Limnology and Water Quality 2017 Report



Paul Smith's College Adirondack Watershed Institute

Acknowledgments

This project was supported by funding from the St. Regis Property Owners Association. We would like to thank the numerous researchers, government agencies, and students who have documented the condition of these lakes for over 50 years. Special thanks to G.W. Fuhs, Patricia Flath, Leo Hetling, James Tofflemine, and Chester Buxton for initiating long term monitoring of the St. Regis Chain. This manuscript was authored by Corey Laxson, with assistance from Elizabeth Yerger, Hunter Favreau, and Dan Kelting. Ned Timbel and Garret Schniewind provided meaningful contributions to the planning of this project.



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Table of Contents

List of Tables	6
List of Figures	7
Executive Summary	9
Introduction	
Background	
Historical Perspective	
Objectives	
Methods	
Data collection	
Data analysis	
Understanding Lake Data	
Temperature and Thermal Stratification	
Dissolved Oxygen	
Phosphorus	
Nitrogen	
Photosynthetic Pigments: Chlorophyll-a and Phycocyanin	
Transparency	
Trophic Status	
Color	20
Acidity: pH and Alkalinity	20
Sulfate	21
Sodium and Chloride	22
Calcium	23
Conductivity	24
Findings: Lower St. Regis	25
Temperature and Dissolved Oxygen	25
Phosphorus	25
Nitrogen	27
Photosynthetic Pigments	29
Chlorophyll-a	29

Phycocyanin	29
Transparency	
Trophic Status	
Color	
Acidity	
Sodium and Chloride	
Calcium	
Conductivity	
Findings: Spitfire Lake	
Temperature and Dissolved Oxygen	
Phosphorus	
Nitrogen	35
Photosynthetic Pigments	35
Chlorophyll-a	35
Phycocyanin	
Transparency	
Trophic State	
Color	
Acidity	
Sodium and Chloride	40
Calcium	40
Conductivity	40
Findings: Upper St. Regis	42
Temperature and Dissolved Oxygen	42
Phosphorus	43
Nitrogen	43
Photosynthetic Pigments	46
Chlorophyll-a	46
Transparency	46
Trophic State	46
Color	47
Acidity	47
Sodium and Chloride	47

Calcium	49
Conductivity	
Recommendations	
Literature Cited	51

List of Tables

Table 1. Lake morphometry and watershed characteristics of the St. Regis Chain. 11
Table 2. Historical data source for the St. Regis Chain. 14
Table 3. Analytical methods employed at the Adirondack Watershed Institute's Environmental ResearchLab.15
Table 4. NYSDEC fixed boundary classification of trophic status
Table 5. Assessment of lake acidification based on pH. 21
Table 6. Acid neutralizing ability and acidification status based on alkalinity concentration (mg/L as CaCO ₃)21
Table 7. Assessment of road salt influence on Adirondack lakes based on chloride concentration23
Table 8. Chemistry and water quality parameters of the surface and bottom water of Lower St. RegisLake during the 2017 field season.26
Table 9. Chemistry and water quality indicators of the surface and bottom water strata of Spitfire Lakeduring the 2017 field season. BDL = below analytical detection
Table 10. Chemistry and water quality indicators of the surface and bottom water strata of Upper St.Regis Lake during the 2017 field season. BDL = below analytical detection.45

List of Figures

Figure 1. The St. Regis Chain of Lakes
Figure 2. The process of thermal stratification and turnover in a typical Adirondack Lake
Figure 3. Indices of acid deposition from the NADP monitoring station in Huntington Forest (central Adirondacks (1977-2017)
Figure 4. Vertical profiles of Lower St. Regis Lake during the ice free period of 2017. From top to bottom: temperature, dissolved oxygen, chlorophyll-a relative fluorescence units (RFU), and phycocyanin RFU. 25
Figure 5. Concentration of total phosphorus in the surface and bottom water strata of Lower St. Regis Lake during the 2017 field season
Figure 6. Time series of annual average values for trophic indicators in Lower St. Regis Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant historical trend (P<0.05)
Figure 7. Total nitrogen to total phosphorus ratio in Lower St. Regis Lake during the sampling events of 2015-2017. Shaded areas indicate the potential for cyanobacteria occurrence
Figure 8. Time series of annual average values for selected water quality indicators in the surface water of Lower St. Regis Lake. Error bars represent 1 SD of the mean. Dashed lines indicate a significant historical trend (P<0.05)
Figure 9. Vertical profiles of Spitfire Lake during the ice-free period of 2017. From top to bottom: temperature, dissolved oxygen, chlorophyll-a relative fluorescence units (RFU), and phycocyanin RFU. 33
Figure 10. Vertical profile of dissolved reactive phosphate and total phosphorus concentrations across the oxygenated and anoxic zones of Spitfire Lake, June 21 st 2017.
Figure 11. Time series of annual average values of key trophic indicators of Spitfire Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant trend in the historical data (P<0.05) 36
Figure 12. Total nitrogen to total phosphorus ratio in the waters of Spitfire Lake during the sampling events of 2015-2017. Shaded areas indicate the potential of cyanobacteria occurrence
Figure 13. Time series of annual average water quality indicators in the surface water of Spitfire Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant historical trend in the data (P<0.05)
Figure 14. Vertical profiles of Upper St. Regis Lake during the ice-free period of 2017. From top to bottom: temperature, dissolved oxygen, chlorophyll-a relative fluorescence units (RFU), and phycocyanin RFU
Figure 15. Concentration of total phosphorus in the surface and bottom water strata of Upper St. Regis Lake during the 2017 field season
Figure 16. Time series of annual average values of key trophic indicators of Upper St. Regis Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant trend in the historical data (P<0.05).

Executive Summary

The purpose of this study is to provide a comprehensive analysis of the limnology and water quality of the St. Regis Lake Chain. The specific objectives are to: (1) synthesis and interpret the physical and chemical properties of the lakes during the 2017 ice free season, (2) create a functioning database that contains all of the available historical water quality data for the lakes, and (3) analyze the historical data for trends in key water quality parameters. The report can be summarized in the following main points.

- Spitfire and Upper St. Regis Lakes are best classified as mesotrophic. Analysis of the available historical data reveals that the trophic state of these lakes has not experienced any major shift in trophic condition over the last 20 years.
- Lower St. Regis Lake has experienced an ecological redemption since the late 1960's. The primary trophic indicators (phosphorus, chlorophyll, and transparency) have exhibited statistically significant improvements, shifting the lake from a eutrophic to a mesotrophic condition.
- All three of the lakes experience rapid oxygen depletion in the bottom strata. Although this information is not news to the SRPOA, the cause of the anoxia is perhaps more complex than described in previous reports. We hypothesize that some degree of bottom water anoxia is natural in the Regis lakes, and has probably always occurred. Ultimately, the controlling factor for anoxia is the ratio of the lakes sediment surface area to hypolimnion volume (SSA:HV). For the relatively shallow lakes in the St. Regis chain this ratio is large, indicating that oxygen depletion should be anticipated. Current and historical nutrient pollution from the watershed has certainly augmented the oxygen depletion by providing a store of organic material for decomposition.

- Anoxia in the bottom water of the lakes creates a reducing environment that allows dissolved reactive phosphate to move out of the sediments. All of the lakes experience a significant increase in phosphorus concentration in the bottom strata. The greatest increase was observed in Spitfire Lake (5x) followed by Upper St. Regis (4x) and Lower St. Regis (2x).
- Examination of the historical data reveals that the annual average concentration of phosphorus has decreased in all of lakes since the 1970's. Because of the small sampling frequency in the 1970's and 1980's, some restraint should be used when interpreting the downward trend in phosphorus concentration.
- Cyanobacteria were detected in all of the lakes at relatively low densities, with the exception of Spitfire Lake, where a productive population of *Planktothrix* thrives near the bottom for most of the summer months. The low light intensity, anoxia, and nutrient supply at the bottom of the lake provide a perfect environment for *Planktothrix*, a species that can photosynthesis in suppressed light, prefer low oxygen, and require a high supply of phosphorus. During most of the summer the *Planktothrix* population is not visible. When growth conditions along the bottom change, the species can constructs gas vacuoles and float to the surface. It is only at this point that they become noticeable to lake users.
- Due to their inherent acid neutralizing ability, the lakes in the chain are circumneutral in terms of their pH and have not experienced noticeable degradation associated with acid deposition. All of the lakes have exhibited a significant downward trend in sulfate concentration, indicating that the acid deposition load to the watershed has decreased over time.
- The chemistry of the St. Regis chain is influenced by salted roads in the watershed. The concentrations of

sodium and chloride have increased in all the lakes over the last 41 years. The greatest impact is in Lower St. Regis Lake, where the concertation of chloride is 90 times greater than the concentration observed in least impacted lakes. Spitfire and Upper St. Regis have similar salt concentration to each other, and are approximately 40 times greater than background values.



Photo 1. The St. Regis Chain of Lakes seen from the summit of St. Regis Mountain (C. Laxson).

Table 1. Lake morphometry and watershed characteristics of the St.

Regis Chain.

Introduction

Background

The St. Regis chain of lakes is 580 hectares (1,433 acres) of connected surface water in Franklin Country NY. The chain is located within a 5,363 hectare (13,252 acre). watershed dominated by forest cover. The chain is morphologically divided into three distinct water bodies known as Upper St. Regis, Spitfire, and Lower St. Regis Lakes (Figure 1).

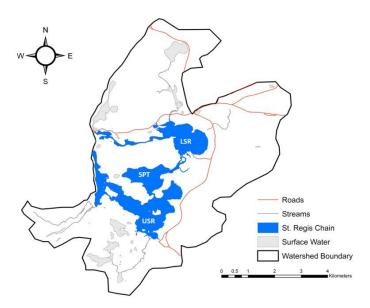


Figure 1. The St. Regis Chain of Lakes

Lake and watershed morphometry of the St. Regis Chain is detailed in Table 1. Upper St. Regis is the first lake in the chain and receives runoff from a 2,313 hectare watershed. The upper lake is also the largest, deepest, and has the greatest surface area. A contour map first published by the New York State Conservation Department in 1930 identifies a 28 meter (90 feet) deep hole in the western arm of the lake (NYSCD 1931). Although this maximum depth of 90ft has spread to numerous other maps for nearly a century, it has not been validated. The maximum depth we have encountered is approximately 20 meters (66 feet). There are and numerous other bathymetric errors in the map as well. Given the inaccuracies of the existing bathymetric

		Lower St. Regi	s Lake	
Location	County:	Franklin	Latitude:	44.426
Location	Town:	Brighton	Longitude:	-74.252
	Lake Area (ha):	141	Z-max (m):	11
Lake	Lake Perimeter (km):	7.1	Volume (m ³):	7.606.12
Characteristics	Luce I ennièrer (kin).	7.1	Flushing Rate (T/Y):	3
	Watershed Area (ha):	5,363	Residential (%):	
	Surface Water (%):	17	Agriculture (%):	
Watershed	Deciduous Forest (%):	35	Commercial (%):	
Characteristics	Evergreen Forest (%):	28	Local Roads (km):	
Characteristics		20	. ,	
	Mixed Forest (%):	3	State Roads (km):	13
	Wetlands (%):	13		
		Spitfire		
Location	County:	Franklin	Latitude:	44.416
Location	Town:	Brighton	Longitude:	-74.270
Lake	Lake Area (ha):	109	Z-max (m):	9
Characteristics	Lake Perimeter (mi):	7	Volume (m ³):	5,036,55
Characteristics			Flushing Rate (T/Y):	2
	Watershed Area (ha):	2,800	Residential (%):	
	Surface Water (%):	22	Agriculture (%):	
Watershed	Deciduous Forest (%):	43	Commercial (%):	
Characteristics	Evergreen Forest (%):	18	Local Roads (km):	
	Mixed Forest (%):	4	State Roads (km):	4
	Wetlands (%):	12		
		Upper St. R	egis	
Location	County:	Franklin	Latitude:	44.18
Location	Town:	Franklin	Longitude:	-74.27
	Lake Area (ac):	287	Z-max (m):	
Lake Characteristics	Lake Perimeter (km):	22	Volume (m ³):	20,400,0
Characteristics			Flushing Rate (T/Y):	C
	Watershed Area (ha):	2,313	Residential (%):	
	Surface Water (%):	21	Agriculture (%):	
Watershed	Deciduous Forest (%):	52	Commercial (%):	
Characteristics	Evergreen Forest (%):	14	Local Roads (km):	
	Mixed Forest (%):	4	State Roads (km):	3
	Wetlands (%):	10	Tenno (mil)	

data, the volume (5,390 MG) and the retention time (1.7 years) is undeniably biased. Water flows north from Upper St. Regis into Spitfire Lake through a 250 meter long channel. Spitfire is the smallest of the lakes in the chain, at 109 hectares (269 acres). It is also the shallowest, reaching a maximum depth of 9 meters. Water drains northeast from Spitfire to Lower St. Regis Lake through a 600 meter long channel referred to as "the slough". Lower St. Regis Lake has a surface area of 142 hectares (350 acres); however, when the 3 km long outlet arm is included in the analysis the surface area increases to 185 hectares.

Historical Perspective

Development within the St. Regis watershed began in 1858 when Apollos A. Smith purchased 50 acres on the shores of Lower St. Regis Lake and began construction of his 17 room hunting lodge. Over the next several decades the rustic hunting outpost called *St. Regis House* grew to

St. Regis Chain: 2017

a world renowned wilderness resort known as *Paul Smith's Hotel*. Well before the end of the 19th century, Paul Smith owned the entirety of the St. Regis watershed. Hotel guests and influential families who desired their own piece of the early Adirondack lifestyle purchased shoreline property from Paul on Spitfire and Upper St. Regis for the construction of their own camps and cottages (Surprenant 2009; Collins 1977). Development on the lakes increased rapidly. Analysis of historical USGS maps reveals a 550% increase in the number of buildings around the lake chain during the first half of the 20th century.

Water quality impacts must have been observed by the turn of the century. We know this because in August of 1901 property owners on the St. Regis Chain, including Dr. E.L. Trudeau, Phelps Smith, and Dr. Walter B. James signed a resolution promising that after June 1st 1902 they would not allow "sewage, kitchen or sanitary water, waste water, or any other refuse of any kind whatsoever to be thrown or drained into any of the waterbodies of the St. Regis Chain". The resolution went on further to say that property owners "will not build or continue to use any dry well or cess pool at a distance of less than 30 feet from the shore of these waters." One can only imagine that if this was the unanimous sentiment in 1901, then surely water quality issues had been observed at that time.

Despite the property owner's efforts to curb pollution, it appears the water quality of the lakes continued to trend down through the middle of the 19th century. Historical documentation of specific water quality concerns focused on Lower St. Regis Lake, and rightfully so. Development associated with the Paul Smith's Hotel, and later Paul Smith's College, outpaced the waste water management technology of the time as well as our scientific understanding of lake ecology. The results to Lower St. Regis Lake were long lasting blooms of cyanobacteria, extreme anoxia, and changes to the fish community (Laxson et al. *in prep*). One of the worst algae blooms occurred in the summer of 1968 when the waters of

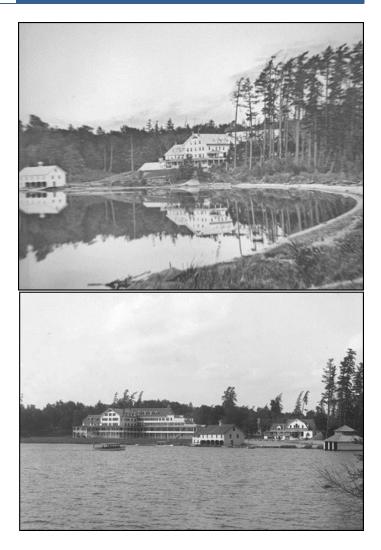


Photo 2. Paul Smith's St. Regis House around 1878 (top), and the Paul Smith's Hotel around the turn of the 20th century (PSC historical archives).

Lower St. Regis were so thick with cyanobacteria that the bloom could be observed 32 km downstream in the St. Regis River. Total phosphorus concentration during this event were as high as 144 μ g/L, nearly six time greater than the total phosphorus values in the adjacent Spitfire Lake (Fuhs et al. 1977). To their credit, Paul Smith's College initiated major changes to waste water handling on campus in the late 1960's. These efforts culminated in 1974 when waste water effluent was diverted from the lake to sand percolation beds for 100% nutrient removal. Subsequent studies of the lower lake reported noteworthy improvements to water quality (Fuhs at al. 1977; Hyde and Martin 1995 Laxson et al. 2017).

In more recent decades the water quality focus has shifted towards the upper lakes. In 1994, the SRPOA (St. Regis Property Owners Association) commissioned a study on the limnology of Spitfire and Upper St. Regis Lake. In the report, Hyde and Martin (1995) described bottom water anoxia, release of sediment bound phosphorus, and cyanobacteria blooms as evidence that both upper lakes had been impacted by shoreline development. The results of this study spurred the SRPOA to support regular water quality monitoring on the lake chain, a task that has been carried out by no less than 6 entities since 1994. Recently, some members of the SRPOA have noted an apparent increase in the prevalence of cyanobacteria blooms, and expressed concern over the oxygen depletion and subsequent internal phosphorus loading in the upper lakes. In an effort to promote stewardship of the lakes, the SRPOA commissioned O'Brien & Gere to use recent lake data to develop a phosphorus budget for the St. Regis Lakes (OBG 2015). The results of the study revealed that internal phosphorus loading from the sediments represented the largest phosphorus input, ranging from 30 to 40% across the three lakes. The OBG report also identified additional monitoring needs, such as extending the time period for sampling, analyzing additional nutrients, and more detailed analysis of oxygen depletion.

Objectives

The purpose of this current study is to provide a comprehensive analysis of the limnology and water quality of the St. Regis Lake Chain. The specific objectives are to: (1) synthesis and interpret the physical and chemical properties of the lakes during the 2017 ice free season, (2) create a functioning database that contains all of the available historical water quality data for the lakes, and (3) analyze the historical data for trends in key water quality parameters.



Photo 3. Students and researchers studying the St. Regis Chain over the last several decades. Clockwise from upper left: PSC students collecting waterthrough the ice on Lower St. Regis Lake (1973). Analysing dissolved oxygen content of the lakes (summer 1984). Collececting plankton from Spitfire Lake (July, 2016).

Methods

Data collection

Historical data was collected from the numerous limnological studies carried out on the lake chain since 1967 (Table 2). All of the available data was combined into one database, which now contains nearly 7,000 records. Field data for 2017 was collected from the R.V. *Clearwater* at the deepest section of the lakes eight times starting on April 27th and ending on October 19th 2016. Transparency was observed using a 20 cm black and white Secchi disk from the shady side of the vessel. Temperature, dissolved oxygen (DO), as well as in situ chlorophyll-a and phycocyanin were determined every meter from the surface to the bottom with an YSI EXO 2 submersible sonde and data logger. Surface water samples were collected using a 2 meter integrated tube sampler. The hypolimnetic water (bottom strata) was collected with a 1 liter Kemmerer bottle from approximately 0.5 meter off the bottom.

250 mL of the surface water was immediately passed through a 0.45µm cellulose membrane filter. The filter was collected, wrapped in foil and put on ice for chlorophyll-a analysis. All samples were kept on ice after collection and chemically preserved or stored at 4°C until analysis could be completed. Samples were analyzed for pH, conductivity, color, alkalinity, total phosphorus, nitrogen series, chlorophyll-a, DOC, chloride, sodium, and calcium at the PSCAWI Environmental Research Lab following the analytical methods described in Table 3. All laboratory analyses included quality control (QC) measures such as check standards, blanks, matrix spikes, and duplicates that were assessed on an on-going basis.

Data analysis

Field and laboratory data from 2017 were combined with historical limnological data from the St. Regis Chain, which has been collected by various research groups in a similar manner since 1967. Trend analysis on the existing data was conducted using Kendall's Tau, a rank correlation coefficient used to test the null hypothesis that there was no association between water quality variables and time. Simple linear trend lines were fit to data with statistically significant (P<0.05) trends and displayed on the corresponding chart. Thus, absence of a line means there was no statistically significant historical trend in the indicator. Average annual values for secchi disk transparency, total phosphorus, and chlorophyll-a in the lake were used to calculate Carlson's Trophic Status Index, (TSI), a commonly used quantitative index for classifying lakes based on trophic status (Carlson 1977). Typically TSI values are between 0 and 100. Lakes with TSI values less than 40 are classified as mesotrophic, TSI values greater than 50 are classified as eutrophic.

Table 2. Historical data source for the St. Regis Chain.

Source	Lower St. Regis	Spitfire	Upper St. Regis	Citation
Dr. Carl Schofield, Cornell University	1967			Fuhs et al. 1977
Brandon Park Fishery Report	1968			Fuhs et al. 1977
S.P. Allen: NYS Department of Health	1970			Fuhs et al. 1977
Paul Smith's College EET Student Data*	1971-1987	1983-1985, 1987	1983-1985, 1987	Martin et al. 1995
New York State Department of Health	1971	1971	1971	NYSDOH 1972
Environmental Protection Agency	1972-1975	1973-1974	1972-1974	EPA 1974 Fuhs et al. 1977
Don Charles	1979			Don Charles pers. com.
Adirondack Lake Survey Corporation	1986	1986		ALSC (2018)
Citizen Science Lake Monitoring Program	2000-2002	1996-2002	1996-2002	CSLAP (2018)
Brass Laboratories		1998	1999	Kalma unpublished reports
Adirondack Ecologists	2000-2002	2000-2002	2000-2002	Lamere unpublished data
Adirondack Watershed Institute	2002-2017	1994, 2002- 2017	1994, 2002- 2017	Martin el al. 1994 AWI unpublished data
Paul Smith's College Limnology Class Data	2013-2017			Laxson unpublished data

St. Regis Chain: 2017

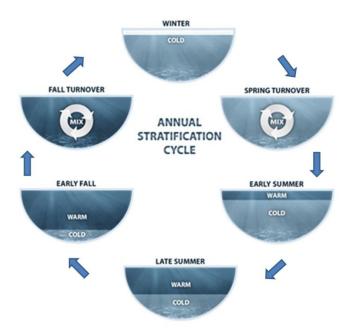
Table 3. Analytical methods employed at the Adirondack Watershed Institute's Environmental Research Lab.

Analyte	Method Description	Reference
Laboratory pH	Mettler Toledo standard pH electrode	АРНА
Spec. Conductivity	Conductance at 25°C via conductivity cell	APHA 2510 B
Apparent Color	Single wavelength method with PtCO standards	APHA 10200 H
Chlorophyll-a	In-vitro fluorescence, non-acidification optical kit	EPA 445
DOC	Oxidative infrared analysis	EPA 415.3
Total Phosphorus	Acid-persulfate digestion, ascorbic acid reduction	APHA 4500 - P H
Total Nitrogen	Oxidative combustion chemiluminescence	APHA 4500 - N
Nitrate + Nitrite - N	Automated cadmium reduction	APHA4500 - NO ₃ I
Ammonium - N	Gas diffusion / pH indicator	Lachat: 10-107-06
Alkalinity	Automated methyl orange method	EPA 301.2
Chloride and Sulfate	Automated ion chromatography	EPA 300.0
Metals	Inductively coupled optical emission spectrophotometry	EPA 200.7

Understanding Lake Data

Temperature and Thermal Stratification

Vertical mixing of a lake is driven by the relationship between waters density and its temperature. Simply put, as the water warms it becomes less dense and floats on top of the colder and denser water. When the ice melts from the lake in the spring the water column is all the same temperature from top to bottom, a condition referred to as isothermal (Greek: *iso* = equal, *thermo* = heat). When a lake is isothermal it's also the same density throughout, allowing the water to vertically mix without impediment. Limnologists refer to this period of complete mixing as spring turnover.





As spring progresses, energy from the sun heats the surface water faster than the heat can be distributed through the water column. The thermal resistance to mixing increases between the warm surface water and the colder and denser bottom water. If the lake is deep enough, the water column will become separated into three distinct strata. The epilimnion is the upper stratum that is uniformly warm and freely mixes with itself. The hypolimnion is the bottom stratum that is uniformly cold and dense. Between the two strata is the metalimnion, a zone of sharp thermal change that prevents mixing between the surface and the bottom (Wetzel 2001). As the lake loses heat in the autumn, the epilimnion becomes cooler and deeper. Eventually the lake is once again isothermal and freely mixes, a period referred to as fall turnover (Figure 2)

Temperature and stratification characteristics are measured on the St. Regis Chain during each sampling trip with a YSI EXO 2 submersible sonde. The sonde is equipped with an instantaneous thermometer that records temperature as it is lowered from the surface of the water to the bottom at the deepest point. The EXO 2 is capable of recording several parameters of the lake described in the subsequent paragraphs.

Dissolved Oxygen

Dissolved oxygen has been described as the most fundamental parameter of a lake, aside from the water itself (Wetzel 2001). Available oxygen is essential for aerobic metabolism and non-biotic chemical reactions. In addition the presence or absence of oxygen directly affects the solubility of a number of important inorganic nutrients such as phosphorus. The primary source of oxygen in a lake is the atmosphere, thus, in lakes that are thermally stratified the hypolimnion is isolated from the When lake sediments contain high oxygen source. amounts of organic material, bacterial decomposition consumes all of the dissolved oxygen resulting in hypolimnetic hypoxia (very low O₂ in hypolimnion). In some lakes a certain amount of hypolimnetic hypoxia may be natural; however, nutrient enrichment resulting from human activities stimulates algal productivity and subsequent algal settlement, decomposition, and oxygen loss.

Several ecological processes are influenced by hypolimnetic hypoxia. The most obvious impact is loss to the fishery. Hypoxia has the potential to negatively affect individual fish growth, survival, reproduction, and ultimately population growth (Wu 2009). A second

important impact of bottom water hypoxia is that it results in internal loading of phosphorus. Lack of oxygen in the hypolimnion influences the solubility of phosphorus and allows the release of dissolved reactive phosphorus from the lake sediments. During fall turnover the phosphorus can then get distributed through the entire water column (Wetzel 2001).

The concentration of dissolved oxygen through the water column of the St. Regis lakes is measured with the YSI EXO 2 submersible sonde. The sonde is equipped with an optical dissolved oxygen sensor that uses luminescence to calculate oxygen concentration.

Phosphorus

Phosphorus is of major importance to structure and metabolism of all organisms. However, in freshwater systems it exists in relatively small amounts compared to other essential nutrients such as carbon, hydrogen, oxygen, and sulfur. Therefore, phosphorus is typically the limiting nutrient in aquatic systems and the addition of extra phosphorus allows production to increase greatly because all other essential elements are typically available in excess (Schindler 1974, Wetzel 2001). Natural weathering releases phosphorus from rocks and soils, and it also enters our watersheds in fertilizers, human waste, and atmospheric deposition. Phosphorus exists in a number of forms in aquatic systems, including readily available dissolved phosphate, and organically and inorganically bound phosphorus. Total phosphorus is all of the forms of phosphorus combined and serves as an important indicator of overall trophic status of a lake. Generally speaking, lakes of low productivity (oligotrophic) have total phosphorus concentrations less than 10 µg/L, while highly productive lakes (eutrophic) have total phosphorus concentrations greater than 20 (NYS DEC assessment criteria).

Water samples from the surface and bottom water strata of St. Regis Chain were analyzed for total phosphorus using EPA Method 365. In this process water samples are run through a digestion procedure to convert all the forms of phosphorus into phosphate. The resulting phosphate is analyzed on a spectrophotometer after ascorbic acid reduction.

Nitrogen

Nitrogen is an essential element that can be the limiting nutrient for algal productivity growth in lakes, but it is generally the second most limiting nutrient after phosphorus. Nitrogen does not typically receive the attention that phosphorus does because it is more abundant and has a variety of sources in the watershed. Nitrogen exists in many forms in a lake, including inorganic and organic molecules. The inorganic forms include nitrogen gas (N_2) , nitrate (NO_3) , nitrite (NO_2) , and ammonium (NH⁺⁴). Nitrogen gas is the most abundant form of nitrogen; it makes up 78% of the earth's atmosphere and readily dissolves into water. This gaseous form of nitrogen is unusable by the vast majority of organisms, only some species of cyanobacteria can "fix" this form of nitrogen into a form they can utilize, giving cyanobacteria a competitive edge in environments with limited useable nitrogen. Plants and algae can assimilate the other forms of inorganic nitrogen. Nitrate, nitrite, and ammonium enter the lake though precipitation, surface runoff, and ground water sources continually cycled and are through bacterial decomposition of organic matter. Inorganic nitrogen concentration in the surface water of lakes is typically quite low, as it is rapidly assimilated by phytoplankton. become Concentrations may elevated due to anthropogenic sources such as waste water discharge, agricultural runoff, and urban development. Organic nitrogen represents the stores of nitrogen that is locked up in organic molecules, such as proteins, amino acids, urea, and living and decomposing organisms. Organic nitrogen is not readily available for algal productivity until bacteria decompose the organic material and excrete useable forms of inorganic nitrogen. Total nitrogen is a measure of all of the non-gaseous inorganic and organic forms of nitrogen in the water.

As the two elements most likely to limit productivity and lakes, the mass ratio of total nitrogen to total phosphorus

(TN:TP) is frequently used as a metric to determine which element limits productivity and which algal groups are likely to dominate. It is generally believed that TN:TP greater than 50 indicates that phosphorus is the limiting nutrient for productivity, while a TN:TP less than 20 indicate nitrogen limitation. TN:TP between 20 and 50 represent a gray area, where either element may be limiting productivity (Guildford and Hecky 2000). Because many species of cyanobacteria can utilize atmospheric nitrogen, these species tend to dominate in nitrogen limited systems. The critical TN:TP ratio at which cvanobacteria tend to dominate is open to debate, with research suggesting ratios as low as 5 to as high as 40 (Schindler 1977; Bulgakov and Levich 1999). For example, Smith (1983) found that cyanobacteria tended to be rare in the water column when the TN: TP mass exceeded 29:1 and have the potential to dominate the planktonic biomass at ratios below 22:1 (Smith et. al 1995). It is important to recognize that cyanobacteria occurrence is not simply dependent on TN:TP ratios, several other variables such as temperature, light, and availability of inorganic carbon and trace elements are all important factors (Dokulil and Teubner 2000).

Water samples from the surface and bottom strata of the St. Regis Chain are analyzed for inorganic forms of nitrogen with a spectrophotometer using the cadmium reduction method for nitrate + nitrite, and the gas diffusion method for ammonium. Total nitrogen is analyzed in a chemiluminescence chamber after combustion.

Photosynthetic Pigments: Chlorophyll-a and Phycocyanin

Chlorophyll-a is the primary photosynthetic pigment found in all freshwater species of algae and cyanobacteria. Quantifying actual algal productivity in a lake is a difficult and expensive undertaking. A measurement of chlorophyll is relatively simple and inexpensive, and can provide a surrogate measure of algal productivity (Wetzel 2001). Chlorophyll is not a direct measure of algal biomass as the concentration of chlorophyll varies somewhat bv species and environmental conditions. This said, increases in chlorophyll are generally associated with increased algal production, and the concentration of chlorophyll is widely considered as the most direct measure of the trophic state of lakes. Algal biomass is affected by the interaction of nutrient availability, light, water temperature, and grazing so there can be considerable variation in chlorophyll concentrations throughout the vear depending on which of these factors is limiting growth at a particular time. Typically, major changes in algal biomass (e.g. an algae bloom), and thus chlorophyll, are usually related to changes in the availability of phosphorus, nitrogen, silica or inorganic carbon (Wetzel 2001). Chlorophyll-a is analyzed by filtering a known volume of lake water through a fine (0.45µm) celluloseacetate filter, which captures the small photosynthetic organisms. In the laboratory the filter is macerated and the chlorophyll is extracted into an acetone solution which is then analyzed with a flourometer. Chlorophyll-a can also be analyzed in the field with a submersible flourometer attached to the YSI EXO 2.



Photo 4. Algal cells from Spitfire Lake captured on a chlorophyll-a filter

Phycocyanin is an accessory photosynthetic pigment found only in cyanobacteria, thus its presence serves as a marker for cyanobacteria presence. Research over the past decade has demonstrated a strong correlation

between phycocyanin concentration and cyanobacterial biomass. We measure relative phycocyanin concentration with a BGA sensor on the YSI EXO 2.

Transparency

Transparency is a simple and inexpensive measurement of water clarity and light penetration. Transparency is a great indicator of lake condition because it is influenced by many factors related to water quality and human perception. Transparency data is used most often to interpret the productivity of a lake. In general, lakes that have low productivity and low algal abundance have greater transparency. As algal productivity increases the transparency of the water body tends to decreases (see Trophic State). There are a number of other water quality issues that can influence transparency depth such as turbidity (cloudiness of the water), suspended sediment, and dissolved chemicals. For example, the transparency of many lakes in the Adirondacks is influenced by the amount of colored dissolved organic material in the water (see Color).

Transparency is measured by lowering a 20 cm black and white disk, called a secchi disk, through the water to the depth where it is no longer visible from the surface. The secchi disk was created by the Italian astronomer Pietro Angelo Secchi in the mid-19th century as a method to measure the depths of the canals in Venice.

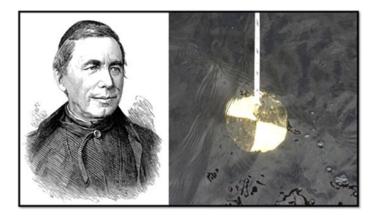


Photo 5. Pietro Angelo Secchi (1818-1878) and the limnological tool named after him.

Trophic Status

Trophic status is a term derived from the Greek word *trophi*, meaning food or nourishment, and is used by limnologists to explain the overall productivity of a lake. Lake productivity is naturally influenced by the rate of nutrient supply from the watershed, climatic condition, and lake and watershed morphology. Human activities and development within a watershed have the potential to increase the rate of nutrient supply into the lake and thereby accelerate lake productivity, a process known as cultural eutrophication.

Most Lakes in the Adirondacks can be assigned into one of three trophic classes; oligotrophic, mesotrophic, or eutrophic based on their overall level of biological productivity.

<u>Oligotrophic</u> - From the Greek words *oligo*, meaning few and *trophi*, meaning nourishment; oligotrophic lakes have low biological productivity due to relatively low nutrient content. As a result of low nutrients oligotrophic lakes have high transparency, low algal abundance, low organic matter in the sediments, sparse aquatic plant growth, and abundant dissolved oxygen throughout the water column the entire year. Oligotrophic lakes are most likely to support a cold water fishery (trout and salmon).

<u>Eutrophic</u> - From the Greek words *Eu*, meaning good. Eutrophic lakes have high biological productivity due to abundant levels of nutrients. As a result of high nutrient availability eutrophic lakes are typified by high algal productivity, low transparency, high organic matter in the sediments, and periods of anoxia in the bottom of the water column (the hypolimnion). Eutrophic lakes tend to support dense aquatic plant growth in the littoral zone. Eutrophic lakes are unlikely to support a viable cold water fishery

<u>Mesotrophic</u> - from the Greek words *Meso*, is an intermediate trophic classification on the continuum between oligotrophy and eutrophy.

Trophic status is typically determined by analyzing lake

data on transparency, chlorophyll and total phosphorus and employing one of the two most commonly used classification approaches, the fixed boundary method or the trophic index method. The fixed boundary method uses predetermined ranges of transparency, total phosphorus, and chlorophyll to classify the lakes trophic status. A good example of a fixed boundary is the traditional method employed by the NYS DEC that appears in Table 4 (NYSDEC Clean Lakes Assessment).

Table 4. NYSDEC fixed boundary classification of trophic status.

Parameter	Oligotrophic	Mesotrophic	Eutrophi
Transparency	>5	2-5	<2
Total Phosphoru	s <10	10-20	>20
Chlorophyll-a	<2	2-8	>8

The most commonly used tropic state index is Carlson's TSI (Carlson 1977). This index uses algal biomass as determined by the three variables of transparency, total phosphorus, and chlorophyll as the basis for the trophic state classification. The range of the index is from approximately zero to 100, although technically there are no upper or lower bounds. Each major TSI division (10, 20, 30, etc.) represents a doubling in algal biomass. The Traditional trophic classification scheme can be overlaid on the index as follows: TSI < 40 = oligotrophic, TSI 40-50 = mesotrophic, TSI > 50 = Eutrophic.

Regardless of the lakes trophic state, or the method used to classify it, it's important to remember that "trophic state" is just an organizing concept limnologists use to locate a particular waterbody on a continuum of productivity, thereby connecting the lake to previous information and knowledge from other lakes. An oligotrophic lake and its biota do not possess a distinct identity or wholeness that separates it from a mesotrophic lake. The physical variables of a lake system are dynamic and exist across a wide gradient and the biological components of a lake change continuously as well (Carlson and Simpson 1996).

Color

The observed color of a lake is an optical property that

results from light being scattered upwards after selective absorption by water molecules as well as dissolved (metallic ions, organic acids) and suspended materials (silt, plant pigments). For example, Lakes rich in dissolved organic matter and humic compounds absorb shorter wavelengths of light, such as green and blue, and scatter the longer wavelengths of red and vellow, thus these lakes appear to be brown in color (Wetzel 2001). Analysis of color can provide us with information about the quantity of dissolved organic matter (DOM) in the water. However, caution should be taken when using color as a surrogate for DOM as color has been shown to behave differently than the total DOM pool in a lake, making it a crude predictor of DOM (Dillon and Molot 1997). In an effort to make color data more objective and quantifiable, color is analyzed in the lab with a spectrophotometer at 455 nm. The absorption of light in each sample is compared to standard concentrations of a platinum cobalt solution (Pt-Co).



Photo 6. Dissolved organic material can cause water to appear brown due to selective absorption of specific wave lengths of light.

Acidity: pH and Alkalinity

In chemistry, pH is used to communicate the acidity. Technically pH is a surrogate measure of the concentration of hydrogen ions in water (acidity). Hydrogen ions are very active, and their interaction with other molecules determines the solubility and biological activity of gasses, nutrients, and heavy metals; thus pH is considered a master variable for its influence on chemical

processes and aquatic life. pH exists on a logarithmic scale from 0-14, with 7 being neutral. pH values less than 7 indicate increasing acidity, whereas pH values greater than 7 indicate increasingly alkaline conditions. Because pH exists on a logarithmic scale a decrease in 1 pH unit represents a 10 fold increase in hydrogen ion activity. Lakes can become acidified when they are influenced by organic acids from wetlands and bogs or when acidic precipitation falls on a poorly buffered watershed (Driscoll et al. 2003, Wetzel 2001). In the Adirondacks acidification status can be assed from pH values based on the guidelines outlined in Table 5. The pH of the St. Regis Lakes is measured in the field as well as in the lab with a pH electrode.

Table 5. Assessment of lake acidification based on pH.

Lake acidity	Status
pH less than 5	Acidic: Critically Impaired
рН 5.0 – 6.0	Acidic: Threatened
рН 6 – 6.5	Acidic: Acceptable
рН 6.5 – 7.5	Circumneutral: non-impacted
pH >7.5	Alkaline: non-impacted

Alkalinity (or acid neutralizing ability) is the capacity of water body to neutralize acids and thereby resist changes in pH. The alkalinity of a lake plays a major role in whether or not a lake is impacted by acid deposition. Alkalinity is a function of the amount of calcium carbonate in the water which is derived mainly from the watershed. Most Adirondack lakes exist on slowly weathering granitic bedrock that has a slow rate of calcium carbonate generation, and therefore lower acid neutralizing ability. The opposite is true for lakes that exist on bedrock derived from ancient ocean deposits, such as limestone or dolomite. Soil depth also plays a role in acid neutralizing capacity, with deeper soils offering more buffering ability than shallower soils. Alkalinity is quantified by analyzing the amount of dilute acid required to lower the pH of a lake sample to 4.3 pH units, the point at which all of the carbonate and bicarbonate alkalinity is consumed. The acid neutralizing ability of a lake can be generally assessed following the parameters

presented in Table 6.

Table 6. Acid neutralizing ability and acidification status based on alkalinity concentration (mg/L as CaCO₃).

Alkalinity (mg/L)	Buffering Ability	Acidification status
< 0	none	acidified
0 - 2	low	extremely sensitive
2 - 10	moderate	moderately sensitive
10 - 25	adequate	low sensitivity
> 25	high	not sensitive

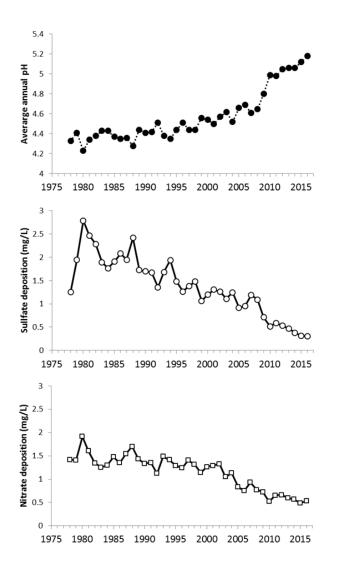
Alkalinity is measured in the lab by quantifying the amount of strong acid required to bring the water to a pH of 4.2. At this pH the buffering ability of the sample has been fully depleted. The results of this analysis are reported in mg/L of $CaCO_3$.

Sulfate

Sulfur is an essential element for all living organisms because of the role it plays in the cellular protoplasm as well as protein synthesis. Sulfur can take many forms in including organic sulfur (products lakes. of decomposition), gaseous hydrogen sulfide (smell of rotten eggs), metal sulfides (iron sulfide), and oxidized ionic form (sulfate). Sulfate (SO₄⁻²) is particularly interesting in the Adirondacks because it is the negative ion deposited on the landscape during acid deposition events. During the 20th century the vast majority of sulfate input to the Adirondack region was derived from industrial emissions in the form of sulfuric acid deposition. For example, Galloway and Whelpdale (1980) estimated that human generated emissions accounted for 93% of the sulfur budget in eastern North America. Tracking sulfate concentrations in surface water serves as a meaningful metric of changes in acid deposition impact to our region. Amendments to the Clean Air Act made in 1990 have resulted in a substantial decrease in sulfur emissions and acid deposition.

Data from the National Atmospheric Deposition Monitoring Program in Huntington Forest (central Adirondacks) reveals that the primary indices of acid

deposition, pH and the acid anions sulfate and nitrate, are all exhibiting significant improvements over the past 35 years (Figure 3). Likewise, recent research from 74 lakes in Northeast (60% in the Adirondacks) illustrate that several acid indicators, such as sulfate concentration and acid neutralizing capacity, are exhibiting significant recovery (Strock et al 2014).





There are several methods used to analyze sulfate in the lab. The AWI uses ion chromatography to separate and quantify negatively charged ions from a waters sample. Sulfate is measured by injecting the water sample through an ion chromatograph where the sulfate is separated from other negatively charged ions by a selective resin and then quantified with a voltmeter.

Sodium and Chloride

Lakes in the Adirondack region have naturally low concentrations of chloride and sodium, with median background concentrations of 0.2 mg/L and 0.5 mg/L respectively (Kelting et al. 2012). However, wide spread use of road deicers (primarily sodium chloride) have significantly increased the concentration of these chemicals in the environment. Each year approximately 98,000 metric tons of road deicers are spread across state roads in the Adirondacks. (Kelting and Laxson 2014). Recent research by Kelting et al. (2012) highlighted that concentrations of sodium and chloride in Adirondack Lakes are directly proportional to the density of state roads within the watershed.

Road salt can have direct and indirect effects on aquatic ecosystems. It is clear that the direct impact of road deicers on organisms is not well understood, and is highly variable across taxa. Based on laboratory studies the lethal concentration for most aquatic organisms is much higher than concentrations encountered in a lake environment. However, at times lethal concentrations can be encountered in near-road environments that receive direct run-off such as road side streams or vernal pools (reviewed by Findlay and Kelly 2011; Kelting and Laxson 2010).

Indirect effects to aquatic systems have also been documented. For example, sodium actively displaces base cations (Ca, K, and Mg) as well as heavy metals from the soil, potentially elevating their concentration in surface waters. In some extreme cases, excessive road salt pollution can interfere with lake stratification due to salts effect on water density (Bubeck et al. 1971; Kjensmo 1997). Sodium and chloride impart an undesirable taste to drinking water. The US EPA has guideline of 250 mg/L for chloride and 20 mg/L for sodium, but these are for drinking water supplies only and are not enforceable standards. Although it is difficult to use sodium and chloride concentration to assess impact to the aquatic

environment, the concentration of these chemicals serve as a reliable index for the level of hydrologic connectivity a lake has with salted roads in its watershed. We propose the boundaries presented in Table 7 as a general guideline for gauging road salt influence on a lake.

 Table 7. Assessment of road salt influence on Adirondack lakes based on chloride concentration.

Chloride (mg/L)	Road Salt Influence
Less than 1.0	Not significant
1 - 5 mg/L	Present - Low
5 - 20	Moderate
20 - 50	High
 1 - 5 mg/L 5 - 20	Present - Low Moderate

Sodium and chloride are analyzed separately from each other in the laboratory using two automated methods. Chloride is measured alongside sulfate with ion chromatography. Sodium is analyzed with an atomic emission spectrophotometer. The water sample is introduced into a very hot argon plasma torch that excites the sodium ion into a higher energy state. When the ion relaxes it emits light in a characteristic wavelength, the intensity of which is proportional to the amount of sodium in the sample.

Calcium

Calcium plays an important role in lake ecology because it is an essential element for the structure and physiology of all organisms. For example, calcium is needed for bones and teeth in vertebrates, exoskeletons and shells in invertebrates, and biochemical regulation in plants to name a few. The ultimate source of calcium in lakes is weathering of the bedrock, and to a lesser extent atmospheric deposition (dust). The majority of lakes in the Adirondacks have low concentrations of calcium, typically between 2 and 5 mg/L. The reason for the relatively low concentration is that the granite bedrock under the Adirondacks weathers slowly resulting in a low rate of calcium generation. There are however many lakes in the Adirondacks that reside on calcium rich bedrock resulting in much higher calcium concentrations, examples include Augur Lake (Ca = 11 mg/L), Long Pond (Ca = 13 mg/L), and Lake Colby (Ca = 12 mg/L).

Environmental stressors can affect the calcium concentration of lakes. Research on northeastern lakes has demonstrated that acid deposition has depleted calcium stores in soils leading to reduced calcium concentrations over time (Strock et al. 2014; Keller et al. 2001). The influence that road salting has on calcium concentrations is an emerging research area. Some municipalities utilize calcium chloride to deice roads, thereby increasing the calcium content of the watershed. When rock salt is used as a deicer the sodium can displace calcium in the soil, potentially leading to increase calcium concentrations in the ground and surfaces water. Kelting and Laxson (2014) observed that the combined concentration of calcium, magnesium and potassium in lakes with paved roads in the watershed was 62% greater than lakes with no paved roads.

Calcium concentration is a good indicator of the overall habitat suitability for the zebra mussel, a non-indigenous species from Eurasia that has been spreading through the world. Researchers have reported that the minimum calcium concentrations needed to support a viable zebra mussel population is in the range of 12-20 mg/L, lower than most, but not all lakes in the Adirondacks (Whittier et al. 2008).

Calcium concentration is analyzed alongside sodium and other metals using an atomic emission spectrophotometer.



Photo 7. Loading road salt (NaCl) into the back of a plow truck (A.P.)

St. Regis Chain: 2017

Conductivity

Conductivity is a measurement of the ability of a water sample to conduct electricity. Pure H_2O is a poor conductor of electricity. The ability of water to conduct electricity increases as the concentration of dissolved ions in the water increases. Thus, conductivity is considered a strong indicator of the amount of dissolved ions in water. Typically the conductivity of a clean undeveloped lake in the Adirondacks is in the range of 10-25 μ S/cm. Elevated conductance may be indicative of road salt pollution, faulty septic systems or the influence of bogs and wetlands in the watershed. Conductivity is a

very useful surrogate when the relationships between ion concentrations and conductivity are known. For example, conductivity can be used to estimate sodium and chloride concentrations in streams (Daley et al. 2009).

Conductivity is measured in the laboratory with a conductivity meter. The instrument applies an alternating electrical current to two electrodes immersed in the water sample and measures the resulting voltage. Electrical conductance is influenced by water temperature so all measurements are scaled to the conductance at 25° C, known as specific conductivity.



Photo 8. Preparing to deploy a submersible data logger in Upper St. Regis Lake.

Findings: Lower St. Regis

Temperature and Dissolved Oxygen

The thermal stratification pattern for Lower St. Regis Lake is typical for shallow Adirondack lakes (Figure 4). Surface water temperature increased from a low of 11.5°C (52.7°F) degrees on April 27th to a maximum observed temperature of 24.2°C (75.6°F) on August 3rd. The epilimnion depth (surface stratum of uniform temperature) ranged from less than one meter in late April to as large as 10 meters during the isothermal condition of late October. The temperature of the bottom water increased from 8.1°C (46.5°F) in late April to as high as 12.7°C after fall turnover (54.9 °F).

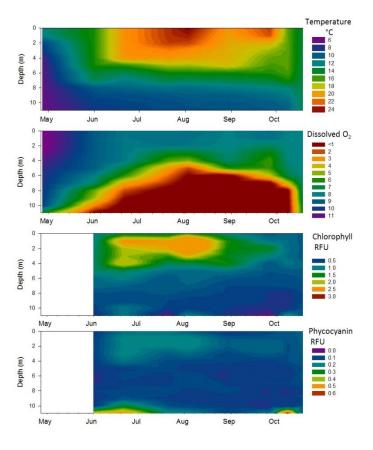


Figure 4. Vertical profiles of Lower St. Regis Lake during the ice free period of 2017. From top to bottom: temperature, dissolved oxygen, chlorophyll-a relative fluorescence units (RFU), and phycocyanin RFU.

Lower St. Regis Lake experienced severe oxygen depletion in the bottom stratum of the lake during 2017

(Figure 4). Dissolved oxygen concentration above the bottom sediments was 6.2 mg/L on April 27th and was depleted to 0.65 mg/L the following month. By early August nearly 60% of the water column of the lake was hypoxic (D.O less than 2.0 mg/L) and 35% of the column was anoxic (essentially no oxygen). The oxygen depletion pattern in Lower St. Regis Lake is an annual occurrence. It was first documented by the EPA in 1972, but has likely been occurring long before that (EPA 1974). Oxygen depletion of this nature occurs when the bottom sediment is rich in organic material. The organic material may have been produced within the lake itself (algae, plankton, etc.), or from the watershed (leaves, terrestrial debris, sewage etc.). Lakes with small hypolimnion volumes relative to the sediment surface area, like Lower St. Regis, are particularly vulnerable to anoxia. It is quite possible that bottom water anoxia is a natural occurrence for this lake; however, long term nutrient pollution would certainly exasperate the situation. The combination of warm surface water and hypoxic bottom water has contributed to, if not driven, the loss of the brook trout fishery in the lake. For example, brook trout and lake trout have temperature preferences of 16°C and 10°C respectively (Coutant 1977, Smith 1985), these preferred temperatures can be found in the deeper waters of Lower St. Regis but the dissolved oxygen in these areas are well below the optimal range of 5 mg/l (Spoor 1990).

The anoxic patter in Lower St. Regis Lake creates reducing conditions along the bottom which drastically affect the concentration of other chemical parameters as described later in this section.

Phosphorus

Surface water phosphorus concentration was greatest in Lower St. Regis Lake. In 2017 surface concentrations ranged from 8.9 to 17.4 μ g/L with a seasonal average of 13.3 μ g/L (Table 8). This value is greater than 65% of lakes that participated in the 2017 Adirondack Lake Assessment Program (n=67; Laxson et. al 2018). Total phosphorus concentration in the bottom stratum was

Table 8. Chemistry and water quality parameters of the surface and bottom water of Lower St. Regis Lake during the 2017 field season.

Water Quality	Lower St. Regis: 2017									
Indicator	4/27	6/1	6/21	7/2	8/3	8/30	9/27	10/19	Avg.	
	Surface Water (0-2 meter)									
Transparency (m)	1.8	2.1	2.0	1.8	2.0	2.0	2.3	1.0	1.9	
Chlorophyll (µg/L)	4.9	2.4	10.6	8.3	8.7	4.7	4.7	2.7	5.9	
Total Phosphorus (μg/L)	17.4	13.1	14.3	16.4	13.2	10.8	8.9	12.5	13.3	
Nitrate (µg/L)	46.0	BDL	2.2	BDL	BDL	BDL	BDL	4.3	17.5	
NH4 (μg/L)	19	18	8	5	15	11	6	84	21	
Total Nitrogen (mg/L)	0.3	0.4	0.2	0.3	0.2	0.2	0.2	0.3	0.3	
Color (Pt-Co)	56.8	56.8	63.2	72.9	69.9	69.7	63.2	124.0	72.1	
DOC (mg/L)	4.5	4.6	4.5	6.1	6.1	6.0	5.6		5.3	
pH (s.u.)	7.1	6.9	7.2	7.3	7.4	7.1	7.3	7.1	7.2	
Alkalinity (mg/L)	12.8	13.5	13.5	11.7	14.7	14.6	17.1	16.8	14.3	
Sulfate (mg/L)	3.2	3.0	3.1	1.1	2.8	2.6	2.8	2.7	2.6	
Conductivity(µS/cm°25)	100.0	85.1	89.4	75.4	79.2	87.8	90.3	94.7	87.7	
Chloride (mg/L)	16.6	17.4	18.7	19.8	17.4	18.4	19.8	20.3	18.5	
Calcium (mg/L)	4.0	4.3	4.6	4.1	4.2	4.6	*16.1	5.1	5.9	
Sodium (mg/L)	8.0	8.8	9.3	8.2	7.6	8.9	5.5	9.1	8.2	
				<u>Bottom</u> V	Vater (10.	5 meters)				
Total Phosphorus (μg/L)	15.3	29.0	31.5	31.7	35.3	59.2	30.1	18.2	31.3	
Nitrate (µg/L)	67.1	12.0	8.0	BDL	BDL	BDL	BDL	5.0	11.5	
NH4 (μg/L)	21	94	197	548	659	701	779	122	390	
Total Nitrogen (mg/L)	0.4	0.4	0.3	0.6	0.7	0.9	0.9	0.3	0.6	
Color (Pt-Co)	79.3	175.8	198.4	246.6	227.0	298.1	291.7	160.0	209.6	
DOC (mg/L)			3.9			4.2	4.2		4.1	
pH (s.u.)	7.1	6.4	6.6	6.7	6.9	6.7	6.9	7.1	6.8	
Alkalinity (mg/L)	13.3	14.4	14.3	21.0	23.1	25.0	25.3	17.2	19.2	
Sulfate (mg/L)	3.0	3.1	2.8	2.6	0.4	0.3	0.1	2.2	1.8	
Conductivity(µS/cm°25)	98.0	95.6	95.1	113.9	124.7	117.0	131.4	96.2	109.0	
Chloride (mg/L)	20.3	19.1	19.6	16.6	17.7	19.4	19.8	20.3	19.1	
Calcium (mg/L)	4.7	4.8	4.9	5.5	5.8	7.0	6.8	5.1	5.6	
Sodium (mg/L)	9.8	9.6	9.5	9.5	9.0	9.5	9.3	9.0	9.4	

markedly elevated, and ranged from 15.3 to 59.8 μ g/L. The steady increase in bottom water phosphorus correlates with the development of anoxic conditions. Depleted oxygen near the bottom creates a reducing environment that allows phosphate to be released out of

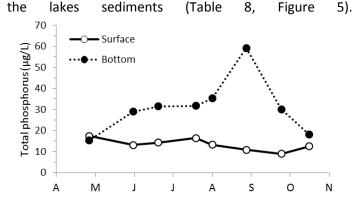


Figure 5. Concentration of total phosphorus in the surface and bottom water of Lower St. Regis Lake during the 2017 field season.

Historically, concentrations of total phosphorus have decreased in Lower St Regis Lake. In the middle of the 19th century Lower St. Regis was experiencing significant water quality degradation (Fuhs et al. 1977). The accelerated lake productivity was due largely to the ineffective management of waste water from the Paul Smith's College campus, which opened in 1946, as well as the historical Paul Smiths Hotel that operated from 1859 to the early 1940's. Fortunately, major environmental progress was made in 1967 when the Paul Smith's College waste water treatment facility went online. The system was considered state of the art for its time, and provided primary (solid settling) and secondary (aerobic digestion) treatment to the college's waste stream; however, the nutrient rich effluent from the plant was discharged into Weller Brook, a primary tributary to the lake. The phosphorus in the effluent stream was responsible for a series of dense cyanobacteria blooms that occurred in the late 1960's and early 1970's (Photo 9)

In 1974 the effluent was diverted from Weller Brook to sand percolation pits for 100% phosphorus removal. Since that time the lake has experienced a statistically significant decrease in the average summer concentration of phosphorus in the surface water, decreasing from $83\mu g/L$ in 1968 to as low as 9.8 $\mu g/L$ in 2015 (P < 0.001, tau = -0.48; Figure 6).

Nitrogen

Nitrate (NO₃-N) and ammonium (NH₄-N) are highly variable during a lakes seasonal cycle as well as across lake depths. For example, a combination of watershed inputs during the snow melt period and low plant uptake typically results in high concentrations of both forms of inorganic nitrogen in the spring. During thermal stratification, the concentration of inorganic nitrogen may become very low due to sequestration by phytoplankton and plants. This pattern is evident in Lower St. Regis Lake. Concentration of nitrate and ammonium in the surface water were greatest in the April 27th sample, at 46 and 19 μ g/L respectively, but decreased to below, or near, the analytical detection level by September (Table 8).



Photo 9. Aerial view of a cyanobacteria bloom on Lower St. Regis Lake, August 5th, 1971. (G.W. Fuhs, NYSDOH).

The typical pattern in the bottom water of stratified lakes is quite different, especially in oxygen depleted water. In anoxic conditions chemoautotrophic bacteria uses the potential energy of nitrate to power their own metabolism, resulting in conversion of nitrate to ammonium. Concurrently, ammonium generated by bacterial decomposition is released from the lake sediments. The result is a rapid decrease in nitrate and a

St. Regis Chain: 2017

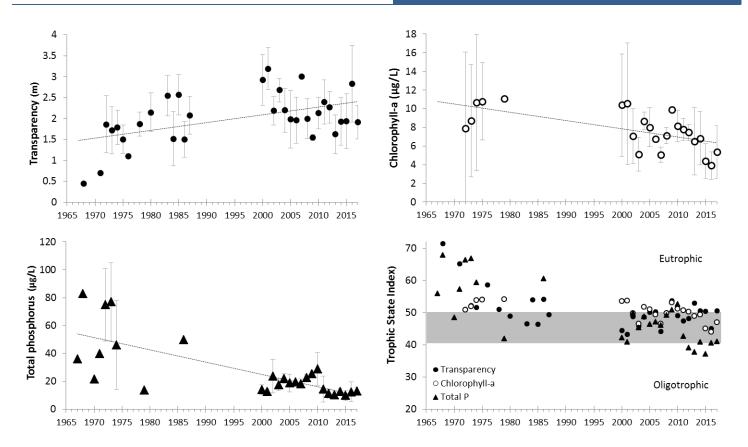
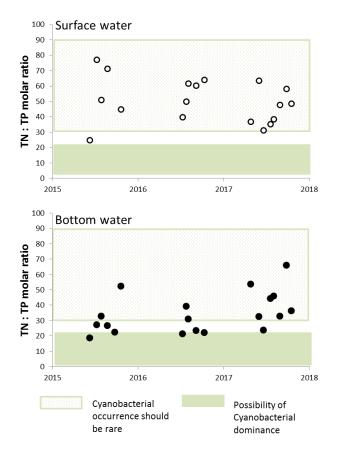
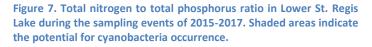


Figure 6. Time series of annual average values for trophic indicators in Lower St. Regis Lake. Error bars represent 1 SD (standard deviation) of the mean. Dashed line indicates a significant historical trend (P<0.05).

simultaneous increase in ammonium. This cycle is evident in the bottom water of Lower St. Regis. Nitrate concentration was greatest in April at 67 μ g/L and decreased to values below detection by early July. Ammonium, however, was lowest in April at 21 μ g/L and increased to as high as 779 μ g/L in late September (Table 8).





The ratio of total nitrogen to total phosphorus (TN:TP) in Lower St. Regis Lake ranged from 31 to 61 in the surface water and 24 – 66 in the bottom water. These results suggest that Lower St. Regis Lake is neither phosphorus nor nitrogen limited, and that cyanobacterial dominance should be rare. In fact, over the last three years the TN:TP ratio in the surface water of Lower St. Regis was in the range were cyanobacterial occurrence should be rare on 95 % of observations, in the bottom water the TN:TP suggest cyanobacteria occurrence should be rare on 58% of the observations (Figure 7).

Photosynthetic Pigments

Chlorophyll-a

Lower St. Regis Lake had the greatest concentration of chlorophyll-a in the surface waters of the St. Regis Chain during 2017. Concentration of the algal pigment was highly variable, and ranged from 2.4 to 10.6 μ g/L with a seasonal average of 5.9 μ g/L (Table 8). Profile measurements of chlorophyll-a taken in the field reveal that the phytoplankton population of the lake is centered in the upper three meters of water, and are most prevalent from the middle of June until the end of August (Figure 4). Although the chlorophyll concentrations of the lake exhibited a great deal of variation, the annual average concentration has experienced a significant downward trend since the early 1970's (Figure 6; P = <0.001; tau = 0.51). Similar to the trend in phosphorus concentration, it's likely that the historical decrease in algal productivity is related to the improvements in PSC waste water treatment that took place between 1967 and 1974.

Phycocyanin

Phycocyanin is a photosynthetic pigment exclusive to the cyanobacteria, thus the strength of its detection serves as a relative indicator of cyanobacteria biomass. We detected phycocyanin throughout the water of Lower St. Regis Lake, but at relatively low concentrations. The greatest density of cyanobacterial pigment was encountered right of the bottom during June and October (Figure 4). Many species of cyanobacteria are adapted to photosynthesis in very low light condition, so it is not uncommon to find the populations centered deeper than common eukaryotic algae. The cyanobacteria species that were observed in the lake in 2017 were *Gloeotrichia* and *Planktothrix*.

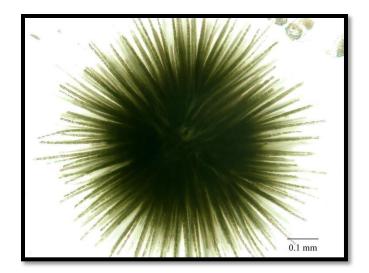


Photo 10. Microscope view of *Gloeotrichia*, a common cyanobacteria colony in Lower St. Regis Lake (Wikipedia).

Transparency

The transparency of Lower St. Regis Lake is the lowest of the lakes in the chain. In 2017 the transparency exhibited little dissimilarity, and ranged from 1.8 to 2.3 meters in depth with a seasonal average of 1.9 meters (Table 8). The 2017 average transparency is lower than 90% of the lakes that participated in the Adirondack Lake Assessment Program (n=67; Laxson et al. 2018). The relatively low transparency of the lake is due in part to algal abundance, but it's primarily a function of the high amount of dissolved organic material in the water from the surrounding wetlands (see Color). Historically, the transparency of Lower St. Regis Lake has exhibited signs of improvement. Limited observation is the late 1960's and early 1970's recorded transparency depths in the 0.5 to 0.7 meter range, since that time observations were most commonly in the range of 1.5 to 2.5 meters. Overall we detected a weak, but a statistically significant, trend in the historical transparency data (P = 0.03; tau = 0.27; Figure 6).

Trophic Status

Overall, the trophic status of Lower St. Regis Lake is best classified as mesotrophic. The Carlson's Trophic State Index (TSI) based on chlorophyll-a (47) and total phosphorus (41) both identify the lake as mesotrophic;

however, the TSI for transparency (51) identifies the lake as being eutrophic. A disparity such as this is common when a lake contains non-algal turbidity or a high amount of dissolved organic material (see Color). Dissolved organic material rapidly attenuates light and reduces transparency depth, but does not necessarily imply increased productivity (Carlson and Havens 2005). Over the past 50 years the trophic state of Lower St. Regis Lake has exhibited encouraging signs of recovery. For example, 74% of the trophic observations between 1967 and 1987 identified the lake as eutrophic (n=27), while only 24% of observations identified the lake as eutrophic during the period of 2000 - 2017 (n=54; Figure 6).

Color

Although color can be affected by a number of dissolved and suspended particles, the color of Lower St. Regis is derived primarily from dissolved organic material, giving the water a brown colored stain. Lower St. Regis Lake is a highly stained water body; with color values more than double that of Spitfire and Upper St. Regis Lake. The source of the color is the lakes watershed, 13% of which is wetlands. In 2017 the color of Lower St. Regis ranged from 56.8 to 124 PtCo units in the surface water, and 70 to 298 in the bottom water (Table 8). Color data only exists back to 2002. Since that time the annual average color of the lake has ranged from 24.2 to 72.5 PtCo units with so significant trend in the data (Figure 8).

Acidity

Lower St. Regis Lake is a circumneutral waterbody, whose acidity has not been negatively affected by acid deposition. The pH of the surface water ranged from 6.9 to 7.4 units in 2017. The pH values were slightly lower (more acidic) in the bottom stratum, where they ranged from 6.4 to 7.1 units (Table 8). The difference between the surface and bottom acidity is a common feature in lakes because photosynthesis near the surface tends to elevate pH, while decomposition near the bottom tends to depress pH. Historically, the acidity of lower St. Regis Lake has been fairly stable, with annual averages typically between 6.5 and 7.5 pH units.

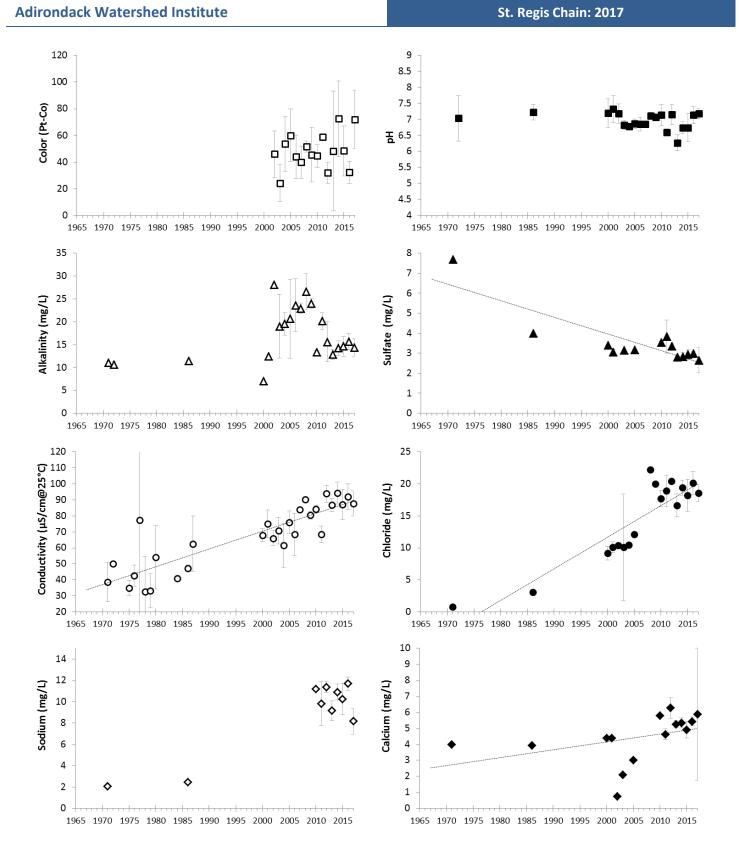


Figure 8. Time series of annual average values for selected water quality indicators in the surface water of Lower St. Regis Lake. Error bars represent 1 SD of the mean. Dashed lines indicate a significant historical trend (P<0.05).

The water of Lower St. Regis Lake is adequately buffered from changes in acidity. The alkalinity of the lake ranged from 11.7 to 17.1 mg/L in the surface, and from 13.3 to 25.3 mg/L in the bottom (Table 8). Historically the alkalinity of the lake has typically been observed to be between 10 and 20 mg/L; however, a series of unusually high values were recorded in the years 2002-2009. We suspect some of these values are erroneous (Figure 8).

Although Lower St. Regis Lake has not exhibited signs of acidification, we know the impact of acid deposition on the watershed has diminished over the last several decades by examining the concentration of the sulfate ion. During acid deposition events, hydrogen (H+) and sulfate (SO_4^{-3}) are deposited across the landscape and eventually make it into the lake. The concentration of sulfate in Lower St. Regis Lake has exhibited a significant downward trend over time, and has diminished from of as high as 7.7 mg/L in 1971 to as low as 2.6 mg/L in 2017 (P = 0.008, tau = -0.54; Figure 8).

Sodium and Chloride

Sodium and chloride concentrations in Lower St. Regis clearly illustrate that the chemistry of the lake is impacted by road salt. Research by Kelting et al. (2012) determined that unimpacted lakes in the Adirondack region typically have sodium and chloride concentrations near 0.5 mg/L and 0.2 mg/L respectively. In Lower St. Regis these chemicals averaged 8.2 mg/L and 18.5 mg/L in 2017, suggesting that the lake has approximately 90 times more chloride than background concentrations alone (Table 8). Although the sodium concentration of the lake was 75% lower in 1971, we were not able to statistically define a trend over time due to the paucity of sodium data through the 1990's. Chloride concentration has exhibited a significant increase over time (P = 0.008, tau = 0.63; Figure 8). For example, the chloride concentration in 1971 was observed to be 0.8 mg/L, the value increased to around 10mg/L in the early 2000's, and is currently approaching 20 mg/L.

The primary source of sodium and chloride in Adirondack waters is from winter road maintenance, particularly on

NYS roads where road salt application averages 23 tons/lane mile (Kelting and Laxson 2010; Kelting et al. 2012; NYSDOT 2012 pers. com). Given that there are 6 miles of state roads in the Lower St. Regis Lake watershed, we can expect an annual salt load of approximately 460 tons. In addition to state roads, the roads and walkways on the 50 acre Paul Smith's College campus are heavily salted and likely play a large role in the elevated salt concentrations in the lake.

Calcium

Calcium concentration in Lower St. Regis Lake ranged from 4.0 to 5.1 mg/L in the surface water and 4.7 to 7.0 mg/L in the bottom water in 2017. The unusually high value of 16.1 mg/L detected in the September surface water sample is an outlier, and likely represents field contamination or laboratory error (Table 8). Historically, average calcium concentrations in the surface water have ranged from less than 1 mg/L to 6.3 mg/L with a significant positive trend detected in the data (P =0.008, tau = 0.52; Figure 7).

Conductivity

The conductivity of the surface water of Lower St. Regis ranged from 75 to 100 µS/cm and averaged 87.7 µS/cm in 2017. Conductivity values in the bottom water were even greater, and averaged 109 µS/cm. The elevated conductivity near the bottom is related to the anoxic conditions that liberate dissolved ions from the sediments (Table 8). The conductivity of Lower St. Regis is approximately 6 times higher than the values we encounter in least impacted lakes (Laxson et al. 2018). Elevated conductance can be attributed to many sources, including development, septic input, permitted discharge, and road salt. In the case of Lower St. Regis, the high electrical conductance is primarily derived from road salt application in the watershed. In the 1970's conductivity values were in the range of 35 to 50µg/L, since that time conductivity has exhibited a strong increasing trend (P <0.0001; tau = 0.70; Figure 8), similar to the concentrations of sodium and chloride.

St. Regis Chain: 2017

Findings: Spitfire Lake

Temperature and Dissolved Oxygen

The thermal stratification pattern for Spitfire is typical for shallow Adirondack lakes (Figure 9). Surface water temperature increased from a low of 12.7°C degrees on April 27th (54.9°F)to a maximum observed temperature of 23°C on July 21st (73.4°F). The epilimnion depth (surface stratum of uniform temperature) ranged from less than one meter in late April to as large as 9 meters during the isothermal condition of late October. The temperature of the bottom water increased from 6.3°C (43.3 °F) in late April to as high as 13.2°C (55.8 °F) after fall turnover.

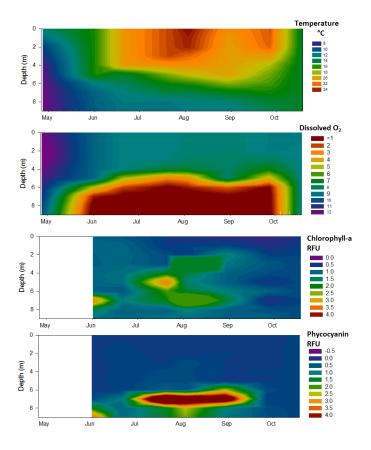


Figure 9. Vertical profiles of Spitfire Lake during the ice-free period of 2017. From top to bottom: temperature, dissolved oxygen, chlorophyll-a relative fluorescence units (RFU), and phycocyanin RFU.

Spitfire Lake also experienced severe oxygen depletion in the bottom stratum of the lake during 2017 (Figure 9). Dissolved oxygen concentration above the bottom sediments was 9.8 mg/L on April 27th (79% saturated) and was depleted to 0.14 mg/L the following month (1.2% saturated). By early August nearly 44% of the water column was hypoxic (D.O less than 2.0 mg/L) and 22% of the column was anoxic (essentially no oxygen). Oxygen depletion of this nature is a function the quantity of organic material in the bottom sediment as well as basin morphometry. It's quite possible that the anoxic condition of Spitfire Lake is a natural occurrence resulting from its relatively shallow basin and elliptic sinusoid morphometry. In shallow lakes the hypolimnetic volume is small relative to the sediment surface area were microbial decomposition occurs, this skewed ratio results in rapid oxygen depletion (Molot et al. 1992; Mathias and Barica 1980). The rate of oxygen depletion is compounded by overall trophic status. For example, Mathias and Barica (1980) found that sediments from eutrophic lakes consumed oxygen 3 times faster than sediments from oligotrophic lakes.

The anoxic pattern in Spitfire Lake creates reducing conditions along the bottom which drastically affect the concentration of other chemical parameters as described later in this section.

Phosphorus

In 2017 the surface concentrations of total phosphorus ranged from 5.5 to 11.8 μ g/L with a seasonal average of 8.4 μ g/L (Table 9). Total phosphorus concentration near the bottom was substantially elevated, and ranged from 12.1 to 57 μ g/L. The steady increase in bottom water phosphorus correlated with the progression of anoxia described above. Depleted oxygen near the bottom creates a reducing environment that essentially allows dissolved reactive phosphate to leak out of the lakes sediments (Table 9).

We examine the concentration of phosphorus species at each meter of depth from the surface to the bottom on June 21^{st} 2017. We found that the concentration of dissolved reactive phosphate (PO₄⁻³) only exhibited a slight enrichment in the bottom water, where it increased from an average of 3.5 µg/L in the epilimnion to an

Table 9. Chemistry and water quality indicators of the surface and bottom water strata of Spitfire Lake during the 2017 field season. BDL = below analytical detection.

Water Quality	Spitfire: 2017										
Indicator	4/27	6/1	6/21	7/2	8/3	8/30	9/27	10/19	Avg.		
	Surface Water (0-2 meter)										
Transparency (m)	2.9	3.0	2.5	3.5	3.2	3.1	4.5	3.1	3.2		
Chlorophyll (µg/L)	6.8	5.8	4.4	2.1	1.9	3.3	2.5	5.2	4.0		
Total Phosphorus (μg/L)	8.2	11.3	11.8	8.5	5.8	6.2	5.5	10.1	8.4		
Nitrate (µg/L)	38.0	BDL	BDL	BDL	BDL	BDL	8.0	7.7	±6.7		
NH4 (μg/L)	BDL	3	3	5	BDL	14	1	46	±7.3		
Total Nitrogen (mg/L)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		
Color (Pt-Co)	31.1	24.6	34.3	27.9	24.6	40.7	21.4	34.3	29.9		
DOC (mg/L)	3.1	3.0	2.9	3.3	3.5	3.5	3.5		3.3		
рН (s.u.)	7.0	6.6	7.0	7.3	7.1	7.0	7.2	7.2	7.0		
Alkalinity (mg/L)	10.5	10.7	10.1	10.5	11.7	11.5	12.7	14.1	11.5		
Sulfate (mg/L)	2.6	2.7	2.5	2.4	2.6	2.4	2.4	1.9	2.4		
Conductivity(µS/cm°25)	48.6	44.8	44.4	44.0	44.0	45.0	46.6	48.9	45.8		
Chloride (mg/L)	7.6	7.5	7.4	7.6	7.7	7.7	7.9	7.7	7.6		
Calcium (mg/L)	2.8	2.8	3.0	3.0	3.3	3.1	3.4	3.1	3.1		
Sodium (mg/L)	3.9	3.9	4.2	4.2	4.4	4.1	4.1	3.8	4.1		
				<u>Bottom</u>	Water (~9) meters)					
Total Phosphorus (μg/L)	12.1	46.3	56.9	44.3	48.3	46.8	58.6	17.1	41.3		
Nitrate (µg/L)	38.1	BDL	BDL	BDL	BDL	BDL	BDL	9.7	±6		
NH4 (µg/L)	40	83	50	26	27	1050	1700	50	493		
Total Nitrogen (mg/L)	0.3	0.4	0.6	0.4	0.4	1.3	1.6	0.2	0.7		
Color (Pt-Co)	43.9	166.2	159.8	282.0	294.9	349.6	349.6	31.1	209.6		
DOC (mg/L)			2.4			3.3	3.3		3.0		
рН (s.u.)	7.2	6.2	6.5	6.4	6.5	6.6	6.8	7.2	6.7		
Alkalinity (mg/L)	10.6	11.9	15.9	17.8	19.0	25.8	26.6	14.2	17.7		
Sulfate (mg/L)	2.5	2.1	1.6	1.3	1.4	0.5	0.5	1.9	1.5		
Conductivity(µS/cm°25)	45.1	47.2	56.3	54.5	62.7	90.0	111.5	47.3	64.3		
Chloride (mg/L)	7.2	7.3	7.3	7.3	7.5	7.6	7.5	7.7	7.4		
Calcium (mg/L)	2.8	3.0	3.4	3.7	4.2	4.8	5.3	3.2	3.8		
Sodium (mg/L)	3.8	3.9	4.1	4.0	4.2	4.2	4.0	3.9	4.0		

average of 5.0 μ g/L in the anoxic zone; however, we found that the total phosphorus concentration increased from 13.8 to 43.5 μ g/L (Figure 10). This result demonstrates the rapid cycling of dissolved reactive phosphate that occurs in aquatic systems. The vast majority of total phosphorus in the anoxic stratum is in an organic form, and likely contained within the biomass of the cyanobacteria population that resides in the deep water of Spitfire (See Phycocyanin in this section). Because phosphorus is the limiting nutrient for aquatic productivity, the essential element is rapidly assimilated as it becomes available.

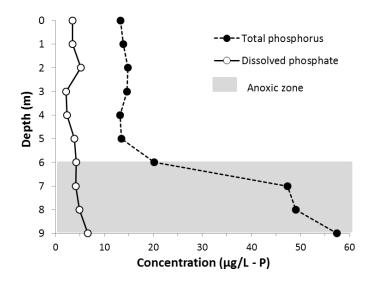


Figure 10. Vertical profile of dissolved reactive phosphate and total phosphorus concentrations across the oxygenated and anoxic zones of Spitfire Lake, June 21st 2017.

Historically, concentrations of total phosphorus in the surface water have ranged from a low of 4.3 μ g/L in 1998 to as high as 62 μ g/L in 1973, with a weak, yet statistically significant downward trend detected in the dataset (P = 0.04; tau = -0.28; Figure 11). Since 2011 annual average concentration has been fairly stable between 7 and 10 μ g/L, we believe this noticeable shift in values around year 2010 is related to the substantial analytical improvements enacted in our lab at that time.

Nitrogen

Nitrate (NO₃-N) and ammonium (NH₄-N) in Spitfire follow

the same pattern observed in Lower St. Regis Lake. In the spring, a combination of snow melt and low autotroph utilization results in high surface concentrations of inorganic nitrogen. Concentration of nitrate in the surface water was greatest in the April 27^{th} sample, at 38 μ g/L, but decreased to near the analytical detection for the majority of the summer (Table 9). The pattern in the bottom water of Spitfire is guite different. In the anoxic conditions chemoautotrophic bacteria uses the potential energy of nitrate to power their own metabolism, resulting in conversion of nitrate to ammonium. Simultaneously, ammonium generated by bacterial decomposition is released from the lake sediments. The result is a rapid decrease in nitrate and a concurrent increase in ammonium. This cycle is evident in the 2017 data. Nitrate concentration was greatest in April at 38.1 μ g/L and decreased to values below detection by early June. Ammonium, however, was lowest in April at 40

The ratio of total nitrogen to total phosphorus (TN:TP) in Spitfire Lake ranged from 34 to 71 in the surface water during 2017, suggesting that the surface waters are not nitrogen limited, and occasionally phosphorus limited. In the bottom water however, TN:TP ranged from 19 to 61, indicating a greater probability of nitrogen limitation. Over the last three years the TN:TP ratio in the surface water of Spitfire was in the range were cyanobacterial occurrence should be rare on 94 % of observations, in the bottom water the TN:TP suggest cyanobacteria occurrence should be rare on only 17% of the observations (Figure 12).

 μ g/L and increased to as high as 1,700 μ g/L in late

Photosynthetic Pigments

Chlorophyll-a

September (Table 9).

Spitfire Lake had the second highest concentration of chlorophyll-a in the surface waters of the chain during 2017. Concentration of the algal pigment was greatest in the April sample at 6.8 μ g/L and lowest in early August at 1.9 μ g/L (Table 9). Profile measurements of chlorophyll-a taken in the field revealed that the phytoplankton

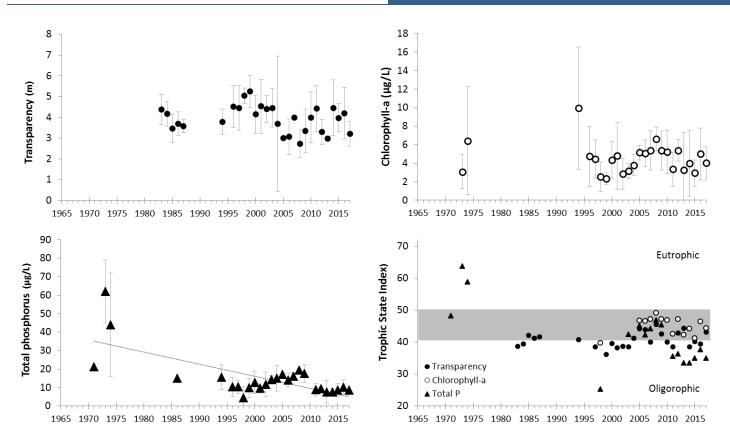
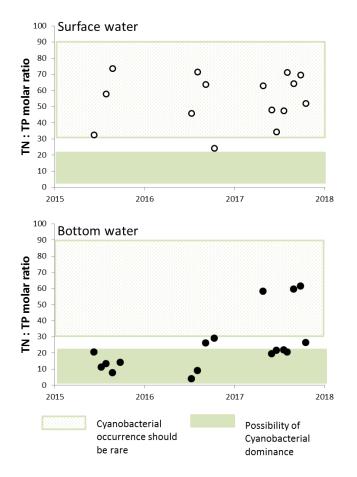


Figure 11. Time series of annual average values of key trophic indicators of Spitfire Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant trend in the historical data (P<0.05).

St. Regis Chain: 2017

population of the lake was centered at approximately 5 meters of water during the month of July (Figure 9). Historically, the annual average chlorophyll concentrations in the lake have exhibited a great deal of variation, ranging from 2.1 to 9.9 μ g/L with no significant trend detected in the data (Figure 11).





Phycocyanin

Phycocyanin is a photosynthetic pigment exclusive to the cyanobacteria, thus the strength of its detection serves as a relative indicator of cyanobacteria biomass. Although we detected phycocyanin throughout the water column of Spitfire, the concentration was exceptionally high at 7 meters of depth from July to mid-September (Figure 9). The deep water bloom of cyanobacteria is primarily comprised of the genus *Planktothrix* (formerly *Oscillatoria*). *Planktothrix* thrives in the bottom stratum

of Spitfire Lake for the following reasons: (1) They contain accessory pigments (phycoeytherin and phycocyanin) that allow them to photosynthesis at very low light levels, (2) The anoxic conditions are beneficial for the species because the nitrogen fixing enzyme nitrogenase is deactivated by the presence of oxygen, and (3) there is an adequate supply of phosphorus and other key elements released from the sediments during anoxic conditions.

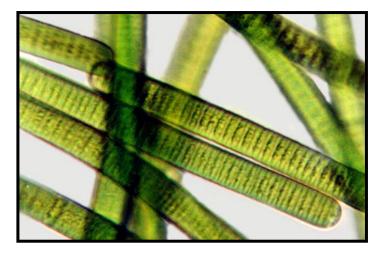


Photo 11. Microscope image of *Planktothrix species*.

One of the more striking characteristics of *Planktothrix* is its ability to change its position in the water column through buoyancy control. When conditions deteriorate in the bottom stratum or a key element becomes unavailable, Planktothrix can construct proteinaceous gas filled inclusions (gas bladders) and float to the surface. If the organisms encounter improved conditions at the surface their photosynthetic rate increases. The fixed carbon stored within their cells increases, as does the turgor pressure within the cell, causing the gas bladders to collapse and sinking the population back down to the depths (Reynolds et al. 1987; Walsby 1977). It is for these reasons that surface blooms of cyanobacteria can occur quickly in Spitfire Lake. The population is typically present during the summer at depths of 7 to 9 meters; however, they occasionally float to the surface. A large proportion of the cells will break the surface tension of the water and not able to sink back down, these individuals are pushed by the wind and congregate on the leeward side

of the lake. In addition, each cell is covered in a mucus membrane to protect nitrogenase from oxygen. The sticky mucus can cause thousands of filaments to clump together and blow to shore as large blue-green kernels (Photo 12).

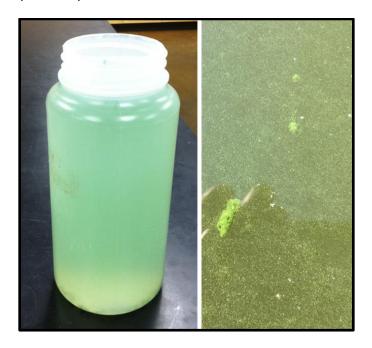


Photo 12. *Plantothrix* sample taken from 1.5 meters off the bottom of Spitfire Lake on July 7th, 2016 (left). By August 20th a portion of the population had moved to the surface and subsequently blew into shore near the outlet (right; C. Laxson).

Transparency

The transparency of Spitfire ranged from 2.5 to 4.5 meters and averaged 3.2 meters in 2017 (Table 9). The 2017 average transparency was greater than 42% of the lakes that participated in the Adirondack Lake Assessment Program (n=67; Laxson et al. 2018). Transparency depth tends to be highly variable in Spitfire with annual average depths ranging from as low as 2.7 meters (2008) to as high as 5.2 (1999). For example, average transparency in 2016 (4.2 meters) was a full meter deeper than in 2017 (3.2 meters). Statistical analysis does not reveal and significant positive or negative trend in the historical transparency data (Figure 11).

classified as mesotrophic. The Carlson's Trophic State Index (TSI) based on chlorophyll-a (44) and transparency (43) both identify the lake as mesotrophic; however, the TSI for phosphorus (35) identifies the lake as being oligotrophic. A disparity such as this is common when a lake experiences phosphorus limitation as described earlier in this section under Nitrogen. Although consecutive annual records are limited prior to 2000, the available data suggests that the trophic condition of the lake has improved, particularly as it relates to phosphorus concentration (Figure 11).

Color

Water color is influenced by suspended and dissolved particles in the water that selectively absorb particular wavelengths of light. In the Adirondack region, dissolved organic material (DOM) has a dominating influence on water color. DOM absorbs blue and green light while it reflects yellow and red light, this selective light absorption gives the water a brown appearance. The amount of color in the surface water of Spitfire Lake is not particularly high, and it 2.5 times less than that of Lower St. Regis. In 2017, the color of the surface water of Spitfire ranged from 21.4 to 40.7 PtCo and averaged 29.9 PtCo units. Decomposition and cyanobacteria biomass resulted in up to 100 times more color near the bottom sediments. In 2017 color in the bottom samples ranged from a low of 43.9 Pt-Co units in April to as high as 349.6 in late September (Table 9).

Color data exists back to 1994 for Spitfire. Since that time, the annual average color of the lake has ranged from 12 to 36 PtCo units with no significant trend in the data (Figure 13). Color exhibits a high amount of variability within each year. This is likely related to weather patterns, as high amounts of precipitation wash a greater amount of organic material into the lake.

Acidity

Like the other lakes in the chain, Spitfire Lake is a

Trophic State

Overall, the trophic status of Spitfire Lake is best

St. Regis Chain: 2017

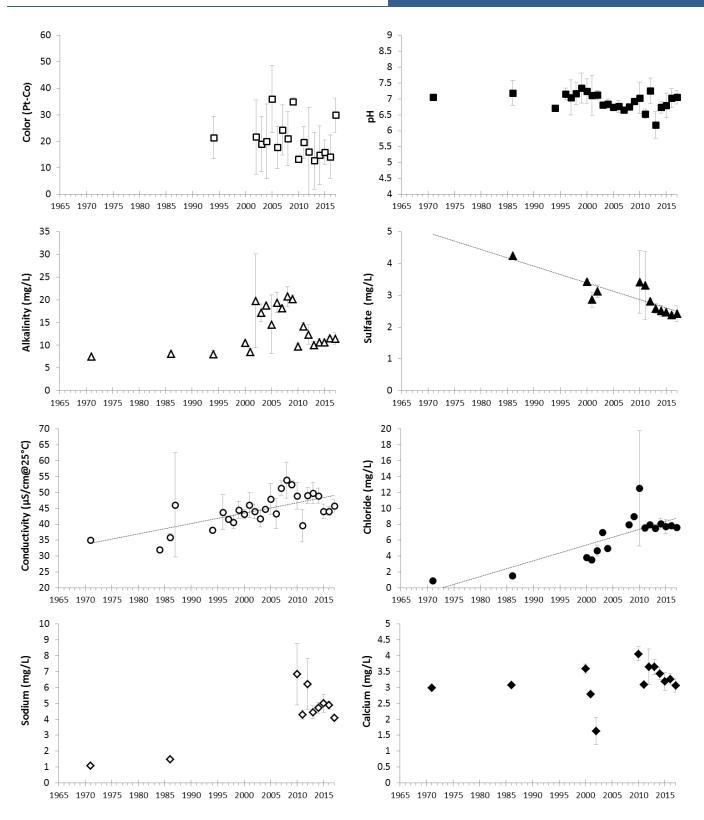


Figure 13. Time series of annual average water quality indicators in the surface water of Spitfire Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant historical trend in the data (P<0.05)

circumneutral water body whose acidity has not been negatively affected by acid deposition. The pH of the surface water ranged from 6.6 to 7.3 units in 2017. The pH values were slightly lower (more acidic) in the bottom water, where they ranged from 6.2 to 7.2 units (Table 9). Historically, the acidity of Spitfire has been unwavering, with annual averages typically between 6.5 and 7.5 pH units.

The water of Spitfire Lake is adequately buffered from changes in acidity. The alkalinity of the lake ranged from 10.1 to 14.1 mg/L in the surface, and from 10.6 to 26.6 mg/L in the bottom stratum (Table 9). Historically, the alkalinity of the lake has typically been observed to be between 8 and 15 mg/L; however, a series of unusually high values were recorded in the years 2002-2009. We suspect some of these values may be in inaccurate (Figure 13).

Although acid deposition has not substantially reduced the pH of Spitfire Lake, we know its impact on the watershed has diminished over the last several decades by examining the concentration of the sulfate ion. During acid deposition events hydrogen (H+) and sulfate (SO_4^{-3}) are deposited across the landscape and eventually make it into the lake. The concentration of sulfate in Spitfire has exhibited a significant downward trend over time, and has decreased from of as high as 4.24 mg/L in 1986 to as low as 2.5 mg/L in 2015 (P = 0.002, tau = -0.82; Figure 13). We believe this decrease is directly related to atmospheric pollution regulations enacted in the early 1990's.

Sodium and Chloride

Sodium and chloride concentrations in Spitfire averaged 4.0 mg/L and 7.6 mg/L respectively in 2017. We have observed that least impacted lakes in the Adirondack have median sodium and chloride concentrations of 0.5 and 0.2 mg/L, respectively, suggesting that Spitfire Lake has approximately 38 times more chloride than background concentrations alone. The concentration of chloride in the lake have exhibited a significant increase over time (P = 0.003, tau = 0.53; Figure 12). For example,

the chloride concentration in 1971 was observed to be 0.9 mg/L, the value increased to around 3.9 mg/L in 2000, and is currently approaching 8 mg/L. We did not detect a statistical association between our available data on sodium concentration and time (P = 0.6); however, the sodium concentration in 2017 (4.1 mg/L) is four times greater than the value observed in August of 1971 (1.1 mg/L).

It is possible that some of the sodium and chloride in Spitfire Lake may be attributed to shoreline development, but the majority of the salt is likely derived from road salt runoff in the watershed. The primary source of these chemicals in Adirondack waters is from winter road maintenance, particularly on NYS roads where road salt application averages 23 tons/lane mile (Kelting and Laxson 2010; Kelting et al. 2012; NYSDOT 2012 pers. com). Given that there are 2.7 miles of state roads in the Spitfire Lake watershed, we can expect an annual salt load of approximately 200 tons.

Calcium

Calcium concentration in Spitfire Lake exhibited little variation around the average value of 3.1 mg/L in the surface water and 3.8 mg/L in the bottom water (Table 9). These values are well below the concentration required to support a viable zebra mussel population. Historically, average calcium concentrations in the surface water have typically ranged from 3 mg/L to 4 mg/L with no significant trend detected in the data (Figure 13). We are suspicious of the 2002 sample because it is much lower than typical values; however, data from 2002 has not been removed from the trend analysis at this time.

Conductivity

The conductivity of the surface water of Spitfire ranged from 44 to 49 μ S/cm and averaged 45.8 μ S/cm in 2017. Conductivity values in the bottom water steadily increased during the period of stratification, and reached as high as 111 μ S/cm. The elevated conductivity near the bottom is related to the anoxic conditions that liberate dissolved ions from the sediments. The conductivity of

Spitfire is approximately 3 times higher than the values we encounter in least impacted lakes (Laxson et al. 2018). Elevated conductance is a marker of human intrusion in the watershed and could attribute to many sources,

including development, septic input, and of course road salt. The conductivity of the water has exhibited a significant increase over time, and has increased from 35 μ S/cm in 1971 to as high as 54 μ S/cm in 2008 (P = 0.009; tau = 0.45; Figure 13).

Findings: Upper St. Regis

Temperature and Dissolved Oxygen

The thermal stratification pattern for Upper St. Regis Lake is typical for Adirondack lakes of moderate depth (Figure 14). Surface water temperature increased from a low of 11.4°C (52.5°F) degrees on April 27th to a maximum observed temperature of 24.3°C (75.7 °F) on August 3rd The epilimnion depth (surface stratum of uniform temperature) ranged from less than one meter in late April to as deep as 10 meters during in late October. The temperature of the bottom water increased from 4.6°C (40.3°F) in late April to as high as 13.5°C (56.3 °F)before fall turnover.

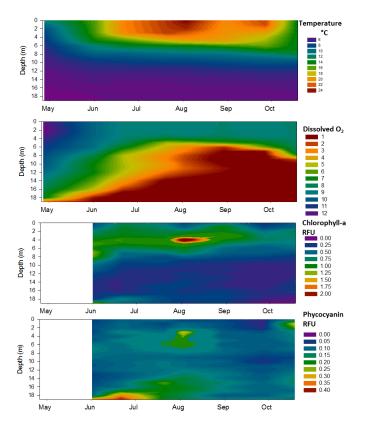


Figure 14. Vertical profiles of Upper St. Regis Lake during the ice-free period of 2017. From top to bottom: temperature, dissolved oxygen, chlorophyll-a relative fluorescence units (RFU), and phycocyanin RFU.

Upper St. Regis Lake experiences extreme oxygen depletion in the hypolimnion (Figure 14). On April 27th (11 days after ice out) the concentration of dissolved oxygen

St. Regis Chain: 2017

right above the bottom was 2.2 mg/L (17% saturated), indicating that oxygen depletion had already been underway. By the 30th of August, 63% of the water column was anoxic. Rapid oxygen depletion in the hypolimnion is an annual occurrence in Upper St. Regis. The earliest documentation of anoxia was from 1972-1974, when Fuhs et al. (1977) illustrated that anoxic conditions existed in 54% of the water column in August of 1972, 50% in 1973, and 28% in 1974.

The impressive oxygen depletion in Upper St. Regis is the result of two limnological features, productivity and basin morphometry. It has long been accepted that lake productivity is related to the development of hypolimnetic oxygen deficits in stratified lakes (Hutchinson 1938, 1957). Organic material produced within the lake eventually falls to the bottom sediments where it is decomposed by aerobic bacteria. In productive lakes the deposition of organic material occurs year after year, resulting in significant accumulation over time. Graneli (1978) suggested that the rate of oxygen uptake along the bottom of a lake reflects long term integration of sedimented organic material rather than short term variation. The annual oxygen depletion observed in Upper St. Regis may be related to current watershed inputs to the lake as well as a legacy effect of over 130 years of shoreline development.

The second, and perhaps more important feature, is basin morphometry. During thermal stratification the thermocline serves as a barrier to vertical oxygen transport from the atmosphere; as a result the hypolimnion is a closed oxygen system, which means it only has as much oxygen as moved in during the spring turnover. When the volume of the hypolimnion is small relative to the sediment surface area, oxygen depletion will occur regardless of trophic condition. For example, Mathias and Barica (1980) examined oxygen depletion in 70 Canadian lakes under the ice and found that the ratio of the lakes sediment surface area to hypolimnion volume (SSA:HV) accounted for 72% of the variation in oxygen depletion rates in eutrophic lakes, and 78% of the variation in oligotrophic lakes. We hypothesize that the SA:HV plays the controlling role in oxygen depletion in Upper St. Regis Lake, particularly in the steep western basin. Another aspect of morphometry that plays a role in this story is the ratio of shoreline length to lake surface area, referred to as shoreline density (Osgood 2005). Upper St. Regis Lake has a convoluted shoreline that is long relative to its surface area. The basins dendritic shape magnifies the importance of terrestrial inputs into the cycle of organic material. Therefore, terrestrial productivity may play a greater role in oxygen depletion in Upper St. Regis than it does in the two lower lakes. The shoreline density index for Upper St Regis is the greatest of the lakes in the chain at 77 m/ha, followed by Spitfire (64 m/ha), and Lower St. Regis (50 m/ha).

The anoxic patter in Upper St. Regis creates reducing conditions along the bottom which drastically affect the concentration of other chemical parameters as described later in this section.

Phosphorus

The surface concentrations of total phosphorus in 2017 ranged from 4.4 μ g/L to an unusually high value of 18.5 μ g/L μ g/L on August 30th (Table 10). Total phosphorus concentrations in the hypolimnion were considerably elevated, and ranged from 8.8 μ g/L on April 27th to a maximum of 50.2 μ g/L on September 27th. As observed in the other lakes in the chain, the steady increase in bottom water phosphorus was linked with the development of anoxic conditions. Depleted oxygen near the bottom forms a reducing environment that permits dissolved reactive phosphate to migrate out of the lakes sediments (Figure 15).

The EPA study of the St. Regis Chain performed in the early 1970's documented surface phosphorus concentration markedly higher than the values we have encountered over the last two decades, suggesting that nutrient concentration of Upper St. Regis has greatly improved. For example, Fuhs et al. (1977) documented total phosphorus concentrations of 44 μ g/L in 1973 and 62 μ g/L in 1974, while concentrations have been in the

range of 5 to 15 μ g/L more recently. Analysis of the available historical data reveals a weak, yet statistically significant, downward trend in average total phosphorus of the lake (Figure 16; P = 0.02, tau = -0.36).

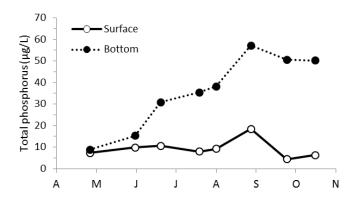


Figure 15. Concentration of total phosphorus in the surface and bottom water strata of Upper St. Regis Lake during the 2017 field season.

Nitrogen

The seasonal pattern of nitrate (NO₃-N) and ammonium (NH₄-N) in Upper St. Regis Lake is similar to that described earlier for the two lower lakes. Concentrations of both forms of inorganic nitrogen are rapidly cycled by autotrophs and microorganisms in the surface water during the summer months, resulting in very low concentrations (Table 10). The inorganic nitrogen cycle in the hypolimnion is guite different, especially in the depleted water. In anoxic conditions oxygen chemoautotrophic bacteria uses the potential energy of nitrate to power their own metabolism, resulting in conversion of nitrate to ammonium. Concurrently, ammonium generated by bacterial decomposition is released from the lake sediments. The result is a rapid decrease in nitrate and a simultaneous increase in ammonium. Nitrate concentration in the hypolimnion of Upper St. Regis was greatest in April at 104 µg/L and decreased to values below detection by early July. Ammonium, however, was below detection in April and increased to as high as 1590 µg/L in late September (Table 10).

The ratio of total nitrogen to total phosphorus (TN:TP) in Upper St. Regis Lake ranged from 35 to 92 in the surface

St. Regis Chain: 2017

St. Regis Chain: 2017

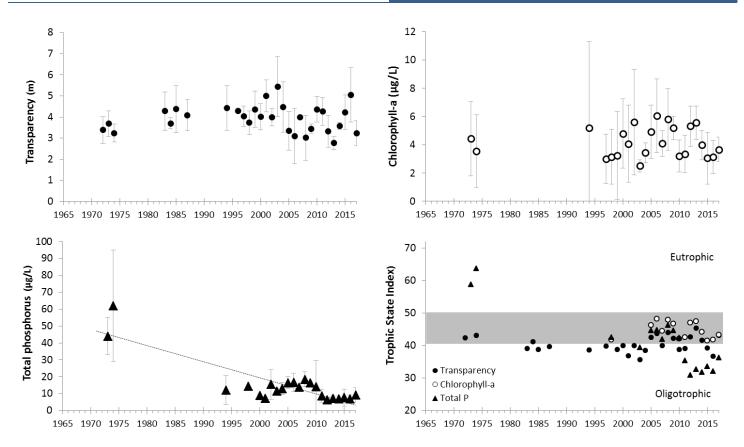


Figure 16. Time series of annual average values of key trophic indicators of Upper St. Regis Lake. Error bars represent 1 SD of the mean. Dashed line indicates a significant trend in the historical data (P<0.05).

Table 10. Chemistry and water quality indicators of the surface and bottom water strata of Upper St. Regis Lake during the 2017 field season.BDL = below analytical detection.

Water Quality	Upper St. Regis: 2017								
Indicator	4/27	6/1	6/21	7/2	8/3	8/30	9/27	10/19	Avg.
	Surface Water (0-2 meter)								
Transparency (m)	2.7	3.2	3.0	3.2	3.5	3.0	4.6	2.9	3.2
Chlorophyll (µg/L)	5.0	3.8	4.0	2.4	3.0	3.9	2.8	4.3	3.7
Total Phosphorus (μg/L)	7.3	9.8	10.6	8.0	9.2	18.5	4.4	6.3	9.3
Nitrate (µg/L)	49.6	BDL	BDL	BDL	BDL	26.1	4.4	2.1	10.2
NH4 (μg/L)	BDL	BDL	BDL	5	7	6	12	23	6
Total Nitrogen (mg/L)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Color (Pt-Co)	27.8	18.2	24.6	24.6	37.5	27.9	18.2	25.6	25.6
DOC (mg/L)	3.2	3.0	2.7	3.4	3.6	3.5	3.6		3.3
pH (s.u.)	7.1	6.7	7.1	7.1	7.1	7.0	7.1	7.1	7.0
Alkalinity (mg/L)	10.9	11.0	10.5	10.3	11.8	11.3	12.5	13.9	11.5
Sulfate (mg/L)	2.8	2.8	2.7	2.6	2.6	2.5	2.6	2.2	2.6
Conductivity(µS/cm°25)	48.6	45.8	47.4	44.8	45.1	46.0	47.9	48.6	46.8
Chloride (mg/L)	7.7	7.7	7.9	7.9	8.2	8.1	8.2	8.2	8.0
Calcium (mg/L)	2.9	2.9	3.0	2.9	3.2	3.2	3.4	3.2	3.1
Sodium (mg/L)	4.1	4.2	4.3	4.0	4.5	4.4	4.4	4.2	4.3
	Bottom Water (~20meters)								
Total Phosphorus (μg/L)	8.8	15.3	30.8	35.4	38.2	57.2	50.6	50.2	35.8
Nitrate (µg/L)	104.0	64.9	17.9	BDL	BDL	BDL	BDL	BDL	23.3
NH4 (μg/L)	91	184	367	498	777	1330	1590	1300	767
Total Nitrogen (mg/L)	0.4	0.5	0.5	0.6	0.9	1.5	1.4	1.3	0.9
Color (Pt-Co)	66.5	98.6	172.6	240.2	127.6	276.6	195.0	198.4	171.9
DOC (mg/L)			2.2			3.0	2.8		2.7
pH (s.u.)	7.1	6.3	6.5	6.4	6.7	6.6	6.8	6.5	6.6
Alkalinity (mg/L)	11.6	13.3	13.1	15.8	19.2	22.7	23.6	22.4	17.7
Sulfate (mg/L)	2.7	2.4	2.4	2.0	1.6	0.3	0.3	0.5	1.5
Conductivity(µS/cm°25)	51.4	53.8	56.7	61.5	76.9	87.8	93.4	96.2	72.2
Chloride (mg/L)	8.5	8.3	8.3	8.5	8.7	8.6	8.6	8.7	8.5
Calcium (mg/L)	3.0	3.2	3.6	3.3	3.9	3.8	4.2	3.8	3.6
Sodium (mg/L)	4.4	4.5	4.8	4.5	4.7	4.5	4.4	4.2	4.5

Findings: Upper St. Regis 45

St. Regis Chain: 2017

water and 35 to 105 in the bottom water. These results suggest that the lake tends to be phosphorus limited, and that cyanobacterial dominance should be relatively rare. In fact, over the last three years the TN:TP ratio in the surface water was in the range were cyanobacterial occurrence should be rare on 94 % of observations, in the bottom water the TN:TP suggest cyanobacteria occurrence should be rare on 100% of the observations (Figure 17).

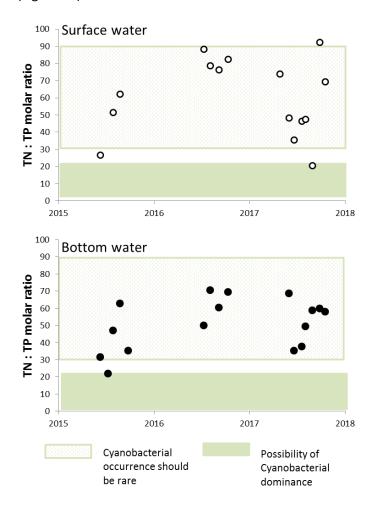


Figure 17. Total nitrogen to total phosphorus ratio in the waters of Upper St. Regis Lake during the sampling events of 2015-2017. Shaded areas indicate the potential of cyanobacteria occurrence.

Photosynthetic Pigments

Chlorophyll-a

Upper St. Regis Lake had the lowest concentration of chlorophyll-a in the surface waters of the St. Regis Chain during 2017. Concentration of the algal pigment ranged

from 2.4 to 5.0 μ g/L with a seasonal average of 3.7 μ g/L (Table 10). Profile measurements of chlorophyll-a taken in the field reveal that the phytoplankton population of the lake is typically centered between the depths of two and seven meters, and they are most prevalent in August (Figure 14). Historically, the annual average chlorophyll-a concentration has ranged from 2.5 to 6.0 μ g/L with no significant trend detected in the data (Figure 16).

Phycocyanin

Phycocyanin is a photosynthetic pigment exclusive to cyanobacteria, thus the strength of its detection serves as a relative indicator of cyanobacteria biomass. We detected phycocyanin throughout the water of Upper St. Regis, but at relatively low concentrations. The greatest density of cyanobacterial pigments were encountered right of the bottom in late June, and at around 3 meters in depth in early August (Figure 14). We did not detect any significant surface blooms of cyanobacteria; however, *Gloeotrichia* was visible from the boat on July 2nd and August 3rd.

Transparency

The transparency of Upper St. Regis ranged from 2.7 to 4.3 meters in 2017, with a seasonal average of 3.2 meters (Table 10). The transparency in 2017 is nearly two meters less that the average from last year (5.1 m), a pattern that is evident in many Adirondack Lakes and likely due to the vast difference in summer precipitation between the two years (Laxson et al. 2018). Increased precipitation washes a greater amount of suspended and dissolved organic material into the lake, resulting in decreased light penetration and overall transparency. Analysis of the available historical data does not reveal any statistical trend in the annual average transparency of Upper St. Regis. Overall, transparency exhibits considerable variability between years and has ranged from 2.5 to 6 meters (Figure 16).

Trophic State

The trophic status of Upper St. Regis Lake is best categorized as mesotrophic. The Carlson's Trophic State Index (TSI) based on chlorophyll-a (43) and transparency

(43) both identify the lake as mesotrophic; however, the TSI for phosphorus (36) classifies the lake as being oligotrophic. A disparity such as this is common when a lake experiences phosphorus limitation. Although consecutive annual data is limited prior to 2000, the available data suggests that the trophic state of the lake has improved since the early 1970's, at least in terms of phosphorus content (Figure 16).

Color

Upper St. Regis Lake is the least stained lake in the St. Regis Chain. Color values in the surface water ranged from 18.2 to 37.5 PtCo units, with a seasonal average of 25.6 PtCo units (Table 10). Overall, the surface color is relatively low. The average color value for Upper St. Regis is less than 71% of the lakes that participated in the 2017 Adirondack Lake Assessment Program (n=67; Laxson et al. 2018). Because water color in Adirondack lakes is primarily influenced by dissolved organic matter (DOM), we can infer that the quantity of DOM entering the lake from the watershed is fairly low. For comparison purposes, the color value of Lower St. Regis was greater by a factor of three, and averaged 72.5 PtCo units in 2017. The concentration of color was significantly greater in the hypolimnion were it generally increased as the season progressed, reaching values as high as 276 PtCo units (Table 10). The augmented color in the hypolimnion is a result of the decomposition of organic material that has settled into the lower strata, as well as s the flux of reduced organic material from the lake sediment.

Color data exists back to 1994 for Upper St. Regis. Since that time the annual average color of the lake has ranged from 7 to 30 PtCo units with no statistical trend in the data (Figure 18). Annual weather patterns result in a high amount of variability in color between years because high amounts of precipitation wash a greater amount of organic material into the lake.

Acidity

Like the other lakes in the chain, Upper St. Regis Lake is a circumneutral water body whose acidity has not been negatively affected by acid deposition. The pH of the

surface water ranged from 6.7 to 7.1 units in 2017. The pH values were slightly lower (more acidic) in the bottom water, where they ranged from 6.3 to 7.1 units (Table 10). Historically, the acidity of Upper St. Regis has been stable, with annual averages typically between 6.5 and 7.3 pH units.

Upper St. Regis Lake has stable pH because the water is adequately buffered from changes in acidity. The alkalinity of the lake ranged from 10.3 to 13.9 mg/L in the surface, and from 11.6 to 23.6 mg/L in the bottom (Table 10). Historically the alkalinity of the lake has typically been observed to be between 9 and 15 mg/L; however, a series of unusually high values were recorded in the years 2002-2009. We suspect some of these values may be in error (Figure 18).

Analysis of the concentration of sulfate in the lake suggests that the amount of acid deposition interacting with the St. Regis watershed has decreased over the last several decades. During acid deposition events hydrogen (H+) and sulfate (SO_4^{-3}) are deposited across the landscape and eventually make it into the lake. The concentration of sulfate in Upper St. Regis has exhibited a significant downward trend over time, and has decreased from of as high as 7.2 mg/L in 1971 to as low as 1.2 mg/L in 2015 (P < 0.001, tau = -0.76; Figure 18).

Sodium and Chloride

Sodium and chloride exhibited little variation around the season averages of 4.3 and 8.0 mg/L respectively (Table 10). These concentrations suggest that the chemistry of the lake is moderately impacted by road salting. For example, the 2017 average chloride concentration of Upper St. Regis is approximately 40 times greater than the concentration we observe in least impacted Adirondack lakes (median concentration = 0.2 mg/L, n = 52; Kelting et al. 2012). Although there are other possible sources of salt in the lake (septic effluent, fertilizers), the Upper St. Regis Watershed contains 7.0 lane-km of state roads, representing one obvious source of salt contamination. In NYS, road salt application rate has been

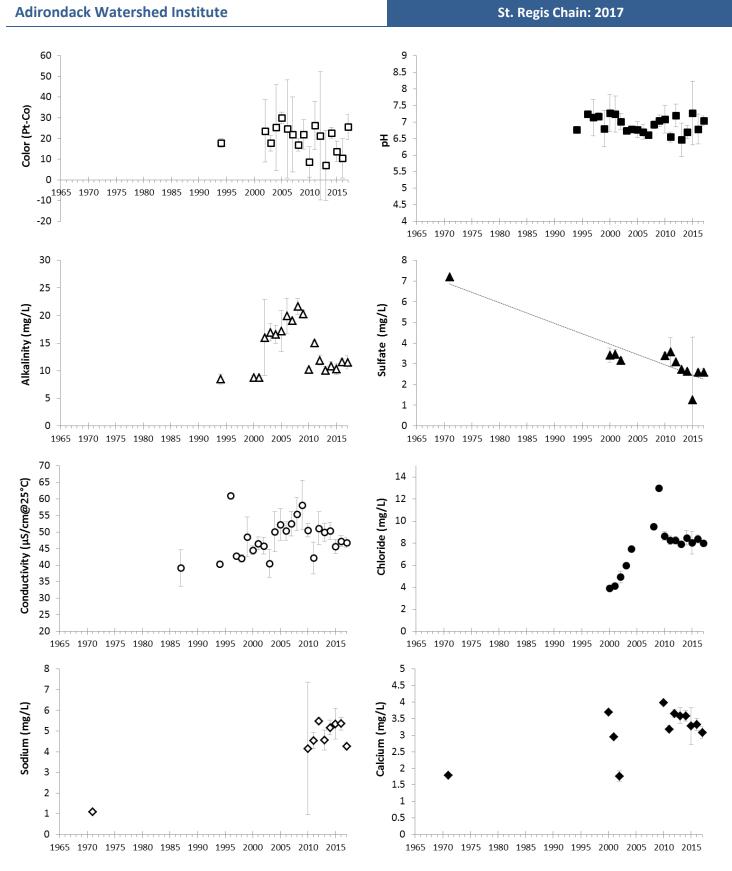


Figure 18. Time series of annual average values of selected water quality indicators in the surface of Upper St. Regis Lake. Error bars represent 1 SD of the mean. Dashed lines indicate a significant trend in the historical data (P<0.05).

estimated at approximately 23 tons/lane mile (Kelting and Laxson 2010; Kelting et al. 2012; NYSDOT 2012 pers. com). Given that there are 4.3 lane-miles of state roads in the Upper St. Regis watershed, we can expect an annual salt load of approximately 161 tons to the watershed.

Clearly, the sodium and chloride concentration has increased above natural levels in Upper St. Regis Lake. For instance, sodium concentration in August of 1971 (1.1 mg/L) was observed to be 75% lower than in 2017 (4.3 mg/L). Despite the obvious increase over time, we were unable to statistically define a trend due to the paucity of data between the 1970's and 2000 (sodium: P = 0.11; chloride; P = 0.09). In addition, we lack confidence in some of the historical chloride data for Upper St. Regis Lake. The sharp increase reported between 2000 and 2009 is highly unusual for a large lake and it does not follow the patter observed in the lower lakes (Figure 17). Our analytical ability to measure chloride greatly increased in 2010 when we launched our new analytical laboratory.

Calcium

Calcium concentration in Upper St. Regis Lake was nearly identical to values observed in Spitfire Lake. In 2017, calcium exhibited little variation around the average value of 3.1 mg/L in the surface water and 3.6 mg/L in the bottom water (Table 10). These values are well below the

concentration required to support a viable zebra mussel population. Historically, average calcium concentrations in the surface water have typically ranged from 3 mg/L to 4 mg/L with no significant trend detected in the data (Figure 18).

Conductivity

Surface water specific conductance in Upper St. Regis Lake exhibited little variation around the seasonal average of 46.8 μ S/cm, a value nearly identical to what was observed in Spitfire Lake. In the hypolimnion the conductance was elevated and generally increased throughout the stratified period, reaching a maximum value of 96.2 μ S/cm by late October (Table 10). The increased conductivity in the bottom stratum is a result of mineralization of organic material in the water as well as in the lake sediments.

The conductivity of Upper St. Regis is approximately 3 times higher than the values we encounter in least impacted Adirondack lakes (Laxson et al. 2018). The elevated conductance is a marker of human intrusion in the watershed and could be attributed to many sources, including development, septic input, and of course road salt. Although the conductivity of Upper St. Regis appears to have increased over the last 31 years, no statistically significant trend exists in the data (P = 0.08; Figure 18).

St. Regis Chain: 2017

Recommendations

Understanding the fundamental components of a lake is critical if we hope to detect ecosystem change or effectively enact management strategies. The St. Regis Chain is fortunate to have historical data to compare the lakes current condition to. Unfortunately, the data is from numerous sources and often suffered from lack of sample continuity and method consistency. This study combined over 7,000 records from a 50 year period and builds a framework for future work. Our primary recommendations are as follows:

The SRPOA should continue to support comprehensive high frequency lake monitoring by the AWI on an annual basis. Long-term data collection using reliable and comparable methodologies is critical for differentiating real trends from short-term fluctuations, as well as identifying emerging water quality issues. This past year monitoring efforts were greatly expanded to include eight sampling trips, collection of surface and bottom water samples, and full lake profiles. This additional data will help us differentiate between processes shaped largely by inherent lake and watershed features from those caused by human influences; thereby providing scientifically sound information to support lake management.

Precise bathymetric data should be collected from the lake chain. Accurate morphometric data is essential for understanding lake productivity, modeling anoxic conditions, and constructing meaningful nutrient budgets.

In an effort to promote informed choices on lake protection and restoration, the SRPOA and the AWI should collaborate on an educational outreach program for the St. Regis community. A program of this nature would strengthen our relationship and improve the public's understanding of lake ecology.

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