



Water Quality Conditions and Patterns on the Grand Portage Reservation and Grand Portage National Monument, Minnesota

Implications for Nutrient Criteria Development and Future Monitoring

Natural Resource Technical Report NPS/GLKN/NRTR—2009/223



ON THE COVER

Margaret Watkins and Victor Aubid of Grand Portage Trust Lands paddling to a sampling site on Trout Lake, September 2006.
Photograph by: Brenda Moraska Lafrancois



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Abstract

Lakes and streams are important natural features in northeastern Minnesota, and their protection is of management interest for the Grand Portage Band of Minnesota Chippewa and Grand Portage National Monument. In 1999, the Grand Portage Band began monitoring water quality intensively in 15 lakes and eight streams, in preparation for developing nutrient criteria. We used the resulting eight-year dataset to provide insights for 1) developing local nutrient criteria for Reservation waters, and 2) developing additional monitoring activities for Grand Portage Creek, through the National Park Service (NPS) Great Lakes Inventory and Monitoring Network. Specifically, we aimed to characterize existing water quality conditions in Grand Portage lakes and streams, evaluate variation among lakes and streams, explore seasonal patterns, relate current water quality conditions to state and federal standards, identify relationships between nutrients and trophic response variables, consider options for setting nutrient criteria, and provide recommendations related to site selection, sampling frequency, and parameter selection for future NPS monitoring of Grand Portage Creek.

Grand Portage lakes and streams tended to be dilute, with intermediate nutrient levels, low transparency, and high dissolved organic carbon concentrations. Streams showed more seasonal variation than lakes, being strongly influenced by hydrologic patterns. The chemistry of Grand Portage Creek was similar to the overall average for Reservation streams. The water quality of Grand Portage lakes differed significantly from that of other lakes in Minnesota's Northern Lakes and Forests (NLF) ecoregion. In particular, Grand Portage lakes were smaller, shallower, more acidic, and more highly stained. Subgroups of Grand Portage lakes were identified, but group divisions were not distinct.

Although the Reservation landscape is relatively undisturbed, some exceedences of state or federal reference criteria were noted. Chloride concentrations in two lakes and one stream were higher than average, which may suggest contamination from local roadways. Concentrations of total nitrogen and total phosphorus were higher than expected for lakes and streams of the NLF ecoregion, and Secchi depths were shallower; such patterns are likely attributable to the humic, dystrophic nature of Grand Portage waters rather than to anthropogenic enrichment. Relationships between nutrients and trophic response variables were somewhat difficult to interpret, perhaps because nutrients were not present in readily bioavailable forms, or because algal responses were limited by high dissolved organic carbon concentrations and resulting low light conditions. Options for establishing reference criteria for Reservation waters were reviewed in the context of the present analysis and recent paleolimnological studies in Reservation lakes.

The Grand Portage Band's monitoring efforts on Grand Portage Creek fit well with the objectives of NPS Great Lakes Inventory and Monitoring Network. The Band's program addresses NPS core water quality variables (e.g., temperature, pH, dissolved oxygen, and specific conductance) as well as more advanced variables. The sampling regime is frequent enough to capture dominant seasonal and interannual patterns in water quality. Future NPS monitoring on Grand Portage Creek should target other aspects of stream hydrology and biological integrity, such as stream discharge, benthic algal biomass, benthic communities, and stream habitat structure. Finally, future monitoring on Grand Portage Creek should account for climate-related changes to stream hydrographs and dissolved organic carbon inputs.

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This work was supported by generous data contributions from Margaret Watkins, Victor Aubid, and Andy Schmidt of Grand Portage Trust Lands Environmental Department, and Joy Ramstack, Mark Edlund, and Dan Engstrom of the St. Croix Watershed Research Station. Joy Ramstack also provided helpful advice on statistical analyses. Ulf Gafvert and Rebecca Key of the National Park Service Great Lakes Network Office assisted by calculating watershed areas and constructing the study area map. The National Park Service Great Lakes Inventory and Monitoring Network, Water Resources Division, and Midwest Region provided funding support for the data analysis aspects of this project. Finally, thanks to several agency reviewers for providing thoughtful comments on an earlier draft of this report.

Introduction

Inland lakes, streams, and wetlands are widespread in northern Minnesota landscapes and throughout the Boreal Shield, and have long been valued for their good water quality and the fish and wildlife resources they support (Steedman et al. 2004). In the Grand Portage Reservation, in far northeastern Minnesota, such water resources are central parts of Ojibwe heritage and culture and remain important for subsistence fishing and wild rice cultivation; these waters also played a fundamental role in the European fur trade era and were key to the establishment of Grand Portage National Monument within the Reservation in 1958 (National Park Service 2003).

The quality of Reservation waters has received increasing attention over the last two decades, through studies by the U.S. Geological Survey, the Grand Portage Band of Minnesota Chippewa (hereafter, Grand Portage Band), and the National Park Service (NPS). Several studies have addressed surface water quality and the hydrology of inland lakes and streams (Boyle and Richmond 1997; Grand Portage National Monument 2000; Winterstein 2000), groundwater chemistry, hydrology, and interactions with surface water (Ruhl and Wolf 1995; Winterstein 2002; Jones 2006), and sediment and water quality in Grand Portage and Wausaugoning Bays of Lake Superior (Ruhl 1997). Winterstein (2002) summarized several of these studies, concluding that Grand Portage watersheds were generally small, with flashy streams and variable lake levels, and that water chemistry and groundwater inputs were influenced mainly by local geologic features.

Because the Reservation landscape consists of relatively undisturbed second growth northern hardwood and boreal forests (Winterstein 2002), its waters are generally considered to be in good condition (Grand Portage National Monument 2000; Winterstein 2002). However, both tribal and NPS biologists are interested in the long-term protection of these water resources, and are concerned about potential effects of changing land use (Goldstein 2000) as well as more subtle stressors, such as climate change and atmospheric deposition (e.g., Schindler 1998; Lafrancois and Glase 2005). Further, because many of the nation's waters have been affected by nutrient over-enrichment, the Environmental Protection Agency (EPA) has mandated that states and tribes develop regional and local nutrient criteria for waters within their jurisdiction (EPA 2000b, c). The state of Minnesota has developed ecoregional nutrient criteria for lakes and has recently promulgated lake eutrophication standards (Heiskary and Wilson 2005; MPCA 2009); state nutrient criteria for streams and rivers are still being developed.

The Grand Portage Band is currently in the process of developing nutrient criteria for the Reservation's many lakes and streams, and began systematically monitoring water quality in 1999 to document current conditions in support of this process. Here we use the resulting dataset (1999-2006) to provide insights for 1) developing local nutrient criteria for Reservation waters, and 2) developing additional monitoring plans for Grand Portage Creek, through the NPS Great Lakes Inventory and Monitoring Network. Specifically, we aimed to:

- a) Characterize current water quality conditions in Grand Portage lakes and streams
- b) Evaluate differences among Grand Portage lakes and streams and between Grand Portage lakes and lakes in the broader ecoregion
- c) Explore seasonal patterns in water quality
- d) Relate current water quality conditions to state and federal standards

- e) Identify relationships between nutrients and trophic response variables
- f) Consider options for setting nutrient criteria
- g) Provide recommendations related to site selection, sampling frequency, and water quality parameter selection for future NPS monitoring of Grand Portage Creek.

Methods

Study Area Description

The Grand Portage Reservation is located in far northeastern Minnesota, bounded to the north by the Pigeon River and the Canadian border and to the east by Lake Superior (Figure 1). Grand Portage National Monument, a protected corridor managed jointly by the NPS and the Grand Portage Band, is situated entirely within the Reservation. It preserves a historic fur trading post and a long-used 13.7 km (8.5 mile) portage route from Lake Superior to the Pigeon River.

The Reservation landscape is characterized by rugged topography (the Grand Portage Highlands), nutrient poor glacial soils, extensive forests, and abundant lakes and wetlands; it is in many ways representative of the Boreal Shield landscape in which it is located (Steedman et al. 2004). The 228 km² Reservation contains a variety of aquatic resources, ranging from intermittent streams to the Pigeon River and from small lakes and wetlands to Lake Superior's Wausaugoning and Grand Portage Bays (Goldstein 2000). Grand Portage National Monument traces a portion of Grand Portage Creek from Lake Superior inland, crosses a large beaver-regulated wetland complex, and intersects Poplar and Snow Creeks (Grand Portage National Monument 2000).

Data Set Description

Two water quality datasets were used for these analyses. The first dataset (hereafter, "Grand Portage") includes data from 15 lakes and eight streams within the Reservation (Table 1). Water quality specialists from Grand Portage Trust Lands sampled each lake or stream monthly, from May through October for lakes and from April or May through October for streams, every other year from 1999-2006, such that the dataset contains information from four growing seasons for each water body. Basic chemical and physical parameters (i.e., pH, dissolved oxygen, specific conductance, and Secchi depth or stream transparency) were measured in the field on each sampling date; pH was also measured directly by the analytical laboratory, and we have used those direct measurements here. Samples for other water chemistry variables were integrated from the entire water column at a single site in most lakes and streams (but from the top 2 m in Taylor and Trout Lakes) and shipped to a laboratory for analysis (Table 2). Dissolved organic carbon (DOC) was measured only in 2005 and 2006 (i.e., one year for each water body). Lake and watershed physical variables (maximum depth, lake area, and watershed area) were measured or calculated by staff from the Grand Portage Trust Lands and NPS Great Lakes Inventory and Monitoring Network using lake surveys, topographic maps, and Geographic Information System analysis.

The second dataset contains environmental data from 59 lakes from Minnesota's Northern Lakes and Forests Ecoregion (hereafter "NLF") (Figure 2). Data for these lakes were compiled by staff from the Minnesota Pollution Control Agency, the St. Croix Watershed Research Station, the Natural Resources Research Institute-Ely Field Station, and Ramstack et al. (2003) as part of a

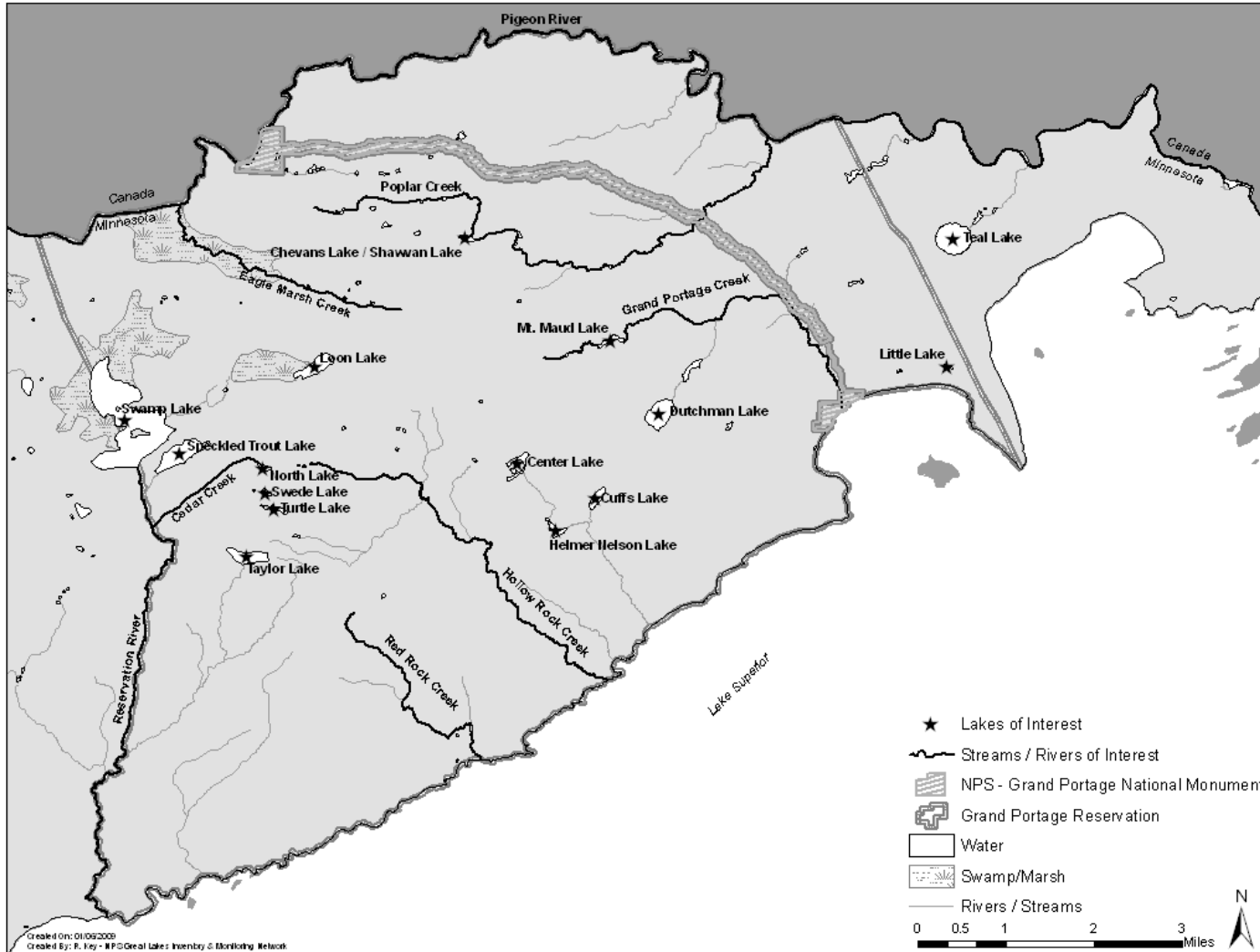


Figure 1. Grand Portage Reservation and Grand Portage National Monument waters analyzed for patterns in water quality data.

145-lake effort to develop water quality models using sediment diatoms and to establish nutrient criteria for Minnesota lakes (Edlund 2005); differences in analytical methods and reporting were reconciled during this process. Of this larger dataset, only the 59 lakes in the NLF ecoregion are included in the present analysis. Water quality variables in this dataset are similar but not identical to those sampled by Grand Portage Trust Lands (Table 2).

Table 1. Lakes and streams sampled by Grand Portage Trust Lands water quality specialists, from 1999-2006. "Odd Years" and "Even Years" refer to the years in which each lake or stream was sampled.

Name	Type	Odd Years	Even Years
Center	Lake	x	
Chevans	Lake	x	
Cuffs	Lake		x
Dutchman	Lake	x	
Helmer Nelson	Lake	x	
Little	Lake		x
Loon	Lake		x
Mt. Maud	Lake	x	
North	Lake		x
Swamp	Lake		x
Swede	Lake	x	
Taylor	Lake		x
Teal	Lake		x
Trout	Lake		x
Turtle	Lake	x	
Cedar	Stream	x	
Eagle Marsh	Stream		x
Grand Portage	Stream	x	
Hollow Rock	Stream		x
Pigeon	Stream	x	
Poplar	Stream	x	
Red Rock	Stream		x
Reservation	Stream		x

Table 2. Physical and water quality variables available from the Grand Portage Trust Lands dataset and the Minnesota Northern Lakes and Forests Ecoregion dataset (“NLF”). “TSI” = Trophic State Index. “Categories” represent subsets of correlated variables based on Spearman correlations. Individual variables noted in bold face were selected to represent their category in the Grand Portage lakes Principal Components Analyses.

Category	Variable	Unit	Grand Portage	NLF
Physical	Lake area	ha	x	x
	Watershed area	ha	x	x
	Maximum depth	m	x	x
Basic Chemistry	pH		x	x
	Dissolved oxygen	mg/l	x	
Conductivity and Ions	Specific conductance	µmhos/cm	x	x
	Alkalinity	mg/l	x	
	Acid neutralizing capacity*	µeq/l	x	x
	Hardness	mg/l	x	
	Calcium	mg/l	x	
	Magnesium	mg/l	x	
	Chloride	mg/l	x	x
	Sulfate	mg/l	x	
Nitrate+nitrite-N	mg/l	x		
Nutrients	Total nitrogen	mg/l	x	x
	Total phosphorus	mg/l	x	x
Trophic and Transparency Indices	Total suspended solids	mg/l	x	
	Chlorophyll-<i>a</i>	µg/l	x	x
	Secchi depth	m	x	x
	Dissolved organic carbon	mg/l	x	x
	Color*	PtCo	x	x
Derived Variables	TSI-Secchi		x	x
	TSI-Chlorophyll- <i>a</i>		x	x
	TSI-Total phosphorus		x	x
	Total nitrogen:total phosphorus		x	x
	Chlorophyll- <i>a</i> :total phosphorus		x	x

*Acid neutralizing capacity was calculated for Grand Portage waters using measured alkalinity values; dissolved organic carbon was calculated for NLF lakes using measured color values.

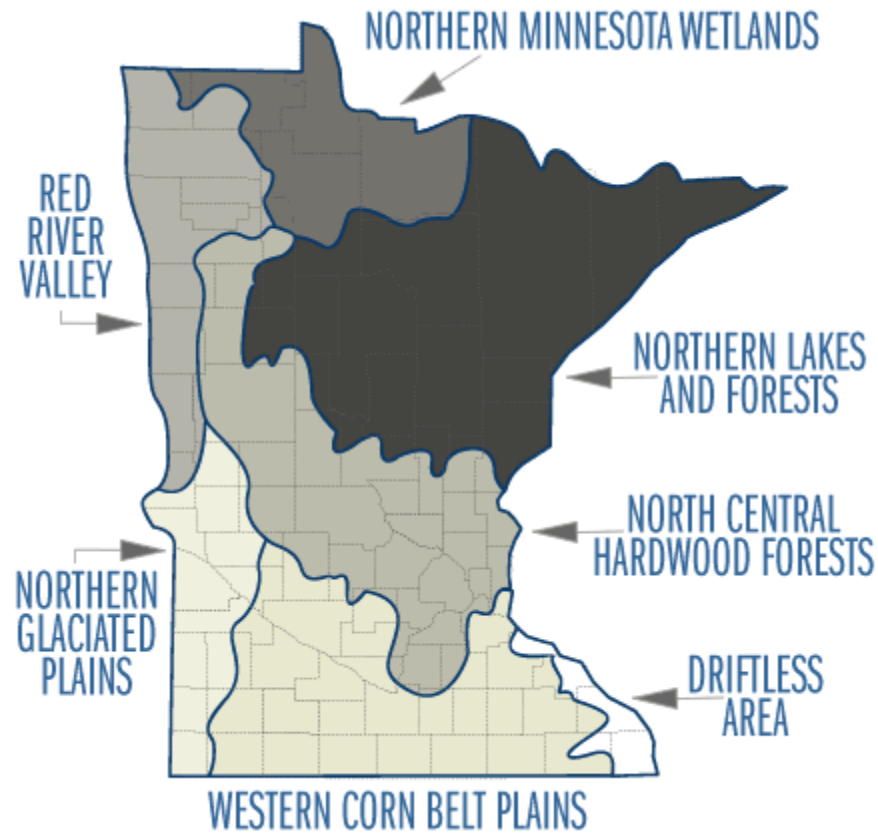


Figure 2. Ecoregions of Minnesota (from Minnesota Sea Grant; www.d.umn.edu/~seawww/depth/limnology/page18.html, accessed November 2008).

Data Analysis

Data Preparation

Data from Grand Portage were screened for outliers by constructing stem and leaf plots for each variable in Systat 10.2.01. All apparent outliers were examined individually, in the context of other values for the water body of origin, and values clearly resulting from sampling or data entry errors were omitted. This process resulted in few deletions overall; in cases of doubt, the value was assumed to represent real system variability and was included in the analysis. Data from the NLF lakes were processed as part of earlier work by Ramstack et al. (2003) and Edlund (2005) and were used here without further screening. Values below laboratory detection limits were set to the detection limit; this step primarily affected nitrate+nitrite-N values, for which detection limits varied by analytical laboratory. Additional water quality indicators were calculated for Grand Portage lakes and streams and NLF lakes based on ratios of existing variables (i.e., total nitrogen:total phosphorus, chlorophyll-*a*:total phosphorus), and Carlson's trophic state index (TSI) equations (Carlson 1977).

A combined Grand Portage-NLF dataset was constructed using water quality variables common to both datasets. In order to harmonize the list of variables, two variables were calculated for

Grand Portage or NLF lakes based on known relationships. First, acid neutralizing capacity (in $\mu\text{eq/l}$) was calculated for Grand Portage lakes based on measured alkalinity values (in $\text{mg CaCO}_3/\text{l}$) (Neal 2001). Secondly, DOC was calculated for NLF lakes in a manner similar to that of Molot and Dillon (1997), using a color-DOC regression from 20 lakes in the NLF dataset for which both variables were measured. For those NLF lakes with actual DOC data available, the measured values were used; for those NLF lakes with only color data available, DOC was calculated as follows: $\text{DOC} = 0.0793(\text{Color}) + 5.4405$ ($r^2 = 0.7482$).

Existing Water Quality Conditions

To circumvent issues associated with skewed data distribution and to account for inter-annual variability, existing water quality conditions were characterized for the entire 1999-2006 monitoring period using median values. First, lake- and stream-specific medians and 25th and 75th percentile values were calculated for each variable. Bar graphs depicting median values were created to compare existing water quality conditions among individual lakes and/or streams. Second, overall means and other summary statistics (among all lakes or streams) were calculated based on these median values and presented in tables.

Patterns in Water Quality

Patterns in Environmental Data: Relationships among environmental variables in Grand Portage lakes and streams were explored using correlation analysis. Due to non-normal data distribution, non-parametric Spearman rank-order correlations with pairwise deletion were calculated in Systat 10.2.01 based on median values for each variable in each lake or stream. Correlations of ρ ($|\rho| > 0.5$) were highlighted.

Differences among Lakes: Patterns among Grand Portage lakes and Grand Portage streams were examined using the lake and stream bar graphs described above. Additionally, Principal Components Analysis (PCA) was conducted to explore relationships among the Grand Portage lakes and environmental variables. Ordination techniques were not used to describe patterns among Grand Portage streams because of the low number of streams available. PCA is an unconstrained, linear ordination technique appropriate for environmental or species datasets with relatively short gradient lengths (Lepš and Šmilauer 2003). In order to simplify the analysis and reduce the number of variables included in the PCAs, subsets of correlated variables were identified based on their Spearman correlations, and a single variable was selected to represent each subgroup (Table 2). Derived variables (nutrient ratios and trophic state indices) were not included due strong covariance with the core variables. Accordingly, seven environmental variables were selected for use in the PCAs: maximum depth (Z_{max}), pH, specific conductance, total nitrogen (TN), total phosphorus (TP), chlorophyll-*a* (chl-*a*), and DOC or Secchi depth (see below).

Two PCAs were conducted (Canoco 4.02, ter Braak and Šmilauer 1998) using this reduced Grand Portage lakes dataset. First, a PCA was conducted using overall median values for each variable in each lake to look for general patterns among lakes across all monitoring years. DOC was selected as the most appropriate transparency variable for this analysis. A second PCA was conducted using median values for each year for each lake to identify any temporal patterns in lake-environment relationships over the monitoring period. Because DOC was not measured in the earlier years, Secchi depth was substituted as the transparency variable for this analysis. Environmental data were $\log(x+1)$ transformed in Canoco 4.02 (ter Braak and Šmilauer 1998)

during the PCA procedure. Ordination biplots showing environmental data and lakes or lake-year combinations were constructed for each PCA. For visual purposes, on the second PCA only those lake-year combinations for which the minimum total fit to the four axes was at least 50 (of a possible 100) were included (Lepš and Šmilauer 2003).

In order to place Grand Portage water quality patterns into a broader ecoregional context, several additional analyses were performed using the combined Grand Portage-NLF lakes dataset. First, overall means for each variable were compared in Grand Portage vs. NLF lakes using graphs and statistical comparisons. Overall means were calculated for Grand Portage lakes based on the median values for each lake and for NLF lakes based on the single data point available for each lake. Bar graphs of means in Grand Portage vs. NLF lakes were created for each variable, with standard deviations provided as error estimates. Means were compared statistically using t-tests in Systat 10.2.01. Data were transformed as necessary to meet the test assumptions. Bonferroni-corrected p-values were reported, to account for multiple tests, and $\alpha=0.05$ was used to identify statistically significant differences between Grand Portage and NLF lakes.

Secondly, a Multi-Response Permutation Procedure (MRPP) was performed. The MRPP procedure tests whether or not two *a-priori* groups of ecological data (in this case, environmental data from Grand Portage lakes vs. NLF lakes) are different from one another. Unlike discriminant analysis, its parametric counterpart, MRPP does not require that assumptions of normality and homogeneity of variance are met (McCune and Mefford 1999). Data were relativized by maximum during the procedure, and Euclidian distance measures were used to compute the test statistic, T , which describes the separation among groups. The chance-corrected within-group agreement statistic, A , and related p-value were evaluated to determine whether or not Grand Portage lakes differed significantly from the lakes in the NLF dataset.

Finally, an ordination analysis was performed on the combined Grand Portage-NLF lakes dataset. Although the combined dataset encompassed longer environmental gradients than the Grand Portage datasets described above, a preliminary Detrended Correspondence Analysis (DCA) indicated that gradient lengths for the first two ordination axes were <1 , and that a linear PCA was still appropriate. A PCA was performed on the combined dataset in Canoco 4.02 (ter Braak and Šmilauer 1998). All data were $\log(x+1)$ transformed in the analysis. Of DOC and color, only color was used. An ordination biplot showing environmental variables and lakes was constructed; for visual purposes, only those lakes for which the minimum total fit to the four axes was at least 75 (of a possible 100) were included (Lepš and Šmilauer 2003).

Seasonal Patterns: To explore intra-annual patterns in the water quality of Grand Portage lakes and streams, overall monitoring season medians (May-October) were calculated for each variable and compared with medians derived from a mid-summer period of high productivity (August). This approach is intended to address sampling frequency considerations for future monitoring, by a) highlighting which water quality parameters showed the most (or least) seasonal stability and b) providing an indication of whether or not a single mid-summer sampling date could adequately represent average growing season conditions. Since streams are more temporally variable than lakes, additional line graphs were prepared showing median concentrations (\pm the 25th and 75th percentiles), by month, for each variable measured in streams. To characterize long-term seasonal streamflow patterns in the Grand Portage area, an annual hydrograph was

constructed for the U.S. Geological Survey's gaging station on the Pigeon River (USGS 04010500, Pigeon River at Middle Falls near Grand Portage, Minnesota). The hydrograph depicts mean monthly flow values at this site for the whole streamflow monitoring period (1921-2007) and for the water quality monitoring period considered in this analysis (1999-2006).

Grand Portage Water Quality in Relation to State and Federal Criteria

Water quality in Grand Portage lakes and streams was characterized as the mean of water-body medians for each water quality variable over the 1999-2006 period of record. These values were compared with existing standards and criteria from the Environmental Protection Agency and Minnesota Pollution Control Agency. Specific attention was given to nutrients and nutrient-related variables.

Relationships between Nutrients and Response Variables

For the purposes of this analysis, factors affecting typical trophic response variables in Grand Portage lakes (i.e., chl-*a*, Secchi depth) were considered to be nutrients (TP and TN) and DOC. Spearman rank-order correlations among these variables were specifically examined. Additionally, regression analysis was used to evaluate the relationship between predictor variables (TP, TN, DOC) and algal response (as chl-*a*). Regressions were performed in Systat 10.2.01 using median values for individual Grand Portage lakes; variables were transformed as necessary to meet the test assumptions. For comparison, regression analyses were also performed using the larger Grand Portage-NLF dataset. Because water column chl-*a* may be a less effective response variable for running waters, these analyses were not performed for Grand Portage streams.

Results

Existing Water Quality Conditions

Lakes

Grand Portage lakes exhibited considerable variation in physical and chemical characteristics. Lake area was 19.2 ha on average, but ranged from 0.6 ha (Little Lake) to 143.7 ha (Swamp Lake) (Table 3, Appendix A-1). Most Grand Portage lakes were shallow (average maximum depth=3.2 m), but maximum depths ranged from a mere 0.9 m in Little Lake to 7.6 m in Taylor Lake. In general, lakes were circumneutral to slightly acidic, with Center and Swede Lakes showing the lowest and highest pH values, respectively (Appendices A-1, A-2). Dissolved oxygen concentrations were generally moderate to low; median concentrations in some lakes (i.e., Center, Chevans, Helmer Nelson, and Mt. Maud) were less than 5 mg/l. Grand Portage lakes were dilute, with a mean specific conductance of 68.3 $\mu\text{mhos/cm}$ overall. The lowest median specific conductance was found in Loon Lake (25.0 $\mu\text{mhos/cm}$); notably higher specific conductance values were found in Little, Swede, and Teal Lakes (138.0, 134.5, and 126.5 $\mu\text{mhos/cm}$, respectively). Grand Portage lakes exhibited a fairly narrow range of alkalinity and hardness, with overall mean values of 26.6 mg/l and 32.9 mg/l, respectively. Loon Lake was the least buffered of the Grand Portage lakes, with a median alkalinity of 8.0 mg/l, whereas Swede Lake was the most buffered, with a median alkalinity of 67.9 mg/l. Patterns in the primary

Table 3. Overall means, standard deviations, minima, maxima, and 25th and 75th percentiles for water quality variables measured in 15 Grand Portage Reservation lakes and eight Grand Portage Reservation streams, 1999-2006. All calculations were derived from lake- and stream-specific medians (see Appendices for water body-specific data). “StDev” = standard deviation, “Min” = minimum, “Max” = maximum, and “n/a” = not applicable for streams. Asterisks (“*”) denote variables that were calculated rather than directly measured.

Variable		Lakes							Streams						
Abbreviation	Variable	Unit	Mean	StDev	Min	Max	25th Percentile	75th Percentile	Mean	StDev	Min	Max	25th Percentile	75th Percentile	
Lake area	Lake area	ha	19.2	35.6	0.6	143.7	3.0	16.5	n/a	n/a	n/a	n/a	n/a	n/a	
Watershed area	Watershed area	ha	520	514	32	1839	149	587	n/a	n/a	n/a	n/a	n/a	n/a	
Z _{max}	Maximum depth	m	3.2	2.0	0.9	7.6	2.0	4.0	n/a	n/a	n/a	n/a	n/a	n/a	
pH	pH		7.06	0.41	6.45	7.70	6.70	7.40	7.35	0.33	6.70	7.71	7.25	7.595	
DO	Dissolved oxygen	mg/l	6.93	2.78	1.35	9.37	5.59	8.82	8.99	1.98	4.45	10.58	8.75	10.26	
SpcCond	Specific conductance	µmhos/cm	68.3	37.3	25.0	138.0	47.2	82.9	118.3	37.3	80.7	189.0	96.1	135.1	
Alk	Alkalinity	mg/l	26.6	15.4	8.0	67.9	18.0	30.5	47.6	12.3	30.5	64.7	39.9	53.6	
Hard	Hardness	mg/l	32.9	16.1	11.0	71.0	22.3	42.5	59.0	13.1	41.5	79.5	51.9	64.5	
Ca	Calcium	mg/l	8.3	5.6	2.5	24.5	5.0	9.3	12.3	3.8	3.8	15.2	11.0	14.8	
Mg	Magnesium	mg/l	2.62	1.15	0.87	4.50	1.65	3.60	3.48	1.05	1.94	5.20	2.89	3.89	
Cl	Chloride	mg/l	2.6	5.3	0.2	19.3	0.3	1.2	4.2	4.5	0.9	14.6	1.7	4.2	
SO ₄	Sulfate	mg/l	1.9	1.6	0.5	6.0	0.6	3.0	4.9	2.2	1.3	8.5	3.6	5.9	
NO ₂ +NO ₃ -N	Nitrate+nitrite-N	mg/l	0.047	0.007	0.030	0.050	0.050	0.050	0.050	0.000	0.050	0.050	0.050	0.050	
TN	Total nitrogen	mg/l	0.81	0.20	0.45	1.15	0.70	0.93	0.65	0.22	0.30	0.98	0.55	0.80	
TP	Total phosphorus	mg/l	0.022	0.011	0.010	0.050	0.012	0.027	0.028	0.012	0.013	0.050	0.022	0.031	
TSS	Total suspended solids	mg/l	3.1	1.8	0.8	6.8	1.9	4.0	4.4	4.4	1.0	13.4	1.9	5.3	
Chl _a	Chlorophyll- <i>a</i>	µg/l	3.0	1.5	1.0	6.0	2.0	3.8	0.9	0.5	0.5	2.0	0.5	1.1	
Secchi	Secchi depth	m	1.30	0.92	0.63	4.38	0.77	1.20	1.01	0.31	0.41	1.20	0.92	1.20	
DOC	Dissolved organic carbon	mg/l	15.14	7.03	5.30	31.80	9.88	18.90	12.41	5.91	6.35	19.85	8.56	15.58	
Color*	Color (calculated)	PtCo	101	66	8	258	52	137	75	55.75	18.26	145.62	39	105	
TSI-Secchi	TSI-Secchi		58	7	39	67	57	64	61	6	57	73	57	61	
TSI-Chl _a	TSI-Chlorophyll- <i>a</i>		40	5	31	48	37	43	28	5	24	37	24	31	
TSI-TP	TSI-Total phosphorus		47	7	37	61	40	51	51	6	41	61	48	54	
TN:TP	Total nitrogen:total phosphorus		38	12	21	66	30	44	24	7	15	39	21	25.71	
Chl- <i>a</i> : TP	Chlorophyll- <i>a</i> :total phosphorus		0.15	0.07	0.05	0.30	0.10	0.20	0.04	0.01	0.03	0.06	0.03	0.05	

cations (calcium and magnesium) were similar to those of alkalinity and hardness. Chloride concentrations in Grand Portage lakes averaged 2.6 mg/l overall; however, concentrations in Little and Teal Lakes were much higher than other lakes (10.7 mg/l and 19.3 mg/l, respectively). Sulfate concentrations averaged 1.9 mg/l and were highest in Little Lake. Nitrate + nitrite-N concentrations were generally near detection limits and showed little variation among lakes.

Concentrations of TN and TP varied somewhat among lakes, averaging 0.81 mg/l and 0.022 mg/l, respectively. Mean total suspended solid (TSS) and chl-*a* concentrations were generally low, with values of 3.1 mg/l and 3.0 µg/l, respectively. TSS concentrations were lowest in Taylor Lake and highest in Swamp Lake, whereas chl-*a* concentrations were lowest in Turtle Lake and highest in Dutchman Lake. Secchi depths tended to be low in Grand Portage lakes, with a mean depth of 1.30 m. Taylor Lake was substantially clearer than other Grand Portage Lakes, with a median Secchi depth of 4.38 m; most other lakes had median Secchi depths < 2 m. Taylor Lake also had the lowest median color value (8 PtCo units) and lowest median DOC concentration (5.30 mg/l) of all the Grand Portage lakes. Other Grand Portage lakes exhibited a range of color and DOC concentrations, with overall means of 101 PtCo units and 15.14 mg/l, respectively.

Carlson's trophic state indices for Secchi depth, chl-*a*, and TP averaged 58, 40, and 47, respectively. Dutchman and Helmer Nelson Lakes tended to have the highest median trophic state indices; Taylor and Trout Lakes tended to have the lowest. The TN:TP ratio was high, on average, with a mean of 38 overall. In fact, the lowest median TN:TP for an individual lake was 21. The ratio of chl-*a*:TP was low in Grand Portage lakes, averaging 0.15.

Streams

Grand Portage streams tended to be circumneutral, with an average pH of 7.35, and, like Grand Portage lakes, tended to have low to moderate dissolved oxygen concentrations (Table 3). Dissolved oxygen concentrations averaged 8.99 mg/l among streams, but were generally very low in Eagle Marsh Creek (median = 4.45) and relatively high in the Reservation River (median = 10.58) (Appendices B-1, B-2). Specific conductance averaged 118.3 µmhos/cm in streams, nearly twice as high as the lake average, and ranged from a median of 80.7 µmhos/cm in the Pigeon River to a median of 189.0 µmhos/cm in Red Rock Creek. Stream waters were slightly better buffered than lake waters, with average alkalinity and hardness values of 47.6 mg/l and 59.0 mg/l, respectively; both alkalinity and hardness were lowest in the Pigeon River and highest in Poplar Creek. Calcium and magnesium concentrations in Grand Portage streams averaged 12.3 mg/l and 3.48 mg/l, respectively. Stream chloride concentrations averaged 4.2 mg/l, but ranged widely, from 0.9 mg/l in Cedar Creek to 14.6 mg/l in Red Rock Creek. Sulfate concentrations were also variable, but averaged 4.9 mg/l among streams. Nitrate+nitrite-N concentrations were near or below detection limits in all reported cases.

Total nitrogen and phosphorus concentrations in Grand Portage streams were similar to those in lakes, averaging 0.65 mg/l and 0.028 mg/l, respectively. Total suspended solids averaged 4.4 mg/l but showed substantial variation among individual streams, with the lowest median TSS concentration occurring in Hollow Rock Creek (1.0 mg/l), and the highest occurring in Poplar Creek (13.4 mg/l). Water column chl-*a* concentrations were uniformly low in Grand Portage streams; mean chl-*a* was 0.9 µg/l, and all streams had median concentrations ≤2 µg/l. Transparency was less than 1.3 m in all Grand Portage streams. Dissolved organic carbon and

color in Grand Portage streams were generally lower than in Grand Portage lakes (12.41 mg/l and 75 PtCo units, respectively) but showed a similar wide range in values. The lowest median DOC concentrations and color were found in Cedar Creek, whereas the highest were found in Poplar Creek. Grand Portage streams had an TN:TP ratio of 24, with the lowest median TN:TP found in Poplar Creek (15) and the highest found in the Reservation River (39). The chl-*a*:TP ratio was substantially lower for Grand Portage streams than for Grand Portage lakes, with an average value of 0.04.

Grand Portage Creek, part of which runs through the Grand Portage National Monument corridor, had median water quality conditions similar to the overall mean water quality conditions in Grand Portage streams (Table 3, Appendices B-1, B-2). Grand Portage Creek had slightly higher median pH, dissolved oxygen, specific conductance, alkalinity, hardness, and anion values than the overall mean for Grand Portage streams, and had the highest calcium and magnesium concentrations. Concentrations of nutrients (TN and TP), suspended solids, and chl-*a* in Grand Portage Creek were somewhat lower than the average for all Grand Portage streams.

Patterns in Water Quality

Grand Portage Lakes

Correlations: Results of the correlation analyses showed that lake area was positively correlated with maximum depth (Table 4a), and that lake area, maximum depth, and watershed area were generally negatively correlated with specific conductance, alkalinity, hardness, and concentrations of major ions. Watershed area was positively correlated with DOC and color. Lower pH was associated with lower dissolved oxygen, lower sulfate concentrations, and lower Secchi depth, and with higher concentrations of TN, TP, DOC, and color. Specific conductance, alkalinity, and hardness were positively correlated with one another and with concentrations of major ions, and were somewhat negatively correlated with chl-*a*. Chloride concentrations were positively correlated with magnesium concentrations, as well as with TN, DOC, and color. Sulfate concentrations were positively correlated with pH and dissolved oxygen, but negatively correlated with TN. Nitrate+nitrite-N concentrations were generally at or near detection limits, and did not show strong correlations with any other variables. Total nitrogen and TP were positively correlated with one another and with DOC, color, and, to a lesser extent chl-*a*, and were negatively correlated with Secchi depth, pH, and dissolved oxygen. Total suspended solids was positively correlated with chl-*a*, and negatively correlated with Secchi depth. Chlorophyll-*a* was negatively correlated with Secchi depth, and Secchi depth showed positive correlations with pH and dissolved oxygen, and strong negative correlations with DOC and color.

Ordinations: The first PCA, conducted using overall median values for each lake, described substantial variation in the environmental dataset on the first and second ordination axes ($\sigma_1=0.436$ and $\sigma_2=0.240$, respectively; Figure 3). The first ordination axis was characterized by a gradient in maximum lake depth and specific conductance, with shallower lakes tending to have higher specific conductance (e.g., North, Swede, Teal, and Little Lakes) and deeper lakes tending to have lower specific conductance (e.g., Taylor, Trout, and Turtle Lakes). The second axis represented a gradient of pH versus chl-*a*, TP, TN, and DOC, with more acidic lakes having

Table 4a. Spearman rank correlations for environmental variables measured in 15 Grand Portage lakes, sampled 1999-2006. "Zmax" = maximum depth. Correlations $\rho > |0.5|$ are noted in boldface.

	Watershed				Dissolved	Specific				
	Lake area	area	Zmax	pH	oxygen	conductance	Alkalinity	Hardness	Calcium	Magnesium
Lake area	1.000									
Watershed area	0.312	1.000								
Zmax	0.608	0.025	1.000							
pH	-0.192	-0.474	0.013	1.000						
Dissolved oxygen	0.089	-0.376	0.127	0.829	1.000					
Specific conductance	-0.589	-0.237	-0.515	0.387	0.150	1.000				
Alkalinity	-0.591	-0.273	-0.343	0.378	0.120	0.910	1.000			
Hardness	-0.584	-0.228	-0.519	0.265	-0.029	0.960	0.916	1.000		
Calcium	-0.621	-0.358	-0.402	0.417	0.121	0.957	0.931	0.960	1.000	
Magnesium	-0.389	0.136	-0.657	-0.132	-0.329	0.764	0.670	0.799	0.639	1.000
Chloride	0.099	0.312	-0.429	-0.472	-0.370	0.287	0.067	0.281	0.126	0.632
Sulfate	0.024	-0.391	-0.049	0.614	0.693	0.204	0.055	0.076	0.178	-0.169
Nitrate+nitrite-N	0.261	-0.023	0.493	0.005	-0.215	0.151	0.213	0.233	0.274	0.069
Total nitrogen	0.215	0.360	-0.242	-0.774	-0.674	-0.068	-0.139	0.043	-0.163	0.495
Total phosphorus	0.027	0.196	-0.001	-0.788	-0.787	-0.292	-0.227	-0.161	-0.222	0.082
Total suspended solids	0.337	0.054	0.214	-0.466	-0.420	-0.488	-0.451	-0.396	-0.474	-0.108
Chlorophyll- <i>a</i>	0.416	0.183	0.103	-0.321	-0.316	-0.543	-0.475	-0.397	-0.535	-0.112
Secchi depth	-0.206	-0.453	0.174	0.756	0.737	0.204	0.245	0.040	0.249	-0.377
Dissolved organic carbon	0.150	0.588	-0.323	-0.759	-0.743	0.036	-0.081	0.147	-0.050	0.568
Color (calculated)	0.150	0.588	-0.323	-0.759	-0.743	0.036	-0.081	0.147	-0.050	0.568

	Chloride	Sulfate	Nitrate + nitrite-N	Total nitrogen	Total phosphorus	Total suspended solids	Chlorophyll- <i>a</i>	Secchi depth	Dissolved organic carbon	Color (calculated)
Chloride	1.000									
Sulfate	-0.112	1.000								
Nitrate+nitrite-N	-0.118	-0.306	1.000							
Total nitrogen	0.621	-0.560	0.114	1.000						
Total phosphorus	0.262	-0.491	0.061	0.602	1.000					
Total suspended solids	0.061	-0.186	0.046	0.550	0.466	1.000				
Chlorophyll- <i>a</i>	-0.072	-0.365	0.022	0.540	0.289	0.761	1.000			
Secchi depth	-0.435	0.479	-0.099	-0.874	-0.600	-0.623	-0.651	1.000		
Dissolved organic carbon	0.722	-0.422	0.107	0.865	0.599	0.411	0.335	-0.868	1.000	
Color (calculated)	0.722	-0.422	0.107	0.865	0.599	0.411	0.335	-0.868	1.000	1.000

higher nutrient concentrations, chl-*a*, and DOC. Eight Grand Portage lakes had generally lower pH and higher nutrient, chl-*a*, and DOC concentrations; these included Center, Chevans, Cuffs, Dutchman, Helmer Nelson, Loon, Mt. Maud, and Swamp Lakes. Within these lakes, the shallower Chevans Lake was closely associated with higher TN and DOC, and the deeper Dutchman, Loon, and Swamp Lakes were associated with higher chl-*a* and TP. The second PCA (not shown), conducted using median values for each year for each lake, described similar amounts of variation in the environmental dataset ($\sigma_1=0.442$ and $\sigma_2=0.334$ for the first and second ordination axes, respectively), and showed similar patterns among environmental variables. Data points for individual years in each lake were clustered closely together, suggesting that among-lake environmental patterns in Grand Portage lakes were not strongly affected by differences among the sampling years.

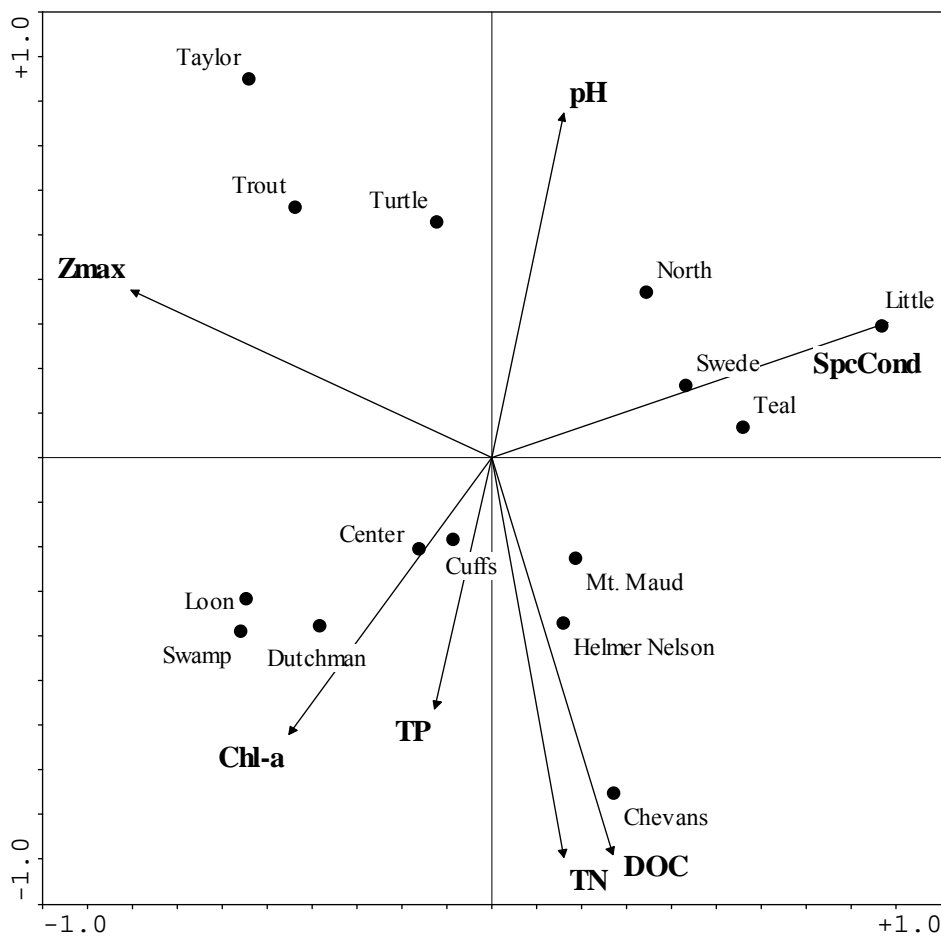


Figure 3. Ordination from a Principal Components Analysis, showing among-lake environmental patterns for 15 Grand Portage lakes, sampled 1999-2006. “Zmax”=maximum depth, “SpcCond”=specific conductance, “Chl-a”=chlorophyll-a, “TP”=total phosphorus, “TN”=total nitrogen, and “DOC”=dissolved organic carbon.

Grand Portage Streams

Correlations: Strong correlations were identified among many of the variables sampled in Grand Portage streams (Table 4b). Dissolved oxygen was positively correlated with pH ($\rho=0.934$), and negatively correlated with TN. As in Grand Portage lakes, specific conductance, alkalinity, and hardness showed strong positive correlations with one another and with concentrations of major ions. Total nitrogen was positively correlated with TP and DOC and color, although DOC and color measurements were limited to four of the eight streams. Total phosphorus, TSS, chl-*a*, DOC, and color were positively correlated with one another, and negatively correlated with transparency.

Grand Portage versus NLF Lakes

Many physical and chemical variables in the 15 Grand Portage lakes differed from those in the larger NLF lakes dataset. In fact, of the variables considered, only watershed area, acid neutralizing capacity, chloride, Secchi depth, TP, and the TSI based on TP showed no significant difference between the two lake datasets ($\alpha=0.05$; Table 5, Appendix C). Grand Portage lakes were significantly smaller and shallower than NLF lakes, and had significantly higher DOC concentrations, color, and TSIs based on Secchi depth. Grand Portage lakes were more dilute than NLF lakes, with significantly lower specific conductance, and were more acidic than NLF lakes, with significantly lower pH values. Total nitrogen concentrations and TN:TP ratios were much higher in Grand Portage lakes than in NLF lakes, but chl-*a* concentrations, TSIs based on chl-*a*, and chl-*a*:TP ratios were much lower. The MRPP supported these t-test results, indicating that the suite of environmental variables, taken together, differed significantly between Grand Portage and NLF lakes ($A=0.081$, $p<0.001$).

The PCA on the combined Grand Portage-NLF dataset helped characterize the nature of these differences. The first ordination axis was associated with gradients of lake and watershed size as well as specific conductance and acid neutralizing capacity (Figure 4), and described substantial variation in the environmental data ($\lambda_1=0.635$). The second axis described somewhat less variation ($\lambda_2=0.191$) and was associated with gradients in color, transparency, and nutrients (TN and TP). Lakes in the NLF dataset (shown as closed circles) were distributed throughout much of the ordination biplot. Grand Portage lakes, however, were consistently associated with smaller lake and watershed sizes, lower specific conductance and Secchi depths, and higher color and nutrient concentrations. In fact, many Grand Portage lakes were among the smallest lakes in the combined Grand Portage-NLF dataset, and Chevans Lake had the highest color and nearly the highest TN concentrations in the dataset.

Seasonal Patterns

Lakes: Overall means (i.e., growing season means, May-October) differed substantially from August-only means for a variety of water quality variables (Table 6). Dissolved oxygen, nitrate+nitrite-N, and Secchi depth showed lower mean values in August than over the entire growing season. Conversely, specific conductance, TN, TSS, and the ratios of TN:TP and chl-*a*:TP each showed higher means in August than overall. Variables that showed relatively little difference in their overall versus August means included pH, alkalinity, hardness, several ions, chl-*a*, TP, DOC, color, and most of the tropic state indices.

Streams: Differences in overall (i.e., growing season means, April or May through October) versus August-only means were more pronounced in Grand Portage streams than in Grand

Table 4b. Spearman rank correlations for environmental variables measured in eight Grand Portage streams, sampled 1999-2006. Correlations $p > |0.5|$ are noted in boldface. "n/a" = insufficient data points available for correlation analysis; "*" denotes variables that were only measured (or calculated) in four of the eight streams and for which results should be interpreted cautiously.

	pH	Dissolved oxygen	Specific conductance	Alkalinity	Hardness	Calcium	Magnesium	Chloride	Sulfate
pH	1.000								
Dissolved oxygen	0.934	1.000							
Specific conductance	-0.084	-0.214	1.000						
Alkalinity	-0.024	-0.024	0.810	1.000					
Hardness	0.000	-0.048	0.881	0.976	1.000				
Calcium	0.446	0.407	0.443	0.635	0.707	1.000			
Magnesium	0.036	-0.024	0.667	0.452	0.571	0.395	1.000		
Chloride	0.204	-0.048	0.643	0.571	0.667	0.671	0.190	1.000	
Sulfate	0.084	-0.024	0.667	0.667	0.738	0.623	0.643	0.595	1.000
Nitrate+nitrite-N	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Total nitrogen	-0.467	-0.530	0.241	0.361	0.361	0.267	-0.325	0.590	0.169
Total phosphorus	-0.205	-0.108	-0.156	0.048	0.084	0.452	-0.192	0.204	0.180
Total suspended solids	-0.367	-0.263	-0.228	-0.263	-0.204	0.024	0.000	-0.168	0.192
Chlorophyll-a	-0.485	-0.342	-0.279	-0.140	-0.140	0.038	-0.254	-0.114	0.101
Transparency	0.576	0.436	0.245	0.109	0.109	0.041	0.000	0.245	-0.245
Dissolved organic carbon*	-0.200	-0.200	0.800	0.800	0.800	0.800	0.600	0.800	1.000
Color (calculated)*	-0.200	-0.200	0.800	0.800	0.800	0.800	0.600	0.800	1.000

	Nitrate + nitrite-N	Total nitrogen	Total phosphorus	Total suspended solids	Chlorophyll-a	Transparency	Dissolved organic carbon	Color (calculated)
Nitrate+nitrite-N	n/a							
Total nitrogen	n/a	1.000						
Total phosphorus	n/a	0.612	1.000					
Total suspended solids	n/a	0.224	0.765	1.000				
Chlorophyll-a	n/a	0.494	0.874	0.919	1.000			
Transparency	n/a	-0.290	-0.686	-0.878	-0.901	1.000		
Dissolved organic carbon*	n/a	1.000	0.949	0.632	0.632	-0.632	1.000	
Color (calculated)*	n/a	1.000	0.949	0.632	0.632	-0.632	1.000	1.000

Table 5. Statistical comparison, using t-tests with Bonferroni-correction, of mean water quality characteristics for 15 lakes in the Grand Portage Reservation and 59 Minnesota lakes in the Northern Lakes and Forests Ecoregion (“NLF”). Transformations to meet test assumptions are noted; and p-values <0.05 are noted in boldface. “TSI” = Trophic State Index.

	Unit	Mean		StDev		T-test	Transformation
		Grand Portage	NLF	Grand Portage	NLF	p-value	
Lake area	ha	19.2	804.7	35.6	3670.9	<0.001	log (x+1)
Watershed area	ha	520.4	11451.8	514.3	47422.9	0.123	log
Maximum depth	m	3.2	16.7	2.0	11.1	<0.001	log (x+1)
Specific conductance	µmohs/cm	68.3	132.1	37.3	91.5	0.002	
Acid neutralizing capacity	µeq/l	532	1294	309	971	0.081	log
Chloride	mg/l	2.58	2.69	5.31	2.00	1.000	log (x+1)
Dissolved organic carbon	mg/l	15.14	7.91	7.03	2.38	0.005	log
Color (calculated)	PtCo	101	32	66	28	0.001	log
pH		7.06	7.51	0.41	0.55	0.027	
Total nitrogen	mg/l	0.810	0.513	0.200	0.207	<0.001	log (x+1)
Total phosphorus	mg/l	0.022	0.021	0.011	0.014	1.000	log (x+1)
Chlorophyll- <i>a</i>	µg/l	2.97	6.89	1.52	5.43	0.002	log
Secchi depth	m	1.30	3.35	0.92	1.42	1.000	
TSI-Secchi		58	44	7	6	<0.001	
TSI-chlorophyll- <i>a</i>		40	47	5	6	0.002	
TSI-total phosphorus		46	45	7	7	1.000	
Total nitrogen:total phosphorus		42	27	15	8	0.032	
Chlorophyll- <i>a</i> :Total phosphorus		0.151	0.318	0.072	0.106	<0.001	

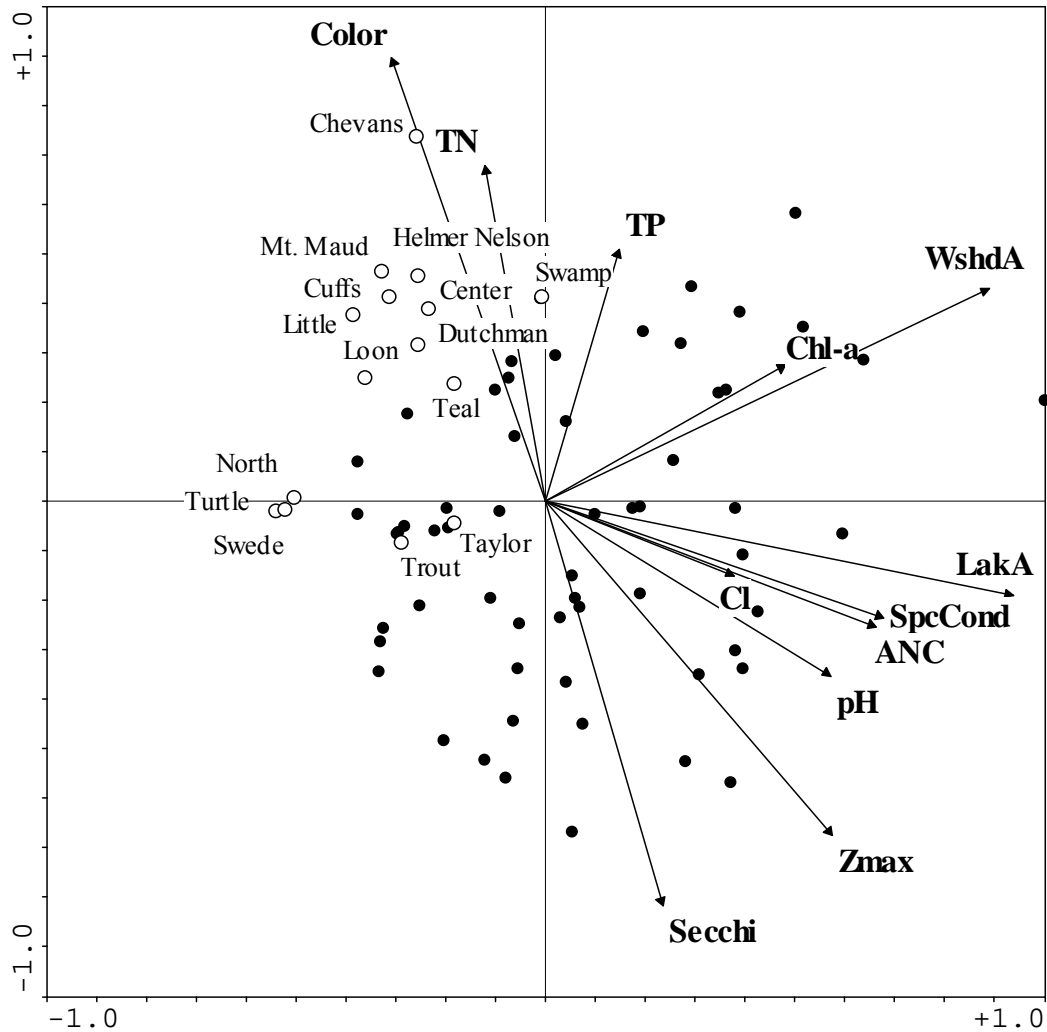


Figure 4. Ordination from a Principal Components Analysis, showing among-lake environmental patterns for the combined Grand Portage-NLF lakes dataset. Grand Portage lakes are noted with open circles, and NLF lakes are noted with filled circles; only Grand Portage lakes are listed by name. “WshdA”=watershed area, “LakA”=lake area, “Zmax”=maximum depth, “SpcCond”=specific conductance, “ANC”=acid neutralizing capacity, “Chl-a”=chlorophyll-a, “TP”=total phosphorus, “TN”=total nitrogen, and “Cl”=Chloride.

Portage lakes (Table 6), and were likely related to seasonal changes in stream discharge (Figure 5). Streamflow at the Pigeon River gaging site showed a unimodal annual pattern, with discharge peaking during snowmelt in April or May and tapering to baseflow conditions by August. The available data suggested a shift toward earlier snowmelt and peak discharge and lower late summer discharge in recent years (i.e., 1999-2006). Specific conductance, alkalinity, hardness, and the concentrations of many ions had higher mean values in August than overall, and showed a seasonal pattern of increasing values from April through August, peaking in September and falling again in October (Appendix D). Ratios of TN:TP and chl-a:TP varied widely, particularly in late summer, but generally showed higher mean values in August than overall. Dissolved oxygen concentrations showed mid-season lows, likely associated with warmer temperatures,

and were substantially lower in August than overall. Sulfate concentrations exhibited a similar pattern. Color and DOC had considerably lower mean values in August than overall, but were highly variable among streams. Water quality variables that differed little in their overall versus August means included nitrate+nitrite-N, which was near detection limits throughout the growing season, TN, TP, and TSS, which were highly variable but generally decreased from April to October, chl-*a*, and transparency.

Table 6. Overall and August means for water quality variables measured in 15 Grand Portage Reservation lakes and eight Grand Portage Reservation streams, 1999-2006, calculated as means of the lake- and stream-specific medians.

	Unit	Lakes		Streams	
		Overall	August	Overall	August
pH		7.06	7.03	7.35	7.50
Dissolved oxygen	mg/l	6.93	5.82	8.99	7.86
Specific conductance	□mhos/cm	68.3	76.5	118.3	152.8
Alkalinity	mg/l	26.6	28.4	47.6	61.4
Hardness	mg/l	32.9	35.2	59.0	73.6
Calcium	mg/l	8.3	9.9	12.3	17.4
Magnesium	mg/l	2.62	2.99	3.48	6.58
Chloride	mg/l	2.6	2.6	4.2	5.3
Sulfate	mg/l	1.9	1.9	4.9	3.6
Nitrate+nitrite-N	mg/l	0.047	0.026	0.050	0.060
Total nitrogen	mg/l	0.81	0.97	0.65	0.71
Total phosphorus	mg/l	0.022	0.026	0.028	0.023
Total suspended solids	mg/l	3.1	5.1	4.4	4.8
Chlorophyll- <i>a</i>	□g/l	3.0	3.8	0.9	0.9
Secchi depth or Transparency	m	1.30	1.18	1.01	0.91
Dissolved organic carbon	mg/l	15.14	16.05	12.41	10.05
Color (calculated)	PtCo	101	110	75	53
TSI-Secchi		58	60	n/a	n/a
TSI-Chlorophyll- <i>a</i>		40	41	n/a	n/a
TSI-Total phosphorus		47	45	n/a	n/a
Total nitrogen:total phosphorus		38	83	24	40
Chlorophyll- <i>a</i> :total phosphorus		0.15	0.34	0.04	0.13

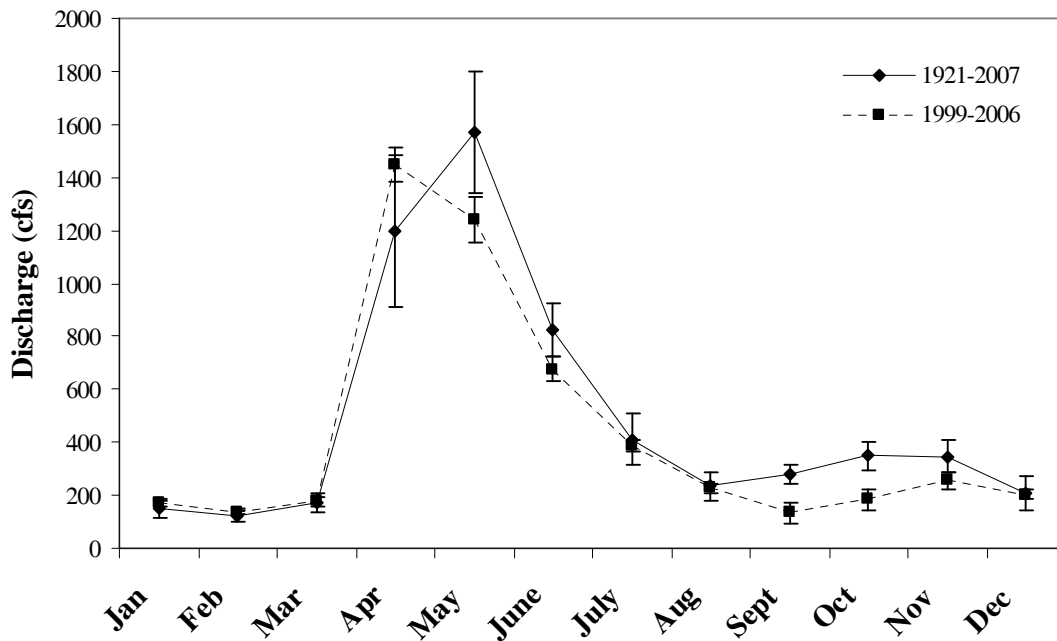


Figure 5. Annual stream hydrograph for the U.S. Geological Survey Pigeon River gaging station (Station USGS 04010500), from 1921-2007 and 1999-2006. Data points are long-term means of monthly mean streamflow values; error bars denote ± 1 standard error of the mean.

Grand Portage Water Quality in Relation to State and Federal Criteria

State and/or federal criteria or standards were available for ten of the water quality variables considered in this analysis (Table 7). Mean pH values for Grand Portage lakes and streams were within the 6.5-9.0 range considered acceptable for freshwater aquatic life (EPA 1986; MPCA 2009). Mean pH in Grand Portage lakes was comparable to ecoregional reference conditions for the state of Minnesota (Heiskary and Wilson 2005). Mean dissolved oxygen concentrations, although lower in lakes than in streams, were above the state and federal standards for warm and cold water systems (EPA 2006; MPCA 2009). Average alkalinity in lakes was low (at 26.6 mg/l) in comparison to Minnesota's ecoregional reference conditions, but mean stream alkalinity was higher (at 47.6 mg/l) and means for both lakes and streams were above the 20 mg/l level considered acceptable for aquatic life (EPA 1986). Mean chloride concentrations in lakes and streams exceeded the state of Minnesota's ecoregional reference conditions, but did not exceed

Table 7. Mean water quality conditions in Grand Portage Reservation lakes and streams (based on means of water body-specific medians), in relation to state of Minnesota and EPA ecoregional reference conditions and federal and state water quality criteria and standards. For total nitrogen, values outside parentheses were calculated based on other nitrogen species; values in parentheses were presented as reported. "F"= fluourometric method, "S"=spectrophotometric method. "zz" = flagged due to low number of observations.

Variable	Unit	Lakes			Streams		All Waters Combined State and Federal Standards ^{3a, b}
		Grand Portage	EPA Reference Conditions ¹	MN Reference Conditions ²	Grand Portage	EPA Reference Conditions ¹	
pH		7.06	-	7.20	7.35	-	6.50-9.00 (freshwater life) ^{3a, b}
Dissolved oxygen	mg/l	6.93	-	-	8.99	-	5 (daily min) ^{3a} , 6.5 (cold water) and 5.5 (warm water) ^{3b}
Alkalinity	mg/l	26.6	-	40.0	47.6	-	20 (aquatic life) ^{3b}
Chloride	mg/l	2.58	-	0.60	4.18	-	230 (chronic) and 860 (maximum) ^{3a, b}
Nitrate+nitrite-N	mg/l	0.047	0.003	-	0.050	0.030	10 (domestic) ^{3b}
Total nitrogen	mg/l	0.810	0.323 (0.40zz)	-	0.651	0.360 (0.440)	-
Total phosphorus	mg/l	0.022	0.010	0.014	0.028	0.012	0.030 (NLF lakes) ^{3a}
Total suspended solids	mg/l	3.1	-	<1	4.4	-	narrative (freshwater) ⁴
Chlorophyll- <i>a</i>	µg/l	2.97	1.38 (F), 2.46 (S)	4.00	0.88	0.60 (F), 2.00zz (S)	9.00 (NLF lakes) ^{3a}
Secchi depth or Transparency	m	1.3	4.2	2.4	1.0	-	2.0 (NLF lakes) ^{3a}
Color (calculated)	PtCo	101	-	10	75	-	75 (domestic), narrative (freshwater) ⁵

¹ "EPA Reference conditions" refers to the 25th percentile value for lakes and streams of Ecoregion VIII, Subcoregion 50 (EPA 2000a, EPA 2001).

² "MN Reference conditions" refers to the 25th percentile value for 32 lakes of Minnesota's northern lakes and forests ecoregion (Heiskary and Wilson 2005).

^{3a} Compiled from MPCA (2009).

^{3b} Compiled from EPA (1976), EPA (1986), EPA (2006).

⁴ Turbidity and total suspended solids criteria for freshwater fish and other aquatic life are reported in EPA (1976): "Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonably established norm for aquatic life."

⁵ Color criteria for freshwater fish and other aquatic life are reported in EPA (1976): "Increased color (in combination with turbidity) should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life".

state or federal standards for chronic or acute concentrations (EPA 2006; MPCA 2009). Median chloride concentrations in a small number of water bodies (i.e., Little and Teal Lakes and Red Rock Creek) were considerably higher than lake or stream mean concentrations (Appendices A-1, B-1). Mean nitrate+nitrite-N concentrations in Grand Portage lakes and streams were well below the EPA limits for health and domestic water use (EPA 1986); however, it is difficult to effectively relate nitrate-N concentrations in Grand Portage waters to ecoregional reference criteria since the criteria are near or below the laboratory detection limits for this study (EPA 2000a; EPA 2001).

Mean TN and TP exceeded EPA and state of Minnesota ecoregional reference conditions, and mean chl-*a* exceeded EPA reference conditions, but mean TP and chl-*a* levels were below new eutrophication standards for Minnesota NLF lakes (MPCA 2009). Mean total suspended solids were higher than state of Minnesota ecoregional reference conditions, but were likely within the federal narrative suspended solids and turbidity criteria (EPA 1976). Mean Secchi depth and transparency in Grand Portage lakes and streams was much lower than state of Minnesota and EPA ecoregional reference conditions (EPA 2000a; EPA 2001; Heiskary and Wilson 2005), and did not meet the proposed Minnesota lake eutrophication standard for the NLF ecoregion (MPCA 2009). Mean color in Grand Portage lakes was ten times higher than ecoregional reference conditions for the state of Minnesota, but likely within the federal narrative criterion (EPA 1976).

Median conditions in individual Grand Portage lakes varied in their relationships to ecoregional reference conditions and proposed state of Minnesota nutrient standards (Figure 6). Most Grand Portage lakes had median TP concentrations below the proposed standard of 0.030 mg/l (MPCA 2009), and several lakes (e.g., Little, North, Taylor, Teal, and Trout Lakes) had median TP concentrations below the 25th percentile of lakes in the NLF ecoregion (Heiskary and Wilson 2005, Figure 6a). However, median TP concentrations in Helmer Nelson and Mt. Maud Lakes exceeded the proposed 0.030 mg/l standard. Median chl-*a* concentrations were less than the proposed state of Minnesota standard of 9 µg/l in all of the Grand Portage lakes, and were less than the 25th percentile of lakes in the NLF ecoregion in most of the 15 lakes (Heiskary and Wilson 2005, Figure 6b). Median Secchi depths met the proposed state of Minnesota standard (2 m) in only two of the Grand Portage lakes (Taylor and Trout Lakes, Figure 6c).

Relationships between Nutrients and Response Variables

Typical trophic response variables (i.e., chl-*a* and Secchi depth) showed mixed correlations with predictor variables in Grand Portage lakes (i.e., TN and TP) (Table 4a). Median chl-*a* concentrations were positively correlated with median TN concentrations ($\rho=0.540$) but more weakly correlated with median TP concentrations ($\rho=0.289$). Secchi depth was negatively correlated with TN and TP ($\rho=-0.874$ and $\rho=-0.600$, respectively) as well as chl-*a* ($\rho=-0.651$). Relationships between trophic response variables and DOC were also considered. Chlorophyll-*a* showed a weak positive relationship with DOC ($\rho=0.335$), whereas Secchi depth was strongly negatively correlated with DOC ($\rho=-0.868$). In Grand Portage lakes, TN, but not TP or DOC, explained significant variation in algal response (as chl-*a*) (Table 8, Figure 7). In NLF lakes, TN, TP, and DOC all explained significant variation in chl-*a*, but TP explained the most ($r^2=0.743$).

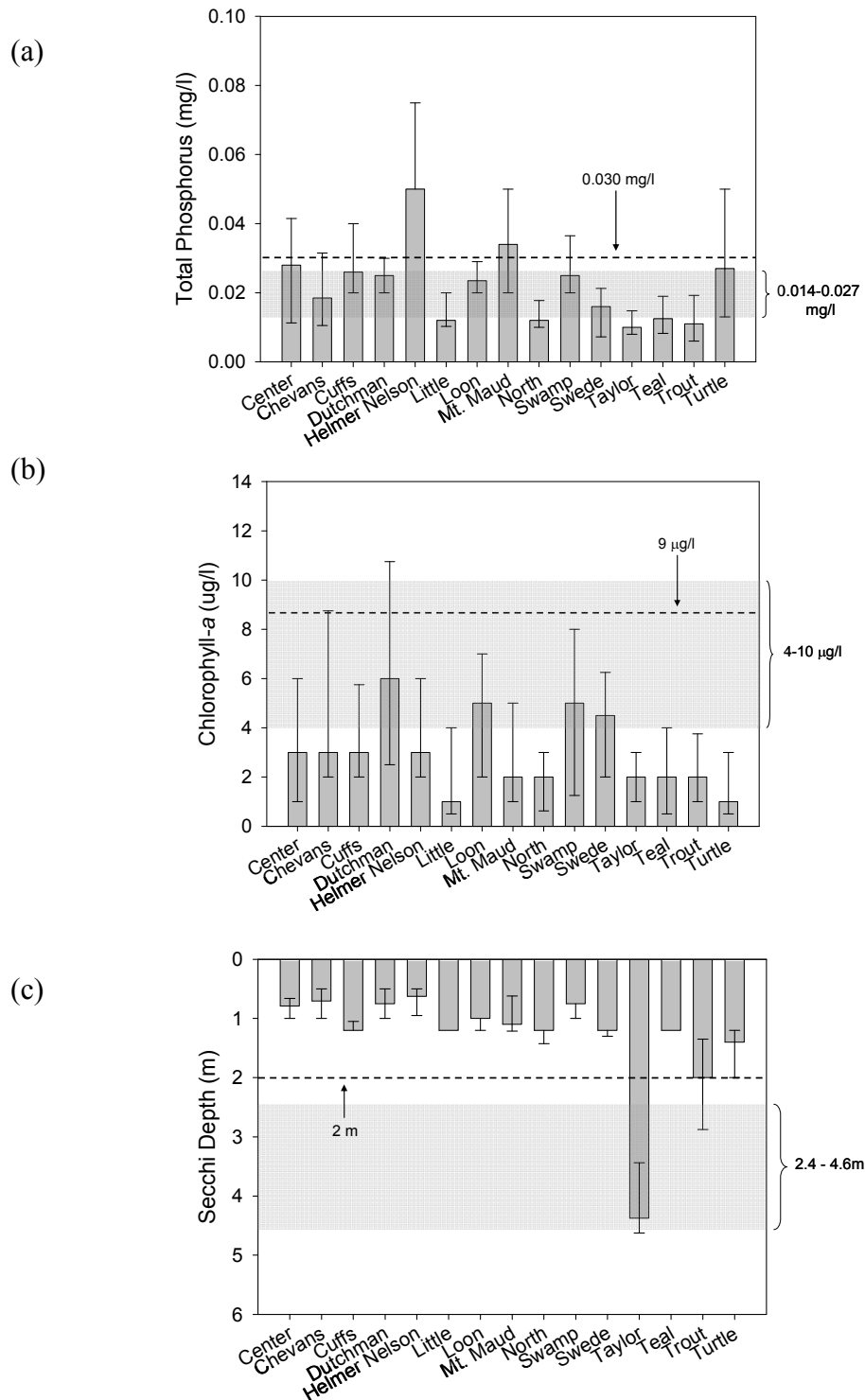


Figure 6. Median levels of (a) total phosphorus, (b) chlorophyll-a, and (c) Secchi depth in individual Grand Portage lakes, in relation to state of Minnesota nutrient standards (dashed line, MPCA 2009) and interquartile ranges (25th and 75th percentiles, shaded area) for reference lakes in Minnesota's northern lakes and forests ecoregion (from Heiskary and Wilson 2005). Error bars denote 25th and 75th percentiles for Grand Portage lakes; if no error bars or only one error bar is shown, 25th and/or 75th percentile values were equal to the median value.

Table 8. Results of simple linear regression analysis, showing relationship of an algal response variable (chlorophyll-a) to various predictor variables, for 15 Grand Portage lakes and 59 lakes in Minnesota's northern lakes and forests ecoregion. p-values ≤ 0.05 are noted in bold face.

Independent variable	Grand Portage			NLF		
	r ²	F-ratio	p-value	r ²	F-ratio	p-value
Total nitrogen	0.291	5.342	0.038	0.595	83.572	<0.001
Total phosphorus	0.060	0.835	0.378	0.743	162.293	<0.001
Dissolved organic carbon	0.093	1.333	0.269	0.179	12.462	0.001

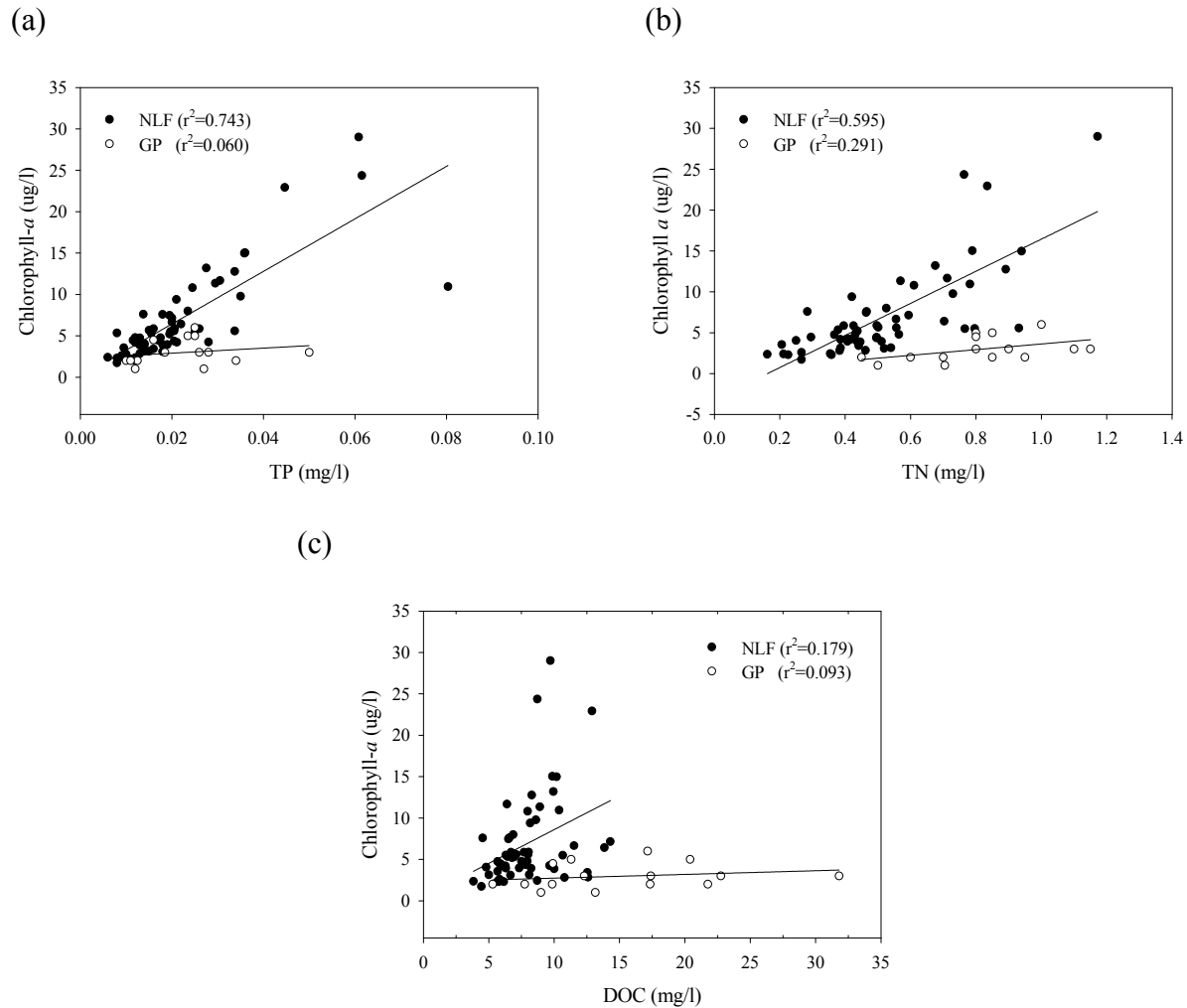


Figure 7. Scatter plots of predictor variables including (a) total phosphorus (TP), (b) total nitrogen (TN), and (c) dissolved organic carbon (DOC) versus chlorophyll-a for 59 lakes in Minnesota's northern lakes and forests ecoregion ("NLF") and 15 lakes in Grand Portage Reservation ("GP"). Plotted lines and r² values are the result of simple linear regressions.

Discussion

Existing Conditions and Patterns

Grand Portage lakes varied substantially in physical characteristics and water quality, but tended to be small, shallow, dilute, and slightly acidic, with intermediate nutrient concentrations, low chl-*a* concentrations, and high DOC and color. Grand Portage streams had nutrient and DOC concentrations similar to those of Grand Portage lakes, but had higher specific conductance, alkalinity, and hardness values. Based on classic trophic state indices, Grand Portage lakes would be considered mesotrophic to eutrophic (Carlson 1977). However, based on their high DOC and relatively undisturbed character, Grand Portage waters are more accurately described as dystrophic (Wetzel 2001). Many of the characteristics common to Grand Portage lakes and streams (e.g., relatively low pH, specific conductance, and alkalinity, high DOC and TSIs based on Secchi depth, and low chl-*a*, chl-*a*:TP ratios, and TSIs based on chl-*a*) are typical of dystrophic waters in northern and boreal regions worldwide (see Järvinen 2002).

Variation among Grand Portage lakes and streams can be explained by land cover patterns (particularly wetlands and beaver activity) and local geology (personal observation, Margaret Watkins, Grand Portage Trust Lands). For example, stream TSS was highest in Poplar Creek and the Pigeon River, which are situated on the portion of the Reservation underlain by erodible shales and siltstones, rather than the more widespread lavas and basalts (see Jones 2006). Seasonal variation in lake water quality was mainly attributable to higher productivity in August versus over the entire growing season (i.e., higher TN, TSS, and chl-*a* in August). In streams, seasonal variation in water chemistry reflected hydrologic patterns, including snowmelt during spring (which corresponded with higher TSS and DOC) and groundwater contributions during late summer base flows (which corresponded with higher specific conductance and alkalinity). Such conditions and seasonal patterns were consistent with those of previous local studies. Winterstein (2000) and Grand Portage National Monument (2000) reported a similar range of water quality characteristics following surveys of several Grand Portage lakes and streams in 1997-1998 and 2000, respectively.

Existing conditions in Grand Portage lakes differed significantly, however, from those of other lakes in Minnesota's NLF ecoregion. In general the Grand Portage lakes were smaller, shallower, more acidic, and more highly stained than their NLF counterparts; were more dilute and less buffered; and had lower algal biomass and Secchi transparency. This pattern of differences is also evident when Grand Portage lakes are compared with interior lakes sampled in nearby Voyageurs and Isle Royale National Parks; however, in the case of Isle Royale, such differences are less pronounced (see Kallemeyn 2000; Kallemeyn et al. 2003). Additionally, many of the lakes in these two parks also exceed ecoregional nutrient criteria (Elias and VanderMeulen 2008; Elias 2009). Many of the differences between Grand Portage lakes and NLF, Voyageurs, and Isle Royale lakes may be linked to the high DOC content and color found in most Grand Portage lakes. For example, in a literature review encompassing more than 600 clear and humic lakes, Nürnberg and Shaw (1999) found that mean summer pH, conductivity, and Secchi depth were significantly lower in humic lakes than in clear lakes.

Grand Portage Water Quality in Relation to State and Federal Criteria

Although Grand Portage Reservation has relatively few anthropogenic disturbances, mean values for several water quality variables approached or exceeded the state or federal reference criteria and standards. Mean dissolved oxygen concentrations in Grand Portage lakes and streams were influenced by very low median values for particular lakes (i.e., Center, Chevans, Helmer Nelson, and Mt. Maud Lakes) and streams (i.e., Eagle Marsh Creek). The four lakes above also had some of the highest DOC and color values in the dataset. Conditions in humic lakes may promote anoxia or net heterotrophy, due to lower light penetration and lower rates of photosynthesis (del Giorgio and Peters 1994) and increased anaerobic consumption of organic matter by bacteria (Nürnberg and Shaw 1999). As with dissolved oxygen, alkalinity values tended to be low in Grand Portage lakes. In fact, all 15 Grand Portage lakes had median alkalinity values <75 mg/l, characteristic of soft water lakes, and ten lakes had median alkalinity values near or below the 20 mg/l threshold considered acceptable for aquatic life (EPA 1986). Lakes in far northeastern Minnesota generally have low alkalinities and may be particularly sensitive to acid deposition due to underlying bedrock geology (Omernik and Griffith 1986). Although no chloride standards were exceeded (EPA 2006; MPCA 2009), mean chloride concentrations in Grand Portage waters substantially exceeded state of Minnesota reference conditions, and high median chloride values were recorded in several Grand Portage lakes and streams. Winterstein et al. (2002) and Jones (2006) noted that some springs and wells on the Reservation were very saline and attributed this to dissolution of the rock matrix and/or upward discharge of brines from underlying Precambrian rocks. Additionally, at least one of the high-chloride water bodies (Little Lake) is situated adjacent to a road and may be affected by road deicing compounds. Salinization related to road deicing compounds is increasingly recognized as a significant threat to freshwater ecosystems in northern climates (Kaushal et al. 2005).

Mean concentrations of primary nutrients (TN and TP) were higher than expected for lakes and streams in the NLF ecoregion, and transparency values were considerably lower (EPA 2000a; EPA 2001; Heiskary and Wilson 2005). This pattern has also emerged from monitoring efforts targeting lakes in nearby national parks, despite their protected status (e.g., at Isle Royale and Voyageurs National Parks; see Elias 2009). Higher than expected TN concentrations have been documented in some systems as a result of anthropogenic nitrogen deposition (Bergström and Jansson 2006) or agricultural inputs (Stanley and Maxted 2008); such elevated TN concentrations are often due to high concentrations of nitrate+nitrite-N. However, nitrate+nitrite-N comprises only a small amount of TN in Grand Portage waters, typical of landscapes dominated by forests and wetlands (Aitkenhead-Peterson et al. 2005; Pellerin et al. 2004). Since TN was highly correlated with DOC, and DOC is generally correlated with the presence of wetlands, it seems likely that naturally-occurring organic forms of nitrogen predominated. Of the trophic state variables (TP, chl-*a*, and Secchi depth), TP exceeded the Minnesota eutrophication standard in only two lakes (Helmer Nelson and Mt. Maud, MPCA 2009). Both lakes are located in wetland-dominated areas, which likely export significant amounts of TN and TP, particularly in the spring, when biological uptake is low and stream flows are high (Devito et al. 1989). Additionally, both lakes are affected by local beaver activity (Margaret Watkins, Grand Portage Trust Lands, personal observation, January 2008). Secchi depth failed to meet the Minnesota eutrophication standard in all but two lakes (MPCA 2009), and was highly negatively correlated with DOC and color.

The pattern of higher than expected nutrient concentrations and lower than expected Secchi transparency is consistent with the finding that Grand Portage lakes are shallower and more humic than many of their NLF counterparts (see Nürnberg and Shaw 1999). Further, Grand Portage lakes tended to have low chl-*a*:TP ratios, low TSIs based on chl-*a*, and high TSIs based on Secchi depth. Collectively, these patterns suggest that the above exceedences are the result of natural processes occurring in Grand Portage waters and watersheds. The state of Minnesota recognizes the potential for natural factors to result in poorer baseline water quality than the numeric eutrophication standards (MPCA 2009), and specifically acknowledges that their numeric eutrophication standards would be less applicable for lakes under 10 acres (~4 hectares). Small, shallow lakes are less likely to stratify seasonally, and are more likely to be subjected to resuspension of bottom sediments and related nutrients (Scheffer 2004). Six of the 15 Grand Portage lakes would fall within the MPCA's small lake category.

Implications for Nutrient Criteria Development

The Environmental Protection Agency has described the process for developing nutrient criteria for lakes and streams separately and in some detail. In general, EPA (2000b, c) recommends the following sequence of steps for developing nutrient criteria (those for which our analysis can offer the most input are noted in bold face):

- 1) **Create a database**
 - a. Evaluate ecoregion
 - b. Classify waters (by type, trophic status)
- 2) Select candidate criteria variables (e.g., TP, TN, chl-*a*, Secchi depth, algae, macrophytes, etc.)
- 3) **Select minimally impacted waters** in each class and a percentile, or select a distribution of all waters in each class and a percentile
- 4) **Establish reference conditions, examine historical record, employ models**, consult experts, and consider downstream effects
- 5) Establish nutrient criteria
- 6) Adopt water quality standards based on criteria
- 7) Institute management response to nutrient-related problems
- 8) Monitor and evaluate

Our analysis provides several insights relevant to this process. First, Grand Portage Trust Lands has created a database based on recent monitoring (1999-2006), and the present work has examined patterns within and beyond the Grand Portage dataset. It is clear that Grand Portage lakes, although situated within the NLF ecoregion, differ from Minnesota's other NLF lakes in important ways. Nutrient and DOC concentrations are significantly higher and Secchi depth is significantly lower in Grand Portage lakes. Since many of these differences are likely related to local geologic, topographic, and land cover features (Winchell 1901; Grand Portage National Monument 2000), this distinction is also expected for Grand Portage streams. Marked intra-ecoregional differences in nutrient conditions and biological response have been noted elsewhere in the Lake Superior basin (Detenbeck et al. 2003) and beyond (Dodds and Welch 2000; Herlihy and Sifneos 2008; Elias 2009). This variation suggests that the Minnesota's NLF nutrient criteria may not be easily applied to Grand Portage lakes (and perhaps other local subsets of lakes), and

that these waters should be considered a distinct subset of NLF waters in developing nutrient criteria.

We noted substantial variation among Grand Portage waters and examined possibilities for classifying Grand Portage lakes based on type or trophic status variables. Because only a small number of streams were included in the Grand Portage dataset, we did not attempt to classify them. Results of the PCA suggested three groups of Grand Portage lakes may exist. The first group consists of deeper, more dilute lakes with low nutrient and DOC concentrations (i.e., Taylor, Trout, and Turtle Lakes). The second group consists of shallow lakes with high specific conductance and intermediate nutrient and DOC concentrations (i.e., Little, North, Swede, and Teal Lakes). The final group consists of remaining lakes with higher nutrient, DOC, and chl-*a* concentrations. However, a review of dot diagrams and frequency histograms for key nutrient and response variables suggested that such group boundaries are not distinct. Although certain lakes had notably a higher TP concentration (i.e., Helmer Nelson Lake), Secchi depth (i.e., Taylor Lake), or color and DOC concentration (i.e., Chevans Lake, and to a lesser extent Helmer Nelson, Mt. Maud, Swamp, and Teal Lakes), values for most variables were distributed continuously rather than in clear groups. Given the relatively small number of lakes and the fact that most Grand Portage lakes are at the shallow, dystrophic end of the NLF spectrum, perhaps no further classification is warranted.

Secondly, our analysis showed that the typical candidate nutrient and trophic response variables are difficult to interpret for Grand Portage waters. The decision to develop nutrient criteria for U.S. and tribal waters was based upon an assumed close relationship between nutrients and nutrient responses (EPA 2000b). However, we found that these relationships were relatively weak in Grand Portage waters. In the case of Grand Portage lakes, TN and TP explained only minimal variation in chl-*a* concentrations, and the negative correlations of Secchi depth with TN and TP were likely due to naturally high DOC concentrations rather than to a trophic response. In Grand Portage streams, both TP and TN were positively correlated with chl-*a*, and TP explained substantial variation in chl-*a*. Similarly, Heiskary and Markus (2001) and Heiskary (2008) found positive relationships between sestonic chl-*a* and TP and total Kjeldahl nitrogen in medium to high order Minnesota streams and rivers. However, the meaningfulness of water column chl-*a* as a productivity measure in shallow, periphyton-dominated stream ecosystems has been debated (e.g., Dodds and Welch 2000). Weak relationships between nutrients and trophic response variables in Grand Portage lakes suggest that trophic responses may be limited by high DOC and color (and thus low light penetration; Williamson et al. 1999) or by low nutrient bioavailability. Nutrients originating in wetlands and peatlands, such as those in the Grand Portage region, are more likely to have undergone conversions from bioavailable inorganic forms to less bioavailable organic forms (Devito et al. 1989).

Although the lack of a strong relationship between nutrients and trophic response variables is understandable in Grand Portage waters, additional trophic response variables should be considered. Endpoints such as benthic algal biomass in streams, frequency of low dissolved oxygen events, or biological community indices (e.g., macrophytes, macroinvertebrates, diatoms, etc.) could be useful in developing nutrient criteria for Grand Portage waters. Additionally, since nutrient effects on trophic response variables (chl-*a* and Secchi depth) appear to be mediated by high DOC concentrations in Grand Portage waters, monitoring for DOC trends should continue.

Thirdly, our analysis of the modern water quality data can be paired with a recent paleolimnological study to determine which Grand Portage lakes and streams represent minimally impacted reference waters. This approach to understanding reference conditions is consistent with the Environmental Protection Agency guidance for lakes and reservoirs (EPA 2000b), which recommends 1) data collection and inference of reference condition based on percentiles, 2) paleolimnological reconstruction, and/or 3) model-based prediction from related datasets or knowledge. It is also consistent with the guidance for streams and rivers (EPA 2000c), which recommends establishing reference reaches by 1) using best professional judgment, 2) identifying the 75th percentile of reference streams for a class of streams, 3) identifying the 5th to 25th percentile of the general population of a class of streams.

Given the small number of lakes and streams involved, for the purposes of this exercise it seems practical to group all Grand Portage lakes into one class and all Grand Portage streams into another. It may be appropriate, then, to characterize reference waters as the best quartile of all Grand Portage lakes or streams (EPA 2000 b, c). Reference conditions in Grand Portage lakes, based on 25th percentile values for TN, TP, and chl-*a* and 75th percentile values for Secchi depth, would be 0.70 mg/l TN, 0.012 mg/l TP, 2.0 µg/l chl-*a*, and 1.20 m Secchi depth (Table 9a). Similarly, reference conditions for Grand Portage streams would be 0.55 mg/l TN, 0.022 mg/l TP, and 0.5 µg/l chl-*a* (Table 9b). However, this strict scenario assumes that Grand Portage lakes represent a mix of impacted and less impacted sites, and many individual lakes and streams would exceed reference conditions. For example, Chevans Lake (which is undisturbed, home to rare plants, and extremely difficult to access) is locally considered pristine (Goldstein 2000; personal communication, Margaret Watkins, Grand Portage Trust Lands, January 2008), but would not meet the reference conditions criteria for Secchi depth.

Since Grand Portage watersheds are minimally impacted relative to other parts of the NLF ecoregion, it is likely fair to assume that Grand Portage lakes and streams represent reference conditions already. Under this more relaxed scenario, we would use the 75th percentile values (25th percentile for Secchi depth) to approximate reference conditions. Accordingly, reference conditions for lakes would be 0.93 mg/l TN, 0.027 mg/l TP, 3.8 µg/l chl-*a*, and 0.77 m Secchi depth (Table 9a). For streams, reference conditions would be 0.80 mg/l TN, 0.031 mg/l TP, and 1.1 µg/l chl-*a* (Table 9b). Such percentile approaches may be reasonable for Grand Portage waters.

Alternatively, Herlihy and Sifneos (2008) suggested that setting criteria based on natural background levels in a collection of undisturbed reference sites may be defensible. A recent paleolimnological study provides some insight into how much Grand Portage lakes have changed over time, and whether or not we can assume they are minimally impacted. Two lakes were selected for paleolimnological study based on contrasting DOC and color conditions. In September of 2006, sediment cores were collected from Swamp Lake (higher DOC) and Trout Lake (lower DOC). Edlund et al. (2007, 2009) found that diatom communities in Swamp Lake were diverse and dominated by soft water benthic taxa, whereas planktonic centric diatoms predominated in Trout Lake; neither lake had seen a substantial change in diatom communities in the last 200 years. Diatom-inferred TP concentrations in Swamp Lake and Trout Lake ranged from 0.017-0.025 mg/l and 0.008-0.014 mg/l, respectively, but showed no systematic change

over time. Modern diatom-inferred TP concentrations for Swamp Lake and Trout Lake were approximately 0.020 mg/l and 0.010 mg/l, respectively, which compared favorably with the measured median concentrations of 0.025 mg/l and 0.011 mg/l, respectively, for these lakes during the 1999-2006 monitoring period (Edlund et al. 2007, Appendix A-1). Results from these paleolimnological studies support the assumption that Grand Portage watersheds are relatively undisturbed, and suggest that setting nutrient criteria based on current conditions may be appropriate.

Table 9. Possible reference conditions, based on percentiles of data distributions among a) 15 Grand Portage lakes, and b) eight Grand Portage streams. "Strict scenario" assumes Grand Portage waters represent a mix of impacted and less impacted sites, and is based on the 25th percentile values for TN, TP, chl-a (75th for Secchi depth). "Less strict scenario" assumes most Grand Portage waters represent reference conditions, and is based on the 75th percentile (25th for Secchi depth). "F"= flourometric method, "S"=spectrophotometric method, "zz" = flagged due to low number of observations.

a) Lake Nutrient Criteria or Standard				
	Strict scenario	Less strict scenario	Minnesota standard¹	EPA criterion²
Total nitrogen	0.70	0.93	n/a	0.32 (0.40zz)
Total phosphorus	0.012	0.027	0.030	0.010
Chlorophyll- <i>a</i>	2.00	3.75	9.00	1.38 (F), 2.46 (S)
Secchi depth	1.20	0.77	2.00	4.2

b) Stream Nutrient Criteria or Standard			
	Strict scenario	Less strict scenario	EPA criterion²
Total nitrogen	0.55	0.80	0.360 (0.440)
Total phosphorus	0.022	0.031	0.012
Chlorophyll- <i>a</i>	0.50	1.08	0.60 (F), 2.00zz (S)
Secchi Depth or Transparency	1.20	0.92	n/a

¹From MPCA (2009).

²From EPA (2006).

Implications for Water Quality Monitoring

Our analysis of Grand Portage stream data provided several insights relevant to the development of NPS water quality monitoring protocols for wadeable streams (particularly for Grand Portage Creek, in Grand Portage National Monument). First, median water quality conditions in Grand Portage Creek approximated average water quality conditions in Grand Portage streams, suggesting that Grand Portage Creek may be generally representative of local streams. Further, although only one site on Grand Portage Creek was included in this analysis, this site integrates water from much of the catchment, is located within the Monument boundaries, and is within the coaster brook trout (*Salvelinus fontinalis*) management zone. Coupled with the Band's additional monitoring of core water quality parameters at an upstream site on Grand Portage Creek, the current monitoring location appears to serve both the Band's and the NPS's purposes well.

Secondly, this analysis offers some insights into which variables are important to include in future monitoring efforts. In addition to the required core parameters (temperature, dissolved oxygen, pH, specific conductance, and streamflow (Irwin 2008)), several other variables should be monitored. Chloride concentrations were higher than expected in several Grand Portage streams, including Grand Portage Creek. Although median chloride concentrations in Grand Portage Creek were below Environmental Protection Agency water quality standards, they should be monitored for any increases related to road salt application and watershed salinization (Kaushal et al. 2005). Because Grand Portage Creek is situated in an area of naturally low alkalinity (Omernik and Griffith 1986), alkalinity and hardness should be monitored. Many watersheds in the northeastern United States have been affected by excess nitrogen deposition (Aber et al. 2003), and experiments in Sweden suggest that phytoplankton in dystrophic systems may be limited by inorganic nitrogen (Jansson et al. 2001). Accordingly, concentrations of both TN and nitrate+nitrite-N should continue to be monitored, with attention to achieving low detection limits for nitrate+nitrite-N.

Like many Grand Portage waters, Grand Portage Creek carries high concentrations of DOC. Given the importance of DOC in attenuating solar radiation, altering contaminant toxicity, and affecting nutrient availability (Williamson et al. 1999), monitoring for DOC trends should continue and attention should be given factors that influence DOC. In general, DOC concentrations in surface waters are tightly linked to catchment land cover, soils, and hydrology, particularly the proportion of wetlands and peatlands (e.g., Engstrom 1987; Gergel et al. 1999; Mattsson et al. 2005). Further, Schindler et al. (1997) found that DOC export from boreal catchments is affected by climate warming, altered hydrology, and lake acidification. Nutrient management and monitoring in Grand Portage Creek should continue to account for DOC and its interactions with trophic response.

As noted above, benthic chl-*a* or periphyton biomass is likely a more appropriate measure of trophic response to nutrients in streams than water column chl-*a* (Dodds and Welch 2000). Further, the significant biomass and spatial coverage of benthic algae in Grand Portage Creek has triggered management interest in recent summers (Brandon Seitz, Grand Portage National Monument, personal communication, December 2008). As such, some measures of benthic algal biomass, periphyton community structure, riparian habitat, and canopy cover should be incorporated into future NPS monitoring efforts for Grand Portage Creek. Such information could be useful in interpreting responses of Grand Portage Creek to changing nutrient conditions, and would complement the Band's existing benthic invertebrate monitoring as well as local coaster brook trout restoration work.

Third, our analysis suggests a high degree of seasonal variation in many water quality variables in Grand Portage streams, including Grand Portage Creek. Much of this variation is due to seasonal changes in stream discharge, which peaks annually in April or May, diluting concentrations of many ions and enhancing concentrations of total suspended solids. Nutrient concentrations varied substantially but inconsistently in Grand Portage Creek, and trophic response variables (chl-*a* values) were low throughout the season. As such, it appears that the Band's monthly sampling frequency, from April to October, effectively captures the periods of greatest hydrologic variation. More frequent sampling is unlikely to reveal substantially different seasonal patterns in the variables of interest, but less frequent sampling may obscure important

seasonal trends. Since no single month or season was especially well suited to understanding overall conditions in Grand Portage streams, maintaining the monthly sampling frequency is likely optimal.

Finally, our analysis underscores that the greatest threats to water quality in Grand Portage are not the obvious agricultural and urban changes occurring elsewhere in Minnesota. Instead, less obvious stressors, such as climate change and atmospheric deposition, are likely the most important. Kling et al. (2003) suggested that climate-related changes in lakes and streams of the Great Lakes region may be substantial (e.g., reduced winter ice cover and lower lake levels, increased duration of summer stratification and occurrence of anoxia, changes in fish communities, changes in the timing of snowmelt and the severity of storm peaks, changes in base stream flow, reductions in thermal refugia for organisms, etc.). Some of these changes might be particularly important in Grand Portage waters. Many Grand Portage lakes already have low dissolved oxygen concentrations, which could be exacerbated by prolonged periods of stratification, and signs of earlier snowmelt peaks and lower summer base flows are already apparent in Grand Portage streams. Further, climate strongly influences DOC in boreal waters (Schindler et al. 1997), and future warming and continued drought conditions could shift the way DOC mediates trophic responses to nutrients in Grand Portage waters. Monitoring climate-linked variables such as streamflow and DOC will be increasingly important.

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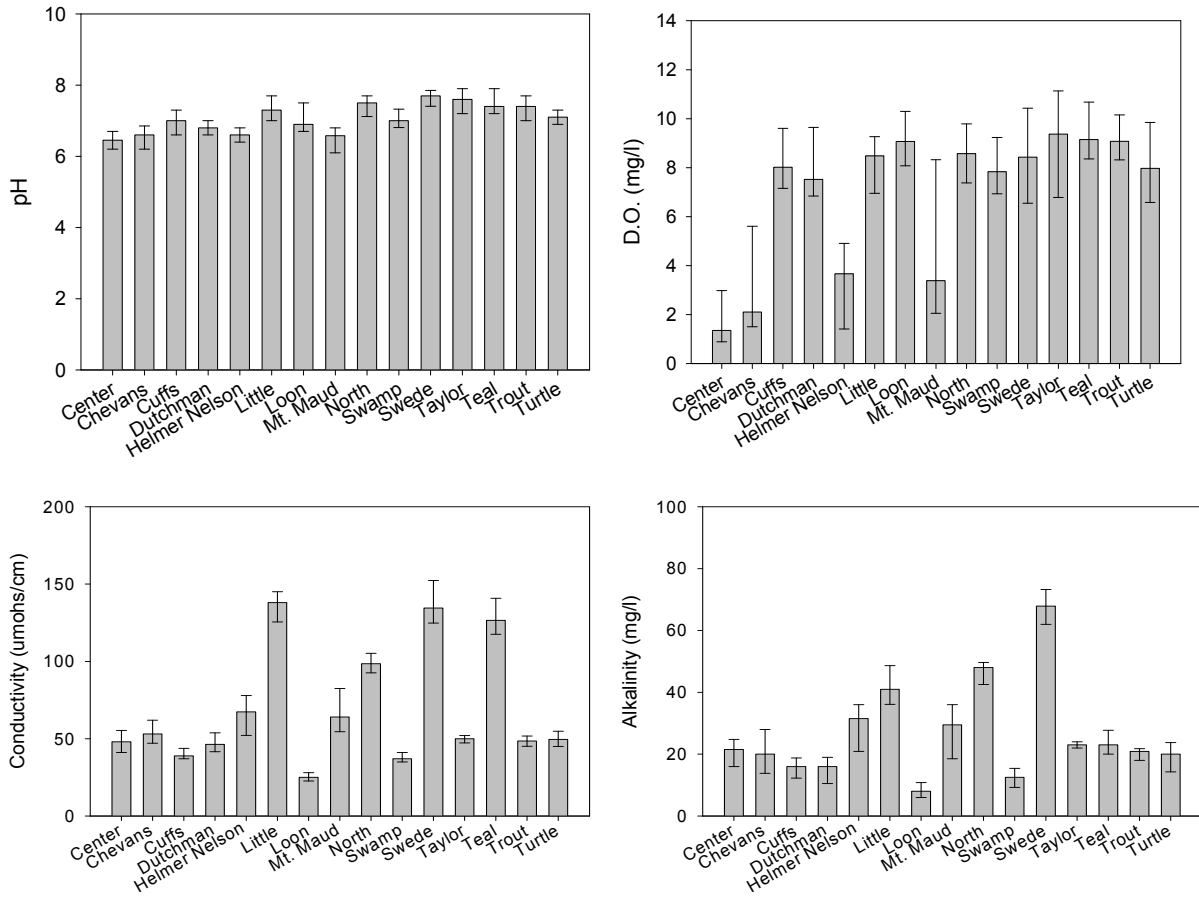
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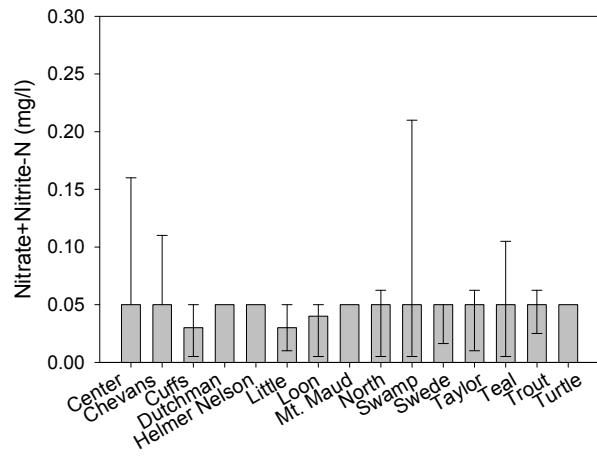
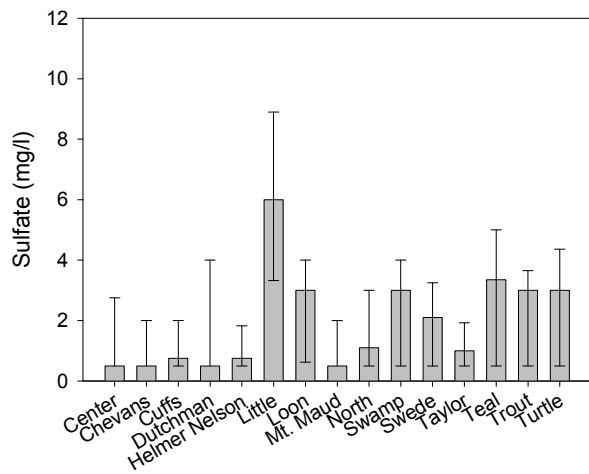
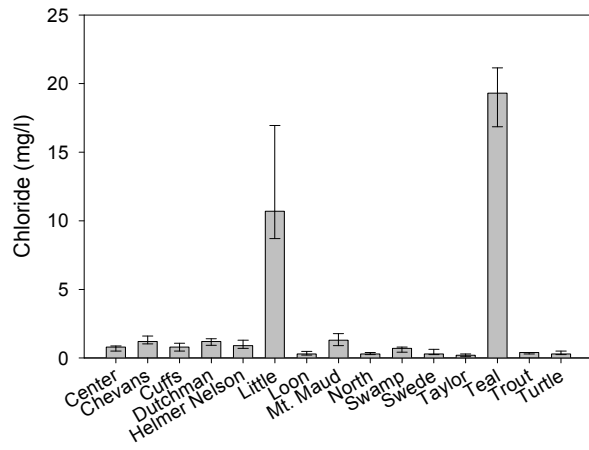
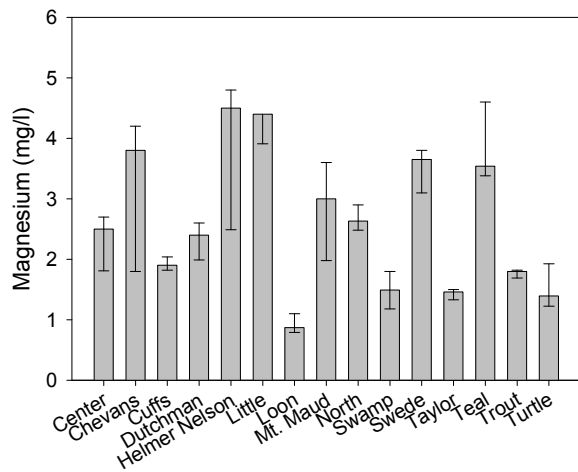
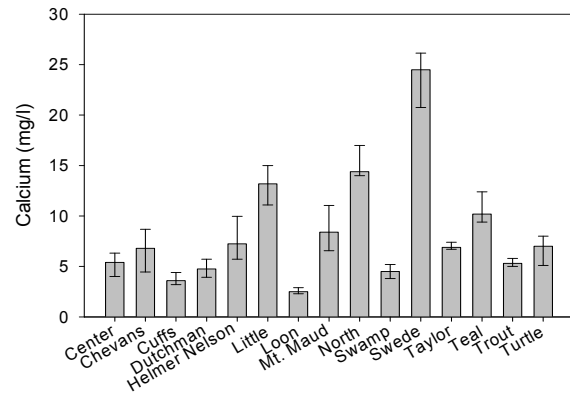
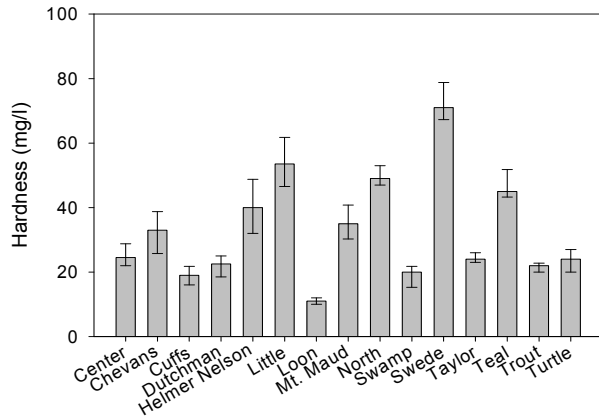
Appendix A-1. Lake-specific median values for water quality variables measured in 15 Grand Portage Reservation lakes, sampled 1999-2006.

Variable	Unit	Helmer														
		Center	Chevans	Cuffs	Dutchman	Nelson	Little	Loon	Mt. Maud	North	Swamp	Swede	Taylor	Teal	Trout	Turtle
Lake area	ha	14.2	3.9	5.8	18.8	9.1	0.6	13.8	3.4	2.2	143.7	1.6	13.0	29.4	25.9	2.5
Watershed area	ha	587	1839	587	335	587	430	184	550	45	1458	32	673	344	114	41
Maximum depth	m	3.4	1.2	1.5	4.3	2.4	0.9	2.4	2.4	2.1	5.8	1.8	7.6	2.1	6.4	3.7
pH		6.45	6.60	7.00	6.80	6.60	7.30	6.90	6.58	7.50	7.00	7.70	7.60	7.40	7.40	7.10
Dissolved oxygen	mg/l	1.35	2.10	8.01	7.52	3.67	8.48	9.07	3.38	8.57	7.83	8.43	9.37	9.14	9.08	7.97
Specific conductance	µmhos/cm	48.0	53.0	38.9	46.3	67.4	138.0	25.0	64.0	98.5	37.0	134.5	50.0	126.5	48.5	49.5
Alkalinity	mg/l	21.5	20.0	16.0	16.0	31.5	41.0	8.0	29.5	48.0	12.5	67.9	23.0	23.0	20.9	20.0
Hardness	mg/l	24.5	33.0	19.0	22.5	40.0	53.5	11.0	35.0	49.0	20.0	71.0	24.0	45.0	22.0	24.0
Calcium	mg/l	5.4	6.8	3.6	4.8	7.3	13.2	2.5	8.4	14.4	4.5	24.5	6.9	10.2	5.3	7.0
Magnesium	mg/l	2.50	3.80	1.90	2.40	4.50	4.40	0.87	3.00	2.63	1.49	3.65	1.46	3.54	1.80	1.40
Chloride	mg/l	0.8	1.2	0.8	1.2	0.9	10.7	0.3	1.3	0.3	0.7	0.3	0.2	19.3	0.4	0.3
Sulfate	mg/l	0.5	0.5	0.8	0.5	0.8	6.0	3.0	0.5	1.1	3.0	2.1	1.0	3.4	3.0	3.0
Nitrate+nitrite-N	mg/l	0.050	0.050	0.030	0.050	0.050	0.030	0.040	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
Total nitrogen	mg/l	0.90	1.10	0.80	1.00	1.15	0.71	0.85	0.95	0.60	0.80	0.80	0.45	0.85	0.70	0.50
Total phosphorus	mg/l	0.028	0.019	0.026	0.025	0.050	0.012	0.024	0.034	0.012	0.025	0.016	0.010	0.013	0.011	0.027
Total suspended solids	mg/l	2.5	3.0	2.2	5.0	4.0	1.8	5.5	4.0	0.8	6.8	4.0	0.8	1.1	3.8	2.0
Chlorophyll- <i>a</i>	µg/l	3.0	3.0	3.0	6.0	3.0	1.0	5.0	2.0	2.0	5.0	4.5	2.0	2.0	2.0	1.0
Secchi depth	m	0.79	0.71	1.20	0.75	0.63	1.20	1.00	1.10	1.20	0.75	1.20	4.38	1.20	2.00	1.40
Dissolved organic carbon	mg/l	17.40	31.80	12.30	17.15	22.75	13.15	11.30	21.75	9.85	20.40	9.90	5.30	17.35	7.75	9.00
Color (calculated)	PtCo	123	258	74	120	173	82	65	164	51	151	52	8	122	31	43
TSI-Secchi		63	65	57	64	67	57	60	59	57	64	57	39	57	50	55
TSI-Chlorophyll- <i>a</i>		41	41	41	48	41	31	46	37	37	46	45	37	37	37	31
TSI-Total phosphorus		52	46	51	51	61	40	50	55	40	51	44	37	41	39	52
Total nitrogen:total phosphorus		34	53	28	38	22	45	32	29	39	32	44	38	66	43	21
Chlorophyll- <i>a</i> :total phosphorus		0.12	0.15	0.11	0.25	0.07	0.09	0.18	0.06	0.15	0.23	0.30	0.16	0.19	0.21	0.05

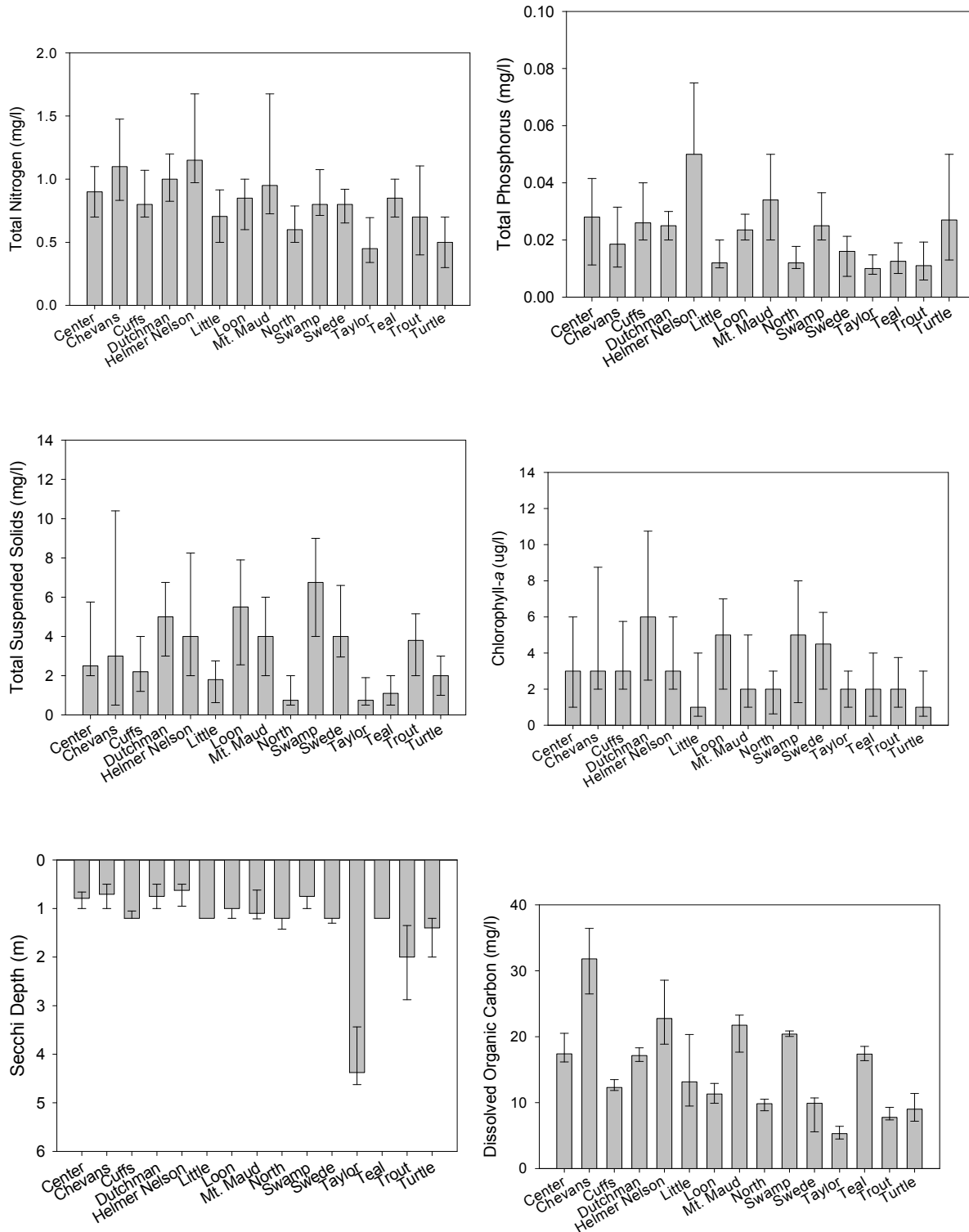
Appendix A-2. Median water quality conditions in 15 Grand Portage lakes, sampled May through October, 1999-2006. Error bars denote the 25th and 75th percentiles; if no error bars or only one error bar is shown, 25th and/or 75th percentile values were equal to the median value. “D.O.” = dissolved oxygen; “TSI”=Trophic State Index.



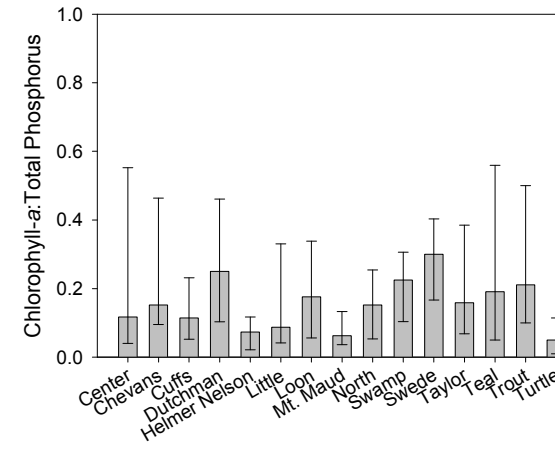
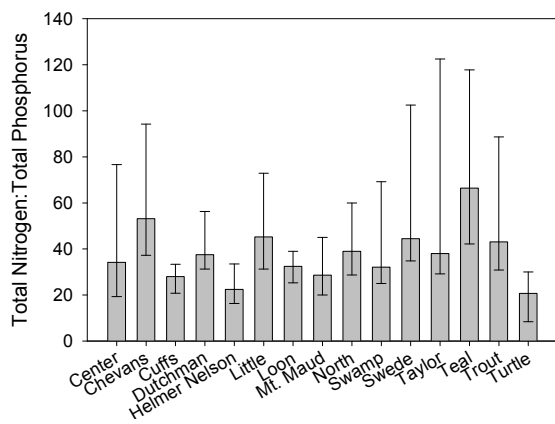
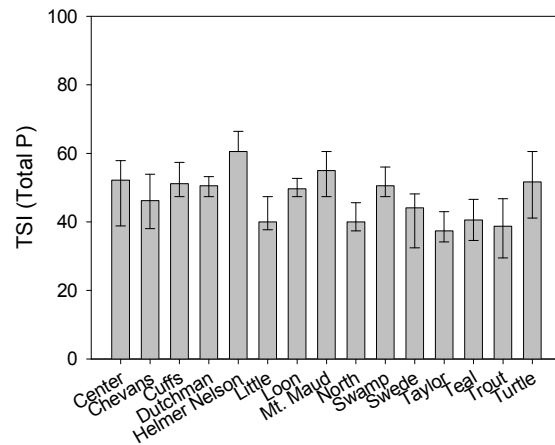
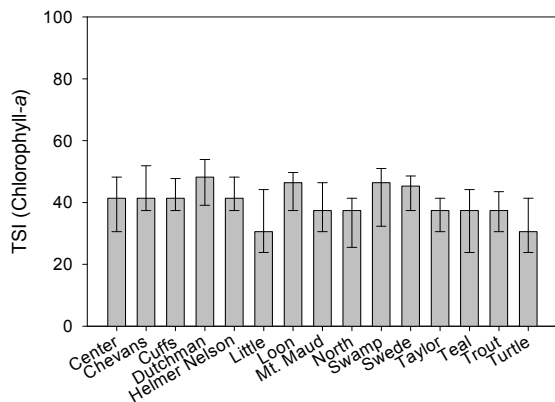
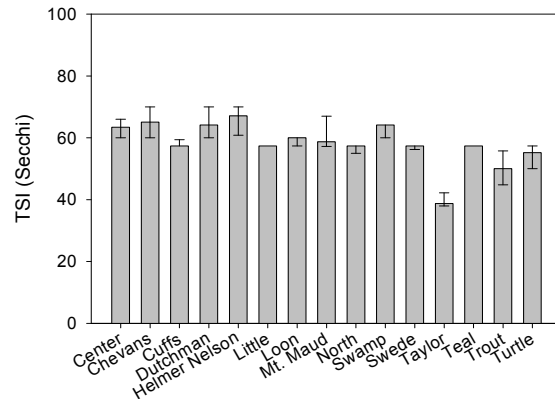
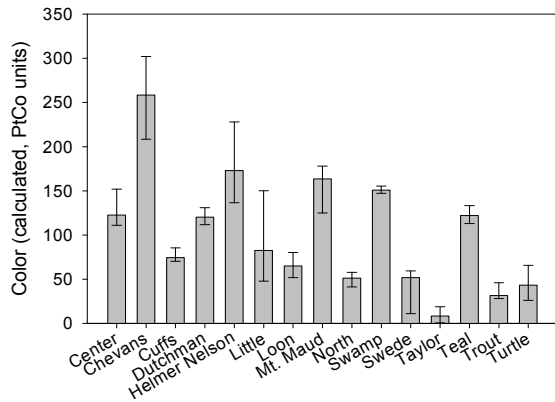
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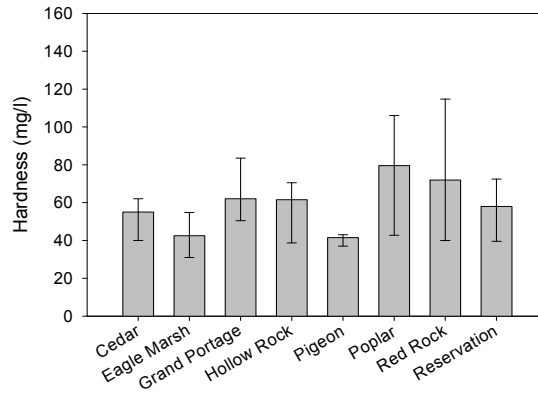
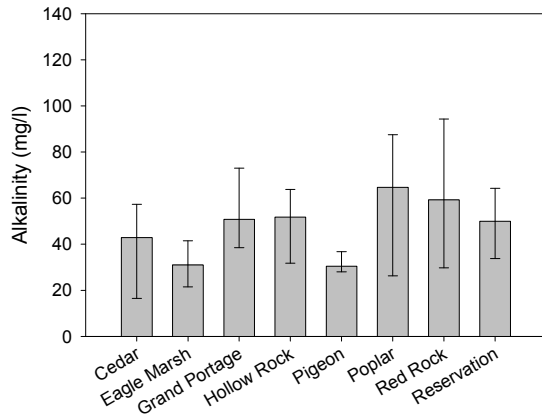
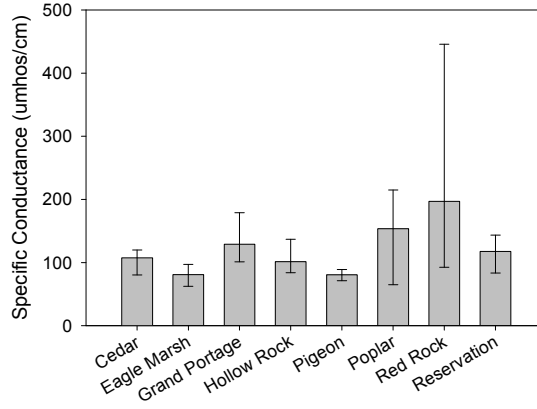
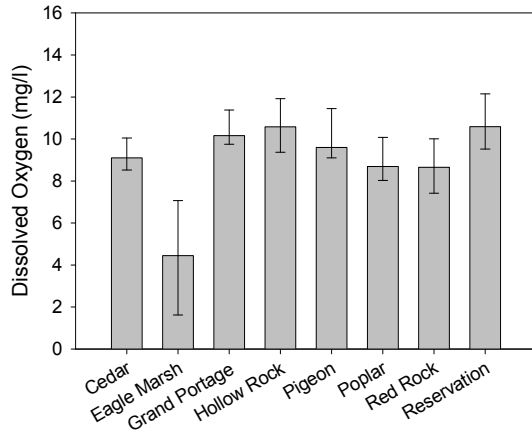
Appendix A-2. Median water quality conditions in 15 Grand Portage lakes, sampled May through October, 1999-2006. Error bars denote the 25th and 75th percentiles; if no error bars or only one error bar is shown, 25th and/or 75th percentile values were equal to the median value. “D.O.” = dissolved oxygen; “TSI”=Trophic State Index (continued).



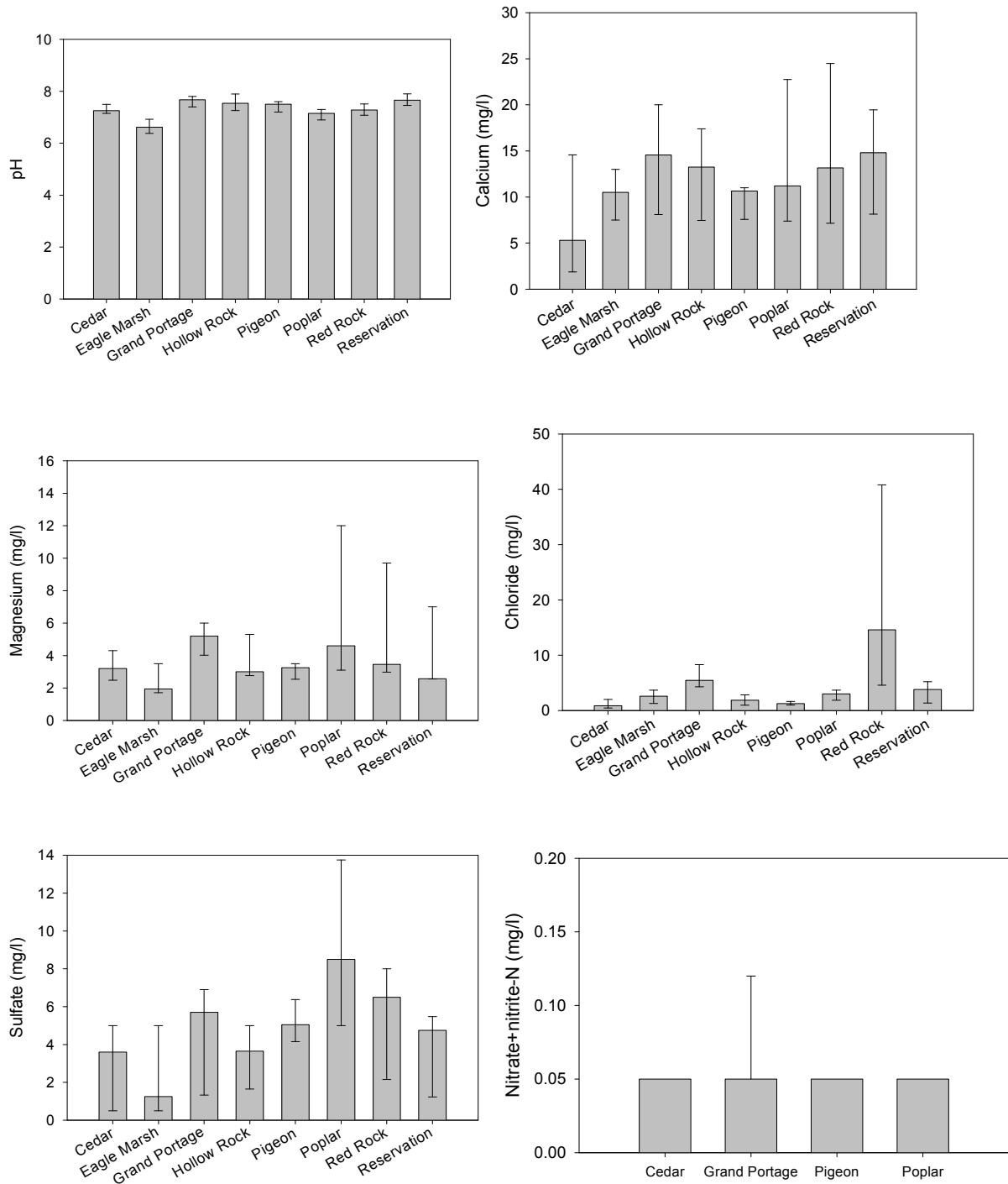
Appendix B-1. Stream-specific median values for water quality variables measured in eight Grand Portage Reservation streams, sampled 1999-2006.

Variable	Unit	Cedar	Eagle Marsh	Grand Portage	Hollow Rock	Pigeon	Poplar	Red Rock	Reservation
pH		7.30	6.70	7.64	7.58	7.50	7.10	7.30	7.71
Dissolved oxygen	mg/l	9.11	4.45	10.16	10.58	9.60	8.79	8.65	10.58
Specific conductance	µmhos/cm	107.5	80.8	129.0	101.2	80.7	153.5	189.0	105.0
Alkalinity	mg/l	42.9	31.0	50.8	51.8	30.5	64.7	59.3	50.0
Hardness	mg/l	55.0	42.5	62.0	61.5	41.5	79.5	72.0	58.0
Calcium	mg/l	3.8	11.0	15.2	14.3	11.0	14.9	13.2	14.8
Magnesium	mg/l	3.65	1.94	5.20	3.00	3.40	4.60	3.46	2.57
Chloride	mg/l	0.9	2.6	5.5	1.9	1.3	3.0	14.6	3.8
Sulfate	mg/l	3.6	1.3	5.7	3.7	5.1	8.5	6.5	4.8
Nitrate+nitrite-N	mg/l	0.050	n/a	0.050	n/a	0.050	0.050	n/a	n/a
Total nitrogen	mg/l	0.30	0.98	0.60	0.60	0.40	0.80	0.80	0.73
Total phosphorus	mg/l	0.013	0.041	0.027	0.022	0.027	0.050	0.020	0.028
Total suspended solids	mg/l	2.0	4.0	2.0	1.0	9.0	13.4	1.5	2.5
Chlorophyll- <i>a</i>	µg/l	0.5	1.3	0.5	0.5	1.0	2.0	0.5	0.8
Transparency	m	1.20	1.00	1.20	1.20	0.66	0.41	1.20	1.20
Dissolved organic carbon	mg/l	6.35	n/a	14.15	n/a	9.30	19.85	n/a	n/a
Color (calculated)	PtCo	18	n/a	92	n/a	46	146	n/a	n/a
TSI-Secchi		57	60	57	57	66	73	57	57
TSI-Chlorophyll- <i>a</i>		24	33	24	24	31	37	24	27
TSI-Total phosphorus		41	58	51	49	51	61	47	52
Total nitrogen:total phosphorus		25	26	22	26	16	15	39	24
Chlorophyll- <i>a</i> :total phosphorus		0.05	0.04	0.03	0.03	0.06	0.05	0.03	0.04

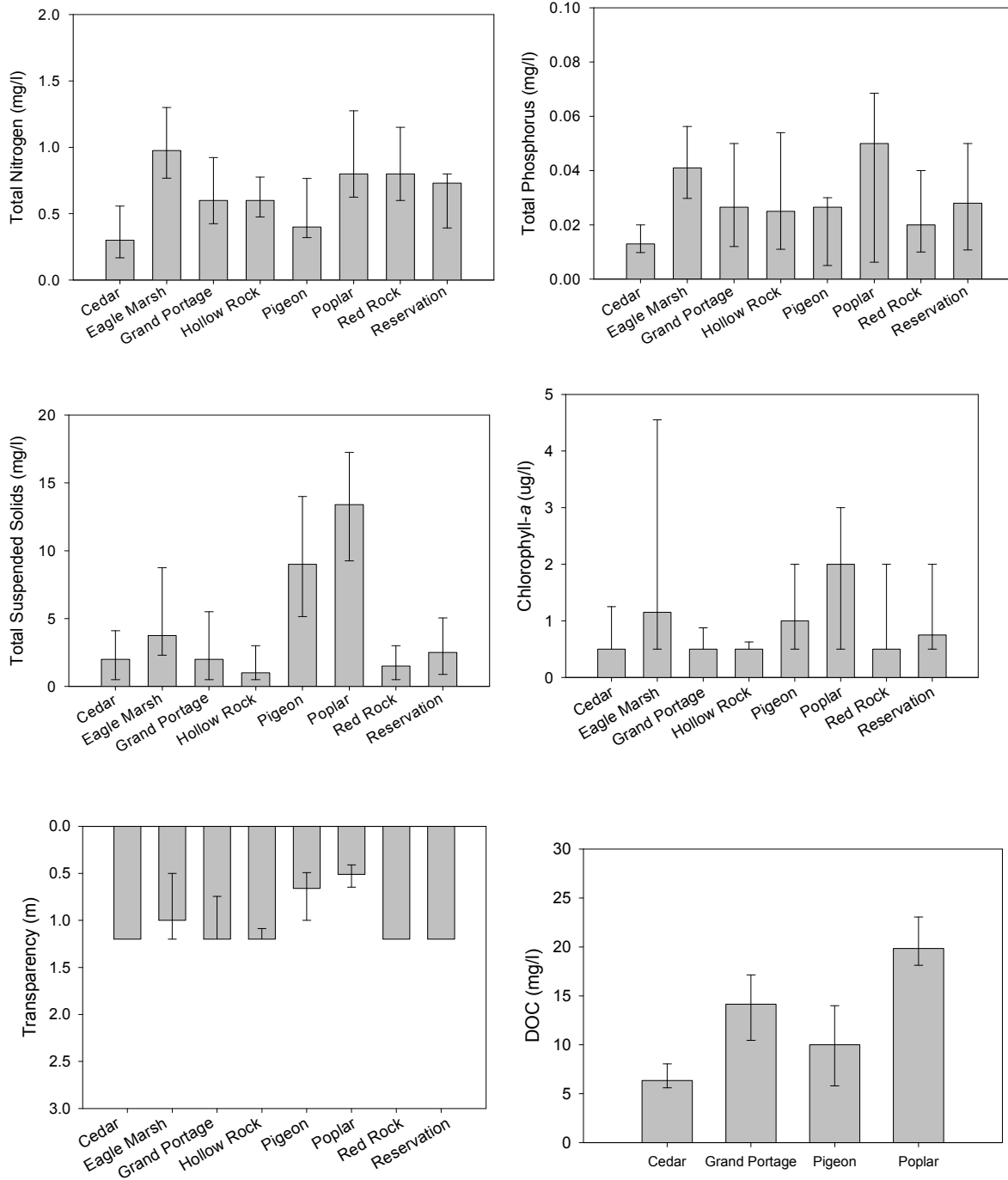
Appendix B-2. Median water quality conditions in eight Grand Portage streams, sampled April or May through October, 1999-2006. Error bars denote the 25th and 75th percentiles; if no error bars or only one error bar is shown, 25th and/or 75th percentile values were equal to the median value.



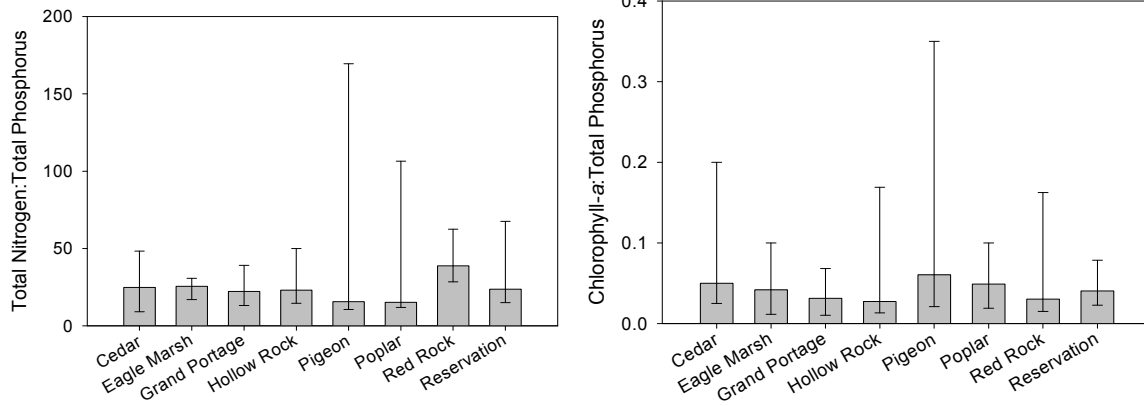
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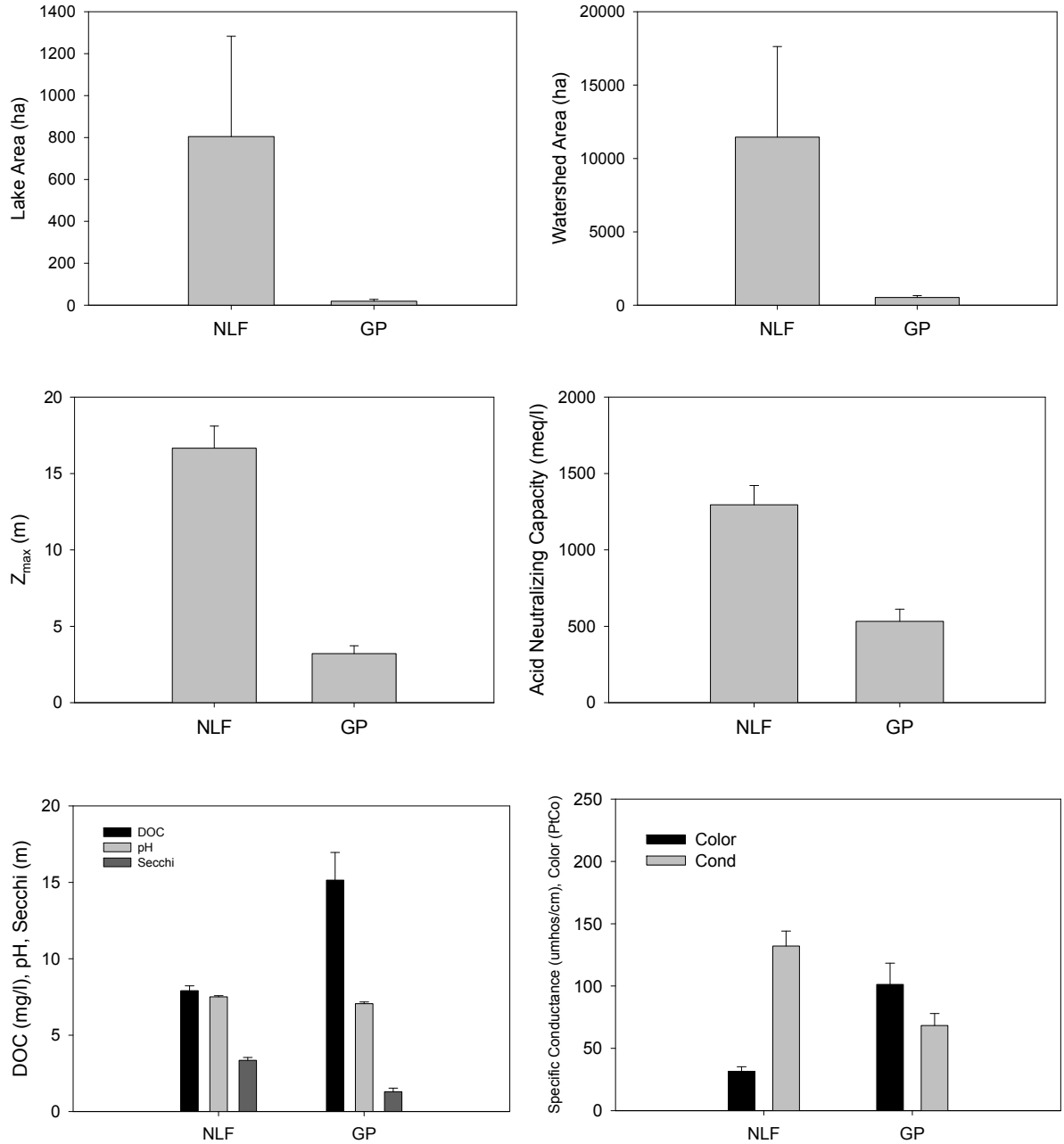
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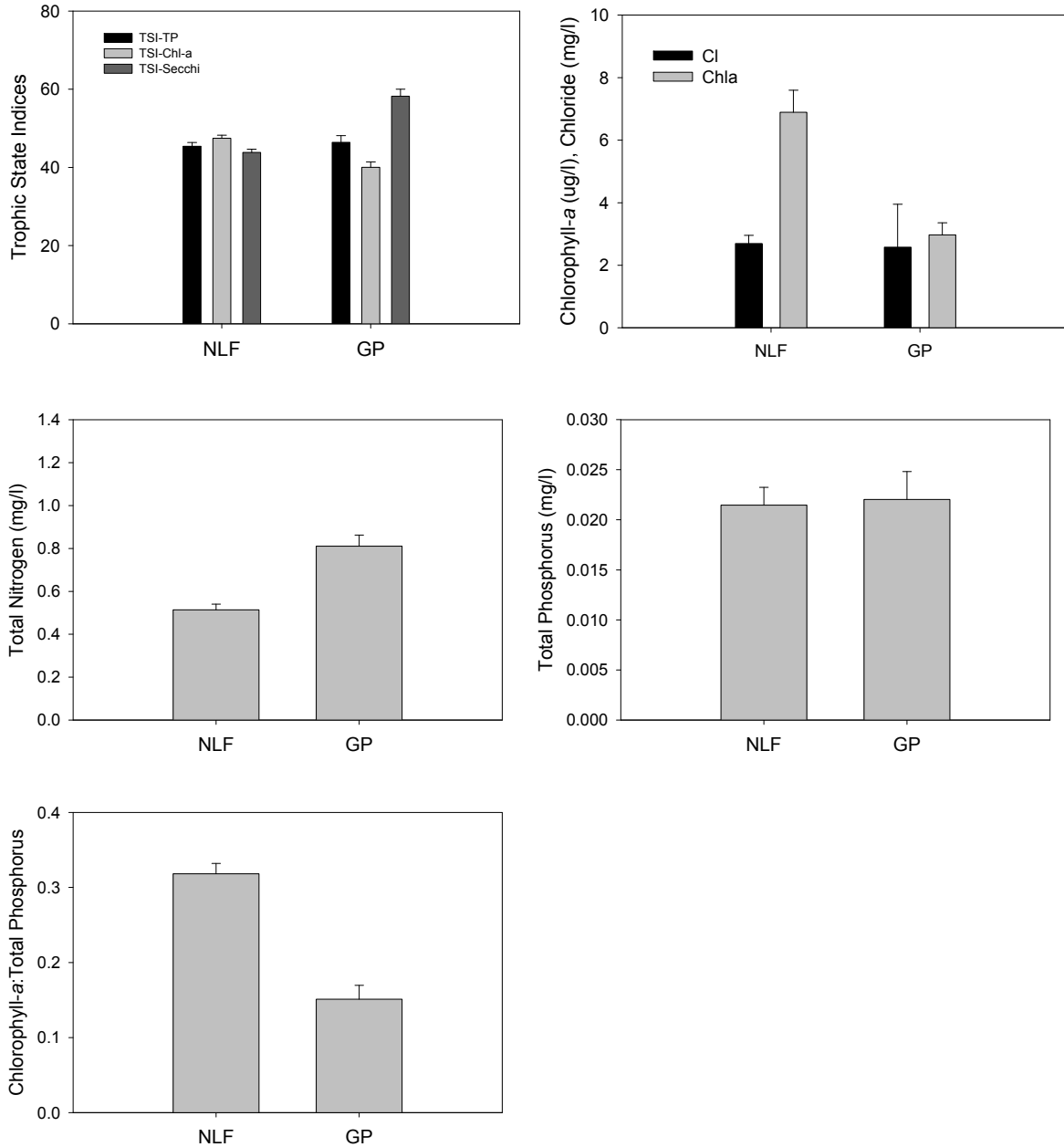
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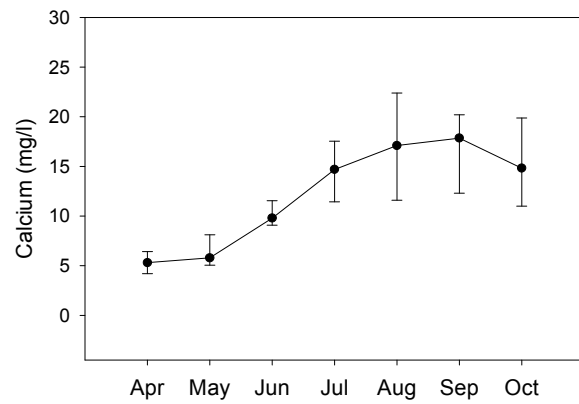
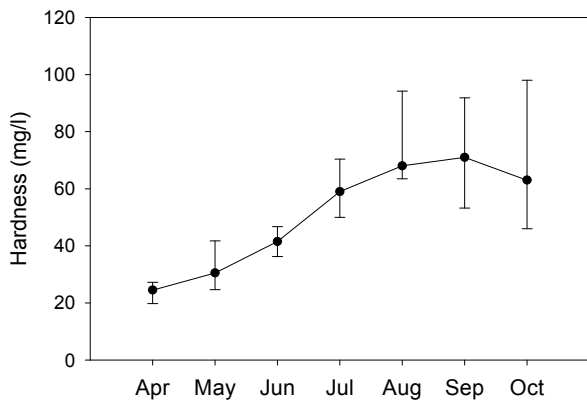
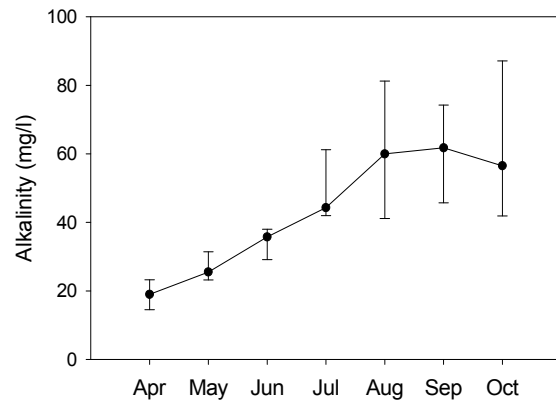
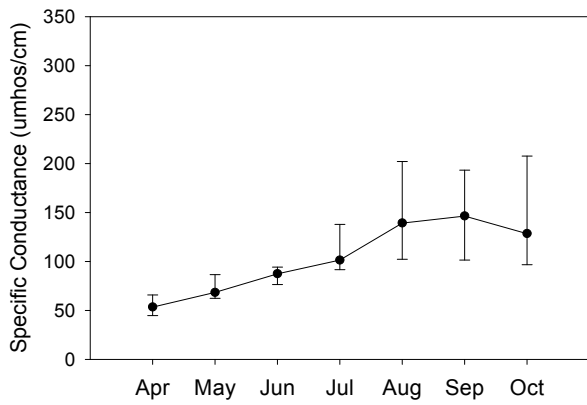
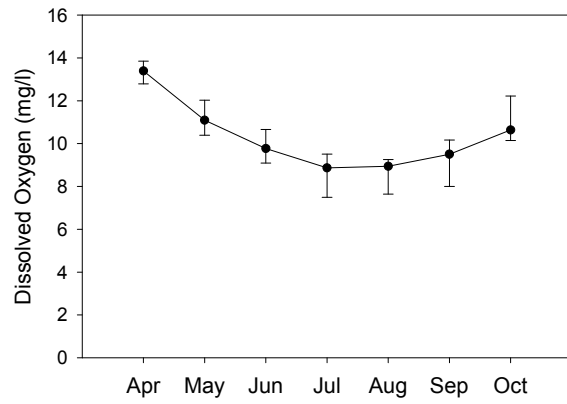
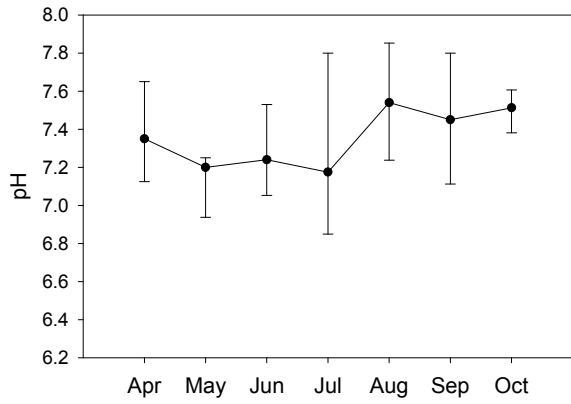
Appendix C. Mean water quality characteristics for 15 lakes in the Grand Portage Reservation (“GP”, based on the mean of individual lake medians) vs. 59 Minnesota lakes in the Northern Lakes and Forests Ecoregion (“NLF”). Error bars denote 1 standard error. Refer to Table 3 for variable abbreviations.



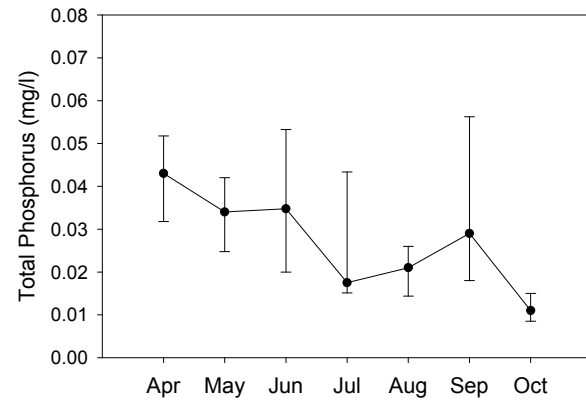
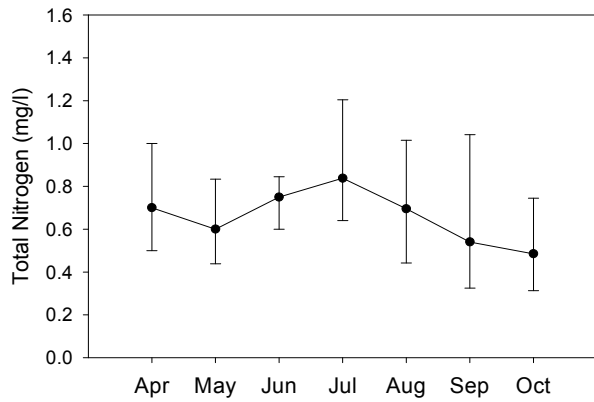
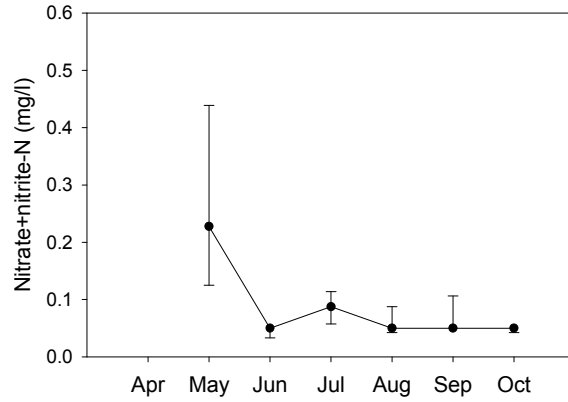
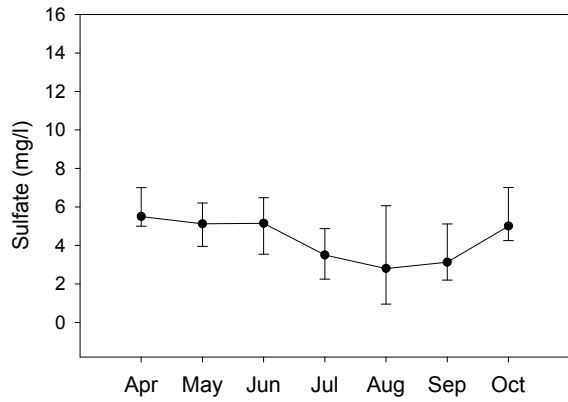
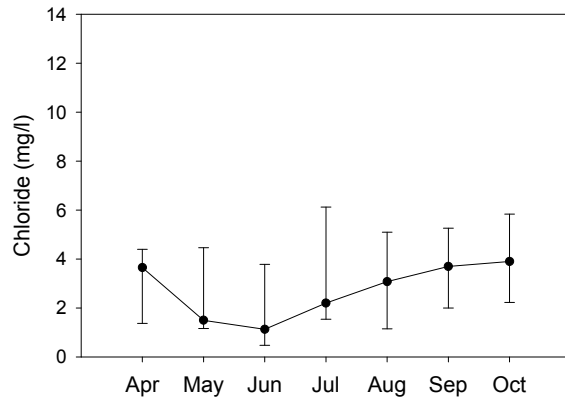
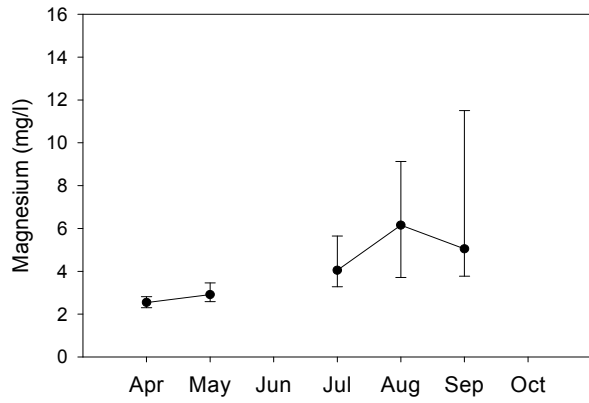
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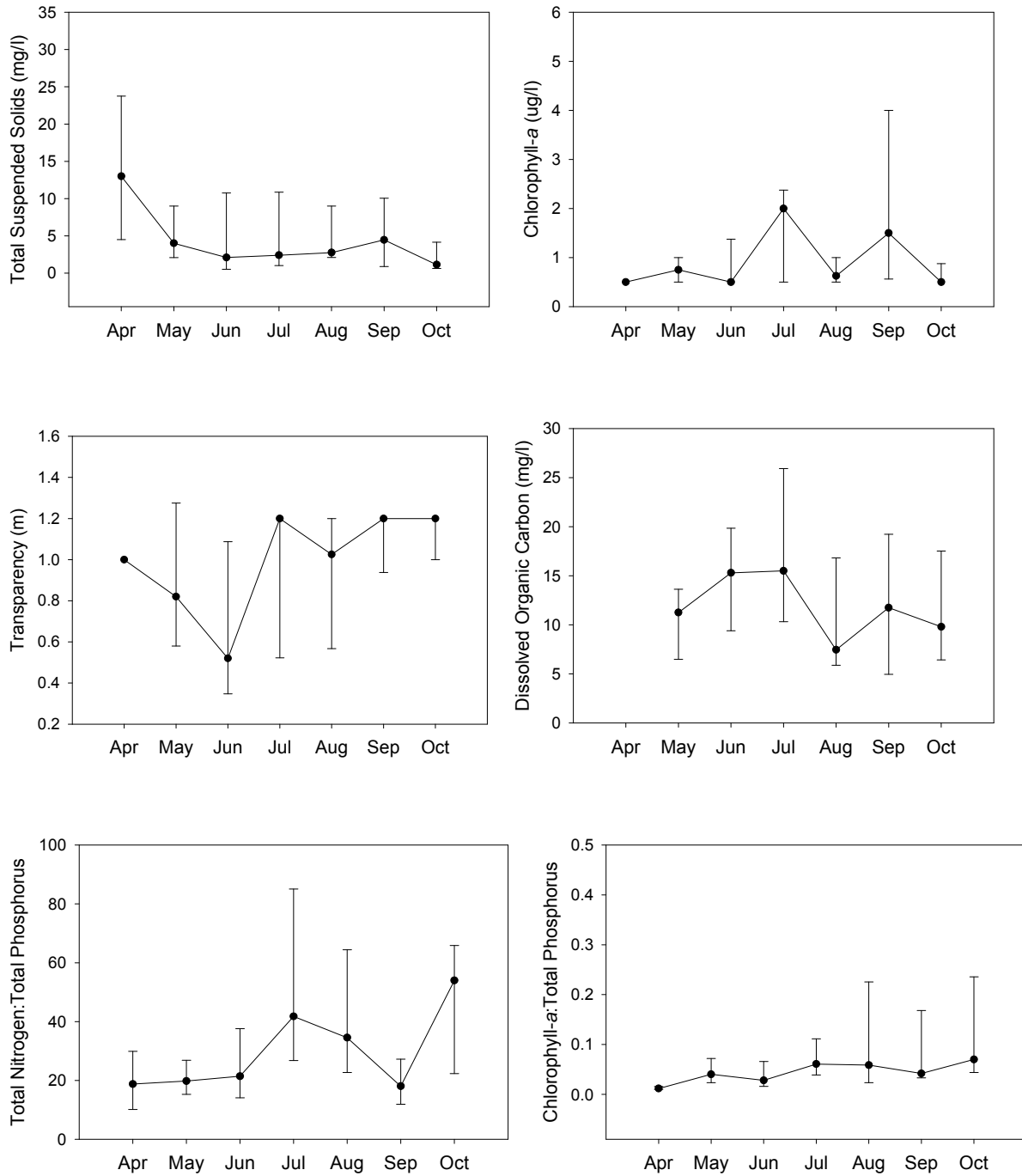
Appendix D. Seasonal patterns in water quality characteristics for eight Grand Portage streams, sampled 1999-2006, shown as median values for each month. Error bars denote 25th and 75th percentiles.



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