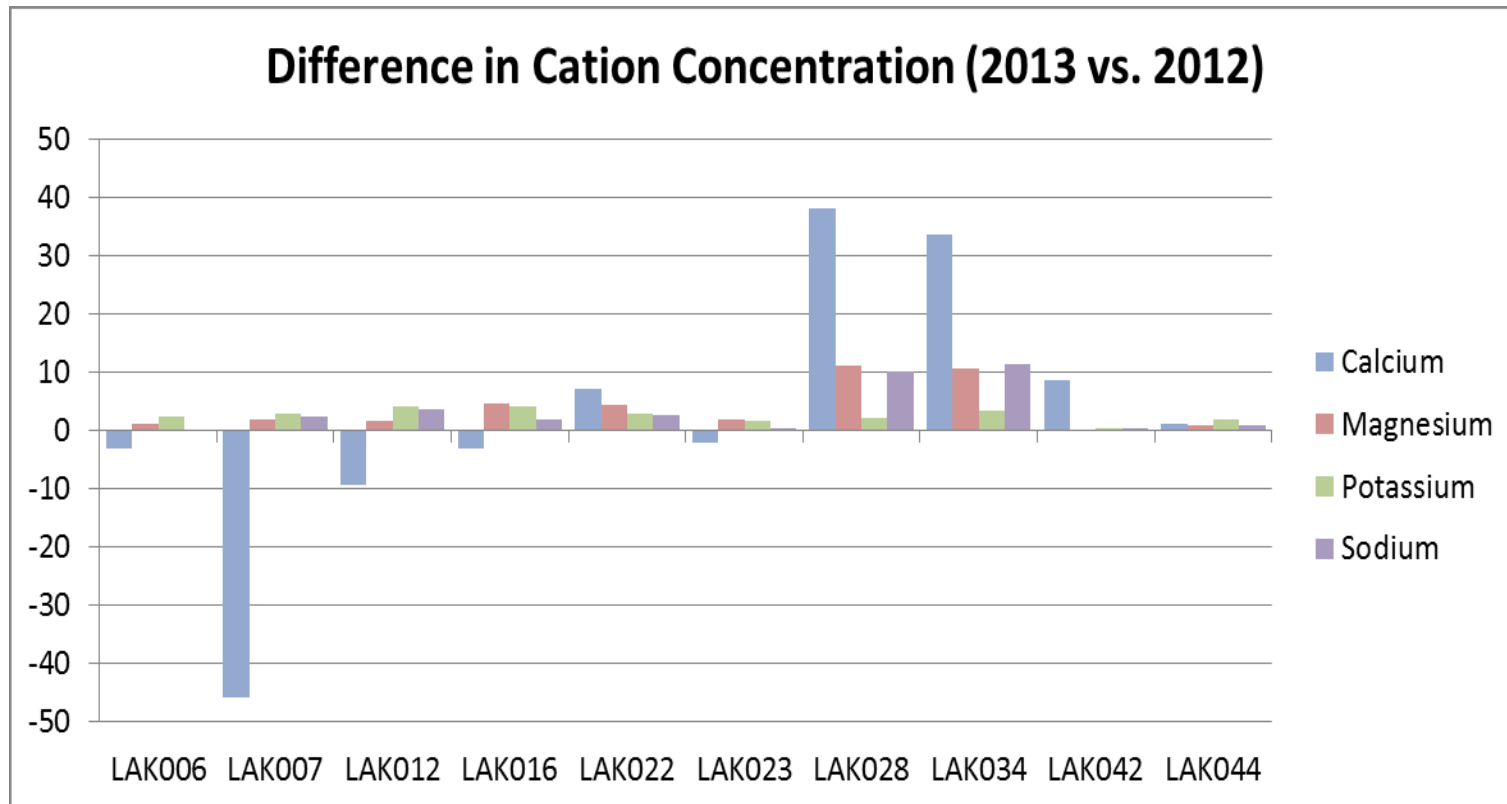


Figure 3-6. Lake-specific differences in the concentration of major cations between 2012 and 2013. Note: The concentrations of these cations have not been corrected for marine influence. Each bar represents 2013 concentrations minus 2012 concentrations.

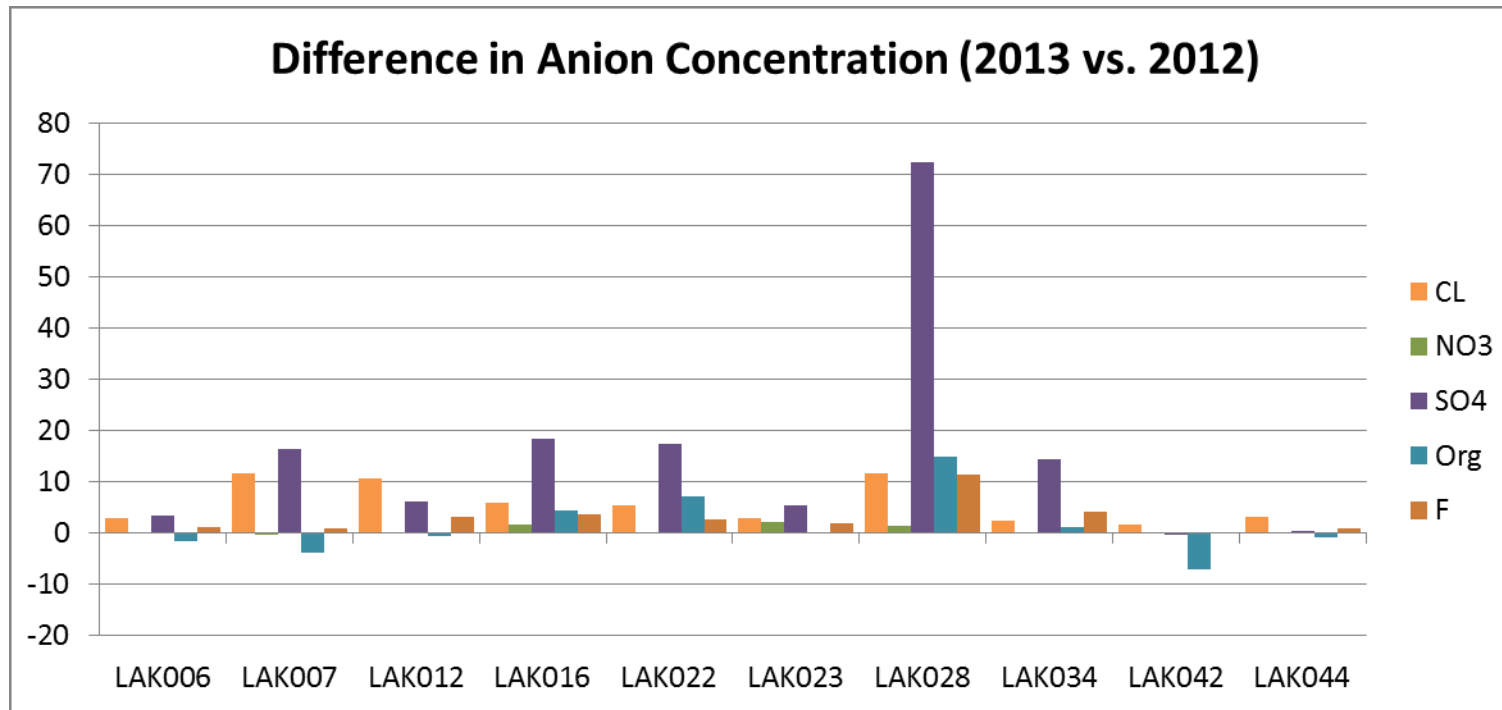


Figure 3-7. Lake-specific differences in the concentration of major anions between 2012 and 2013. Note: SO₄ has not been corrected for marine influence. Each bar represents 2013 concentrations minus 2012 concentrations..

Non-EEM Sites – Water Chemistry Properties ③⑧

Table 3-3 provides a summary of the results for the non-EEM sites for some of the key water chemistry properties.

Table 3-3. Select chemical properties of non-EEM sites sampled during 2013 and 2014. 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	SO ₄ * (µeq/L)	Cl (µeq/L)	F (µeq/L)	BC* (µeq/L)	DOC (mg/L)
MOE3	2013	167.7	7.10	122.6	7.4	2.8	260.4	0.4
Cecil Creek 1	2013	275.2	7.16	68.1	17.6	4.5	390.4	3.3
Cecil Creek 2	2013	367.7	7.17	57.1	16.0	4.7	477.5	4.6
Cecil Creek 3	2013	111.1	6.35	108.9	16.3	6.5	285.8	14.0
Average of EEM sensitive lakes	2013	26.7	5.8	33.8	11.1	9.9	77.0	5.1
Average of EEM less sensitive lakes	2013	589.8	7.2	53.8	19.0	8.4	625.6	3.0

MOE6	2014	175.8	7.06	63.7	16.4	2.2	267.6	3.2
Goose Creek 1	2014	93.2	6.37	128.9	18.3	27.6	274.9	6.3
Goose Creek 2	2014	82.5	6.27	139.4	16.6	28.0	251.2	5.6
Goose Creek 4	2014	41.1	5.47	112.1	18.9	42.2	210.1	14.7
Goose Creek 5	2014	332.6	6.68	188.2	18.6	22.4	601.0	4.5
Goose Creek 6	2014	284.9	7.36	185.2	15.2	18.1	488.9	4.5
Goose Creek 7	2014	283.4	6.90	167.6	14.1	12.2	458.0	4.2
Average of EEM sensitive lakes	2014	34.4	5.9	24.9	8.0	7.6	80.3	5.2
Average of EEM less sensitive lakes	2014	557.1	7.3	33.3	25.2	5.3	618.2	3.4

MOE3, MOE6

Despite having high SO₄ levels, both of these lakes have low F levels and pH values greater than 7. Both lakes also have high ANC and high base cations, and are therefore not sensitive to acidification.

Cecil Creek

Cecil Creek sites 1 and 2 have moderately high SO₄ levels with moderately low F levels and pH values greater than 7. These two sites have high ANC and high base cations. Cecil Creek site 3 has high SO₄ with moderate F levels and pH of 6.35. ANC and BC concentrations for site 3 are substantially lower than sites 1 and 2 but still quite high. ANC is well above the 50 ueq/l level, below which acidic episodes are more common (Driscoll et al. 2001).

Goose Creek

All of the Goose Creek sites have high to very high SO₄ levels and very high F levels. Sites 5, 6 and 7 all have high pH, high ANC and very high base cations. Sites 1 and 2 have pH values of ~6.3-6.4, moderate ANC values, and high base cations. Goose Creek site 4 has a low pH, extremely high F values relative to all other observed sites, moderate ANC, high DOC and high base cation

levels. With a high DOC level (14.7 mg/l), Goose Creek site 4 may have been naturally acidified. With relatively low ANC, it may also be sensitive to anthropogenic acidification, and may have been influenced by the smelter given the relatively high fluoride concentrations.

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 2015) and in the water quality report by Perrin and Bennett (2015).

The results from these three lakes show that there is high variability in pH, substantially higher than previously expected. The results show that for each of the lakes there is variability in pH over time, between the continuous monitors and lab measurements, between in-situ field measurements and lab measurements, and between measurements from different labs. As noted in Perrin and Bennet (2015):

“At best, precision on pH measurement using a field instrument or at a lab is 0.2 pH units. It is 0.3 pH units at ALS. These values are essentially the same as the amount of change in pH that is to trigger more intensive monitoring and decisions about mitigation within the EEMP (0.3 pH units, ESSA et al. 2013b). It may be difficult to resolve this amount of change in pH when instrument precision is the same amount.”

This variability has important implications for the design of the EEM program, which are discussed in Section 4.1.

3.4 Flow Data

The following three graphs show when the sampling of the EEM lakes occurred in the context of the three available stream flow stations, taken as a proxy for regional hydrologic conditions (Figure 3-8, Figure 3-9, and Figure 3-10.). Each of the hydrographs shows the sample dates for the EEM lakes (i.e., all EEM lake samples, not specific to those lakes closest to each stream flow location, all of which are to the south of the study area). The three figures show that sampling in August 2012 was done on a descending limb of the hydrograph, sampling in October 2013 was done near the top of an ascending limb of the hydrograph (though not at peak monthly flow), and sampling in October 2014 was done near the beginning of the fall ascending limb of the hydrograph but in a localized depression immediately following a late September storm flow event.

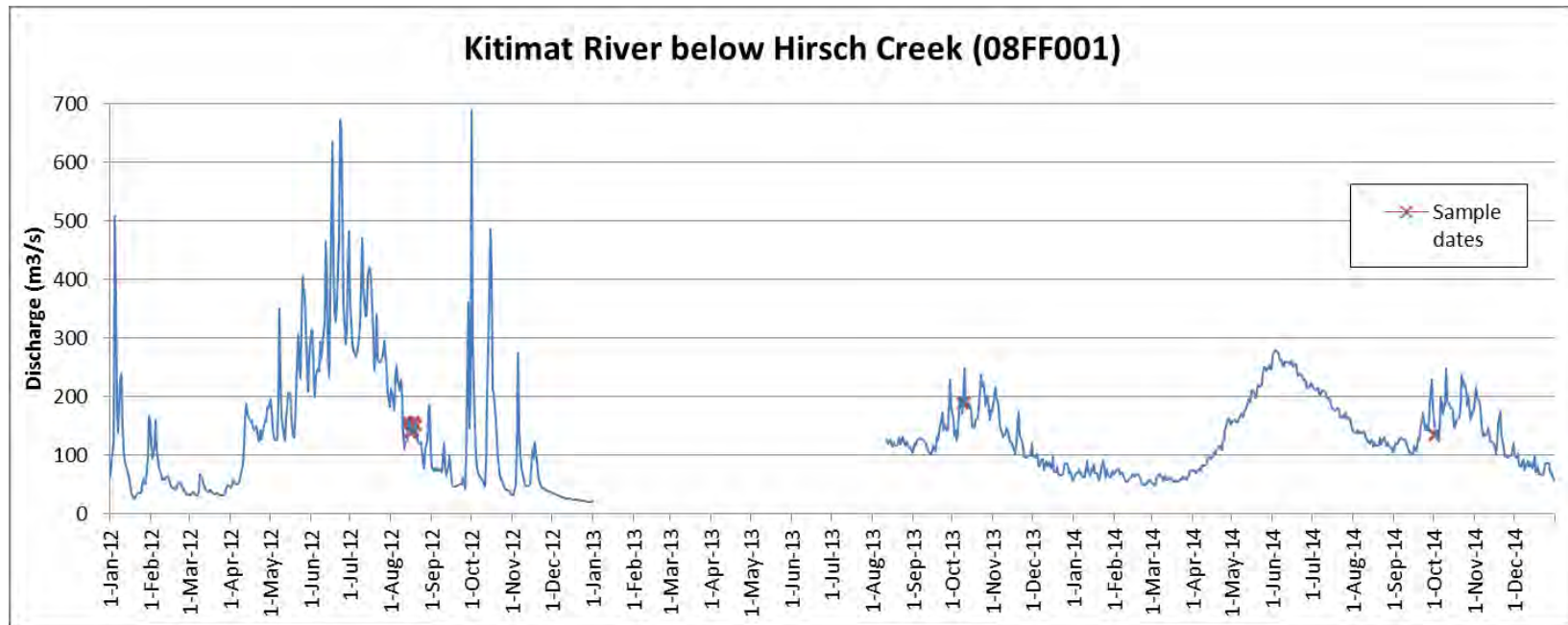


Figure 3-8. Hydrograph of Kitimat River. The data were acquired from the Water Survey of Canada's Wateroffice website. The 2012 data are from the "historic" records and the more recent data are from the "real-time" records, which represent different levels of processing and validation by the Water Survey. The gap between the two data sets is currently unavailable. Red crosses indicate the dates on which EEM lakes were sampled.

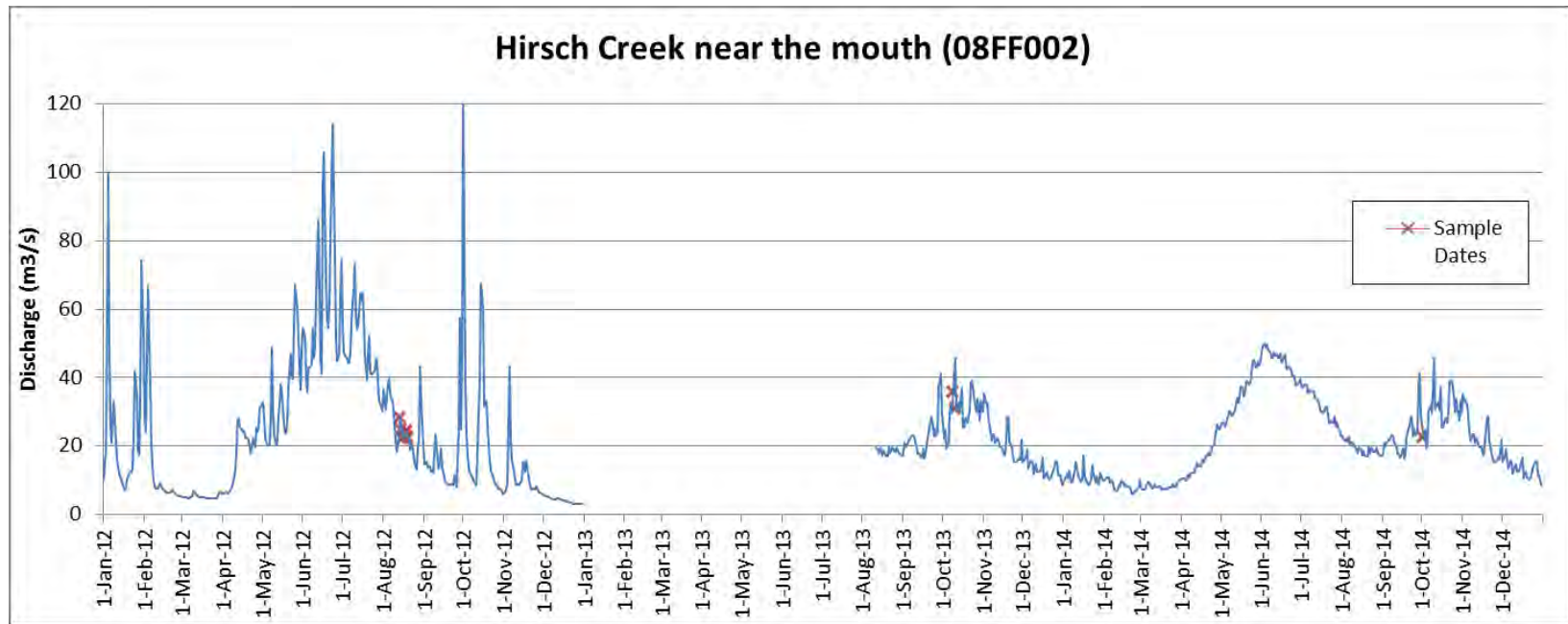


Figure 3-9. Hydrograph of Hirsch Creek. The data were acquired from the Water Survey of Canada's Wateroffice website. The 2012 data are from the "historic" records and the more recent data are from the "real-time" records, which represent different levels of processing and validation by the Water Survey. The gap between the two data sets is currently unavailable. Red crosses indicate the dates on which EEM lakes were sampled.

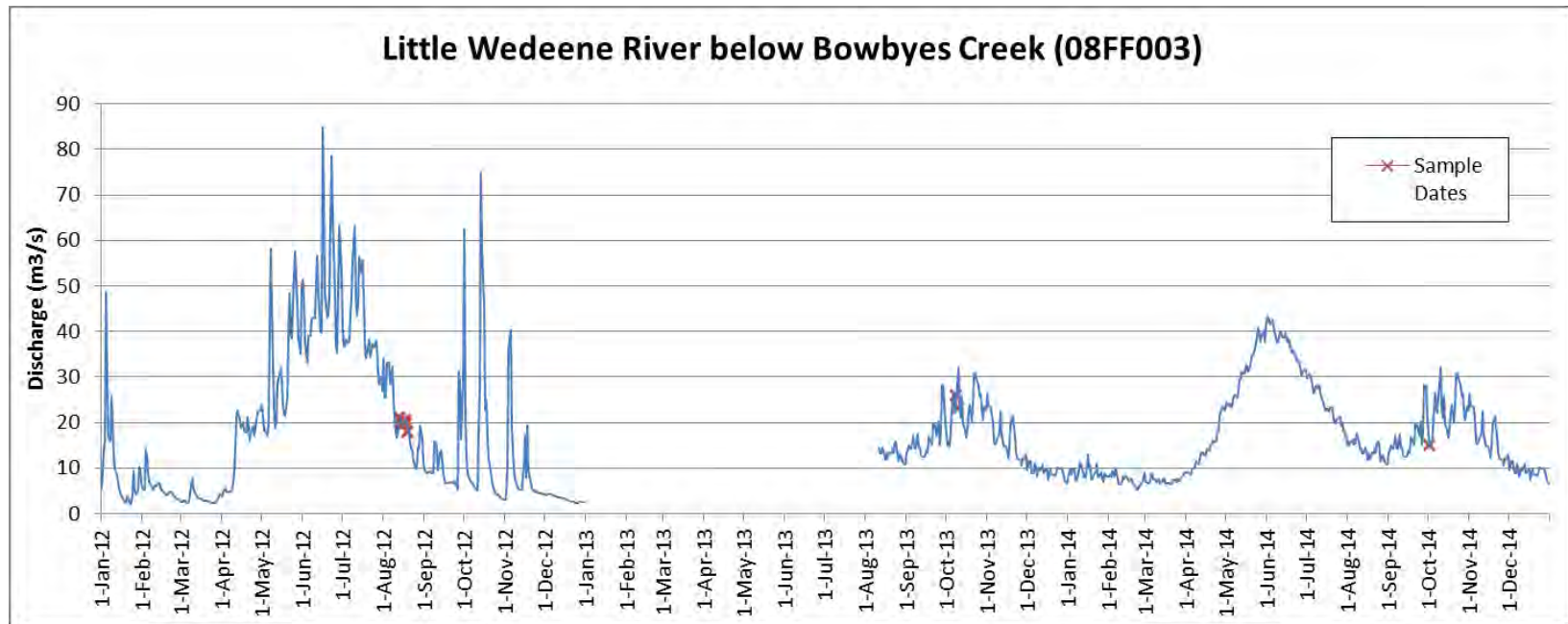


Figure 3-10. Hydrograph of Little Wedeene River. The data were acquired from the Water Survey of Canada's Wateroffice website. The 2012 data are from the "historic" records and the more recent data are from the "real-time" records, which represent different levels of processing and validation by the Water Survey. The gap between the two data sets is currently unavailable. Red crosses indicate the dates on which EEM lakes were sampled.

3.5 Critical Loads and Exceedances ①

STAR vs. KAA watershed methods

The implications of calculating watershed area using the improved methods applied in the KAA (compared to the initial methods employed in the STAR) were assessed by comparing the calculated critical loads and predicted exceedances for 2012 and 2013 using each of the methods. Table 3-4 shows the critical loads and exceedances based on using the STAR methodology for defining watershed area, and Table 3-5 shows the same results when using the KAA methodology. Comparing these two tables shows that there are minimal, often negligible, differences as a result of the selection of the method for watershed definition. In no case does the choice of method change the sensitivity class or exceedance class for any of the lakes. Differences in critical load and exceedances based on the sampling year yield much more substantial differences. These results of this comparison show that the improved method does not change the baseline of the STAR results in a meaningful way and thus continuing with the improved method is fully justified.

Table 3-4. Critical loads and exceedances for EEM lakes using STAR methodology for calculating watershed area, for 2012 and 2013.

	2012 STAR data		2013 EEM data		2013 vs. 2012	
	CL(Ac)	Ex(A)	CL(Ac)	Ex(A)	CL(Ac)	Ex(A)
EEM Lakes	(meq/m2/yr)	(meq/m2/yr)	(meq/m2/yr)	(meq/m2/yr)	%	%
End Lake (006)	28.41	14.23	33.70	9.06	5.29	-5.17
Little End Lake (012)	79.14	-37.38	80.62	-38.81	1.48	-1.42
Lake 022	53.95	-12.22	73.06	-31.29	19.11	-19.07
West Lake (023)	31.94	9.03	36.39	6.45	4.45	-2.58
Lake 028	46.15	51.23	132.43	-33.04	86.28	-84.27
Lake 042	15.88	0.21	25.36	-9.45	9.48	-9.66
Lake 044	0.00	16.71	0.00	16.78	0.00	0.07
Lake 007	1390.01	-1353.65	1379.02	-1342.76	-10.99	10.89
Lake 016	115.51	-70.93	127.80	-81.58	12.29	-10.65
Lake 034	125.09	-105.90	171.94	-152.83	46.85	-46.93

Table 3-5. Critical loads and exceedances for EEM lakes using KAA methodology for calculating watershed area, for 2012 and 2013.

	2012 STAR data		2013 EEM data		2013 vs. 2012	
	CL(Ac)	Ex(A)	CL(Ac)	Ex(A)	CL(Ac)	Ex(A)
EEM Lakes	(meq/m2/yr)	(meq/m2/yr)	(meq/m2/yr)	(meq/m2/yr)	%	%
End Lake (006)	28.43	14.31	33.27	9.59	4.84	-4.72
Little End Lake (012)	79.38	-37.47	80.86	-38.89	1.48	-1.42
Lake 022	53.92	-12.26	73.02	-31.32	19.10	-19.06
West Lake (023)	31.92	9.11	36.35	6.54	4.43	-2.57
Lake 028	47.45	49.81	135.82	-36.51	88.37	-86.32
Lake 042	15.92	0.20	25.42	-9.48	9.50	-9.68
Lake 044	0.00	16.71	0.00	16.78	0.00	0.07
Lake 007	1393.45	-1358.43	1382.44	-1347.52	-11.01	10.91
Lake 016	115.62	-71.05	127.92	-81.71	12.30	-10.66
Lake 034	124.71	-105.46	171.42	-152.26	46.71	-46.79

2012 vs. 2013

The comparison of critical loads and exceedances for the EEM lakes between 2012 and 2013 are shown in Table 3-6, Figure 3-11, and Figure 3-12. Two of the lakes with predicted exceedances based on the 2012 data no longer have predicted exceedances when using the 2013 data. The critical load calculated for Lake 028 using 2013 data was more than double the critical load computed from 2012 data (109 vs. 47 $\mu\text{eq/l}$), and shifted that lake from exceedance (based on 2012 chemistry) to non-exceedance (based on 2013 chemistry). However, the other three lakes with exceedances calculated in 2012 show increases (very small for 044) in the exceedances calculated. Figure 3-11 and Figure 3-12 show that the EEM lakes generally show similar critical loads as calculated with the two data sets.

The predicted exceedances suggest that the results based on the August 2012 sampling period may have been more conservative than those based on the October 2013 sampling period. It is not possible to extract the separate effects of year and season; however, these results at least partly support the hypothesis put forth in the STAR that although fall sampling was preferred, summer sampling was acceptable because if anything it would likely be more conservative.

Table 3-6. Critical loads and exceedances for the EEM lakes, comparing 2012 and 2013.

	2012 STAR data		2013 EEM data		2013 minus 2012	
	CL(Ac)	Ex(A)	CL(Ac)	Ex(A)	CL(Ac)	Ex(A)
EEM Lakes	(meq/m2/yr)	(meq/m2/yr)	(meq/m2/yr)	(meq/m2/yr)	µeq/l	µeq/l
End Lake (006)	28.43	14.31	25.33	17.52	-3.09	3.21
Little End Lake (012)	79.38	-37.47	67.84	-25.88	-11.54	11.60
Lake 022	53.92	-12.26	62.39	-20.69	8.47	-8.43
West Lake (023)	31.92	9.11	29.48	13.41	-2.44	4.30
Lake 028	47.45	49.81	109.48	-10.16	62.02	-59.97
Lake 042	15.92	0.20	20.43	-4.49	4.52	-4.70
Lake 044	0.00	16.71	0.00	16.78	0.00	0.07
Lake 007	1393.45	-1358.43	1343.96	-1309.04	-49.49	49.39
Lake 016	115.62	-71.05	116.33	-70.11	0.70	0.93
Lake 034	124.71	-105.46	164.84	-145.68	40.13	-40.21

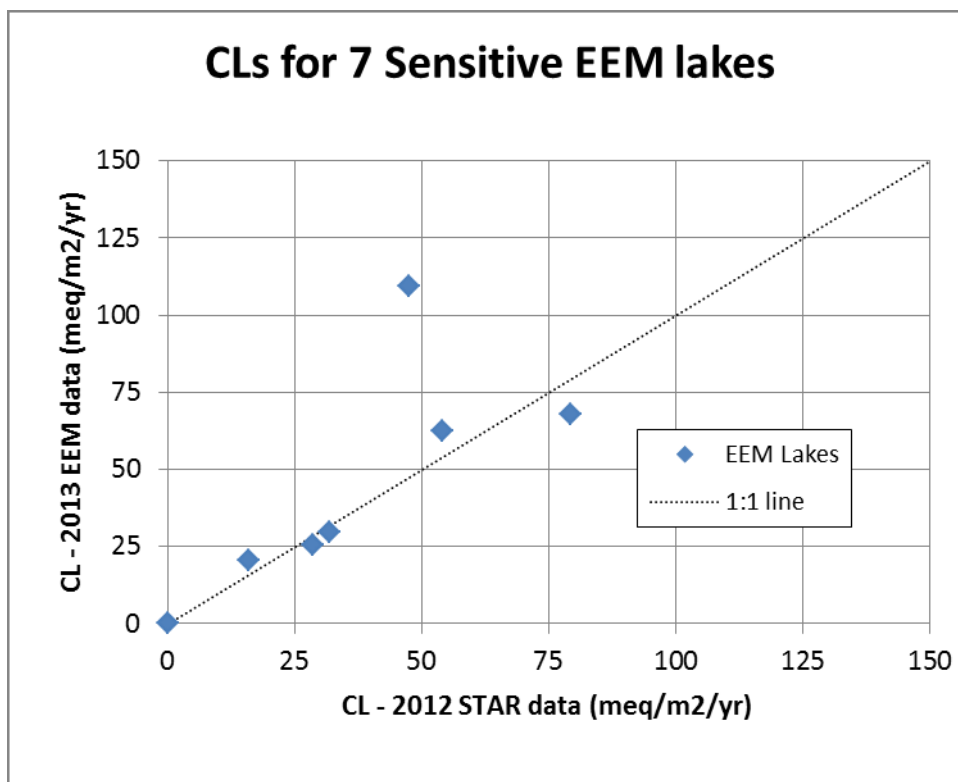


Figure 3-11. Critical loads for sensitive EEM lakes, comparing 2013 versus 2012.

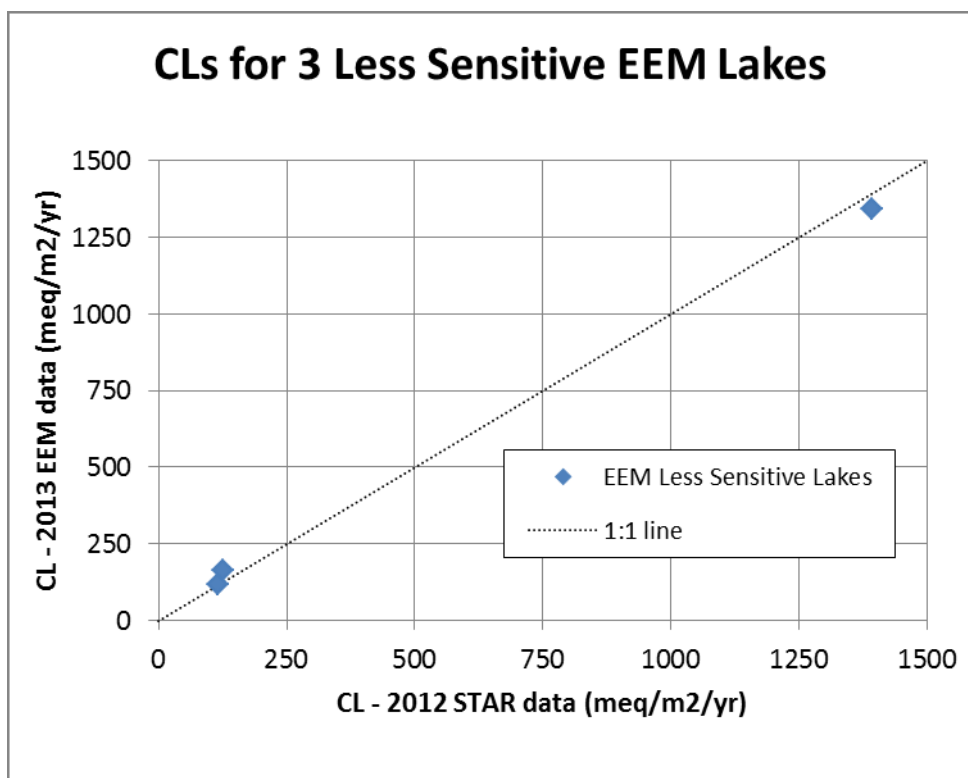


Figure 3-12. Critical loads for less sensitive EEM lakes, comparing 2013 versus 2012.

Non-EEM lakes and streams

The critical loads and predicted exceedances for MOE3, MO6 and Cecil Creek are shown in Table 3-7. All of these non-EEM sites show critical loads that are multiple times higher than the threshold for the “very low sensitivity” class (i.e., 100 meq/m²/yr). These sites all appear to be very insensitive to potential acidification.

Table 3-7. Critical loads (CL(Ac)) and predicted exceedances (Ex(A)) for the non-EEM sites, MOE3, MOE6, and Cecil Creek.

Site	Year	CL(Ac) (meq/m ² /yr)	Ex(A) (meq/m ² /yr)
MOE3	2013	598.3	-576.3
MOE6	2014	413.5	-413.5
CECIL1	2013	429.9	-380.8
CECIL2	2013	469.3	-388.3
CECIL3	2013	225.5	-180.5

3.6 Predicted Changes in pH (Δ pH)

The ESSA/DFO model for the calculation of predicted future pH was run with the 2013 data (as was done in the STAR with the 2012 data). The results of Δ pH (i.e., the difference between predicted future steady state pH and current pH) for the EEM lakes using both the 2012 and 2013

data are shown in Table 3-8. Two of the lakes predicted to have $\Delta\text{pH} < -0.3$ based on the 2012 data are predicted to not exceed the threshold of 0.3 pH units based on the 2013 data. Conversely, there is one lake for which the reverse applies. A graphical comparison of the predicted changes in pH between the two years' data is shown in Figure 3-13.

Table 3-8. ΔpH for EEM lakes, 2012-2013. Decreases in pH of greater than 0.3 pH units are shown in red. The three shaded rows indicate the less sensitive EEM lakes.

	2012 STAR Data	2013 EEM Data	2013 vs. 2012
EEM Lakes	ΔpH	ΔpH	ΔpH
End Lake (006)	-0.48	-0.40	0.08
Little End Lake (012)	-0.13	-0.11	0.02
Lake 022	-0.39	-0.24	0.15
West Lake (023)	-0.54	-0.43	0.11
Lake 028	-0.38	-0.21	0.17
Lake 042	-0.20	-0.32	-0.12
Lake 044	-0.54	-0.58	-0.04
Lake 007	0.00	0.00	0.00
Lake 016	-0.07	-0.05	-0.05
Lake 034	-0.03	-0.01	-0.01

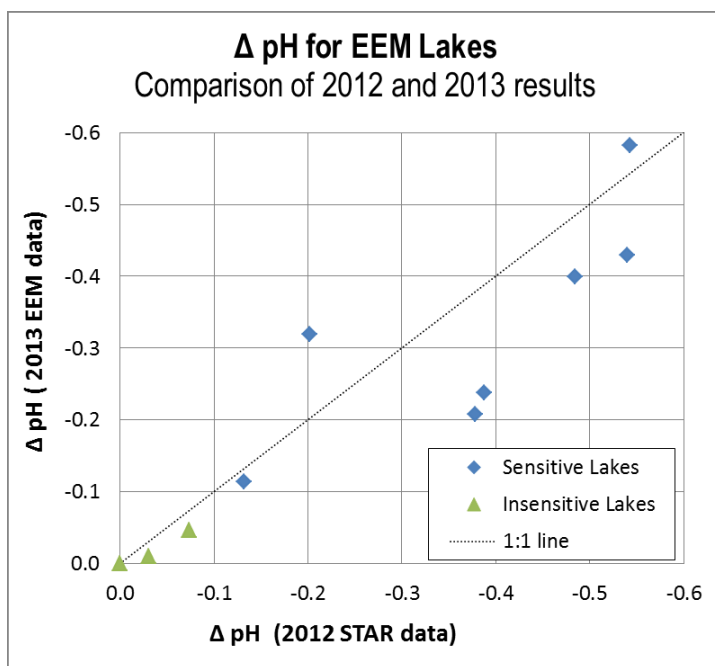


Figure 3-13. ΔpH for EEM lakes, comparing 2013 versus 2012.

3.7 Inter-annual Changes

Inter-annual changes in pH, Gran ANC, SO₄, DOC, sum of base cations, and chloride are shown in Table 3-9 (absolute changes) and Table 3-10 (relative changes). Changes are shown for the three time periods of comparison, 2012-2013, 2013-2014, and 2012-2014. The sensitive EEM lakes and less sensitive EEM lakes are presented separately within each of the tables.

Figure 3-14 and Figure 3-15 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 2013 and 2014. Although the tables show changes from 2012 as well, these figures have only been prepared for the changes from 2013 to 2014. Changes from 2013 to 2014 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.

Table 3-9. Inter-annual changes in select water chemistry attributes for EEM lakes, 2012-2013, 2013-2014, and 2012-2014. SO₄ = sulphate, DOC = dissolved organic carbon, Σ BC = 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 value in later year minus value in earlier year.

	pH			Gran ANC (ueq/L)			SO ₄ * (µeq/L)			DOC (mg/L)			Σ BC* (µeq/L)			Cl (µeq/L)		
From To	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014
Lak006	0.37	0.08	0.45	3.3	7.8	11.1	3.0	-3.4	-0.4	-0.4	0.2	-0.2	-3.0	8.7	5.7	2.9	-2.2	0.7
Lak012	0.65	-0.02	0.63	6.5	16.8	23.3	5.2	-5.5	-0.3	-0.4	0.3	-0.1	-11.8	2.7	-9.0	10.5	-8.5	2.1
Lak022	0.23	0.11	0.33	8.5	10.5	19.0	16.9	-9.3	7.6	0.9	-0.6	0.3	11.0	4.9	15.9	5.4	-3.3	2.1
Lak023	0.25	0.11	0.36	4.0	11.7	15.7	5.0	-7.4	-2.3	-0.1	0.7	0.6	-2.1	7.4	5.3	3.0	-1.8	1.2
Lak028	0.23	0.12	0.35	8.8	17.8	26.6	71.2	-33.7	37.5	2.2	-1.1	1.1	48.4	4.4	52.8	11.7	-6.7	4.9
Lak042	0.78	-0.35	0.43	41.4	-8.5	33.0	-0.5	-1.8	-2.2	-3.5	0.9	-2.6	7.6	-5.3	2.3	1.6	4.1	5.7
Lak044	0.26	0.09	0.35	7.3	-2.7	4.6	0.0	-1.6	-1.6	-0.2	0.3	0.1	3.0	0.1	3.1	3.3	-2.9	0.3
Average (Sensitive Lakes)	0.39	0.02	0.41	11.4	7.6	19.1	14.4	-8.9	5.5	-0.2	0.1	-0.1	7.6	3.3	10.9	5.5	-3.1	2.4

Lak007	-0.05	0.14	0.10	24.5	-16.4	8.2	15.1	-35.8	-20.7	-0.5	0.6	0.1	-51.9	63.5	11.6	11.7	-17.1	-5.4
Lak016	0.38	0.04	0.42	28.3	8.8	37.1	17.9	-8.7	9.1	0.5	-0.2	0.3	0.8	13.7	14.5	6.0	-3.0	3.0
LAK024			0.49			172.6			12.3			0.3			170.3			38.5
Lak034	0.12	-0.12	0.00	111.0	-5.4	105.6	14.0	-21.1	-7.0	0.1	2.4	2.5	56.0	8.6	64.6	2.5	-1.8	0.7
Average (Less Sensitive Lakes)	0.15	0.02	0.25	54.6	-4.3	80.9	15.7	-21.9	-1.6	0.0	0.9	0.8	1.6	28.6	65.3	6.7	-7.3	9.2

Table 3-10. Inter-annual changes (%) in select water chemistry attributes for EEM lakes, 2012-2013, 2013-2014, and 2012-2014. SO₄ = sulphate, DOC = dissolved organic carbon, Σ BC = sum of base cations (e.g., Mg, Ca, K, Na), Cl = chloride. The * indicates that the ionic concentrations have been corrected for marine influence.

From To	pH			Gran ANC (mg/L)			SO ₄ * (µeq/L)			DOC (mg/L)			Σ BC* (µeq/L)			Cl (µeq/L)		
	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014	2012 2013	2013 2014	2012 2014
Lak006	6%	1%	8%	13%	27%	43%	26%	-24%	-4%	-10%	6%	-5%	-5%	15%	9%	51%	-25%	13%
Lak012	12%	0%	11%	11%	26%	41%	84%	-49%	-5%	-9%	7%	-2%	-10%	2%	-8%	254%	-58%	49%
Lak022	4%	2%	6%	31%	29%	68%	56%	-20%	25%	17%	-9%	6%	11%	5%	16%	78%	-27%	30%
Lak023	4%	2%	6%	20%	49%	80%	26%	-31%	-12%	-3%	18%	15%	-3%	12%	8%	67%	-24%	26%
Lak028	5%	2%	7%				125%	-26%	66%	45%	-16%	22%	66%	4%	72%	193%	-38%	81%
Lak042	17%	-6%	9%				-7%	-31%	-36%	-26%	9%	-19%	14%	-9%	4%	26%	53%	93%
Lak044	5%	2%	6%	576%	-32%	361%	0%	-26%	-26%	-12%	17%	3%	21%	1%	22%	59%	-33%	6%
Lak007	-1%	2%	1%	2%	-1%	1%	29%	-54%	-40%	-84%	610%	15%	-3%	4%	1%	48%	-47%	-22%
Lak016	6%	1%	7%	41%	9%	54%	46%	-15%	23%	14%	-4%	9%	0%	8%	9%	95%	-24%	47%
LAK024			7%			58%			50%			23%			50%			141%
Lak034	2%	-2%	0%	112%	-3%	106%	58%	-55%	-29%	3%	51%	55%	28%	3%	32%	42%	-21%	12%

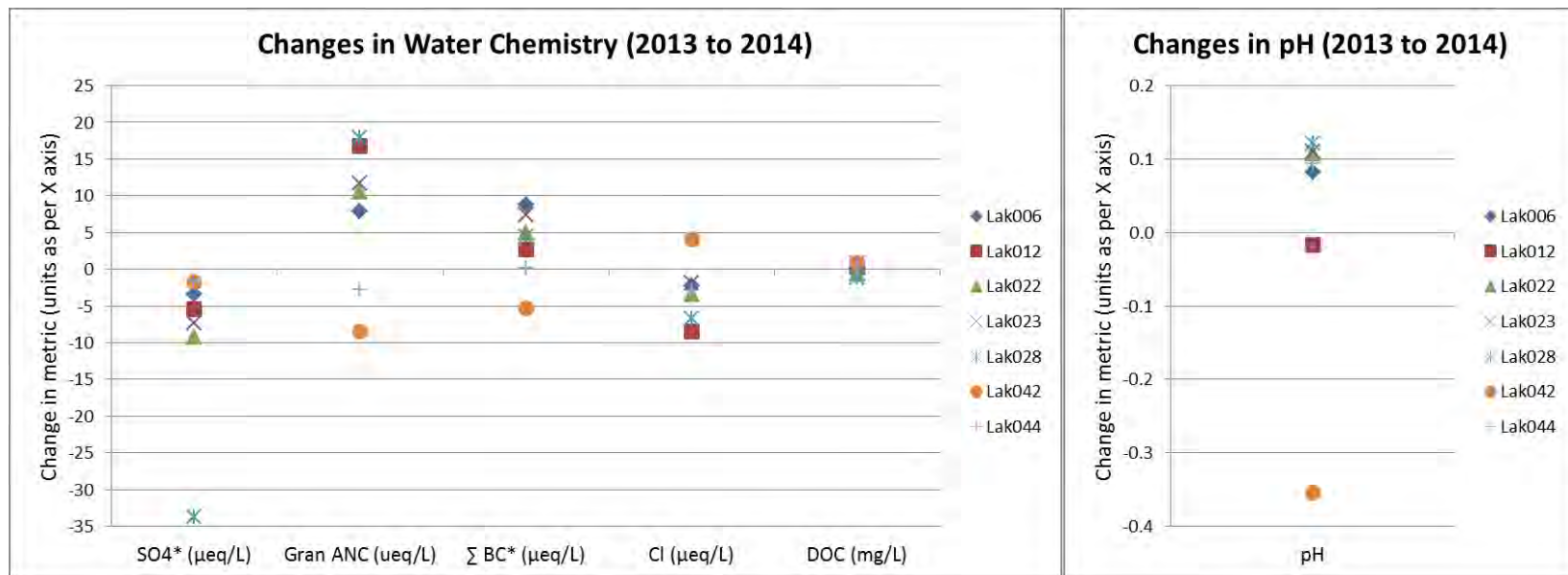


Figure 3-14. Changes in water chemistry parameters (left panel) and pH (right panel) across all of the sensitive EEM lakes, from 2013 to 2014. Values shown are 2014 value minus 2013 value.

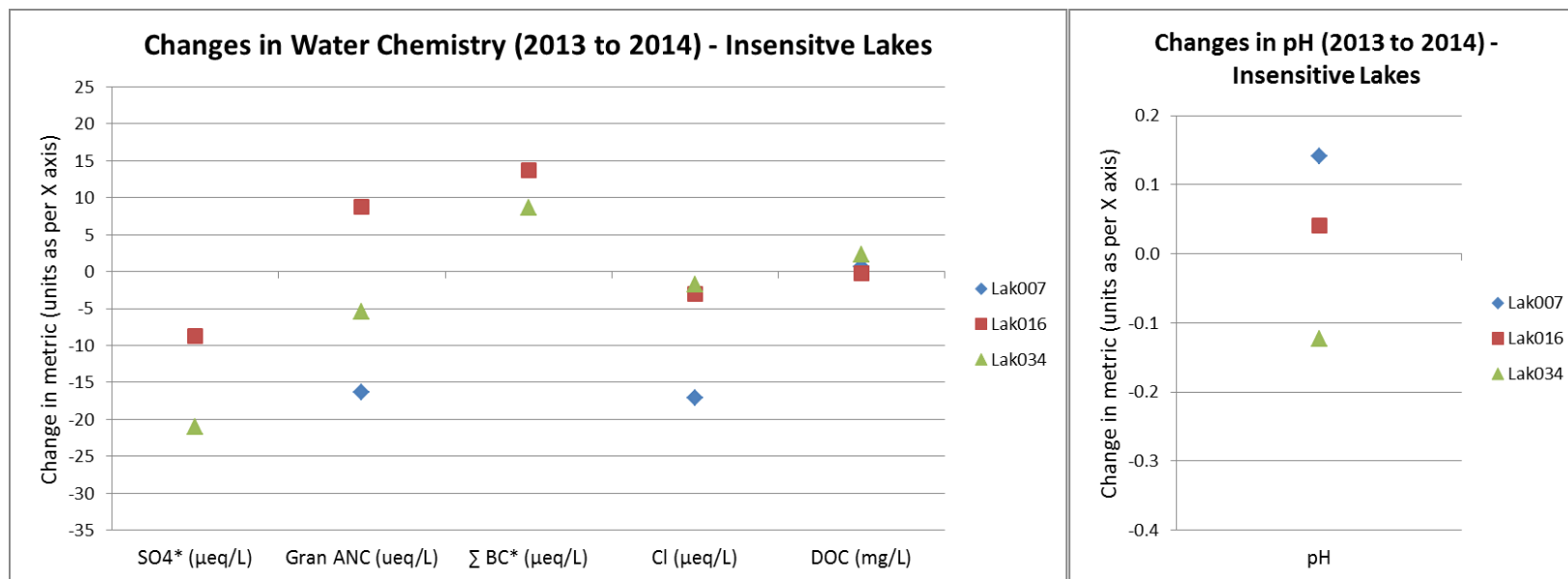


Figure 3-15. Changes in water chemistry parameters (left panel) and pH (right panel) across all of the less sensitive EEM lakes, from 2013 to 2014. Values shown are 2014 value minus 2013 value.

3.8 Fish Sampling ⑦

Results from the fish sampling are documented Section 3.6 of Limnotek's technical report (Perrin et al. 2013), and discussed in Section 4.2 of the same report.

The executive summary of the Limnotek technical report provides this summary of the results of the fish sampling:

*Three of the four lakes sampled using gill nets contained fish. Finlay Lake had no inlets or outlets and no fish were caught. Stickleback (*Gasterosteus aculeatus*, TSB) were common in the other three lakes. Both of the End Lakes had coastal cutthroat trout (*Oncorhynchus clarkii clarkii*, CCT), coho salmon (*Oncorhynchus kisutch*, CO), and Dolly Varden char (*Salvelinus malma*, DV) whereas West Lake only had CO and TSB. The CO in West Lake had morphologies indicating residualism (fish did not migrate out of the lake after rearing as juveniles), which is rare in coastal lakes. DNA analysis of tissue from the CO in 2014 will be used to confirm species identification and the apparent occurrence of coho residualism. The condition may be caused by intermittent access to West Lake between wet and dry years. In dry years, lack of wetted channels may have prevented smolts from outmigrating. Very low numbers of DV may result in difficulty detecting the presence of this species in future sampling.*

Perrin et al. (2013, p. iv)

4 Discussion

The discussion is not separated based on the year in which the information was collected. The discussion 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 added in either year. The discussion of each of these sets of sites integrates all available information collected and analyzed thus far (i.e., 2012, 2013, 2014).

4.1 EEM Lakes

Critical Loads – 2012 vs. 2013

Of the seven sensitive EEM lakes, the calculated critical loads in 2013 decreased in three lakes, increased in three lakes and remained the same in one lake. None of the lakes with decreased critical loads changed sensitivity class, but the three lakes with increased critical loads all resulted in being reclassified in lower sensitivity classes (Table 4-1). Because exceedances were calculated based on the same deposition values (i.e., post-KMP), all of the lakes with increased critical loads showed decreased exceedances and vice versa. Of the three less sensitive EEM lakes, critical loads increased in one lake, decreased in one lake and changed negligibly one lake; all remained in the lowest sensitivity and exceedance classes.

Overall, these results show that when assessed using the October 2013 sampling data, the sensitivity of the EEM lakes predominantly appears to be similar or lower than when previously assessed using the August 2012 sampling data. These results are consistent with the hypothesis, as described in the STAR, that sampling done in the summer (which was necessary due to logistical constraints during the STAR work) would be more conservative than sampling done in the fall – that is, it would tend to overestimate the sensitivity of lakes to increased emissions. Though there is lake to lake variability, it appears that base cations and critical loads were more likely to increase

when based on the October 2013 sampling (relative to the August 2012 sampling) than to decrease. The possible explanations for this pattern (including for Lake 028) include: an increase in the proportion of groundwater contributions in the fall of 2013 compared to the summer of 2012; decreases in vegetation uptake of base cations in the fall of 2013 compared to the summer of 2012; and watershed flushing of base cations in the fall of 2013 following the storms which preceded the sampling in that year. It isn't possible to test these hypotheses with just a couple of years of data.

Table 4-1. Sensitivity and exceedance classes of EEM lakes, 2012 and 2013. Classification system is defined in the STAR.

	2012 STAR data	2013 EEM data	2013 vs. 2012
EEM Lakes	Sensitivity Class	Sensitivity Class	Change in Sensitivity Class
End Lake (006)	4	4	-
Little End Lake (012)	2	2	-
Lake 022	3	2	(1)
West Lake (023)	4	4	-
Lake 028	3	1	(2)
Lake 042	5	4	(1)
Lake 044	5	5	-
Lake 007	1	1	-
Lake 016	1	1	-
Lake 034	1	1	-

Variability in pH

The results of the intensive monitoring of pH at three of the EEM lakes (Bennett and Perrin 2015) show substantial variability in pH measurements, both over time and among different field and lab approaches. This has important implications for the ongoing design of the EEM plan.

Firstly, the high variability in pH supports the need to continue both frequent and continuous pH monitoring to improve our knowledge of the variability across time (both intra-season and inter-annual) and among methods (i.e., continuous monitors, field samples, lab analyses). From these initial results, it appears necessary to both maintain the continuous monitoring of pH and collect samples for lab analysis of pH four times during the fall for each of the three accessible lakes. Secondly, the high variability indicates that the EEM would be strengthened by jointly evaluating patterns of change in pH, ANC and SO₄, rather than solely relying on pH as a critical indicator. Given the variability in pH, it is important that ANC and SO₄ be analyzed as part of the weekly samples described above. Thirdly, the high variability indicates a significant need to conduct power analyses on our ability to correctly detect changes in pH, as well as ANC and SO₄, both within a single lake, and across the set of seven sensitive lakes. Power analyses will evaluate our level of confidence that the observed changes reflect true changes and how to improve our confidence (power) to correctly identify true changes in water chemistry.

Application of the Evidentiary Framework

The Evidentiary Framework (ESSA et al. 2014b, Section 7) has been used as a basis for expectations about observed patterns of change. Table 4-2 contains relevant questions from the Evidentiary Framework and expected implications for these processes in the context of *decreasing emissions* (whereas the Framework was developed in the context of assessing patterns of change in the context of the *increasing emissions* that will occur as the transition to KMP is completed). Table 4-3 assesses the extent to which the patterns of change observed between 2013 and 2014 align with the expected changes in water chemistry. A similar exercise was conducted with the changes between 2012 and 2013 but is not included because the mixed effect of changing season and year made interpretation of the patterns of change much more difficult.

In general, changes from 2013 to 2014 show rapid responses of lakes to changes in S emissions, which is consistent with the hypothesis that future reductions in emissions (if required) would also result in rapid changes in water chemistry. Further years of data collection are required to test this hypothesis. Both pH and ANC predominantly show increases from 2012 to 2013 and 2013 to 2014, in response to two sequential years of decreases in S emissions.

Table 4-2. Expected patterns of change based on the Evidentiary Framework. Questions are taken directly from the Evidentiary Framework and interpreted in the context of decreasing emissions.

Questions from Evidentiary Framework	Expectations in the context of decreasing emissions prior to KMP implementation (particularly for changes between October 2013 and October 2014)
Has lake [SO ₄] increased post-KMP in a manner consistent with predicted increases in deposition of SO ₄ , and deposition levels inferred from monitoring observations?	Lake [SO ₄] would be expected to decrease with increases in emissions and consequent deposition of SO ₄ .
Do the observed spatial and temporal changes in climate, pH, ANC, dissolved organic carbon (DOC) and sulphate suggest drought-caused oxidation of sulphate stored in wetlands, related to KMP rather than due to climate fluctuations affecting wetland storage of historical S deposition?	<i>This is independent of emissions. It is associated with whether or not drought conditions have been observed.</i>
Has lake ANC decreased post-KMP in a manner consistent with increases in lake [SO ₄] and watershed neutralizing abilities (F-factor)?	If lake [SO ₄] has decreased, we expect ANC to have increased. Lakes with a higher F-factor value should exhibit a larger increase; lakes with an F-factor of 0 should exhibit minimal/no change in ANC. If lake [SO ₄] has increased, we expect ANC to have decreased.
Has lake pH decreased post-KMP in a manner consistent with SO ₄ increases, ANC decreases, and lake-specific titration curves?	If lake ANC has increased (as predicted with decreases in lake [SO ₄]), then we expect pH to increase, as consistent with the pH-ANC relationship characterized by the titration curve.
Have lake pH and ANC values decreased beyond identified thresholds (Table 27)?	No thresholds are identified in the context of decreasing emissions and deposition.
Are observed changes in Cl, NO ₃ and DOC consistent with causes of acidification other than KMP (i.e., sea salt driven episodes, N emissions, organic acidification)?	In the context of decreasing emissions, increasing acidification is not expected to be observed. Given this expectation, changes in pH that are inversely correlated with changes in lake [SO ₄], (with no corresponding changes in Cl, NO ₃ or DOC) would suggest that lake acidity is primarily driven by smelter influence. If there are changes in Cl, NO ₃ or DOC that are inversely correlated with pH, this would suggest that other causes of acidification are contributing to the lake's level of acidity.
<i>Not directly connected to specific questions from the Evidentiary Framework</i>	May expect slight increases in organic anion charge density and possibly DOC with decreasing deposition of S, but this is not certain (Marmorek et al. 1988).

Table 4-3. Comparison of observed changes from 2013 to 2014 versus expected changes based on the interpretation of the Evidentiary Framework in the context of decreasing emissions.

Expected changes in lake chemistry		Observ. match expect.	Results - observations from annual sampling	Possible explanations for results that differ from expectations, other comments, and suggested analyses
Factor	Expectations based on KMP changes			
Decreased S emissions, decreased SO ₄ deposition	Decreased [SO ₄]	YES	[SO ₄] decreased in 10/10 lakes	
	Changes in deposition will be affected by distance from the smelter: ▪ largest [SO ₄] decrease in Lake 028 ▪ smallest [SO ₄] decreases in Lakes 034, 042, 044 ▪ intermediate [SO ₄] decreases in other lakes	YES/NO	YES/NO - Lake 028 has 2nd largest decrease YES - smallest decreases in Lakes 042, 044 NO - Lake 034 has large decrease	Changes in [SO ₄] are generally (but not always) consistently related to distance from the smelter
	Increased [ANC] (for sensitive lakes)	YES	ANC increased in 5/7 sensitive lakes (not Lakes 042 and 044, which are furthest away)	
	No change in [ANC] (for less sensitive lakes)	YES	3 less sensitive lakes have low proportional changes in ANC (1↑, 2↓), substantially lower than the sensitive lakes	
	Increased pH (for sensitive lakes)	YES	YES - pH increased in 5/7 sensitive lakes NO - pH decreased in 2/7 lakes (-0.35 in Lake 042, which is further away) pH increased in 2/3 less sensitive lakes	
	No change, or small increase in DOC	YES	YES - increase in 7/10 lakes (moderate in Lake 034, small in all others) YES/NO - decreases 3/10 lakes are small	
If [SO ₄] is driving [BC]	Decreased [BC]	NO	NO - [BC] increased in 9/10 lakes	It is possible that there have been changes in BC deposition due to other factors (e.g., fires, dust). Need to look at BC deposition at wet deposition monitoring sites.
Chloride	No change in [Cl]	NO	NO - [Cl] decreased (substantially) in 9/10 lakes	Consistent decreases in lake [Cl] implies: 1. decreased sea salt contribution 2. more dilution of Cl in 2013 than 2014 (sampling 2013 was after low Q in Sept)

4.2 Non-EEM Sites

MOE3

Lake MOE3 was sampled in 2013. Lake chemistry and critical loads have been assessed for MOE3. It has been assessed as insensitive to potential acidification due to its very high critical load and high pH. MOE3 has very high SO₄ levels, which demonstrate an influence of smelter emissions; however, its overall lake chemistry suggests that it is insensitive to acidification.

MOE6

Lake MOE6 was sampled in 2014. Lake chemistry and critical loads have been assessed for MOE6. It has been assessed as insensitive to potential acidification due to its high critical load and high pH. MOE6 has high SO₄ levels, which demonstrate an influence of smelter emissions; however, its overall lake chemistry suggests that it is insensitive to acidification.

Cecil Creek

Cecil Creek was sampled in 2013 at 3 sites. Lake chemistry and critical loads have been assessed for Cecil Creek. Although SO₄ levels are moderately high to high, all three sites have been assessed as insensitive due to their high critical loads. For two of the sites, pH > 7, and for the third, pH = 6.35.

Goose Creek

Goose Creek was sampled in 2014 at 6 sites. Lake chemistry has been assessed for Goose Creek, but not critical loads.

All of the sites show definite influence of the smelter emissions, due to their very high levels of both SO₄ and F. However, three of the sites (5-7) appear to be insensitive to potential acidification based on having high pH, high ANC and very high base cations. Sites 1 and 2 are unlikely to be sensitive to acidification because although ANC and pH are lower, they are still relatively high, with base cations are still quite high. Site 4 shows evidence of natural acidification due to its high DOC, and has some potential to be an acid sensitive site, depending on emissions and runoff levels, due to low pH and moderately low ANC; however, base cations are still high. Critical loads will be calculated for Goose Creek in 2015.

In the absence of critical loads results, a simple sensitivity analysis was conducted (not reported). The results suggested that site #4 could potentially show an exceedance if its deposition is high and its runoff is low relative to nearby sites. Site 2 could also potentially show an exceedance, but only under the unlikely conditions of unexpectedly high deposition and low runoff relative to nearby sites.

5 Recommendations

Recommendations are only briefly summarized here, as they are described in more detail in the discussion section above.

5.1 Recommendations regarding EEM lakes

- Maintain the continuous monitoring of pH at the three accessible lakes for at least one more year
- Collect water chemistry samples for lab analyses from the three lakes with continuous pH monitors four times during the fall sampling period
- Conduct power analyses on changes in pH, ANC and SO₄ to assess our ability to correctly identify important changes in water chemistry
- Use the KAA approach for defining watershed area for all future analyses

5.2 Recommendations regarding non-EEM sites

- MOE3, MOE6 and Cecil Creek are insensitive and therefore not necessary to sample in further years.
- Critical loads should be calculated for Goose Creek sites to assess its sensitivity, especially Goose Creek 4.

6 References

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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 and 2014, 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 and 2014, the pH of the water samples was measured by two different laboratories (Trent University and ALS).

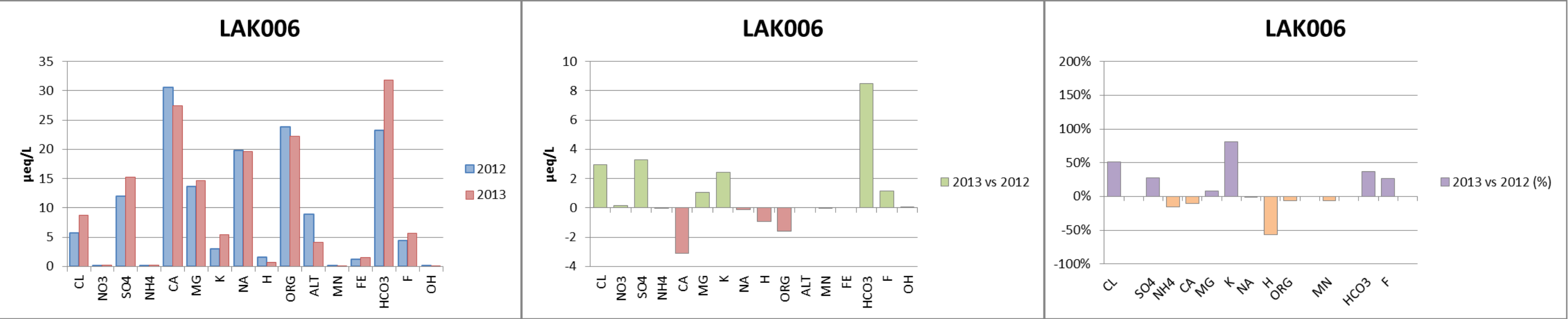
Lake	Year	Lab pH (Trent)	Lab pH (ALS)	DOC (mg/L)	Gran ANC (µeq/L)	SO ₄ (µeq/L)	Cl (µeq/L)	F (µeq/L)	Ca (µeq/L)	Mg (µeq/L)	K (µeq/L)	Na (µeq/L)	Σ BC (µeq/L)
LAK006	2012	5.79		3.6	25.7	12.0	5.8	4.5	30.5	13.6	3.0	19.8	67.0
LAK007	2012	7.98		0.6	1437.6	53.9	24.6	2.8	1273.1	161.8	19.8	76.5	1531.2
LAK012	2012	5.64		4.6	57.0	6.6	4.2	5.0	74.7	21.6	5.3	23.6	125.2
LAK016	2012	6.31		3.7	68.7	39.7	6.3	7.8	117.9	21.8	7.4	26.2	173.3
LAK022	2012	5.92		5.3	27.8	30.9	6.9	6.1	58.4	17.4	3.3	26.7	105.8
LAK023	2012	5.70		4.2	19.8	19.5	4.5	5.6	39.6	12.9	3.7	14.7	70.9
LAK024	2012	7.14		1.4	299.5	27.6	27.3	1.6	274.2	38.4	4.7	53.0	370.3
LAK028	2012	4.98		4.9	-4.0	57.5	6.1	20.7	47.8	10.7	3.2	18.0	79.6
LAK034	2012	6.74		4.5	99.4	24.7	5.8	5.8	119.5	32.8	5.9	49.9	208.1
LAK042	2012	4.68		13.2	-20.4	6.8	6.1	3.2	7.6	23.9	3.2	25.5	60.2
LAK044	2012	5.40		1.7	1.3	6.8	5.6	2.9	7.0	4.3	4.2	4.8	20.4
LAK006	2013	6.16	6.14	3.2	29.0	15.3	8.7	5.6	27.4	14.7	5.4	19.7	67.2
LAK007	2013	7.93	8.06	0.1	1462.1	70.3	36.3	3.7	1227.3	163.7	22.6	78.8	1492.4
LAK012	2013	6.29	6.14	4.2	63.5	12.8	14.7	8.2	65.4	23.2	9.5	27.2	125.2
LAK016	2013	6.69	7.19	4.2	96.9	58.2	12.3	11.5	114.9	26.3	11.4	28.1	180.8
LAK022	2013	6.15	6.13	6.2	36.4	48.3	12.4	8.7	65.6	21.7	6.2	29.4	122.8
LAK023	2013	5.95	6.00	4.0	23.8	24.8	7.5	7.4	37.4	14.8	5.3	14.7	72.2
LAK028	2013	5.21	5.47	7.1	4.8	129.9	17.7	32.0	85.8	21.8	5.3	28.2	141.0
LAK034	2013	6.86	7.43	4.7	210.4	39.0	8.2	10.0	153.0	43.3	9.3	61.2	266.9
LAK042	2013	5.46	5.42	9.7	21.0	6.5	7.7	3.2	16.3	23.8	3.6	25.9	69.6
LAK044	2013	5.66	5.97	1.5	8.6	7.1	8.9	3.8	8.1	5.3	6.0	5.6	25.1
LAK006	2014	6.24	6.69	3.4	36.8	11.7	6.5	5.1	31.8	15.9	4.3	21.5	73.5
LAK007	2014	8.07	7.95	0.7	1445.7	32.7	19.2	1.9	1277.5	160.5	20.6	78.3	1536.9
LAK012	2014	6.27	6.69	4.6	80.3	6.5	6.2	5.7	65.4	21.4	6.2	25.5	118.5
LAK016	2014	6.73	6.65	4.0	105.7	49.1	9.3	9.5	122.8	26.8	10.2	31.3	191.1
LAK022	2014	6.26	6.42	5.7	46.9	38.7	9.0	6.9	68.9	20.7	5.3	29.1	124.1
LAK023	2014	6.06	6.24	4.8	35.5	17.3	5.6	6.7	42.4	15.6	3.9	15.6	77.5
LAK024	2014	7.63	7.49	1.7	472.1	43.9	65.7	2.3	404.7	63.1	9.0	106.6	583.4
LAK028	2014	5.33	5.68	5.9	22.6	95.6	11.0	23.3	86.3	19.9	4.6	27.1	137.9
LAK034	2014	6.74	7.03	7.0	205.0	17.7	6.5	7.7	161.7	44.8	9.5	57.4	273.5
LAK042	2014	5.11	5.42	10.6	12.5	5.2	11.8	2.6	10.9	25.9	3.9	28.1	68.8
LAK044	2014	5.75	5.60	1.8	5.9	5.2	5.9	2.8	8.0	5.1	5.4	5.5	23.9

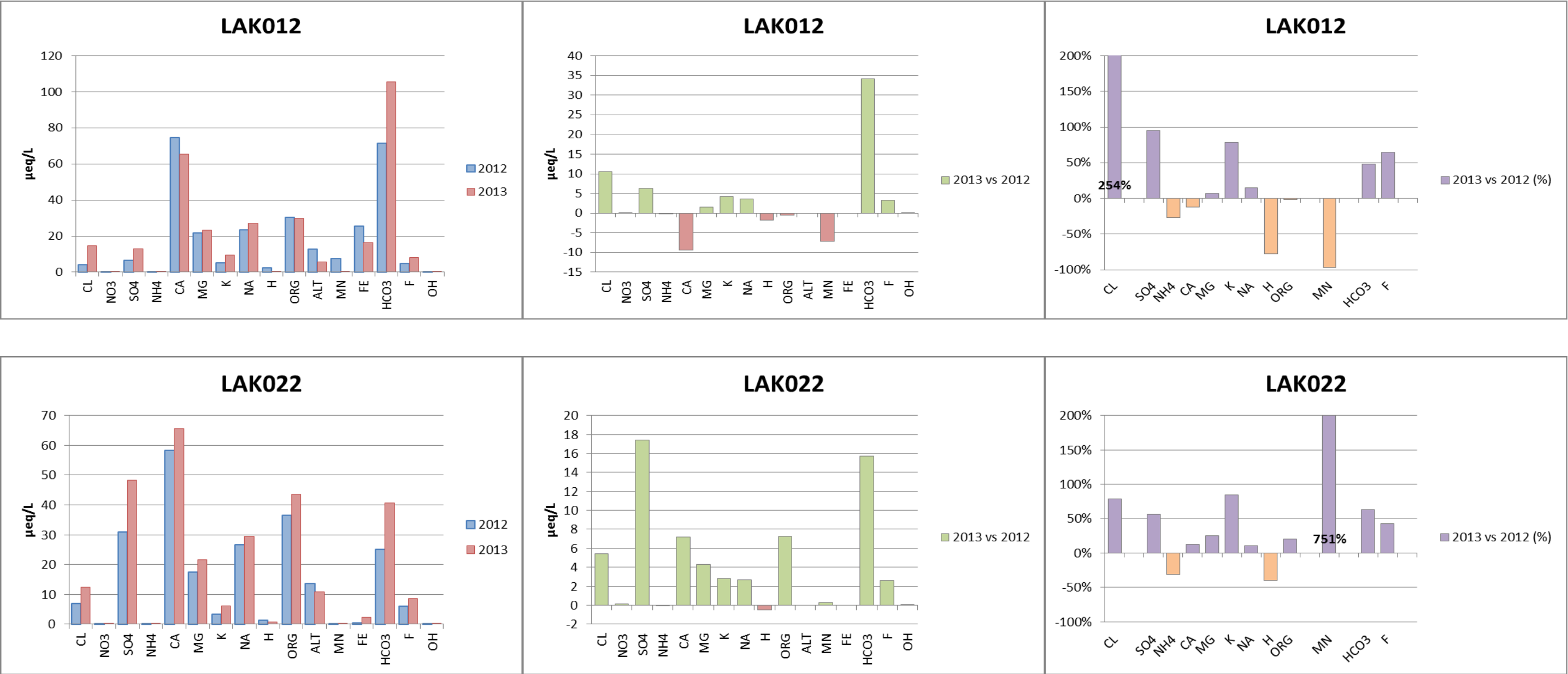
Appendix 2: Changes in Ion Concentrations from 2012 to 2013

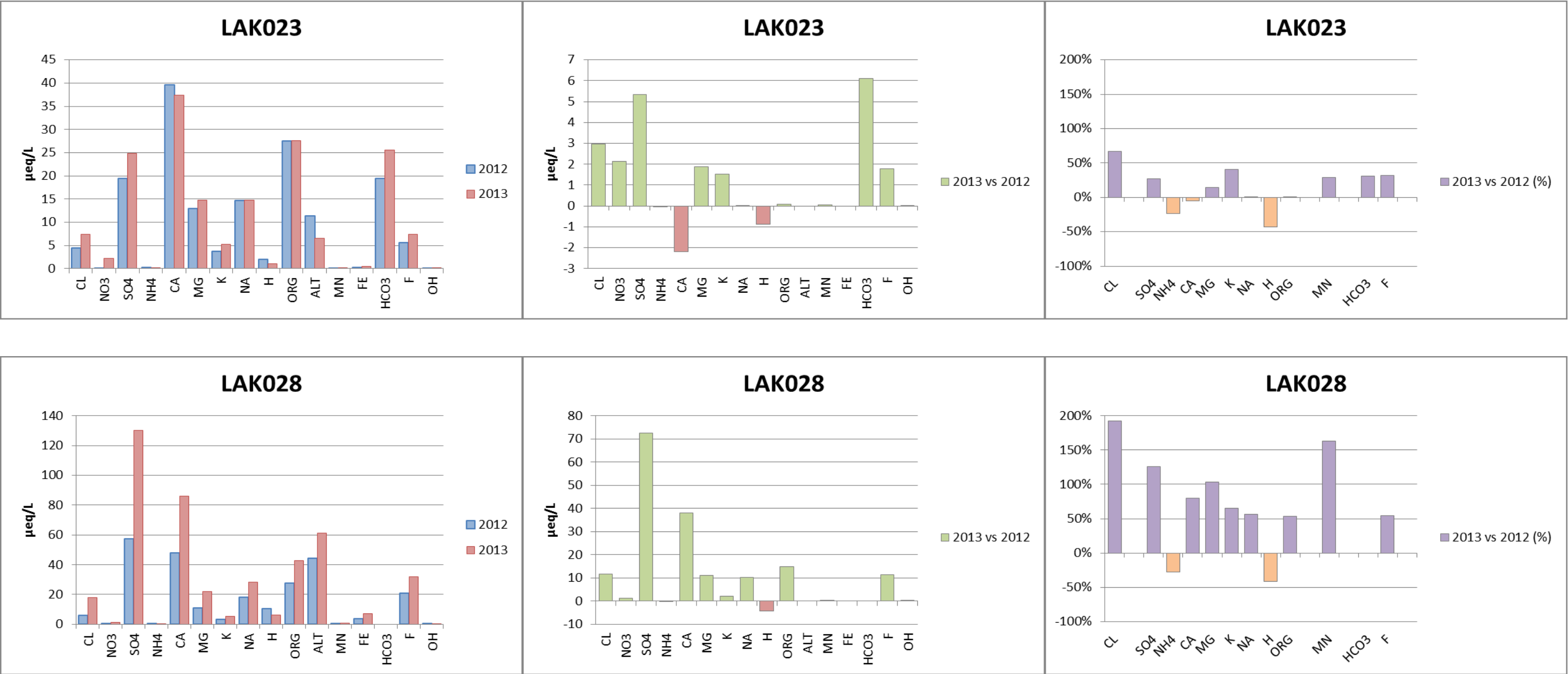
For each of the EEM lakes, the figures in this appendix show the concentrations for each ion in 2012 and 2013 (left panel), the changes in each ion from 2012 to 2013 in absolute terms (centre panel), and the changes in each ion from 2012 to 2013 as a percentage.

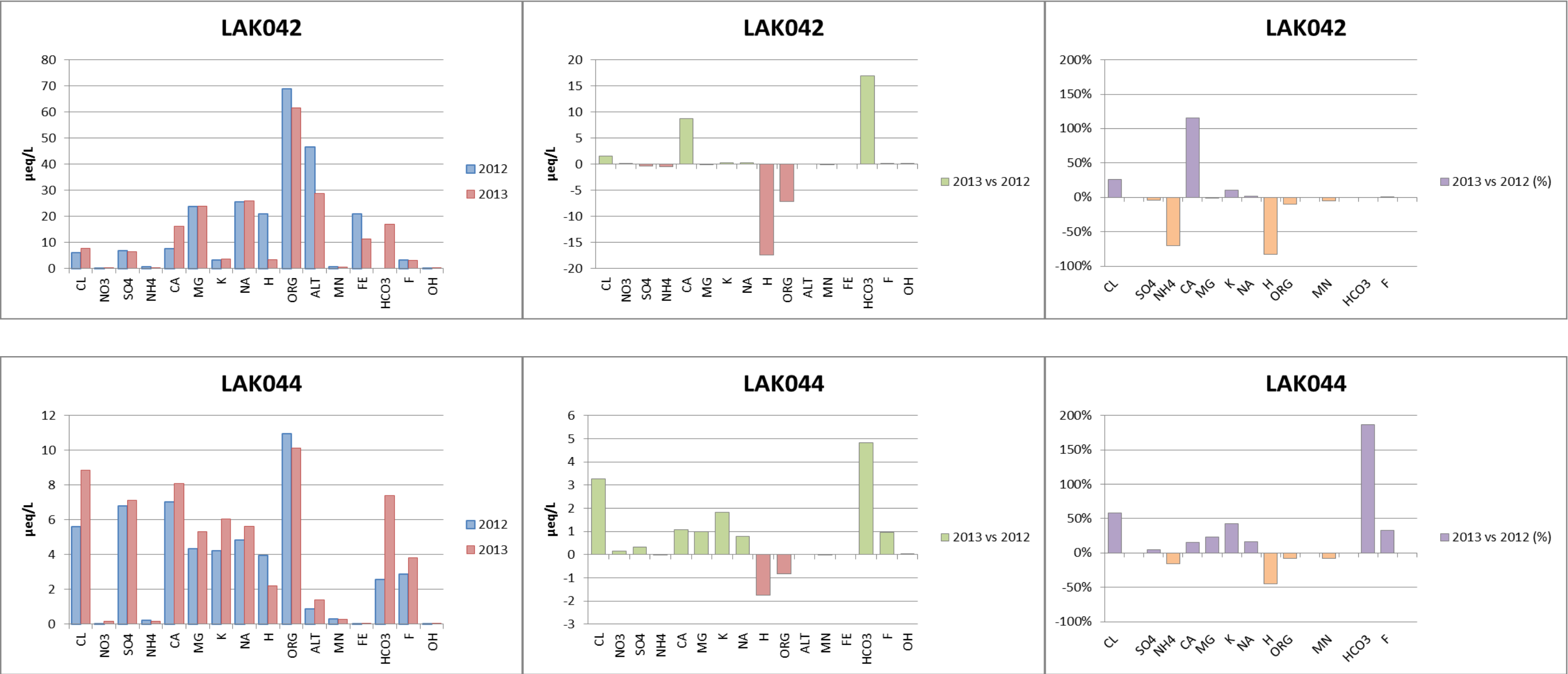
The labels are as follows: CL = chloride, NO3 = nitrate, SO4 = sulphate, NH4 = ammonium, CA = calcium, MG = magnesium, K = potassium, NA = sodium, H = hydrogen, ORG = organic anions, ALT = aluminum, MN = manganese, FE = iron, HCO3 = bicarbonate, F = fluoride, OH = hydroxide. The centre panel only reports changes in ions contributing to the charge balance calculation, therefore ALT and FE are not reported (labels not removed). In the right panel, ALT and FE are removed for the same reason, OH is removed because both it occurs at such low concentration that slight changes that are meaningless show up as enormous proportional changes, and NO3 was commonly below the lab detection limit (which differed between years) making it inappropriate to compare between years (labels removed).

Sensitive Lakes

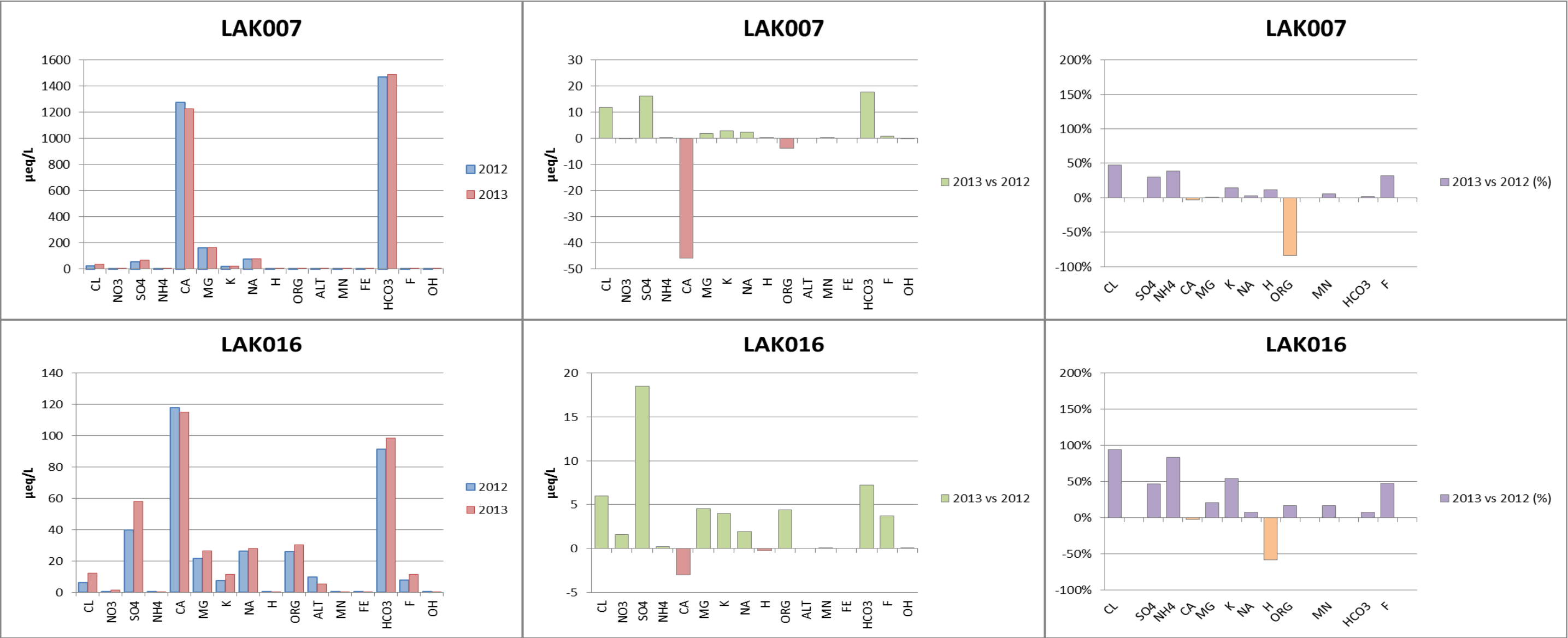


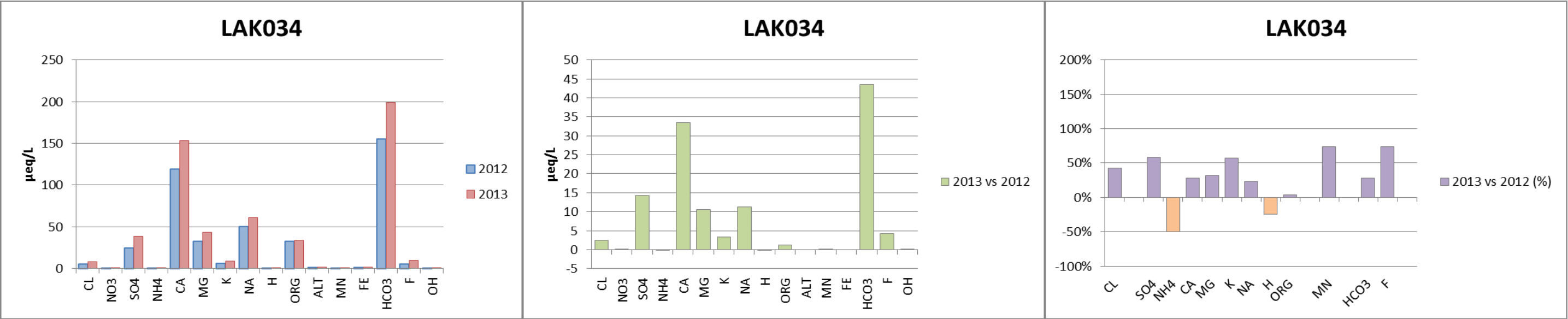






Less Sensitive Lakes







KMP SO₂ EEM Program – Technical Memo W02

Continuous Monitoring of pH in West Lake, End Lake and Little End Lake in Fall, 2014

January 19, 2015

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1 Overview

Early in 2014, a decision was made to begin continuous monitoring of pH and temperature in each of End Lake (LAK006), Little End Lake (LAK012) and West Lake (LAK023). These lakes were selected for the long term monitoring by Rio Tinto Alcan (RTA) with decision support from ESSA Technologies Ltd. (ESSA). The objective was to document variability in pH and related chemistry in each of the three lakes over the fall season. Limnotek set up and installed the instrumentation and conducted routine maintenance and calibration of the instruments during a period of deployment from August 29, 2014 through November 25, 2014. Results of pH measurement are reported in this memo.

2 Methods

RTA supplied a Manta2 model 2.5 multiprobe (<http://waterprobes.com/>) to continuously monitor pH in each lake. Each Manta 2 instrument was configured at the factory with three pH sensors and a temperature probe. Three sensors were required rather than the typical one sensor to capture variance associated with instrument error that was independent of environmental variability in pH. The pH is measured as the electrical potential created across a very thin glass membrane located at the tip of a glass bulb on each sensor when it is immersed in water. This part of the instrument is called the glass electrode because it looks like a glass bulb. A silver wire that is coated with a layer of silver chloride connects between a buffer inside the glass bulb to the pH meter to record output. A reference electrode is used to complete the voltage-measuring circuit. The difference in potential between the glass electrode and the reference electrode is used to calculate pH by the instrument. The Manta is designed to use one reference electrode to complete the voltage-measuring circuit for each of the three separate pH sensors.

Safe access to the three lakes was confirmed on August 1 by Andy Lecuyer (RTA) and Shauna Bennett (Limnotek). On August 29, a Limnotek field crew launched an inflatable boat with a small motor at each of the three lakes and used a hand held depth sounder to conduct a quick survey to determine the position having greatest water depth in each lake (Table 1). That location, marked with red circles in Figure 1, was selected for installation of a Manta2 in each lake.

Table 1. Water depth and position where a Manta 2 instrument was installed in each of West, End and Little End Lakes in 2014.

Station ID	Station Name	UTM zone	Easting	Northing	Water depth (m)
LAK006	End Lake	9U	524225	6020667	24.4
LAK012	Little End Lake	9U	524117	6021012	6.1
LAK023	West lake	9U	522764	6018914	9.1

Methods for installation of the instruments were as follows. Weights were tied to one end of a 5/16th inch double braided line to serve as an anchor, and the line was cut to a length equal to 2 meters less than the water depth at the chosen site. The line was held vertical through the water column with submerged floats and the Manta2 protective case was attached to the line just beneath the floats using a locking carabiner clip. A weighted protective cap on the Manta2 kept the instrument vertical on the anchor line. Figure 2 shows a photo of the Manta and floats submerged in End Lake.

The instruments were set up to record a measurement once every 30 minutes beginning on August 29, 2014 (West Lake) or August 30, 2014 (End Lakes) with servicing at intervals of 7 to 19 days. On service dates, each Manta was pulled out for an hour to perform various tasks either on shore or on the boat. When a Manta was removed, a tag line and surface float was attached to the anchor line to facilitate ease in finding the gear following instrument servicing (Figure 2). The battery pack was removed, an Archer Field PC was connected to the Manta2 with an underwater cable, and data was uploaded from the Manta to the Archer. Following the data upload, the weighted sensor guard was replaced with a calibration cup. Screenshots on the Archer were captured with the sensors submersed in pH 4, pH 7 or both standard buffer solutions. The purpose of these readings was to determine the degree of sensor drift since the previous calibration. Following those measurements, the pH electrodes were gently cleaned with a Q-tip and the electrolyte solution in the reference electrode was replaced with fresh solution supplied according to manufacturers specifications. A two-point calibration was run for each of the three pH sensors on each Manta following the steps in the instrument manual¹. Post-calibration checks were conducted in one or both of the buffer solutions of known pH (pH 4 and 7) and screenshots were captured. The weighted sensor guard was then replaced along with the battery pack, and the instrument was redeployed in the lake. Every 4 to 6 weeks, the eight C cell batteries in the battery pack were replaced with new ones.

¹ Measurement Specialties, Inc. Multiprobe User Manual: Manta 2, Sub2 and Sub3 Water-Quality Multiprobe Manual. Austin, TX. www.meas-spec.com

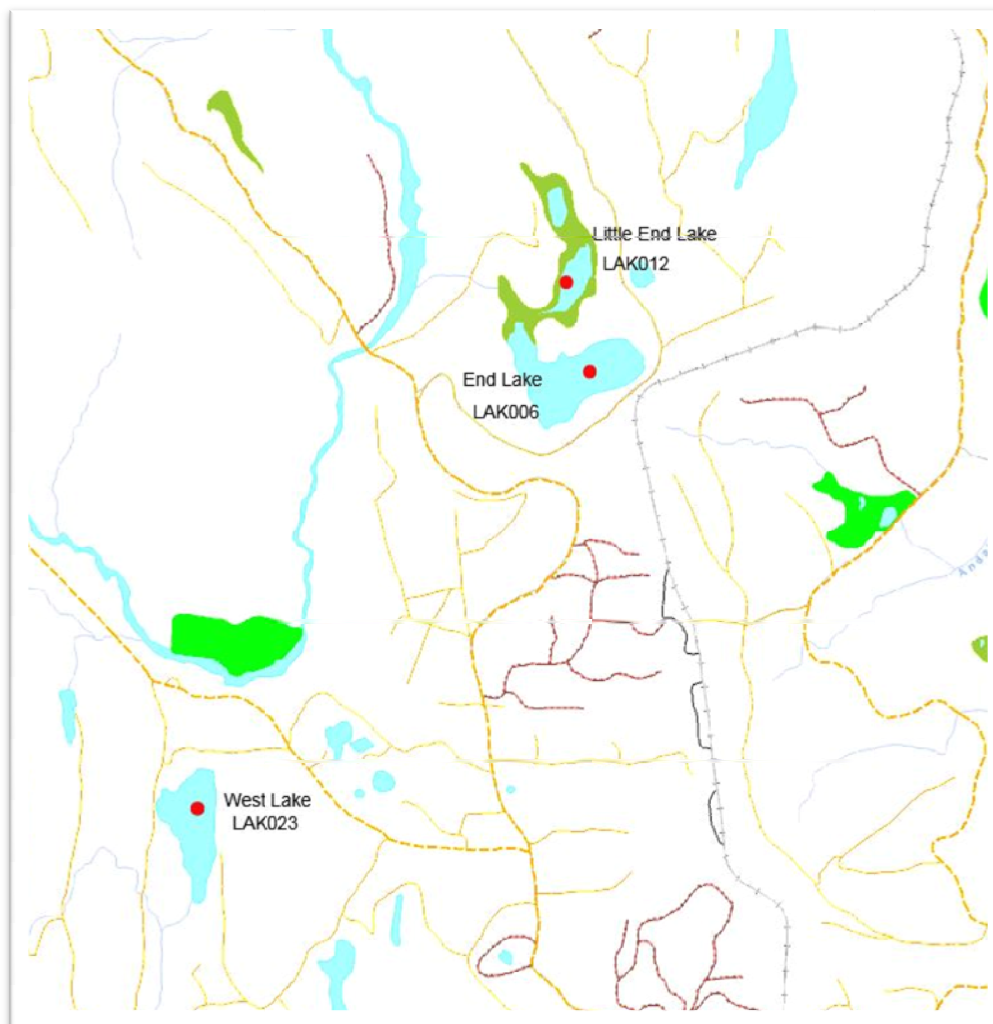


Figure 1. End, Little End and West lakes with Manta instrument deployment locations shown as red solid circles. Image created in iMapBC 2.0² and the yellow dotted lines represent roads or ATV trails.

Water samples were collected at the time of servicing the instruments for two independent analyses of pH and additional analyses. One pH measurement was in a surface grab sample using a WTW Profilline 3210 portable pH meter (<http://www.wtw.de/en/products/lab/ph/portable-meters.html>). That measurement was made within 10 minutes of collection. The other was measurement of pH in a surface grab sample that was sent to ALS Environmental, an accredited laboratory in Burnaby, B.C., following shipment of the sample from Terrace to Burnaby on the day after collection. That measurement was made within 3 days of collection. On Oct 2, Oct 9, Oct 16, Oct 23 and Nov 11, an additional water sample was collected from the surface of each lake for analysis of a full suite of anions and cations as well as Gran alkalinity and pH from all three lakes. Those analyses were the same as those run on samples collected from 10 lakes that are part of the annual environmental effects monitoring (EEM) by RTA. The Gran alkalinity and pH in those samples were analysed at Trent University and the suite of anions and cations were analyzed at

² http://www.data.gov.bc.ca/dbc/geographic/view_and_analyze/imapbc/index.page? Last accessed on Dec 19, 2014

ALS in Burnaby. The pH data from all sources are the subject of this memo while the anion, cation, and Gran alkalinity data will be used later as part of interpretation of water chemistry for the EEM annual report to be prepared by ESSA.

On November 25, the Manta instruments in West and End Lakes were removed for the winter. Ice had formed on Little End Lake, which prevented the field crew from safe access. The instrument in that lake will be left submerged for the winter and recovered in spring 2015.

All the discrete data from the handheld pH meter and laboratories were appended to the continuous data from the Mantas in an excel spreadsheet that accompanies this memo.

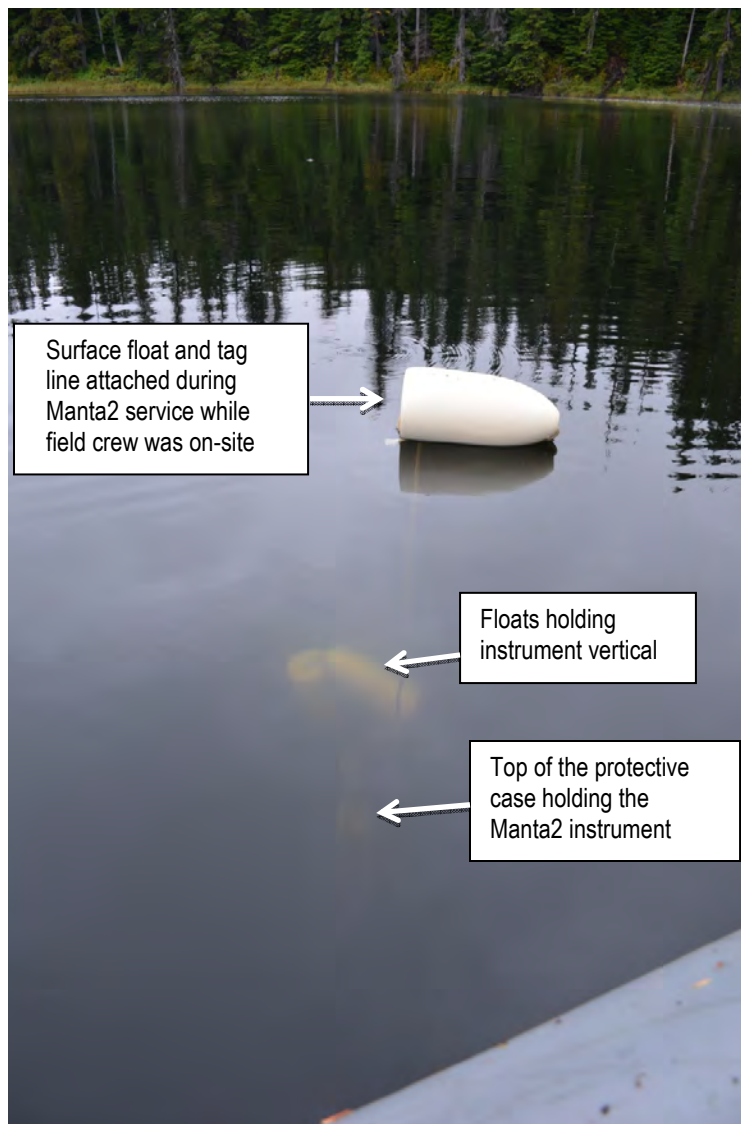


Figure 2. Photo showing the Manta2 installed in End Lake. The instrument was encased in a protective case which hung roughly 2 meters below the lake surface. The surface float and tag line were attached to the float set-up during instrument calibration to ease instrument redeployment but removed before the crew left the lake.

3 Results and Discussion

Mean daily pH from the Mantas was plotted with the discrete sampling data from the WTW meter and lab pH measurements for each lake as shown in Figure 3. The duration of continuous data was 74 days in Little End Lake (Aug 29 to Nov 11), 88 days in End Lake (Aug 30 to Nov 25), and 89 days in West Lake (Aug 29 to Nov 25). The three pH sensors on each Manta showed the same temporal changes, indicating no difference among sensors on an instrument in detecting ambient change in pH (Figure 3).

Within each lake, pH was less variable in the later part of the fall season (late October and November) than it was in September and early October (Figure 3).

Over the fall period, the range of pH measurements from a single sensor on the Mantas was 0.63 to 1.05 in West Lake, 0.88 to 0.95 in End Lake and 0.98 to 1.15 in Little End Lake (Table 2). Average pH over the period was lowest in Little End Lake (5.99 to 6.11) and highest in End Lake (6.28 to 6.4) with West Lake falling in between (6.21 to 6.39).

A noticeable shift in pH corresponded with instrument calibrations after the first field deployment of 14 days, on September 14 (Figure 3). In West Lake, pH sensor 1 (called pH in Figure 3) and sensor 2 (called pH2 in Figure 3) shifted upwards by 0.6 and 0.63 pH units respectively after calibration, while sensor 3 (called pH3 in Figure 3) pH shifted upwards by only 0.16 units. In End Lake, the pH shifted upwards by 0.29 to 0.53 pH units, while in Little End Lake, the pH shifted upwards by 0.46 to 0.56 pH units. This coincidence of the time of calibration and the time of pH shifts in all instruments suggests that the abrupt change in pH readings was due to corrections following calibration. There were no pre- and post-calibration checks run during that site visit, so we are not able to determine if the change was entirely a calibration effect or whether an actual change in water column pH was also present.

A second shift occurred in End Lake. After removal of the Manta from End lake on Nov 11, a pre-calibration test of the sensors in a standard pH 7 buffer found that the three sensors were reading high by 0.34 to 0.41 pH units. Calibration of the instrument corrected the sensor drift and after calibration, the sensors were reading 0.3 pH units lower in End Lake than they were reading before calibration. However, the pH continued to drop another 0.2 pH units over the following 48 hours. The continued decrease of 0.2 pH units seen in Figure 3 appeared to be due to environmental effects because all three sensors responded similarly, and post-calibration tests of the sensors in standard pH 7 buffer found that the three sensors were reading within ± 0.02 pH units.

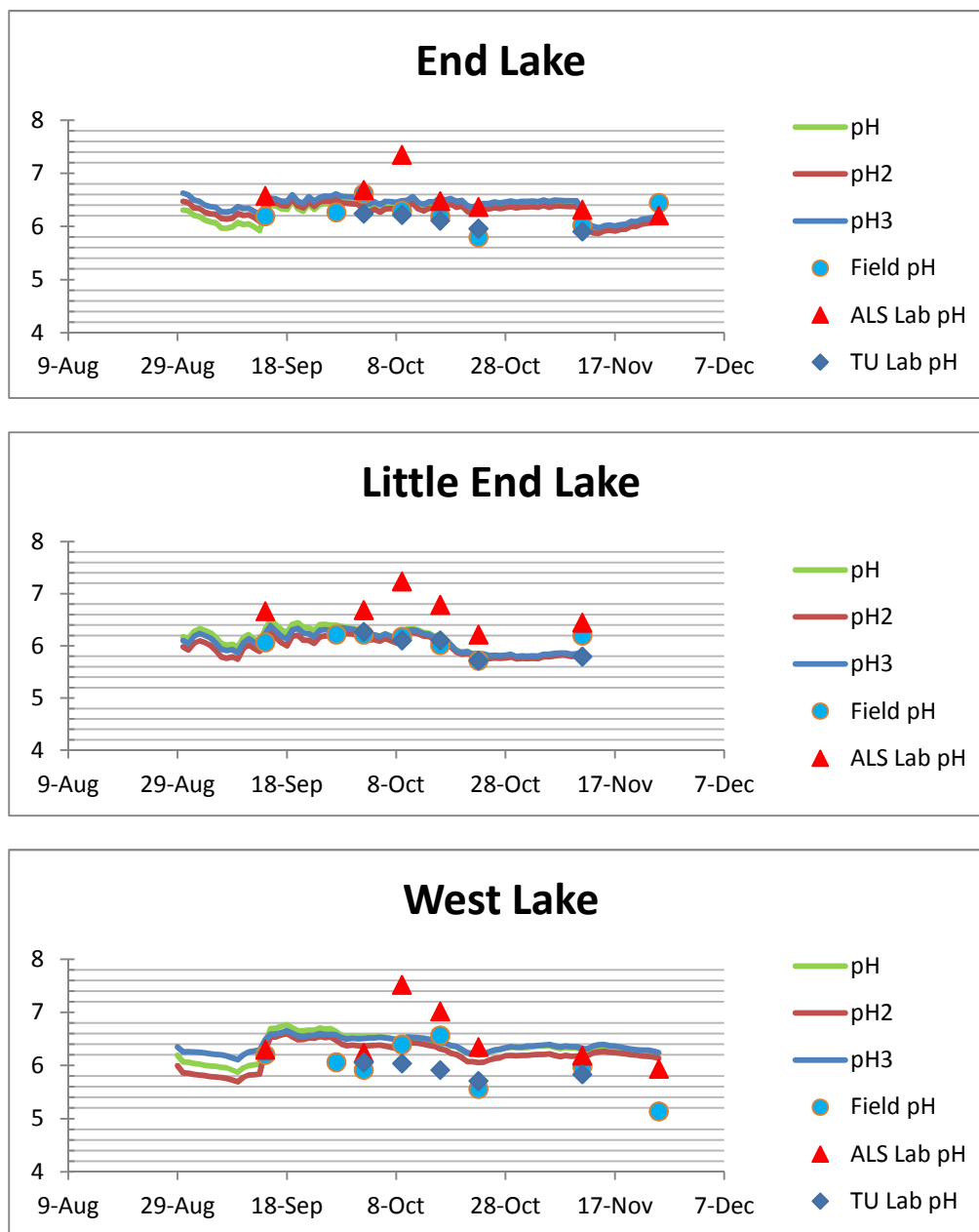


Figure 3. Mean daily pH for three sensors (pH, pH2 and pH3) in each of three lakes shown with discrete pH sampling results³. Discrete sampling results correspond to calibration dates with the exception of Oct 2.

³ Field pH indicates pH readings using a handheld WTW pH meter in the boat to measure pH of a surface collected water sample. Lab pH indicates pH readings using a bench top pH meter in the ALS Burnaby lab (ALS Lab) or the Aherne Trent University lab (TU Lab).

Table 2. Minimum, maximum, average and range of pH measurements taken every 30 minutes in each of End, Little End and West lakes in fall 2014.

Lake	Sensor	Number of observations	Minimum pH	Maximum pH	Range of pH	Mean pH \pm SD
End	pH	4169	5.71	6.66	0.95	6.28 \pm 0.19
End	pH2	4169	5.82	6.70	0.88	6.29 \pm 0.17
End	pH3	4169	5.94	6.86	0.92	6.40 \pm 0.17
Little End	pH	3501	5.50	6.65	1.15	6.11 \pm 0.23
Little End	pH2	3501	5.46	6.44	0.98	5.99 \pm 0.18
Little End	pH3	3501	5.49	6.55	1.06	6.08 \pm 0.20
West	pH	4210	5.77	6.82	1.05	6.35 \pm 0.22
West	pH2	4210	5.65	6.66	1.01	6.21 \pm 0.23
West	pH3	4210	6.07	6.70	0.63	6.39 \pm 0.13

3.1 Discrete pH samples

Figure 3 shows that discrete measurements of pH in the lab and field were frequently >0.2 pH units different from the continuous Manta results. Discrete samples from five dates in October and November were summarized for each lab (Trent and ALS) in Table 3. The highest mean pH values were consistently reported by ALS for all three lakes, while mean pH values reported by the TU lab were consistently the lowest (Table 3). The average pH in samples collected on five dates in October and November ranged from 6.09 to 6.64 in End Lake, 6.00 to 6.68 in Little End Lake and 5.91 to 6.66 in West lake. The difference in mean pH between instruments was 0.55 pH units in End lake, 0.68 pH units in Little End lake and 0.75 pH units in West lake.

Values reported by the Trent lab and measured in the field were more similar to each other than to the values reported by ALS. In addition, on most occasions, these values were more similar to the pH values measured with the Manta in each lake (Figure 3).

A common explanation for differences between field and lab pH measurement is that CO₂ can purge from water to air in a sample bottle, resulting in higher pH readings in a lab compared to those taken in the same water in the field. In the present case all sample bottles were filled without air space, which would have limited or prevented gas exchange in the sample bottle. This action means that differences between the lab and field measurements were related to other factors. These factors cannot be resolved with existing data. Consistently low pH from the Trent lab and consistently high pH from ALS with field measurements in between suggests that instrument or operator bias may have contributed to the differences.

Table 3 Mean (\pm standard deviation) pH of discrete samples collected on Oct 2, Oct 9, Oct 16, Oct 23 and Nov 11 at each of the three lakes.

Source of measurement	End Lake	Little End Lake	West Lake
Field pH	6.19 \pm 0.31	6.07 \pm 0.21	6.08 \pm 0.40
Trent University lab pH	6.09 \pm 0.15	6.00 \pm 0.23	5.91 \pm 0.15
ALS lab pH	6.64 \pm 0.42	6.68 \pm 0.38	6.66 \pm 0.58

3.2 Sensor Bias

Sensor bias on the Mantas can be defined as the difference in pH that is detected between the three sensors on a given instrument. That bias declined over the deployment period (Figure 3). In all lakes, the maximum difference between any two sensors was >0.35 pH units, which occurred during the first two weeks of September (Table 4, Figure 3). Sensor bias decreased thereafter, and the maximum difference between any two sensors was <0.11 pH units in the last few weeks of deployment (Figure 3). The average sensor bias over the deployment period was ≤ 0.14 pH units, which was consistent across all instruments (Table 4). Since the instruments have specifications of ± 0.2 pH units, the sensors were behaving according to specs at all three lakes.

Table 4 Sensor bias calculated as the difference between each pair of sensors on a single instrument.

Sensor Pair	End		Little End		West	
	Mean \pm SD	Max	Mean \pm SD	Max	Mean \pm SD	Max
pH and pH2	0.06 \pm 0.05	0.21	0.12 \pm 0.09	0.35	0.14 \pm 0.04	0.24
pH and pH3	0.12 \pm 0.09	0.35	0.05 \pm 0.04	0.29	0.07 \pm 0.08	0.37
pH2 and pH3	0.12 \pm 0.09	0.35	0.05 \pm 0.04	0.29	0.07 \pm 0.08	0.37

3.3 Sensor Drift

The difference between observed and expected values in pH readings taken in standard buffer solutions of a known pH with a newly calibrated Manta were similar to pH readings taken with the WTW handheld meter (Figure 4). However, after an average 12 day deployment in one of the lakes, the difference between observed and expected values in pH readings taken in standard buffer solutions with the Manta instrument had increased. This sensor drift, caused by slow leak of hydrogen ions across the glass membrane which leads to a dilution of the reference solution, is the cause of this increase in measurement error. The magnitude of sensor drift was consistently less than 0.2 pH units across all sensors on all three instruments. Since the instruments have specifications of ± 0.2 pH units, the sensors were behaving according to specs at all three lakes.

However, the degree of sensor drift varied with the time of deployment between servicing dates, which ranged from 7 to 19 days (Figure 5). Over a shorter deployment period (2 weeks or less), the average sensor drift was <0.15 pH units. The sensor drift increased by two-fold to an average value

close to 0.3 pH units when the deployment period was increased to 19 days. Therefore, to minimize the effect of sensor drift on the collected data, the electrolyte solution in the reference electrode should be changed and the instrument calibrated not less than once every two weeks.

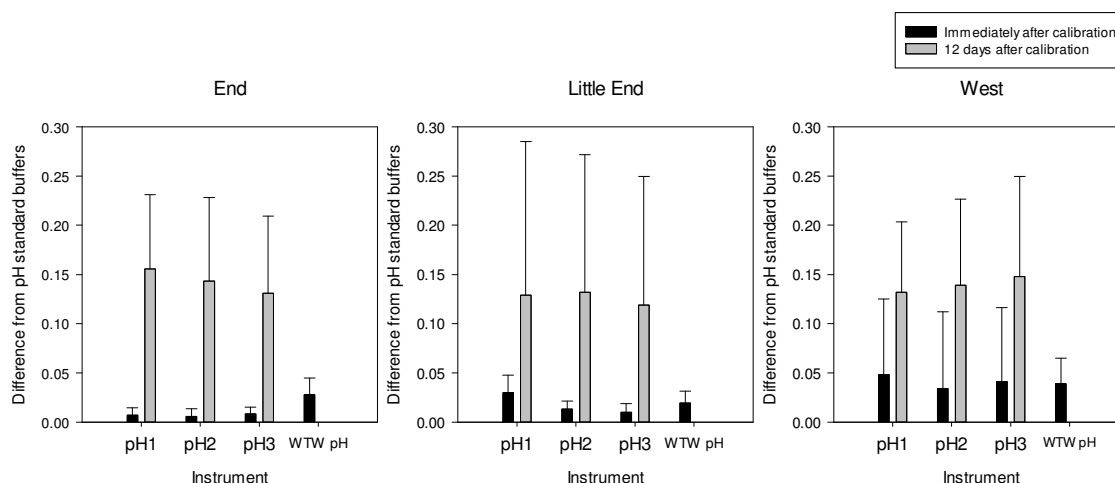


Figure 4. Manta pH instrument drift shown as the difference between observed and expected values of pH measured in standard pH 4 and 7 buffers before and after deployment in one of the three lakes for an average period of 12 days compared to the hand held WTW pH instrument reading in a standard buffer of pH 4 or pH 7. The pH probes on the Manta instrument were field calibrated immediately prior to deployment.

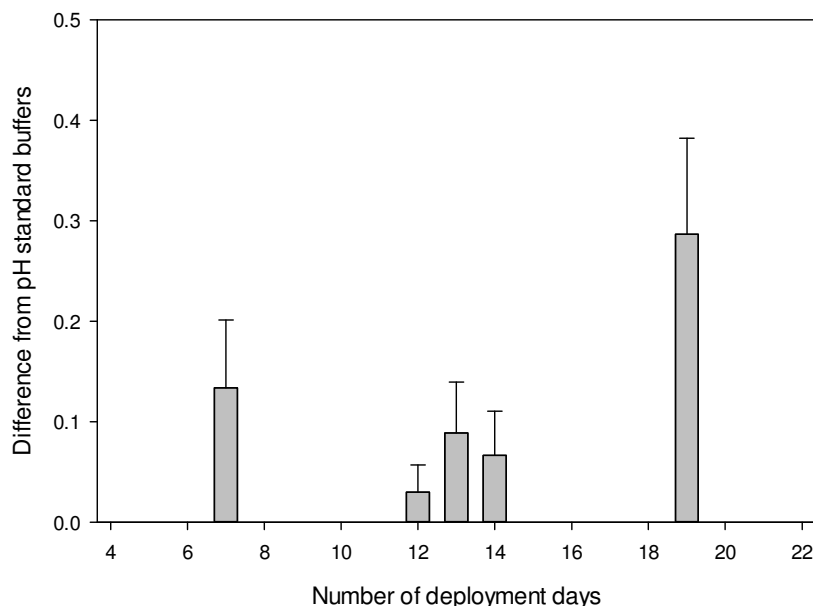


Figure 5. Sensor drift shown as the difference between observed and expected values of pH measured in standard buffers immediately after instrument removal from each lake. Data for all instruments and all sensors have been pooled and plotted against the number of days of deployment (*i.e.* number of days since the last calibration).

Although End and Little End lakes share a common outlet, there were several lines of evidence from the Manta data to suggest that the two lakes are distinct waterbodies. First, the plots of mean daily pH over the deployment period in fall 2014 showed that the two lakes had unique patterns of change in pH (Figure 3). Second, on Nov 25 Little End Lake was fully covered with ice, while there was no ice cover on End lake, which indicates differences in heat content and lack of mixing between the lakes. Further, each of the lakes had a different pattern of change in temperature, despite the general cooling through the fall, again indicating lack of mixing (Figure 6). The difference in ice cover and the distinct temperature patterns in End and Little End lakes despite the close proximity of the lakes provides evidence that the two lakes do not mix and the common channel between them is an outflow channel for both lakes that does not backwater.

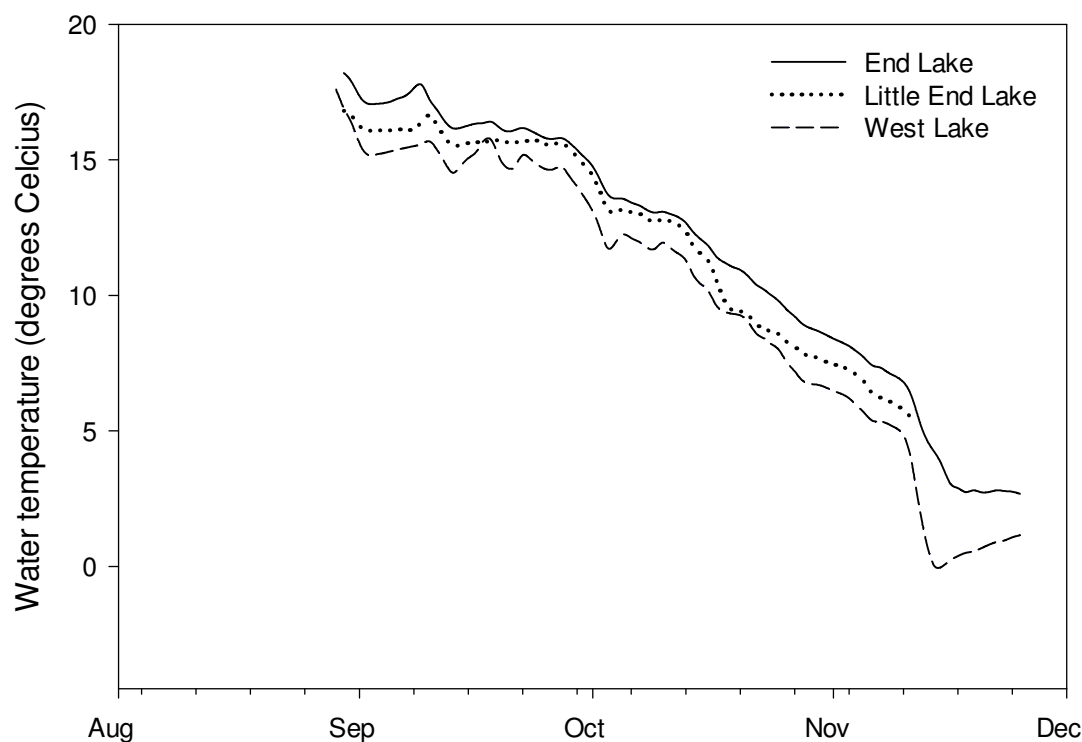


Figure 6. Average daily temperature in each of three lakes.