

Summary of Results  
Kawartha Highlands Provincial Park  
Summary 2015 Lake Sampling

Drs. Paul C. Frost and Clay Prater  
Department of Biology  
Trent University  
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Contact information: [paulfrost@trentu.ca](mailto:paulfrost@trentu.ca); 705-748-1011 x7903

## Summary

During the late summer of 2015, staff from the Kawartha Highlands Provincial Park sampled 25 lakes to examine patterns of water quality in the park. Measured properties were chosen to match past surveys and to thoroughly assess water quality in these selected park lakes. These data will be used to assess current patterns and serve as an important benchmark in future sampling years. Sampled water was transferred to Trent University for analysis where all analysis followed conventional and well-established methodology to ensure data accuracy and precision. This report summarizes the methods used to collect and analyze the water and presents the primary findings. We have attached electronic copies of all data with this report including that raw analyses and compiled, summary datasheets.

## Background

The establishment of the Kawartha Highlands Provincial Park coincides with a greater awareness of human effects on the landscape and embedded water bodies. As a park, there is a need to mitigate potential human effects by assessing patterns and effects of use. One necessary ingredient in such assessment is sound environmental data that allows the current and future state of ecosystems to be compared against reference conditions. As a first step in establishing management strategies and as a means to increase our understanding of aquatic ecosystems in the Kawartha Highlands Provincial Park, water quality data was comprehensively sampled from a subset of lakes inside its park boundaries.

## Methods

Sampled lakes were chosen by Park Staff to include a range of lake size and potential human use. Many selected lakes may see increased usage in future years but currently remain relatively unvisited and most have few, if any, shoreline residences. Their watersheds are largely forested and are currently protected and undisturbed. A list of sampled lakes, dates of sampling, their locations and maximum depths is provided in Table 1.

Table 1. Lakes sampled in the KHPP 2015 water quality survey.

Lake	Date Sampled	Easting <sup>a</sup>	Northing <sup>a</sup>	Maximum Depth (m) <sup>b</sup>
Adams	9/8/2015	771526	4945044	23.5
Bottle	8/31/2015	715210	4960259	22
Buzzard North Basin	9/1/2015	721910	4950690	43
Buzzard South Basin	9/1/2015	721232	4949677	26.5
Cold	8/31/2015	716078	4953383	7.5
Compass	9/2/2015	719121	4950355	8.5
Crab	8/19/2015	722605	4956220	7
Elm	8/25/2015	723860	4949670	17
Little Turtle	9/10/2015	721435	4944500	23.5
Long East Basin	9/3/2015	724690	4952550	24
Long West Basin	9/3/2015	723475	4952050	22.5
Loon Call North Basin	8/19/2015	726540	4958750	16
Loon Call South Basin	8/19/2015	724735	4958750	13.8
Loucks	9/3/2015	720300	4951360	18.6

North Rathbun	8/27/2015	720395	4936920	14.5
Sawmill	9/8/2015	721007	4945211	8
Mountain	9/1/2015	720223	4948653	16
Stouples North Basin	9/2/2015	719685	4948021	16
Stouples South Basin	9/2/2015	719791	4947420	15.5
Sucker	8/31/2015	717213	4960432	20
Wolf NB	8/18/2015	723587	4958312	8.3
Wolf SB	8/19/2015	722071	4956912	7.1

<sup>a</sup>Easting and Northing UTM coordinates are provided for northern hemisphere, zone 17.

<sup>b</sup>Maximum reported from time of sampling.

At each lake, park staff first measured water temperature and dissolved oxygen concentrations using a calibrated hand-held sensor (Model: YSI Pro20 or YSI ProODO) at 1 m increments in the water column. They assessed the Secchi depth using a standard disk (200 mm) that was lowered into the water on the sunny side of the boat until it disappeared. Water was collected 1 m below the surface and 1 m above the bottom of the lake using a 1.2L PVC Kemmerer sampler and placed into carboys (1 L without filtration; 4 L with 60  $\mu$ m filtration; 40 ml with 0.2  $\mu$ m filtration) and transported on ice to Trent University.

Once at Trent, water and samples were processed, preserved, and analyzed. For dissolved nutrients, water was sequentially passed through a glass fiber filter (GFF) and a 0.2  $\mu$ m polycarbonate filter to remove most bacteria and other small microbes. Filtered water was saved either in dark brown amber bottles (DOC and DIC), plastic bottles for dissolved P and N fractions, or 50 ml falcon tubes (TP and trace metals) in the refrigerator.  $\text{NH}_4$  samples were frozen in plastic bottles until analyzed. Additional water was passed through GFF to collect suspended particles for chlorophyll and suspended solids/particulate P analysis. These filters were either frozen (chlorophyll) or dried (TSS+PP) and stored until subsequent analysis.

Water chemistry generally followed standard protocols (APHA 2003) and was accompanied by analysis of standards to ensure good recovery and high precision.

Carbon: We measured DOC concentration using an OI analyzer following persulfate digestion. DIC was also measured at the same time on unsparged samples. DOC absorbance at 280 nm was measured with a spectrophotometer using a 1 cm path length.

Nitrogen:  $\text{NO}_3$  was measured using a second derivative spectroscopy method. We added concentrated acid (HCl) and calculated the second derivative for absorbance values at 224 nm. TDN was measured using the same method after oxidizing samples by autoclaving them at 122°C for 30 min after adding NaOH and K-persulfate.  $\text{NO}_2$  was measured using a sulfanilamide method by measuring absorbance at 543 nm.  $\text{NH}_4$  samples were thawed and analyzed using a phenol alcohol alkaline citrate method. Reagents were added to samples and absorbance was measured after one hour of incubation at room temperature at 640 nm using a spectrophotometer.

Phosphorus: Samples were measured for SRP using a molybdate blue ascorbic acid reduction method by measuring absorbance at 885 nm. TP and TDP were measured on unfiltered samples and samples filtered at 0.2  $\mu\text{m}$  respectively, using the same method following persulfate oxidation for 30 min at 122°C in an autoclave. Particulate phosphorus samples were analyzed on GFF following persulfate oxidation using identical ascorbic reduction methods.

Chlorophyll: We estimated chlorophyll on ethanol-extracts of frozen filters in a fluorometer calibrated with spinach standards.

Physical measurements: We assessed TSS by filtering 500 ml of water on a pre-weighed GFF, drying, and reweighing filters. pH was measured using a calibrated desktop probe.

Metals: Unfiltered water samples were analyzed using a TXRF Picofox after adding a gallium standard to samples, loading samples onto quartz discs, and comparing X-ray readings to internal elemental standards.

Table 2. Sampled water quality parameters.

Parameter	Abbreviation	Method	Sample preparation
pH		laboratory probe	Whole
Secchi depth		In situ	n.a.
Dissolved oxygen	DO	Lake sensor	n.a.
Temperature	Temp	Lake sensor	n.a.
Dissolved organic carbon	DOC	TOC analyzer	Filtrate
Dissolved inorganic carbon	DIC	TOC analyzer	Filtrate
Absorbance 280	Abs280	Spectrophotometer	Filtrate
Total dissolved nitrogen	TDN	Wet chemistry	Filtrate + digested
Nitrate	NO <sub>3</sub>	Wet chemistry	Filtrate
Ammonium	NH <sub>4</sub>	Wet chemistry	Filtrate
Total phosphorus	TP	Wet chemistry	Whole + digested
Total dissolved phosphorus	TDP	Wet chemistry	Filtrate + digested
Particulate phosphorus	PP	Wet chemistry	Filter + digested
Soluble reactive phosphorus	SRP	Wet chemistry	Filtrate
Chlorophyll a	Chl	Fluorometer	Filter + extraction
Total suspended solids	TSS	Scale	Filter
Total dissolved iron	TDFe	X-ray fluorometer	Filtrate
Total dissolved calcium	TDCa	X-ray fluorometer	Filtrate
Total dissolved potassium	TDK	X-ray fluorometer	Filtrate
Total dissolved manganese	TDMn	X-ray fluorometer	Filtrate
Total dissolved zinc	TDZn	X-ray fluorometer	Filtrate
Total dissolved bromide	TDBr	X-ray fluorometer	Filtrate
Total dissolved tin	TDSr	X-ray fluorometer	Filtrate
Total dissolved barium	TDBa	X-ray fluorometer	Filtrate

## Source Methods:

APHA. 2003. Standard Methods for the Examination of Water and Wastewater. American Public Health Association.

## Nitrogen:

NO<sub>2</sub>: Wetzel RG, Likens GE (2000) Limnology Analysis, 3<sup>rd</sup> edition. Springer, New York  
TDN and NO<sub>3</sub>: Crumpton WG, Isenhardt TM, Mitchell PD (1992) Nitrate and organic N analyses with second-derivative spectroscopy. Limnology and Oceanography 37:907-913.  
NH<sub>4</sub>: APHA 1992/ Benliel 1994

## Phosphorus:

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27:31-36

## Trace metals:

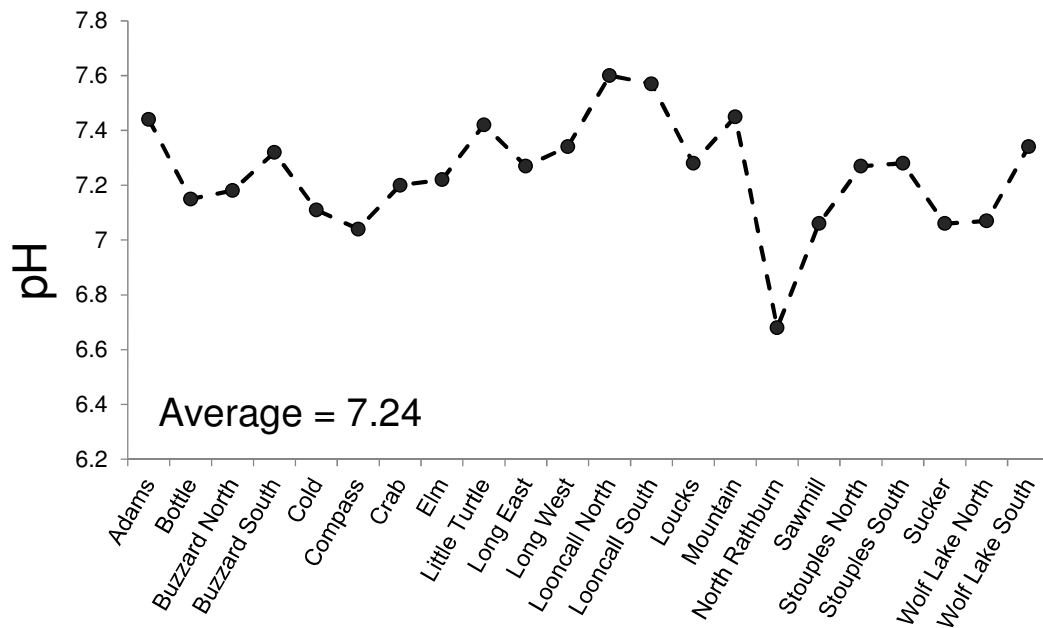
Margu\_I, E., J. C. Tapias, A. Casas, M. Hidalgo, and I. Queralt. 2010. Analysis of inlet and outlet industrial wastewater effluents by means of benchtop total reflection X-ray fluorescence spectrometry. Chemosphere 80:263-270.

## Results

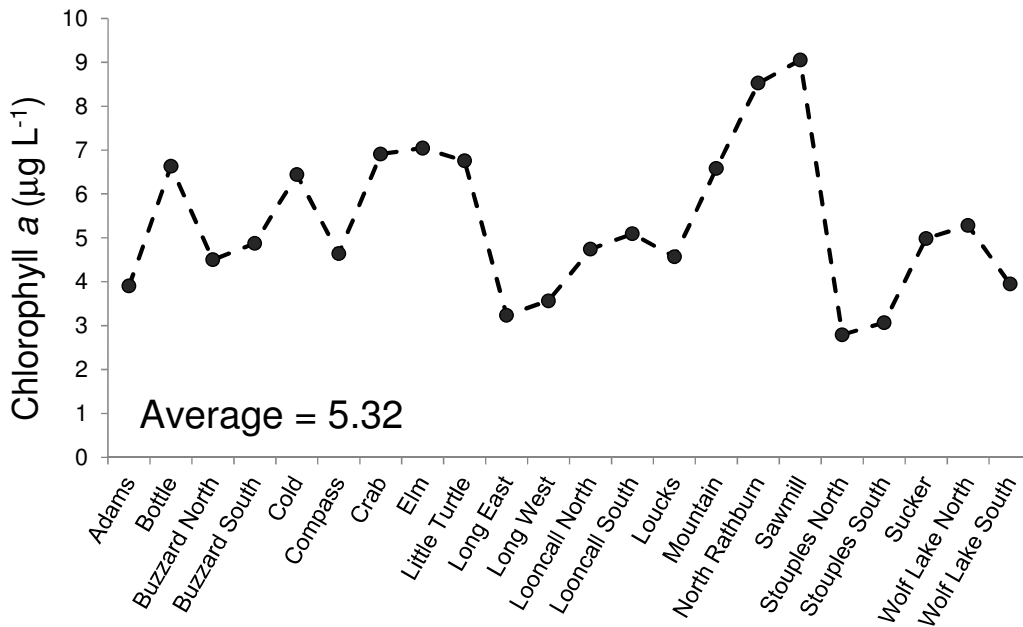
### 1. Surface water chemistry.

*Summary.* We found lakes in the KHHP to have good water quality and to fall largely within expected ranges. Low Ca concentrations were found in a few lakes and given declines reported elsewhere in this region, these lakes should be resampled to determine the trajectory of these concentrations. Two lakes were found to have slightly above average TP and should be further sampled and assessed to better understand the causes and nature of this phosphorus loading. Raw data for variables presented here and all variables measured are available in an electronic database.

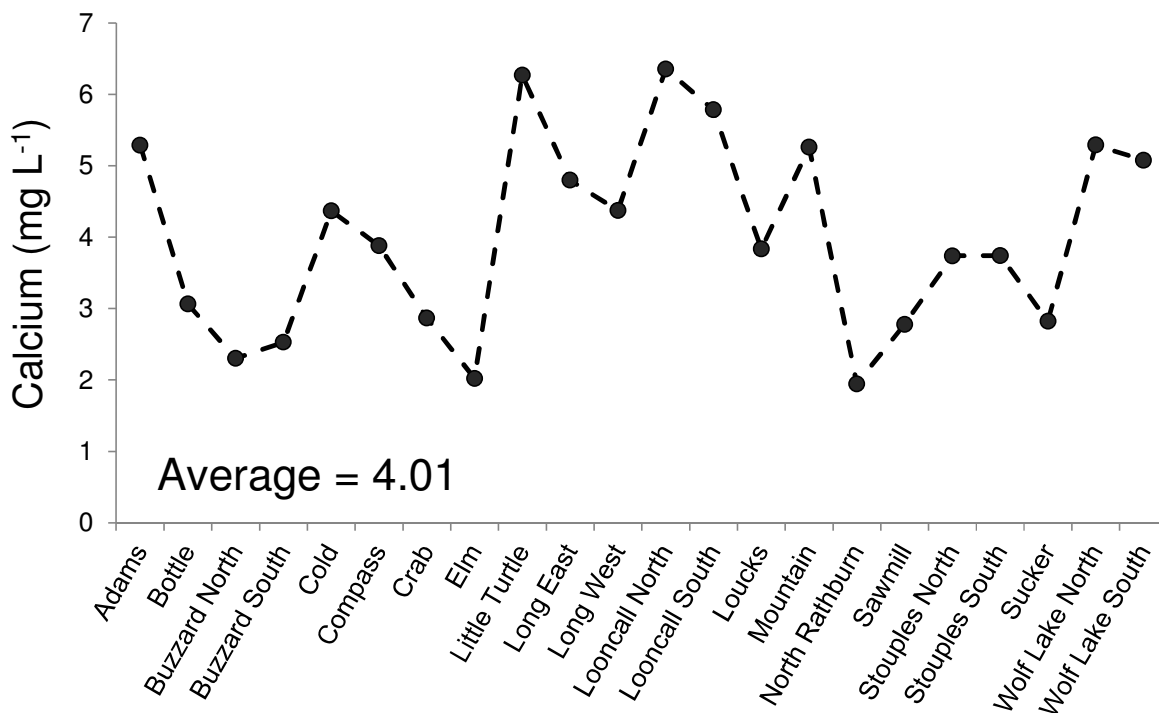
*pH.* We found pH in the surface waters to fall with the 7.0 to 7.4 range for most lakes in the KHHP. The average lake value for this sampling period was 7.24 with the highest pH (~7.6) in Looncall Lake (both north and south basins) and a low value of 6.68 in North Rathbun. These are pH readings are within the expected range for southern Canadian Shield, boreal lakes.



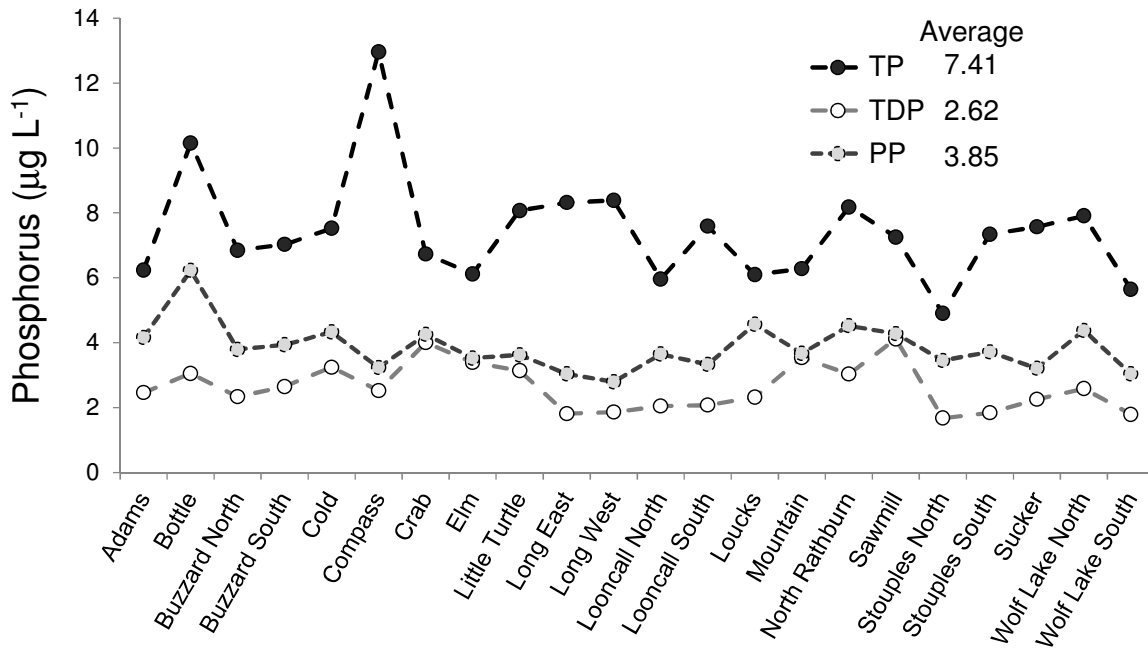
*Chlorophyll a.* Chlorophyll a (CHL) provides an index of algal biomass and is a very widely used metric in assessing water quality. Lakes in the KHHP were found to have low CHL concentrations (typical of unproductive lakes) with an average concentration of  $5.32 \mu\text{g L}^{-1}$ . The highest concentrations ( $\sim 9 \mu\text{g L}^{-1}$ ) were seen in North Rathburn and Sawmill are still relatively low but are at the threshold where lakes are considered more productive. Future and more intensive monitoring of these lakes is necessary to determine whether these results are indicative of potential water quality problems.



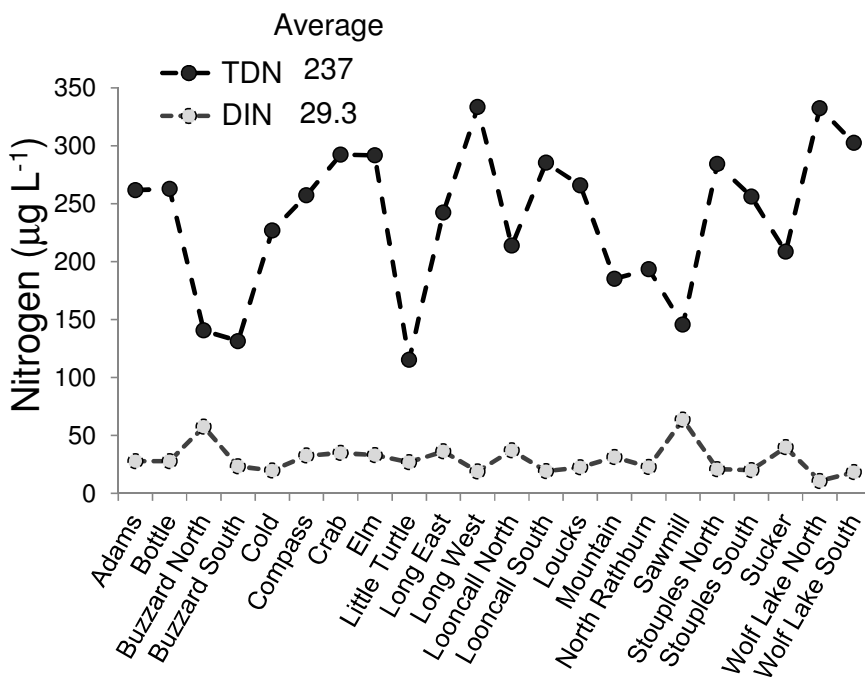
*Dissolved calcium.* There have been recent reports of declining calcium (Ca) concentrations in lakes of this general region. We found an average Ca concentration of 4 mg L<sup>-1</sup> in the Kawartha Highlands PP lakes with values ranging from <2 mg L<sup>-1</sup> to about 6 mg L<sup>-1</sup>. About ½ the lakes were found above 4 mg L<sup>-1</sup> and at concentrations that should elicit no concern. We found four lakes close to the 2 mg L<sup>-1</sup> concentration: Buzzard North, Buzzard South, Elm, and North Rathburn. Continued monitoring of these lakes and other below average lakes (Bottle, Crab, and Sawmill) should be considered given the possible effects of Ca-limitation on lake foodwebs.



*Phosphorus.* We measured the concentrations of total phosphorus and three separate fractions (total dissolved, TDP; particulate, PP; and soluble reactive P, SRP). For TP, we found an average of 7.41 µg L<sup>-1</sup> with most lakes found between 6 and 8 µg L<sup>-1</sup>. Two lakes (Compass and Bottle) were above 10 µg L<sup>-1</sup> but well within the range typical of oligotrophic lakes. It is likely that the Compass value is from contamination as neither TDP nor PP were elevated in this lake. Both fractions of phosphorus, TDP and PP, were found at lower concentrations (as would be expected) and in the range typical of oligotrophic, chronically P-limited lakes. In most lakes, the sum of TDP and PP nearly matched the measured TP, which further indicates little inorganic P being present in the water column. We measured SRP concentrations and found low concentrations in all lakes near or below the detection limit and suspect these values are largely the result of measuring labile organic P sources (data not shown on graph).

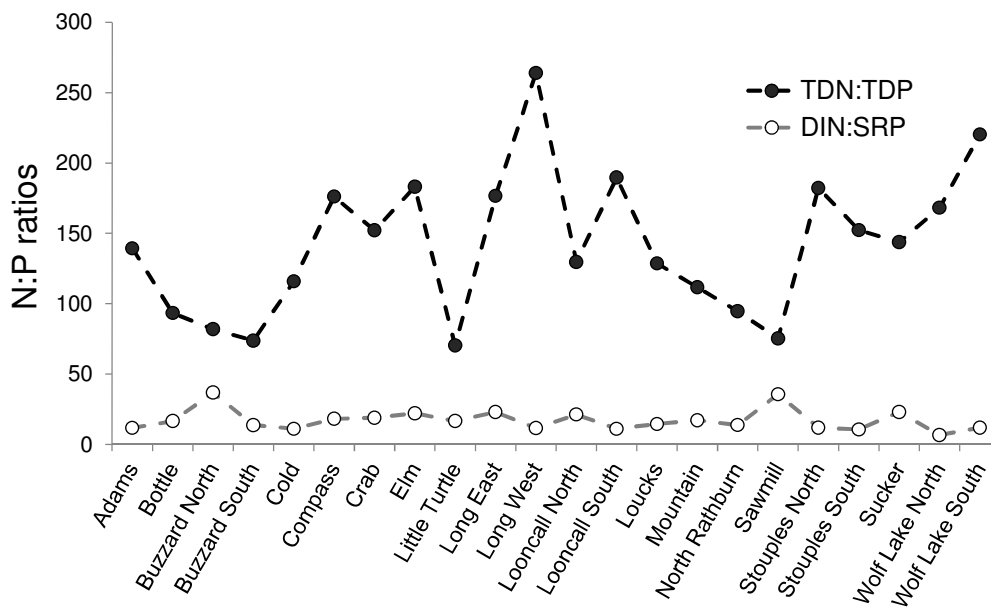


*Nitrogen.* We found most dissolved nitrogen in KHHP lakes in dissolved organic forms due to the relatively high TDN concentrations (150-350 µg L<sup>-1</sup>) and the much lower concentrations of dissolved inorganic nitrogen (10-50 µg L<sup>-1</sup>). TDN varied considerably among lakes with higher values seen in Long and Wolf lakes and low values present in Buzzard and Little Turtle. The DIN was largely found in the form of ammonia (~90%) with very little nitrate or nitrite measured in our samples. As our nitrate assay had a relatively high detection limit (~50 µg L<sup>-1</sup>), future work should use more sensitive methods to better describe nitrogen and its species composition in these lakes.

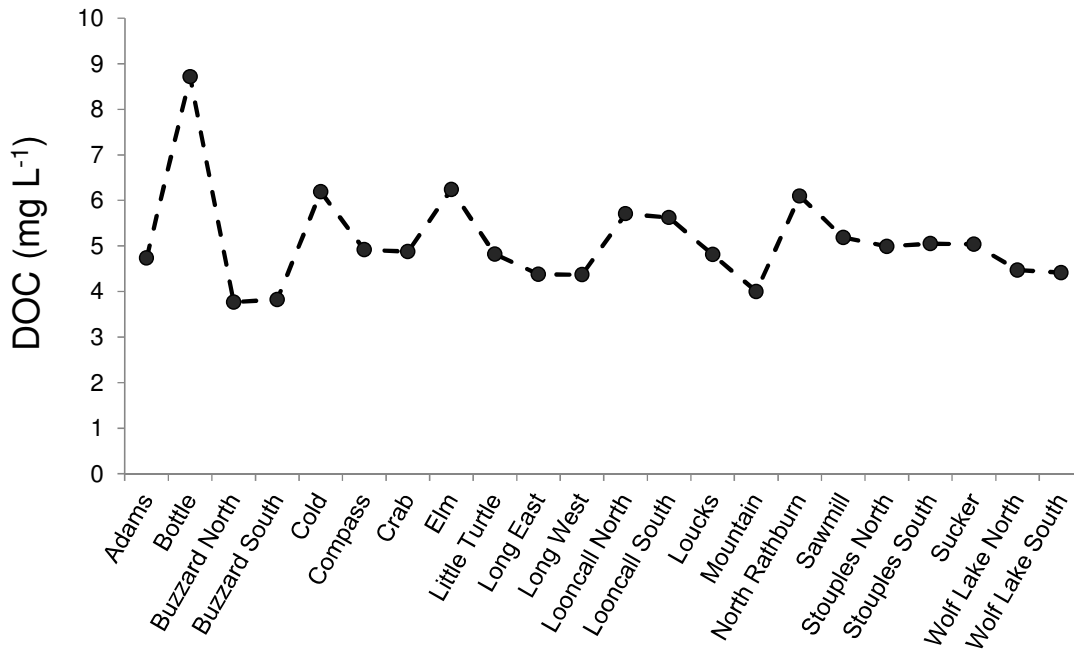




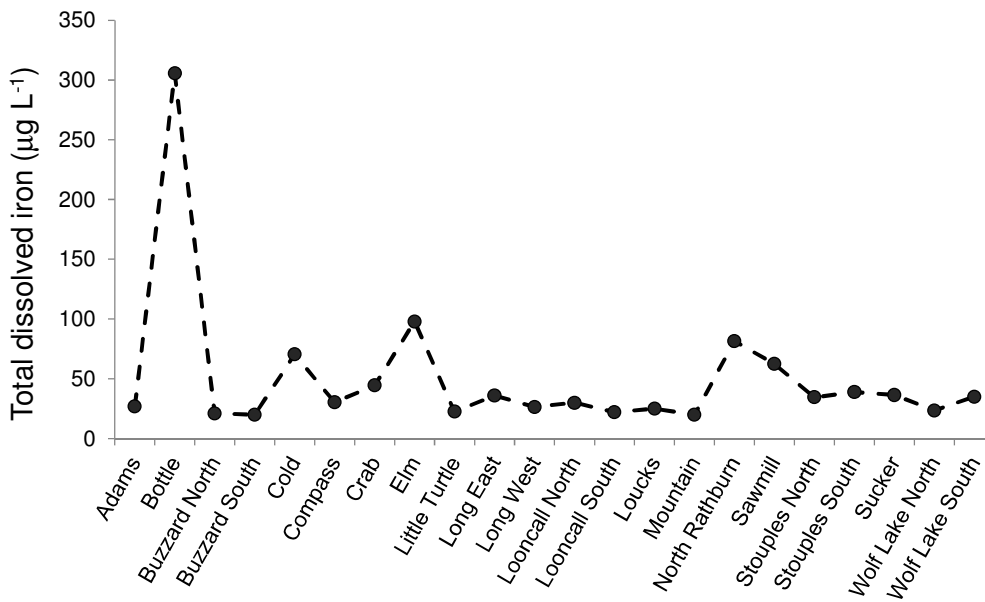
*N:P ratios.* The ratios of N to P in the dissolved nutrient pool provide another important indication of the nature of nutrient-limitation in the lake of interest. We found TDN:TDP ratios (by mol) in the 50-300 range, which is elevated above ratios normally seen in phytoplankton cells (~15-30). This is highly indicative of P-limitation in the KHPP lakes and the wide range further indicates large differences in the relative availability of these two important nutrients. We found much lower ratios of DIN:SRP (7-35), which are closer to being stoichiometrically balanced with regards to algal growth requirements. We suspect these ratios are not representative of those actually present in the lake due to the over-estimation of SRP (as noted above) and the under-detection of nitrate (as noted above), which would artificially lower the measured ratios. The differences between TDN:TDP and DIN:SRP nonetheless indicate a potentially important role of DON as a nitrogen source to primary producers, which is a possibility that should be further evaluated. If DON is largely inaccessible to algal producers, the KHPP may experience more frequent or intense N-limitation than we suggest here.



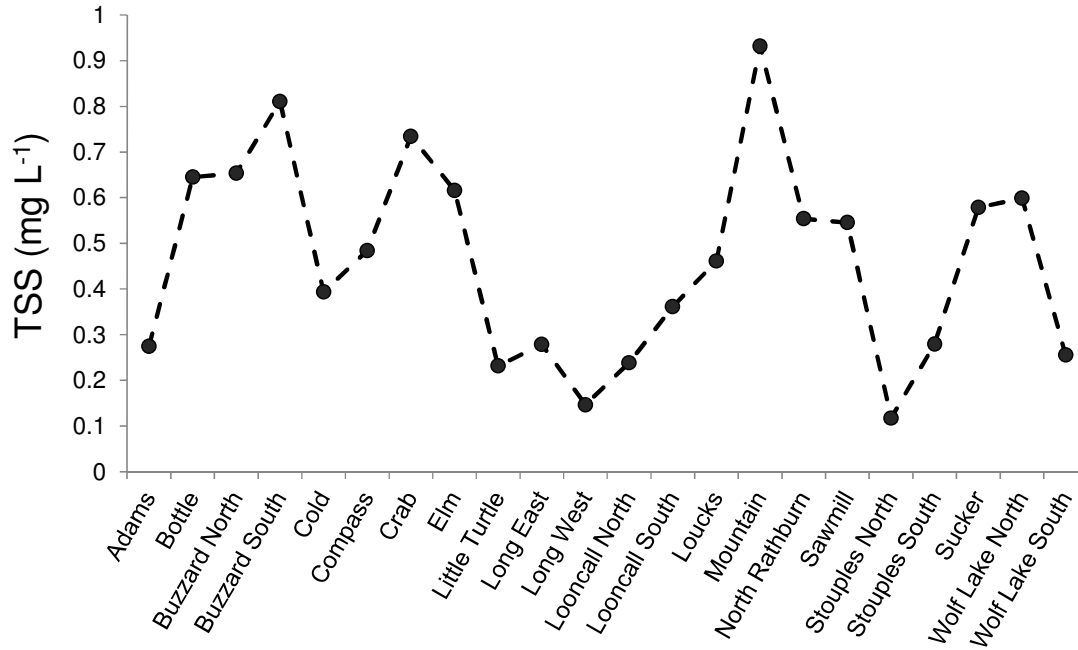
*DOC concentrations.* The concentration of dissolved organic carbon ( $\text{mg C L}^{-1}$ ) can vary widely among lakes and streams. The average value for KHPP lakes found here ( $\sim 5.10 \text{ mg C L}^{-1}$ ) is within the normal range for southern boreal lakes. Most lakes were between 4 and 6  $\text{mg C L}^{-1}$ , which is expected given the similar upstream landuse (undisturbed forest) and similar lake sizes. It is unclear why Bottle Lake was much higher ( $\sim 9 \text{ mg C L}^{-1}$ ) but this should be determined in the future.



*Total dissolved iron.* Iron is another essential element for phytoplankton growth but one that is rarely considered to limit growth of primary producers in freshwater ecosystems. Despite this assumption, dissolved iron concentrations are sometimes low in lake surface waters. Total dissolved iron (Td-Fe) concentrations in most KHPP lakes were in the range (20-50  $\mu\text{g L}^{-1}$ ) expected for humic, surface waters of the boreal ecosystem and likely not low enough to limit algal growth. The very high value found for Bottle Lake corresponds to its much high DOC concentration.



*Total suspended solids.* Total suspended solids (TSS) in most lakes usually consist mainly of organic particles (e.g., algal cells, detritus) unless shoreline or upstream disturbance produces high rates of erosion or sediment resuspension. Elevated TSS can also be observed during algal blooms when suspended algal mass is elevated. We found low TSS concentrations ( $<1.0 \text{ mg L}^{-1}$ ) in the KHPP lakes as would be expected for relatively undisturbed, forested lakes and are indicative of good water quality.



## 2. Surface-bottom comparisons.

*Summary.* Due to thermal stratification, bottom waters of lakes can become isolated from surface waters over the summer growing seasons. Most lakes in this region experience complete water column mixing twice each year (spring and fall), which homogenizes the water chemistry across all depths. Significant deviations in surface-bottom water chemistry found during summer periods can be produced by loss processes at the surface (uptake and sedimentation) and generation processes in the bottom waters (decomposition and redox release of mineralized nutrients). Such differences are usually exacerbated in productive lakes where excessive algal sedimentation leads to O<sub>2</sub> drawdown and hypoxic conditions in the hypolimnion. Under these conditions, nutrient concentrations tend to increase substantially and can indicate poor water quality. As surface and bottom waters were sampled simultaneously, we compared the surface and bottom conditions in the KHHP as a first order assessment of overall lake water quality. These data are summarized in the table below.

Parameter	units	Avg. Top	Avg. Bot	Difference
pH		7.24	6.61	0.64
TSS	mg/L	0.46	5.41	-4.95
CHL	µg/L	5.32	29.87	-24.54
TP	µg/L	7.41	29.93	-22.52
Seston P	µg/L	2.83	19.27	-16.44
TDP	µg/L	3.85	14.74	-10.89
TDN	µg/L	237.63	363.72	-126.09
NO <sub>3</sub>	µg/L	6.18	180.79	-174.62
NH <sub>4</sub>	µg/L	27.04	227.17	-200.13
DOC	mg/L	5.10	4.94	0.16
A <sub>280</sub>		0.08	0.16	-0.08
Ca	mg/L	4.02	5.02	-1.00
Fe	mg/L	0.05	0.94	-0.89

We generally found more particulate and dissolved nutrients in lake bottom waters of the KHHP. This was especially for N, P, and Fe and is mirrored by higher concentrations of TSS and CHL. This accumulation of nutrients and materials in hypolimnetic waters are likely due to high rates of sedimentation, low light levels (due to high DOC concentrations), low primary production (no uptake), and considerable nutrient release (due to low O<sub>2</sub> conditions). As this sampling occurred at the end of the summer, the net accumulation of materials over the course of the summer growing season may have amplified these depth related difference. While not necessarily of high concern, this pattern nonetheless indicates algal growth may be relatively high during late spring and early summer, which leads to high sedimentation and material transfer to the bottom of the lake. Our results indicate that seasonal sampling, especially during spring to summer transition, will be necessary to fully assess water quality in the KHPP.