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Water Quality Sampling at St. Croix National Scenic Riverway, 2007

David VanderMeulen and Joan Elias
Great Lakes Network

Great Lakes Network Report GLKN/2008/03 **March 2008**

Photo credits clockwise from upper left: early spring sampling on the Apple River (J. Sieracki); Railroad Bridge over Lake St. Croix at Prescott, WI (D. VanderMeulen), David VanderMeulen and Peter Deurkop, sampling from bridge over the Namekagon River at Earl, WI (J. Elias); upper Namekagon River at Phipps Landing (D. VanderMeulen).

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Abstract

The Great Lakes Inventory and Monitoring Network (Network or GLKN) began monitoring water quality in the St. Croix National Scenic Riverway (SACN) in 2007. Monitoring began at eleven sites in April, with two additional sites added in May, and continued through November. In the field, we measured water temperature, pH, specific conductance, and dissolved oxygen with a multiprobe. We also measured water clarity with a transparency tube and Secchi disk, and recorded environmental conditions, such as weather and flow conditions. Water samples were collected during each sampling period and sent to contract analytical laboratories for analysis of chlorophyll-*a*, nutrients (total phosphorus, total nitrogen, nitrate+nitrite-nitrogen, ammonia-nitrogen), total suspended solids, dissolved organic carbon, alkalinity, chloride, sulfate, cations (calcium, magnesium, potassium, sodium), and dissolved silica. We also collected surface sediment samples at five sites for analysis of diatom communities, which are a good integrator of water quality conditions.

Monitoring sites were categorized into two general groups; lake sites and river sites, based mainly on hydrology and channel morphology. In general, water quality conditions were good at SACN, with somewhat degraded conditions at downstream sites in Lake St. Croix and in the Willow River, especially with respect to excess nutrient levels. These sites integrate upstream water quality conditions, which indicate that upstream nutrient additions are impacting downstream sites in a cumulative fashion. The Apple, Willow, and Kinnickinnic Rivers had very high concentrations of nitrate+nitrite-nitrogen. The watersheds associated with these tributaries are dominated by agriculture and increasing development, and have coarse-textured highly permeable soils over carbonate bedrock, which makes groundwater more susceptible to contamination from nitrate+nitrite-nitrogen fertilization associated with agriculture and increasing urbanization.

Although water quality was generally good, EPA-recommended nutrient reference conditions were exceeded at most of the monitoring sites in 2007. These exceedances may only be leading to a reduction in beneficial uses at sites furthest downstream. Applicable state (Minnesota and Wisconsin) water quality standards were met at SACN throughout the season, except for low dissolved oxygen concentrations in the lower portion of the water column for two sites on Lake St. Croix in mid-summer.

Additional monthly water quality monitoring is scheduled to take place in 2009 and 2011, with quarterly monitoring in the interim years dependant on additional funding. Upon completion of three full years of monthly monitoring, we will analyze the data for potential trends over time and will produce a report that synthesizes our data and those of other monitoring efforts.

Introduction

The Great Lakes Inventory and Monitoring Network (hereafter the Network or GLKN) measured water quality variables and collected water samples for laboratory analyses at the St. Croix National Scenic Riverway in 2007, after implementing the Network's large rivers water quality monitoring protocol (Magdalene et al. 2007) at Mississippi National River and Recreation Area in 2006. Water quality as a vital sign ranked high across Network parks and monitoring water quality is mandated by the National Park Service Water Resources Division. Of the vital signs discussed and ranked by park and GLKN staff as well as outside experts (Route 2004), the water quality monitoring protocol encompasses the following:

- core suite (temperature, dissolved oxygen, conductivity, pH, clarity)
- water level/flow
- advanced suite (alkalinity, dissolved organic carbon, silica, chloride, sulfate, calcium, sodium, potassium, magnesium, chlorophyll-a, total phosphorus, total nitrogen, ammonium-nitrogen, nitrate+nitrite-nitrogen)
- primary productivity (as estimated by chlorophyll-a measurements)
- nutrient dynamics (as measured by the phosphorus and nitrogen species)
- diatoms (not included within the water quality monitoring protocol, but closely tied to it)

The overall goal of the monitoring program for water quality of large rivers is to contribute to an understanding of the health of ecosystems and provide insights on likely water resources issues in the parks. The Network's objectives for monitoring water quality at SACN, listed in order of priority, are:

1. Monitor flow to determine changes in mean monthly and mean annual flow
2. Monitor mean annual concentrations of core and advanced suite parameters, accounting for seasonality in water quality conditions
3. Relate current water quality conditions to known historical conditions
4. Analyze water quality parameters for trends, and correlate any observed trends with potential causes (such as weather, climate, land use, point sources, exotic species, and atmospheric deposition)

This report summarizes the Network's activities related to water quality monitoring at SACN in 2007. The report concludes with a summary of findings and park-specific recommendations. Network data from 2007 will be compared with data collected by other agencies and data collected in previous years only after the details of field and laboratory methods for other work are known and deemed comparable.

Methods

Sampling Locations and Site Descriptions

The Network originally selected 11 sites for long-term monitoring, and added two sites after the first month of sampling (see list below for explanation) for a total of 13 water quality monitoring sites (Figure 1). During the site selection process, three upper SACN stations (Namekagon River near Earl, Wisconsin, St. Croix River near Norway Point, and St. Croix River about one mile downriver from the confluence with the Trade River) and three lower SACN stations on the St. Croix River (Pool 1 near Bayport, Minnesota, Pool 2 near Lake St. Croix Beach, Minnesota, and Pool 4 near Prescott, Wisconsin) were randomly chosen. The remaining seven sites were chosen non-randomly in consultation with members of the St. Croix Basin Water Resources Team

(Basin Team), which is composed of federal, state, and regional water resources professionals. Water quality monitoring at these seven sites is designed to fill spatial gaps in monitoring coverage, and to serve as integrator sites for contributions from select large tributaries. A complete description of the site selection process can be found in the Large Rivers Water Quality Monitoring Protocol (Magdalene et al. 2007). Site descriptions follow (Note: randomly-selected sites are indicated by an 'R' in parenthesis):

- **SACNa** was added in May, 2007 and is located in the upper St. Croix River above its confluence with the Namekagon River. It was selected to represent relatively pristine conditions in the northern lakes and forest ecosystems, and to expand water quality monitoring to the upper St. Croix River at a site where other water resource related projects are taking place. Sampling takes place from the CCC bridge on St. Croix Trail Road.
- **SACNb** was added in May, 2007 and is located in the upper Namekagon River and was selected to represent relatively pristine (reference) conditions in the northern lakes and forest ecosystems. The site is also downstream of nearby cranberry farm operations. Sampling takes place at Phipps Landing.
- **SACN01 (R)** is located on the Namekagon River at Earl, Wisconsin, and represents water quality conditions downstream of hydroelectric facilities at Hayward, Wisconsin. Sampling takes place from the North Road bridge.
- **SACN02 (R)** is located just upstream of Norway Point on the St. Croix River. This is the first water quality monitoring site to integrate both the upper St. Croix and Namekagon Rivers, and is co-located with a United States Geologic Survey (USGS) gage that will begin operation in 2008. Sampling takes place in the center of the river just upstream of the Norway Point landing.
- **SACN03** is located near the mouth of the Snake River. The site was identified as a high-priority site by Basin Team to supplement other monitoring efforts through more frequent sampling, and is downstream from an active USGS gage. The site is accessed from the Snake River Campground in Minnesota.
- **SACN04 (R)** is located on the St. Croix River approximately 1 mile upstream from Nevers Dam, just downstream of the confluence with the Trade River. This is the last water quality monitoring site on the St. Croix River where hydrologic processes are classic mainstem river flow rather than akin to a lake.
- **SACN05** is located on the St. Croix River just above the dam at St. Croix Falls. Monitoring at this 'lake-like' site was deemed a high priority by the Basin Team, as flow is also monitored here, and downstream land uses and land cover begins to be dominated by agriculture, mixed forest, and urban development. Sampling takes place at a site adjacent to SACN headquarters, just before the river channel widens significantly near the dam.

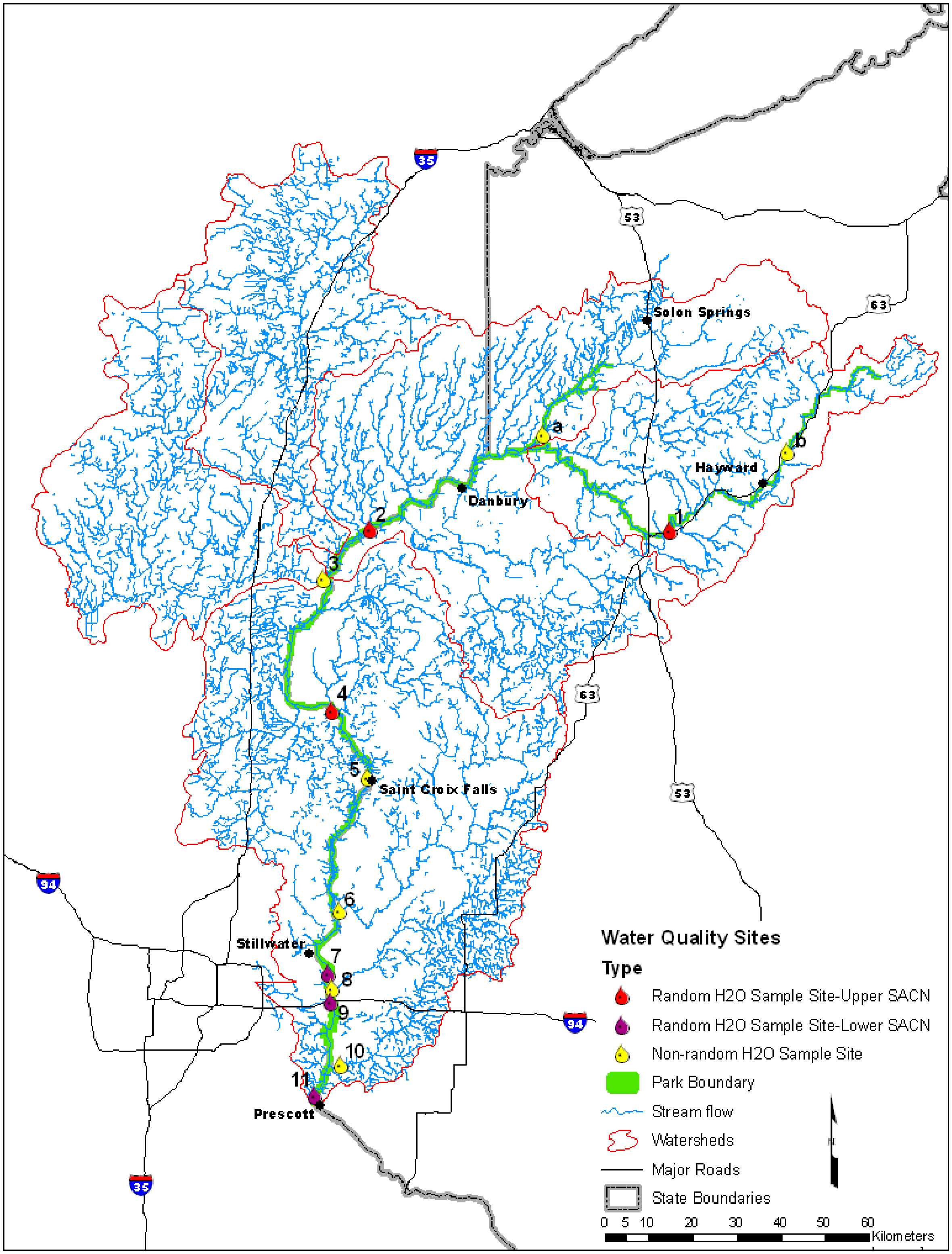


Figure 1. Location of water quality monitoring sites in St. Croix National Scenic Riverway.

- **SACN06** is located on the Apple River just upstream from its terminus with the St. Croix River. This site was identified as a high priority site by the Basin Team, as monitoring by the Network will fill a substantial gap in current monitoring by other agencies. The site is located downstream from an active USGS gage, and is accessed from private land at the end of Apple River Trail road.
- **SACN07 (R)** is located in Pool 1 of Lake St. Croix near Bayport, Minnesota. The site represents water quality conditions near the upstream end of Lake St. Croix, and also is located near the U.S. Army Corps of Engineers water elevation gage in Stillwater, Minnesota. Monitoring at this site will be used to assess nutrient conditions for Lake St. Croix, which is now 303(d) listed for phosphorus. Sampling takes place in the main channel across from the public boat launch in Bayport.
- **SACN08** is located in Lake Mallalieu, which is an impoundment (reservoir) of the Willow River near its terminus with the St. Croix River. The Willow River watershed is heavily dominated by agriculture and is undergoing intense development. The Willow River is currently the subject of a Total Maximum Daily Load study, and monitoring in Lake Mallalieu was identified as a top priority site by the Basin Team. The site is accessed by the public boat ramp on Lake Mallalieu in North Hudson, Wisconsin.
- **SACN09 (R)** is located in Pool 2 just downstream of the mouth of the Willow River and the I-94 Bridge. Monitoring at this site supports Basin Team modeling efforts and will be used to assess nutrient conditions for Lake St. Croix, which is now 303(d) listed for phosphorus. The site is accessed from the public boat ramp in Hudson, Wisconsin.
- **SACN10** is located on the Kinnickinnic River approximately 1.5 miles upstream of its mouth at the St. Croix River. Deemed a high-priority by the Basin Team, this site is co-located with an active USGS gage, and water quality work here will fill gaps in current monitoring by other agencies. Sampling takes place just upstream of the County F bridge.
- **SACN11 (R)** is located in Pool 4 of Lake St. Croix near the terminus of the St. Croix River. Monitoring at this site integrates all upriver water quality parameters, and is located near a newly-installed USGS flow gage at Prescott, Wisconsin. Monitoring at this site will be used to assess nutrient conditions for Lake St. Croix, which is now 303(d) listed for phosphorus. Sampling takes place in mid-channel across from Carpenter Nature Center in Minnesota. The site is accessed from the public boat ramp on the Mississippi River at Prescott, Wisconsin.

Field Methods

We conducted water quality sampling at each site once a month throughout the open water season (Table 1). Samples were not collected in March (per Magdalene et al. 2007), due to unsafe, iced-up conditions on the river. In addition, samples also were not collected in April at sites SACNa and SACNb, as they had not yet been added to the list of sites to be monitored. Whenever feasible, we conducted field sampling at approximately the deepest part of the channel and the centroid of flow. In a few instances high water and unsafe currents prohibited sampling in the center of the channel, and sampling occurred closer to the riverbank.

Table 1. Dates of water quality sampling at SACN in 2007.

Sampling Dates, 2007
April 2-6, 10
May 3-4, 7
June 6-8, 11
July 9-12
August 6-8, 10
September 10-14
October 9-12
November 5-8

Profile data on temperature, dissolved oxygen concentration, specific conductance, and pH were collected near the surface and at 0.5 or 1 m intervals with a Hydrolab multiprobe. At each site, we also measured water clarity using a transparency tube and/or Secchi disk, took a GPS reading, recorded environmental conditions (e.g., wind speed and direction, wave height, sky cover, air temperature), and noted field personnel and instrumentation.

The multiprobe was calibrated daily for specific conductance and pH, and prior to sampling at each site for dissolved oxygen and depth. The temperature probe was checked with a NIST-calibrated thermometer prior to the season and was found to read within acceptable limits (Ledder and Elias 2007). A brass chain with precise length markers was used to check previously marked depth increments on the nylon rope attached to the Secchi disk.

We collected 0-2 m integrated water samples for laboratory analyses using an integrated tube sampler (MPCA 2004a, b; WDNR 2004). When the water was 1-2 m deep, we used the tube sampler on an angle to collect a sample from the full water column. When the water was < 1 m deep, an elbow-deep grab sample was collected. Water was composited in a 9 L high density polyethylene carboy that had been cleaned in the lab prior to sampling and rinsed three times with sample water on-site. The composited water was used for the transparency tube reading and to fill 1 L brown and translucent polyethylene bottles for chlorophyll-*a* and total suspended solids (TSS) samples. The composite container was then topped off with additional water from the integrated sampling tube for the remaining laboratory analyses. The 1 L bottles and the composite container were stored in a cooler on ice until further processing could be completed. Samples were further processed later the same day or the following day.

Equipment blanks were conducted prior to field sampling in April and midsummer to ensure we were not introducing any contamination to the samples. During each round of sampling, we collected duplicate samples from one randomly selected site. Duplicates were split samples taken from the same composite water sample. We fabricated a station code, date, and time of collection for each sample to disguise its status as a duplicate sample. Every site had an alphanumeric identification code.

Analytical Laboratories

We contracted with White Water Associates (WWA) and Natural Resources Research Institute (NRRI) for analytical laboratory services. Samples were sent to NRRI for nutrient analysis. All other analyses were conducted by WWA.

Sample Processing

Samples were processed at the St. Croix National Scenic Riverway lab. Both a hand pump and electric vacuum pump were used to process samples requiring filtration. Sample handling and processing is detailed below and summarized in Table 2.

Handling and Processing Samples for White Water Associates Laboratory: Water from the 1 L brown bottle was filtered through a Whatman GF/C paper filter for analysis of chlorophyll-*a* (chl-a). The volume of water passed through the filter was recorded (1000 ml or until the filter began to clog, whichever came first). The filter was then folded into quarters, wrapped in aluminum foil, placed in a small plastic bag, and frozen for later analysis.

Water from the 1 L translucent bottle was filtered through a dried, pre-weighed paper filter provided by WWA for analysis of total suspended solids (TSS). The volume of water passed through the filter was recorded (1000 ml or until the filter began to clog, whichever came first). The filter was placed back into its original aluminum tray, and then in a bubble wrap bag, which was placed in a small plastic bag, and refrigerated for later analysis.

Water from the composite container was processed in various ways, depending on the analyte to be measured. One bottle was filled with raw sample water without a preservative and refrigerated for analysis of alkalinity (alk), chloride (Cl^-), and sulfate (SO_4^{-2}). Water from the remaining composite sample was filtered through a Millipore 0.45 µm membrane filter, then split into three bottles: 1) preserved with H_2SO_4 for analysis of dissolved organic carbon (DOC), 2) preserved with HNO_3 for analysis of cations (calcium (Ca^{+2}), sodium (Na^+), magnesium (Mg^{+2}), and potassium (K^+)), and 3) without a preservative for analysis of dissolved silica (SiO_2). All bottles were then stored in a refrigerator until shipped to the laboratory.

Handling and Processing Samples for Natural Resources Research Institute Laboratory: Raw sample water from the composite container was used to fill one bottle for analysis of total phosphorus (TP) and total nitrogen (TN). For analysis of ammonium-nitrogen (NH_4-N) and nitrate+nitrite-nitrogen (NO_3+NO_2-N), water was filtered through a Millipore 0.45 µm membrane filter and placed into one bottle. All nutrient samples were frozen until analysis at the laboratory.

Shipping Samples to the Laboratory

Samples that were completed before noon on Thursday were shipped Thursday afternoon via overnight FedEx to the laboratories. Samples that were completed after noon on Thursday were shipped the following Monday via overnight FedEx. In several instances monthly NRRI samples were delivered personally by Network staff. Refrigerated samples and frozen nutrient samples were packed in a cooler surrounded by bags and bottles of ice. Frozen filters for chlorophyll-*a* analysis were bundled together in double plastic bags and sandwiched between bags and bottles of ice. All samples arrived at the respective laboratories within recommended holding times in good condition and at acceptable temperatures with the exception of the June nutrient samples that had not frozen solid prior to shipping. They were frozen immediately upon receipt at the laboratory.

Table 2. Water sampling frequency, sample handling and processing procedures; analyte abbreviations as in text. M=monthly samples, Q=quarterly samples

Analyte	Sampling Frequency	Processing	Handling
Alkalinity	Q	raw water sample	refrigerate
Anions (Cl^-, SO_4^{-2})	Q	raw water sample	refrigerate
Cations (Ca^{+2}, Na^+, K^+, Mg^{+2})	Q	filter sample - 0.45µm membrane filter; preserve with HNO_3	refrigerate
Chlorophyll-*a*	M	filter sample – Whatman GF/C filter; record volume filtered	freeze
DOC	Q	filter sample - 0.45µm membrane filter; preserve with H_2SO_4	refrigerate
NO_3+NO_2-N	M	filter sample - 0.45µm membrane filter	freeze
NH_4-N	M	filter sample - 0.45µm membrane filter	freeze
TP/TN	M	raw water sample	freeze
SiO_2	Q	filter sample - 0.45µm membrane filter	refrigerate
TSS	M	filter sample –weighed filter provided by lab; record volume filtered	refrigerate

Results and Discussion

General Water Quality Observations

The thirteen water quality monitoring sites at SACN can be broken down into two general categories based mainly on hydrology and channel morphology:

- **Lake-like sites** – These sites are generally >3 m deep, have little to no evidence of flow through visual observation, and have the potential to thermally stratify. Sites that exhibit these conditions include the three stations on Lake St. Croix (SACN07, SACN09, and SACN11), and the two impoundments above the dams at St. Croix Falls (St. Croix River) and North Hudson (Lake Mallalieu on the Willow River) (SACN05 and SACN08, respectively). These sites will be referred to as 'lake sites'.
- **River-like sites** – These sites are generally <3 m deep, have obviously flowing water, and are well-mixed. Sites that exhibit these conditions include the two stations on the Namekagon River (SACNb and SACN01), three stations on the St. Croix River north of St. Croix Falls (SACNa, SACN02, and SACN04), and the remaining stations on the Snake, Apple, and Kinnickinnic Rivers (SACN03, SACN06, and SACN10, respectively). These sites will be referred to as 'river sites'.

Range and average values of field and laboratory variables measured at all thirteen sites are shown in Table 3; all data are shown in Appendices A and B. The next few paragraphs are devoted to a discussion of noteworthy results across all sites and over the complete sampling season. Seasonal (temporal) and geographic (spatial) trends and comparisons to water quality standards will be addressed later in this document.

Alkalinity, Specific Conductivity, and Cations/Anions

Alkalinity is a term that refers to the buffering capacity of a solution. The buffering capacity is essentially the ability of the solution (water) to resist changes in pH through additions of acids or bases. Mean alkalinity values at the river sites ranged from a low of 38 mg/L at the CCC bridge in the upper St. Croix River (SACNa) to 184 mg/L at the Kinnickinnic River (SACN10). Mean alkalinity values at the lake sites ranged from a low of 61 mg/L at the impoundment above the dam at St. Croix Falls (SACN05) to 131 mg/L at Lake Mallalieu (SACN08-Lake Mallalieu). Alkalinity values at both river and lake sites indicate that waters at SACN are reasonably well-buffered, especially in the lower portion of the basin.

Specific conductance is a measure of the ability of sample water to conduct electricity. Waters with higher concentrations of ions will have higher values of specific conductance. Listed in order of importance, CO_3^{-2}, SO_4^{-2}, Cl^- (anions) and Ca^{+2}, Mg^{+2}, Na^+, K^+ (cations) are the major contributors to specific conductivity in the St. Croix River basin. We observed a marked difference in mean specific conductance values for samples from the Apple, Willow (Lake Mallalieu), and Kinnickinic Rivers (267 µS/cm, 329 µS/cm, and 484 µS/cm, respectively) compared to the other water quality monitoring sites, which were all less than 205 µS/cm. Because conductivity is related to the concentration of ions, it is not surprising that concentrations of measured anions (SO_4^{-2}, Cl^-) and cations (Ca^{+2} Mg^{+2}, Na^+, K^+) were correlated to values of specific conductance (Table 3). Much of the calcium (Ca^{+2}) and sulfate (SO_4^{-2}) was most likely weathered from the underlying clay-rich, calcareous glacial deposits and sedimentary rocks, especially in the Apple, Willow, and Kinnickinnic watersheds (Juckem 2007). Concentrations of the remaining anions and cations are derived through weathering of the surrounding rocks and soils, and from anthropogenic inputs including fertilizers and runoff from urban and industrial areas (Stark et al. 2000).

Nitrate+Nitrite-Nitrogen

The Apple (SACN06), Willow (SACN08-Lake Mallalieu), and Kinnickinnic (SACN10) Rivers had very high concentrations of NO_3+NO_2-N, with mean values ranging from 729 µg/L at SACN06 to 5010 µg/L at SACN10 (Table 3 and Appendix C). In comparison, site SACN11 in Pool 4 of Lake St. Croix, which integrates water quality for the complete St. Croix Basin, had a mean NO_3+NO_2-N value of 364 µg/L. The watersheds associated with these tributaries are dominated by agriculture and increasing development. In addition, soils generally are coarse textured and highly permeable, which makes groundwater more susceptible to NO_3+NO_2-N loading via fertilizer application (Juckem 2007). This is especially evident in the Kinnickinnic River, which not only has highly permeable soils but is underlain by carbonate bedrock, making this watershed more susceptible to groundwater contamination (Juckem 2007).

Chlorophyll-a

Chlorophyll pigment (chlorophyll-*a*) concentrations can be used to estimate algal biomass, and serve as a basis for evaluation of trophic status. Chlorophyll-*a* concentration in samples from all 13 monitoring sites over the 2007 monitoring season was much lower than expected, with many chlorophyll-*a* samples reported as having a non-detectable concentration by the laboratory. Preliminary investigations (e.g., comparison of GLKN chlorophyll-*a* data with chlorophyll-*a* data collected by other organizations on the St. Croix River near GLKN monitoring sites, and regression analysis of TP with chlorophyll-*a*) into these low chlorophyll-*a* values have confirmed that our chlorophyll-*a* results are unreliable and will not be assessed in this report.

TN/TP

Although chlorophyll-*a* data collected in 2007 are suspect, past water quality studies have shown that SACN is sensitive to increased nutrient loading (Lafrancois et al. *in press*), which is expressed through increased concentrations of chlorophyll-*a* (i.e., increases in algal biomass), and also through changes in diatom assemblages (Edlund and Engstrom 2001). Because high values of chlorophyll-*a* concentrations can be indicative of ecosystem degradation, it is useful to explore which nutrient, nitrogen or phosphorus, is potentially limiting growth of phytoplankton. This is most often accomplished by examining the ratio of nitrogen to phosphorus in the area of interest. High values of TN:TP usually indicate that phosphorus is limited, while low values of the ratio usually indicate that nitrogen is limited. Lower TN:TP provide conditions that favor cyanobacteria, as this group can fix nitrogen. Cyanobacteria, also known as blue-green algae, can form unsightly algal blooms and potentially lead to low oxygen concentrations in the water when they die and decompose. Cyanobacteria are usually not common at TN:TP greater than 29 (Wetzel 2001) and often dominate at values lower than 5 to 10 (Bulgakov and Levich, accessed 2/16/2007).

Most samples collected in SACN at the lake sites during 2007 (SACN05, 07, 08, 09, 11) had TN:TP values greater than 15 (Table 4), indicating possible phosphorus-limitation. Although use of TN:TP values to examine nutrient limitations at the river sites is applicable, chlorophyll-*a* concentrations for rivers is typically much lower than lakes given the same concentration of nutrients (Wetzel 2001). Several of the lake sites could be considered as transitional between phosphorus and nitrogen limitation during the August round of sampling, with ratios between 13 and 16 (Shaw et al. 1996). If 10 (Dillon et al. 2004) or 7 (Scheffer 2004) is used as the critical value, all sites were phosphorus limited throughout the sampling season. Although these ratios suggest that algae are likely limited by phosphorus at the lake sites, other factors such as water color and amount of dissolved organic carbon may to some extent suppress algae growth (Kent Johnson, personal communication). It should be noted, however, that although phosphorus may be a limiting nutrient, algal growth is abundant and total phosphorus values are relatively high. Visible algal blooms are common on Lake St. Croix in the summer, especially in the last decade (Kent Johnson, personal communication).

Table 3. Range and mean values of field and laboratory variables measured at St. Croix National Scenic Riverway, 2007. N = number of samples (Note: number of samples for SACNa and SACNb = N-1). Field measurements are transparency tube, Secchi depth, pH, specific conductance (SC25), dissolved oxygen (DO), and temperature. Near-surface values were used for pH, specific conductance, DO, and temperature. ND = not detected. Dash (-) = not measured or calculated.

		SACNa		SACNb		SACN01		SACN02		SACN03	
Variable	N	range	mean	range	mean	range	mean	range	mean	range	mean
Temperature (°C)	8	6.56-26.47	17.2	5.53-18.59	13.1	5.81-22.46	14.3	2.91-24.45	14.4	2.2-27.84	15.8
DO (mg/L)	8	8.04-12.79	9.6	8.22-11.53	10.0	6.86-11.53	9.2	6.81-12.64	9.0	8.75-11.72	10.1
pH (std. units)	8	6.36-8.09	7.55	6.50-8.53	7.56	6.54-8.16	7.59	6.94-7.90	7.48	6.67-8.64	7.80
SC25 (µS/cm)	8	90.2-99.1	92.3	126.7-172.8	151.0	130.8-185.3	161.4	84.6-161.4	132.1	92.0-248.8	185.1
TSS (mg/L)	8	ND-14	3.1	2-3	2.3	1-12	5.4	2-11	5.3	3-12	6.6
Trans. Tube (cm)	8	79.3-120+	-	>120+	>120+	87.8-120+	-	87.9-120+	-	57.7-120+	-
Secchi Depth (m)	8	-	-	-	-	-	-	-	-	-	-
TP (µg/L)	8	16-48	22.7	9-25	16.1	13-47	27.9	21-65	34.1	65-109	82.2
TN (µg/L)	8	258-1022	521.1	155-703	312.4	199-996	491.0	390-1204	650.4	929-1338	1154.1
NO_3+NO_2-N (µg/L)	8	ND-93	28.8	ND-110	37.6	32-216	103.3	9-279	95.2	31-367	153.3
NH_4-N (µg/L)	8	5-19	12.6	4-25	9.6	3-24	11.3	7-100	27.3	4-89	34.6
DOC (mg/L)	3	5.3-18.0	11.7	2.7-14.0	8.4	3.1-18.0	9.9	4.9-17.0	11.8	14.0-16.0	14.7
Alkalinity (mg/L)	3	32-44	38.0	54-79	66.5	55-83	64.3	34-75	53.7	32-99	74.7
Cl^- (mg/L)	3	1.9-2.7	2.3	2.6-3.1	2.9	3.9-4.2	4.1	3.1-3.7	3.3	4.8-7.5	6.1
SO_4^{-2} (mg/L)	3	3.60-9.94	6.8	5.00-6.29	5.7	4.59-6.40	5.2	3.90-7.28	5.5	4.50-5.79	5.2
Ca^+ (mg/L)	3	11.0-11.4	11.2	17.3-23.8	20.6	17.6-23.0	19.6	11.1-19.4	15.0	10.6-27.0	20.5
Mg^{+2} (mg/L)	3	3.54-4.26	3.9	4.86-7.02	5.9	5.24-7.46	6.0	3.62-6.96	5.2	4.23-10.70	8.24
K^+ (mg/L)	3	0.15-0.89	0.5	0.65-0.87	0.8	0.70-1.11	0.9	0.68-1.51	1.1	1.90-3.28	2.5
Na^{+2} (mg/L)	3	2.30-2.53	2.4	2.60-2.98	2.8	3.00-3.55	3.22	2.10-3.28	2.7	2.80-5.00	4.2
SiO_2 (mg/L)	3	2.8-10.0	6.4	5.7-13.0	9.4	5.4-14.0	10.5	3.4-11.0	7.6	2.5-14.0	7.7

Table 3 (continued). Range and mean values of field and laboratory variables measured at St. Croix National Scenic Riverway, 2007. N = number of samples. Field measurements are transparency tube, Secchi depth, pH, specific conductance (SC25), dissolved oxygen (DO), and temperature. Near-surface values were used for pH, specific conductance, DO, and temperature. ND = not detected. Dash (-) = not measured or calculated.

		SACN04		SACN05		SACN06		SACN07		SACN08	
Variable	N	range	mean	range	mean	range	mean	range	mean	range	mean
Temperature (°C)	8	3.61-25.77	15.1	4.22-27.37	16.1	5.03-23.48	15.4	2.69-27.26	17.2	5.9-24.80	16.5
DO (mg/L)	8	7.27-12.39	9.0	8.46-11.48	9.3	7.00-12.99	9.6	7.39-13.3	8.8	8.37-12.84	10.97
pH (std. units)	8	6.77-8.14	7.61	6.77-8.52	7.73	7.36-8.55	7.87	6.89-8.36	7.71	7.28-9.06	8.28
SC25 (µS/cm)	8	94.0-182.1	144.4	106.5-202.6	161.8	227.3-300.1	266.9	106.8-238.5	189.7	294.7-359.1	328.5
TSS (mg/L)	8	2-18	7.4	4-20	6.6	3-10	4.5	3-6	4.5	2-15	10.3
Trans. Tube (cm)	8	52.2-120+	-	-	-	89.9-120+		-	-	0.31-1.30	0.78
Secchi Depth (m)	8	-	-	0.70-2.00	1.25	-	-	0.67-2.25	1.28	-	-
TP (µg/L)	8	26-112	48.3	29-96	51.3	37-108	59.0	36-73	48.6	55-105	83.0
TN (µg/L)	8	482-1337	790.6	568-1305	845.9	933-1580	1243.5	580-1315	905.8	1600-3149	2313.0
NO_3+NO_2-N (µg/L)	8	17-315	102.5	6-414	143.0	415-1033	791.5	44-399	196.1	647-2626	1624.9
NH_4-N (µg/L)	8	4-154	28.3	4-165	31.1	13-88	36.5	14-163	73.4	8-195	57.0
DOC (mg/L)	3	6.4-17.0	12.5	6.4-16.0	12.1	3.7-9.2	5.9	7.2-15.0	10.7	4.0-7.0	5.7
Alkalinity (mg/L)	3	26-82	54.3	37-87	61.0	99-133	112.3	39-106	72.0	118-142	131.0
Cl^- (mg/L)	3	4.7-4.9	4.8	4.9-5.4	5.2	7.9-8.6	8.2	5.5-7.5	6.6	12.0-14.7	13.5
SO_4^{-2} (mg/L)	3	4.30-7.72	6.4	4.60-7.33	5.7	5.27-5.80	5.6	5.70-7.00	6.1	8.59-10.60	9.5
Ca^+ (mg/L)	3	11.1-22.8	16.8	12.1-24.1	17.9	26.1-32.4	28.7	12.8-27.7	21.0	26.9-35.4	31.1
Mg^{+2} (mg/L)	3	4.06-8.01	6.0	4.41-8.99	6.5	10.6-16.0	12.5	4.56-10.80	7.9	15.4-22.7	18.9
K^+ (mg/L)	3	0.97-2.83	1.8	1.03-2.71	1.7	1.13-2.27	1.74	1.21-2.73	3.8	1.28-3.83	2.8
Na^{+2} (mg/L)	3	2.80-4.30	3.5	3.00-4.49	3.7	4.10-4.62	4.3	3.00-5.03	4.2	4.60-5.60	5.2
SiO_2 (mg/L)	3	3.3-12.0	7.6	3.5-12.0	8.0	6.2-17.0	12.4	6.2-12.0	8.7	4.9-16.0	11.6

Table 3 (continued). Range and mean values of field and laboratory variables measured at St. Croix National Scenic Riverway, 2007. N = number of samples. Field measurements are transparency tube, Secchi depth, pH, specific conductance (SC25), dissolved oxygen (DO), and temperature. Near-surface values were used for pH, specific conductance, DO, and temperature. ND = not detected. Dash (-) = not measured or calculated.

		SACN09		SACN10		SACN11	
Variable	N	range	mean	range	mean	range	mean
Temperature (°C)	8	2.77-26.24	17.0	4.68-17.35	11.6	4.35-25.54	17.2
DO (mg/L)	8	7.56-12.49	9.1	9.12-14.20	11.2	6.28-10.98	8.5
pH (std. units)	8	7.01-8.62	7.83	7.55-8.66	7.97	6.73-8.80	7.84
SC25 (µS/cm)	8	82.2-250.7	183.6	464.7-493.2	484.0	140.4-244.3	204.8
TSS (mg/L)	8	3-7	4.6	2-6	3.0	2-6	3.5
Trans. Tube (cm)	8	-	-	>120+	>120+	-	-
Secchi Depth (m)	8	1.05-1.55	1.25	-	-	0.80-3.28	1.65
TP (µg/L)	8	31-60	45.4	19-51	33.4	21-70	38.6
TN (µg/L)	8	620-1241	914.1	4510-5400	5083.1	769-1342	1032.7
NO_3+NO_2-N (µg/L)	8	20-428	212.5	4620-5320	5010.3	193-608	363.7
NH_4-N (µg/L)	8	7-177	57.5	5-22	10.1	8-183	56.6
DOC (mg/L)	3	7.0-14.0	9.4	2.4-5.0	3.4	4.6-10.0	7.7
Alkalinity (mg/L)	3	43-104	79.7	173-195	184.3	58-106	88.1
Cl^- (mg/L)	3	5.8-7.8	7.0	20.1-21.5	20.9	4.0-8.5	7.0
SO_4^{-2} (mg/L)	3	5.94-6.65	6.3	15.3-19.3	17.7	5.62-7.00	6.4
Ca^{+2} (mg/L)	3	14.4-27.1	22.3	53.9-55.0	54.4	17.6-27.8	24.12
Mg^{+2} (mg/L)	3	5.28-11.30	8.7	24.30-28.20	26.1	6.43-11.80	9.9
K^+ (mg/L)	3	1.20-2.57	1.8	1.42-1.94	1.7	1.31-2.78	1.8
Na^+ (mg/L)	3	3.20-5.03	4.3	7.30-8.00	7.7	3.60-5.30	4.7
SiO_2 (mg/L)	3	5.4-11.0	8.2	6.2-14.0	11.1	3.8-10.0	7.5

Table 4. Total nitrogen to total phosphorus (TN:TP) values for sampling sites in the St. Croix National Scenic Riverway.

	SACN05	SACN08	SACN07	SACN09	SACN11
Apr	14	29	18	21	22
May	20	41	22	21	26
Jun	20	32	20	19	47
Jul	16	19	17	19	23
Aug	15	15	13	16	32
Sep	23	35	18	21	32
Oct	12	25	18	20	26
Nov	23	40	22	23	24
mean	18	29	19	20	29

Dissolved Organic Carbon

Dissolved organic carbon (DOC) for the river sites ranged from a low of 3.7 mg/L at the Kinnickinnic River (SACN10) to a high of 14.7 mg/L at the Snake River (SACN03) (Table 3). Sources of DOC for vegetated streams and rivers are both allochthonous and autochthonous (Hauer and Lamberti 2006). DOC for the lake sites ranged from a low of 5.7 mg/L at Lake Mallalieu (SACN08) to a high of 12.1 mg/L at impoundment above the dam at St. Croix Falls (SACN05). DOC values >3 mg/L are high enough to attenuate light and thus reduce photosynthesis (Schindler and Gunn 2004), which is of greater relevance at the lake sites where an abundance of nutrients has the potential to fuel excessive algal growth.

Temporal Variability – Comparison of Seasons

Basin-wide Flow

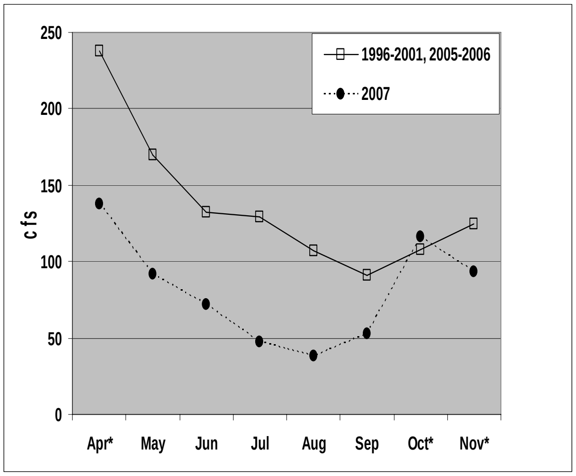
Six USGS streamflow gages currently operate within or near SACN park boundaries (Table 5). Two additional USGS streamflow gages were installed or re-activated in 2007: on the St. Croix River near Norway Point (site#05336000, 2007-present) and at the outlet of the St. Croix River at Prescott, WI (site#05344490, 2007-present). Discharge rating curves for these sites are under development and will be available in 2008. In addition, staff from Metropolitan Council Environmental Services is measuring water velocity of the St. Croix River at Stillwater Minnesota, and will use water elevation data collected by the U.S. Army Corps of Engineers to develop a discharge rating curve for the river as it enters Lake St. Croix.

Table 5. Active USGS streamflow gage sites at SACN.

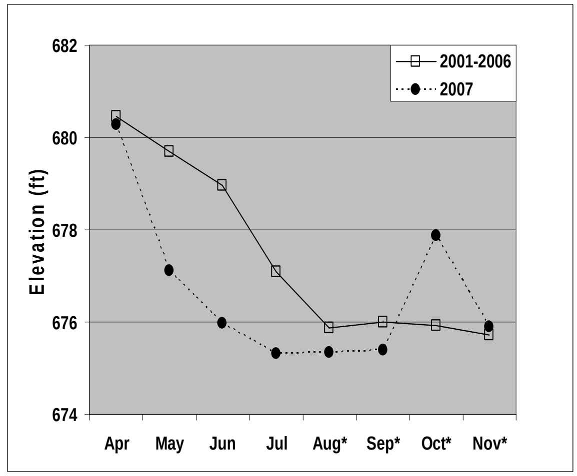
Site #	Period of Record	Location
05331833	1996-present	Namekagon River near Leonards, WI
05332500	1927-present	Namekagon River near Trego, WI
05333500	1914-present	St. Croix River at Danbury, WI
05340500	1902-present	St. Croix River at St. Croix Falls, WI
05341500	1914-1970, 1986-present	Apple River near Somerset, WI
05342000	1916-present	Kinnickinnic River near River Falls, WI

Flow conditions throughout the St. Croix River basin were well below average from the onset of water quality sampling in April until mid-September, when heavy rains beginning in mid-August and continuing throughout the fall caused flow to increase to average or above average conditions (Figure 2).

(a) Namekagon River at Leonards, Wisconsin



(c) St. Croix River at Stillwater, Minnesota



(b) St. Croix River at St. Croix Falls, Wisconsin

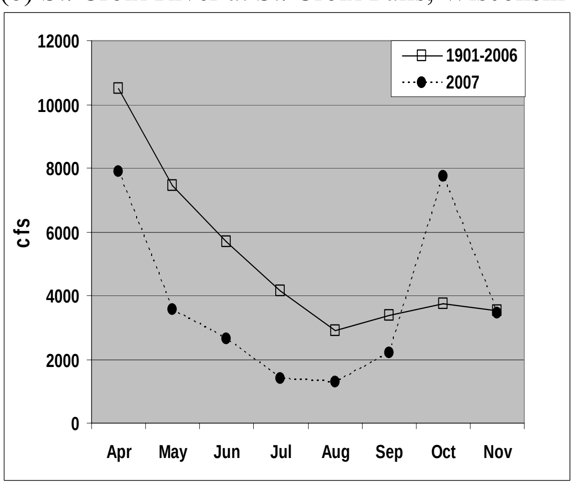
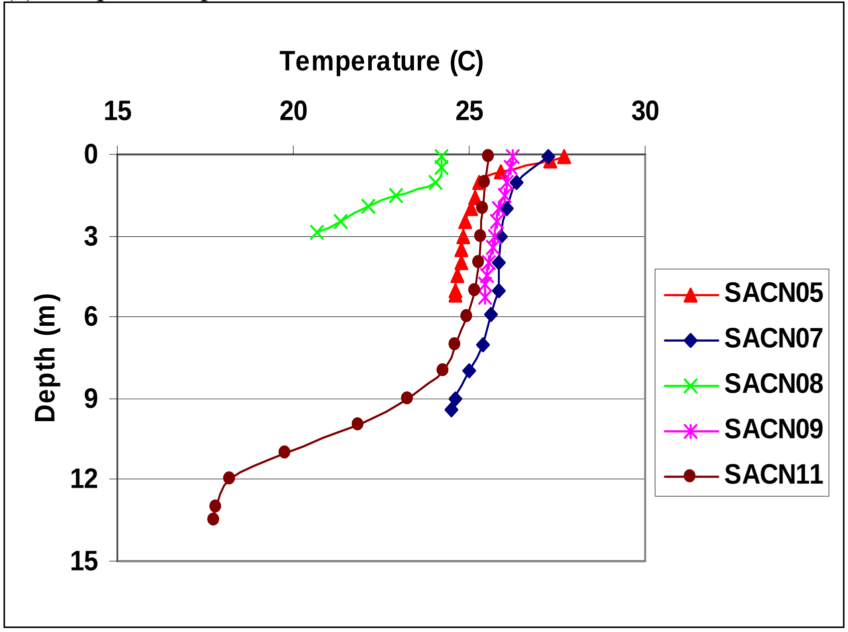


Figure 2. Mean monthly discharge at select sites (a - Namekagon River at Leonards, b - St. Croix River at St. Croix Falls) during the 2007 water quality monitoring season and over several past years. Mean monthly water elevation for the St. Croix River at Stillwater, Minnesota shown in c (http://waterdata.usgs.gov/ accessed 1/15/08). * indicates some data not available for years before 2007.

Temperature and Dissolved Oxygen

Profiles of temperature and dissolved oxygen concentration show all eight river sites were well mixed throughout the open-water season. However, at the lakes sites, the upper and lower stations on Lake St. Croix (SACN07, 11) and the station on Lake Mallalieu (SACN08) became stratified with respect to temperature and dissolved oxygen by mid-summer. Water temperature and dissolved oxygen were the most stratified during the August sampling event (Figure 3), with near-bottom dissolved oxygen levels at 1.18, 0.07, and 3.18 mg/L, respectively.

(a) Temperature profiles at lake sites



(b) Dissolved oxygen profiles at lake sites

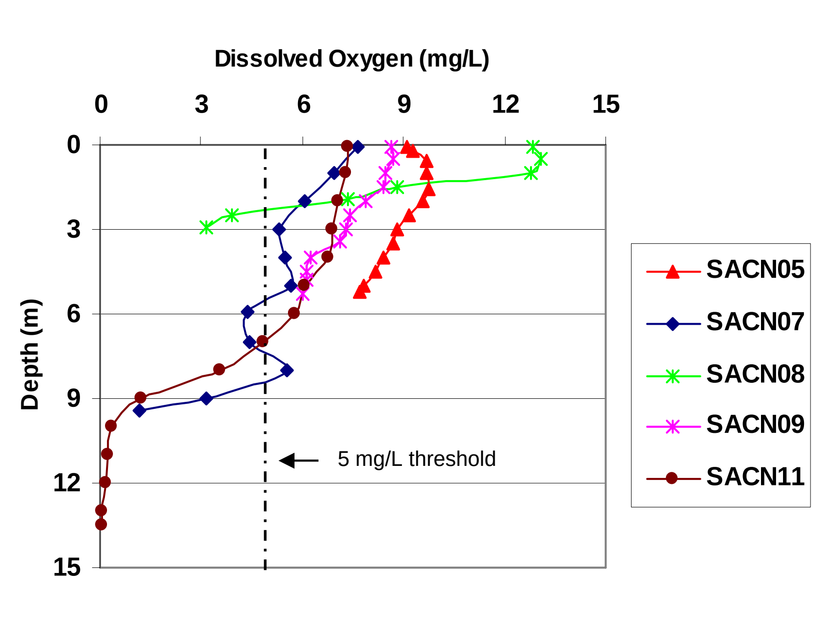


Figure 3. Temperature (a) and dissolved oxygen (b) values at lake sites in August, 2007.

Dissolved oxygen levels <5 mg/L as a daily minimum are considered below the standard for Class 2B waters (Minnesota water quality standards), and may be detrimental to aquatic life. Stratified waters with low (<5 mg/L) oxygen levels were also found at several sites in Lake St. Croix during August sampling in 2005 and 2006 by volunteers working with NPS staff (Brenda Moraska Lafrancois, personal communication). The potential for stratification at lake sites is increased during years of high air temperatures and low flow, which was the case in 2007. By mid-August heavy rain caused increased flow and rising water levels in the St. Croix River Basin, and by September water at all sites was well-mixed.

Anaerobic conditions in the lower water column of stratified waters typically lead to a significant decrease in pH, increased specific conductivity, and the release of soluble phosphorus from the sediment. Both near-surface and bottom TP samples were collected at lake sites in August that exhibited stratification (Table 6). Both sites in Lake St. Croix had much higher concentrations of TP near the bottom compared to near the surface. Although Lake Mallalieu was stratified with respect to temperature and dissolved oxygen, TP near the surface was higher than near the bottom, perhaps due to the relatively shallow (< 3m) nature of water.

Table 6. Near-surface (0-2 m) and bottom TP values in August 2007 for select sites. Bottom TP samples collected ≤1 m from sediment-water interface.

Site	Depth (m)	TP (µg/L)
SACN07	near-surface	43
	9.2	107
SACN08	near-surface	105
	2.6	82
SACN11	near-surface	28
	13.0	472

Nutrients
A large portion of the annual nutrient and sediment loading to the St. Croix River occurs during snowmelt runoff and storm events (Lenz et al. 2001, Robertson and Lenz 2002). Therefore, for the 2007 monitoring season at SACN, the hydrological characteristics shown earlier (i.e., early spring snowmelt and rains, spring to late-summer drought, late-summer to fall rains) should be reflected in concomitant increases and decreases in nutrient concentrations. In general, TP and TN (including NO_3+NO_2-N and NH_4-N) concentrations across all sites were highest in the spring, lowest in August or September, and increased throughout the fall (Appendices B and C). A large spike in nutrients and total suspended solids occurred in October, most likely as a result of large storm events and inputs of organic material from the landscape during leaf senescence. The spike in total suspended solids in October also resulted in reduced water clarity, which otherwise was quite high at most sites throughout the year.

pH
The pH of natural waters is defined as the logarithm of the reciprocal of the concentration of free hydrogen ions. As pH decreases below 7.00 waters become progressively more acidic; as pH increases above 7.00 waters become more basic. Because organisms can only tolerate a pre-

defined range of pH values, the mean and range of pH values at a given site often determine what organisms could exist there. At SACN in 2007, mean monthly near-surface pH values typically were generally lower in early spring, reached a maximum in mid-summer, and decreased in the fall (Figure 4). The increase in pH in the summer is most likely due to increased water temperatures (less dissolved CO_2) and less dissolved organic carbon (i.e., lower concentration of organic acids), as well as conditions of high primary productivity.

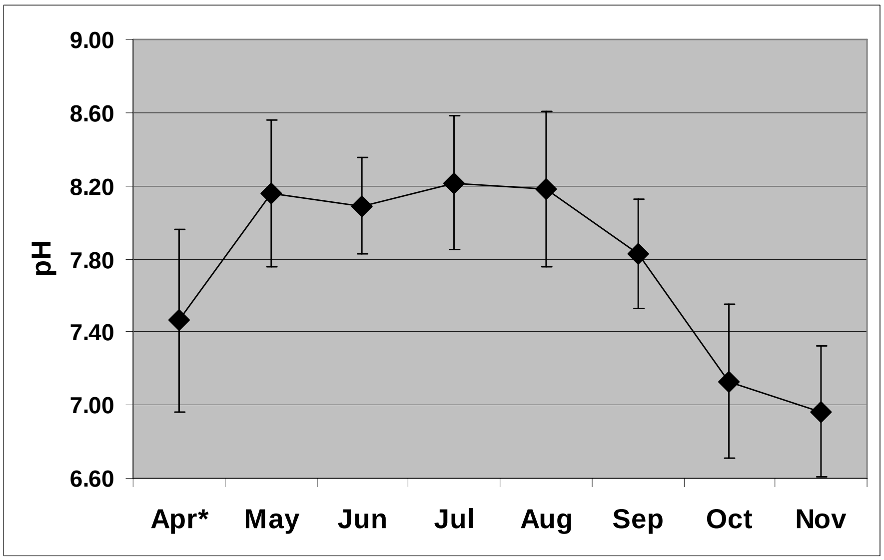


Figure 4. Mean monthly near-surface pH of all sites. Error bars are ± 1SD. * no pH data for SACNa and SACNb in April.

Spatial Variability – Comparison of Sites

Although comparisons of water quality parameters have been made within two broad categories (river and lake sites), in terms of spatial variability it is most useful to compare water quality monitoring sites on the mainstem of the St. Croix River, upstream to downstream. Mean water quality values for select parameters are shown in Table 7, starting with the site farthest upstream (SACN02) on the mainstem of the river and ending at the last mainstem site (SACN11) just upstream from the river's terminus at the Mississippi River.

Temperature, pH, specific conductivity, TN, alkalinity, cations, and anions typically increased from upstream to downstream. There were no clear patterns among these five sites for DO, TSS, Secchi Depth, TP, DOC, and silica. However, by examining only those sites on Lake St. Croix (SACN07, 09, and 11), concentrations of TSS, TP, DOC, and silica generally decreased from upstream to downstream. From a hydrologic and channel morphology perspective, Lake St. Croix is fundamentally different from the other two upstream sites. Historically, TSS and TP have been consistently higher at the upstream site on the lake, due to allochthonous sources of TSS and TP from upstream sources (Kent Johnson, personal communication). TP decreases as it is taken up algae, which then settle out in the slow-moving waters. TSS and silica also decrease as suspended particles settle out (Triplett et al. 2008). TSS, TP, DOC, and silica concentrations may also be decreasing as mixing occurs in progressively deeper waters, which causes overall concentrations to be diluted.

Table 7. Mean values of select water quality variables from sites on the mainstem of the St. Croix River, 2007. Sites are listed upstream to downstream, left to right. Sites SACN04 and 05 were similar, therefore only SACN05 is shown. Near-surface values are used for pH, specific conductance (SC25), dissolved oxygen (DO), and temperature.

Variable	N	SACN02	SACN05	SACN07	SACN09	SACN11
Temperature (°C)	8	14.4	16.1	17.2	17.0	17.2
DO (mg/L)	8	9.0	9.3	8.8	9.1	8.5
pH (std. units)	8	7.48	7.73	7.71	7.83	7.84
SC25 (µS/cm)	8	132.1	161.8	189.7	183.6	204.8
TSS (mg/L)	8	5.3	6.6	4.5	4.6	3.5
Secchi Depth (m)	8	-	1.25	1.28	1.25	1.65
TP (µg/L)	8	34.1	51.3	48.6	45.4	38.6
TN (µg/L)	8	650.4	845.9	905.8	914.1	1032.7
DOC (mg/L)	3	11.8	12.1	10.7	9.4	7.7
Alkalinity (mg/L)	3	53.7	61.0	72.0	79.7	88.1
Cl^- (mg/L)	3	3.3	5.2	6.6	7.0	7.0
SO_4^{-2} (mg/L)	3	5.5	5.7	6.1	6.3	6.4
Ca^{+2} (mg/L)	3	15.0	17.9	21.0	22.3	24.12
Mg^{+2} (mg/L)	3	5.2	6.5	7.9	8.7	9.9
K^+ (mg/L)	3	1.1	1.7	3.8	1.8	1.8
Na^+ (mg/L)	3	2.7	3.7	4.2	4.3	4.7
SiO_2 (mg/L)	3	7.6	8.0	8.7	8.2	7.5

Comparison with Water Quality Standards

The State of Minnesota lists the entire St. Croix River as an Outstanding Resource Water. The State of Wisconsin has listed the St. Croix River as an Outstanding Resource Water, except between the St. Croix Falls city limits to one mile below the STH 243 Bridge at Osceola, where it is listed as an Exceptional Resource Water (a category of lesser protection). Wisconsin also lists the Namekagon River as an Outstanding Resource Water.

The St. Croix River and its tributaries are governed by state-specific water quality criteria. Whether the water quality standards of Minnesota, Wisconsin, or both apply depends on the location of the water quality monitoring site. A summary of state-specific water quality standards was compiled by Ledder (2005) for the Network during development of the Network's Monitoring Plan (Route and Elias 2007). In the following sections water quality monitoring results from SACN in 2007 are compared with federal standards and the criteria listed in Ledder's (2005) state-specific summary.

Minnesota

The State of Minnesota designated beneficial uses for all surface waters in the state, defined in Minn. R. 7050.0200 as follows:

- Class 1 - protected for drinking
- Class 2 - protected for aquatic life and recreation
- Class 3 - protected for industrial uses
- Class 4 - protected for agricultural uses
- Class 5 - protected for aesthetics and navigation
- Class 6 - other uses
- Class 7 - limited resource value waters

Use classes 1, 2, 3, and 4 have subclasses. Of these, the Class 2 subclasses are most pertinent to natural resource considerations:

- 2A: Cold-water fisheries, trout waters, also protected as a source of drinking water
- 2Bd: Cool-and warm-water fisheries, also protected as a source of drinking water
- 2B: Cool-and warm-water fisheries (not protected for drinking water)
- 2C: Indigenous fish and associated aquatic community (not protected for drinking water)
- 2D: Wetlands (not protected for drinking water).

The State of Minnesota has assigned designated use classes for the portion of the St. Croix River that form the border between Minnesota and Wisconsin, and on Minnesota tributaries flowing into the St. Croix River. For the St. Croix River, waters north of Taylors Falls, Minnesota are designated Class 1B, 2Bd, 3B, 3C, 4A, 4B, 5, and 6, while waters south of Taylors Falls are designated Class 1C, 2Bd, 3B, 3C, 4A, 4B, 5, and 6. Water quality monitoring site SACN03 near the mouth of the Snake River is designated Class 2B, 3B, 4A, 4B, 5, and 6.

The State of Minnesota has established criteria for some water quality parameters based on the designated uses (MnRule 7050.0220). Criteria that apply to sampling sites within SACN are shown in Table 8. Note that Minnesota state water quality standards are not applicable for sites SACNa, b, 01, 06, 08, and 10. At site SACN03 (Snake River), mean pH for July and August was 8.66 and 8.62, respectively, exceeding the standard of 8.50. At sites SACN 07 and 11 on Lake St. Croix, dissolved oxygen concentrations were less than 5 mg/L below the thermocline in July and August (Figure 3). All other standards listed in Table 8 were met during the 2007 sampling season.

Table 8. Minnesota state water quality standards (MnRule 7050.0220) for monitored variables, based on designated use classifications (MnRule 7050.0200) that apply to SACN sampling sites. All limits are chronic standards and maximum values, except dissolved oxygen, which is a minimum allowable value, and pH, which is an allowable range of values. The most conservative values are used when differences occur among use classifications. * Site SACN03 has designated water use classifications 2B, 3B, 4A, 4B, 5, and 6.

Water Quality Parameter	Designated Water Use Classifications 1B & C, 2Bd, 3B , 3C, 4A, 4B, 5, 6 (sites 2, 3*, 4, 5, 7, 9, 11)
temperature (°F)	± 5 of natural
pH (standard units)	6.50-8.50
dissolved oxygen (mg/L)	5 daily min
specific conductance (µS/cm)	1000
nitrate+nitrite-N (mg/L-N)	10
ammonia, unionized (ug/L-N)	40
chloride (mg/L)	100
sulfate (mg/L)	10, for wild rice
sodium (% total cations)	60%

Wisconsin

The State of Wisconsin categorizes all waters of the state according to the following designated uses (NR 102.04):

- Fish and Other Aquatic Life Uses – Cold water communities, warm water sport fish communities, warm water forage communities, limited forage fish communities, limited aquatic life (marginal surface water).
- Recreational Use – A sanitary survey and/or evaluation to assure protection from fecal contamination is the chief criterion determining suitability for recreational use.
- Public Health and Welfare – All surface waters shall meet the human threshold and human cancer criteria specified in NR 105.08 and NR 105.09, respectively.
- Wildlife Use – All surface waters shall be classified for wildlife uses and meet the wildlife criteria specified in NR 105.07.

In accordance with Wisconsin's NR104 Uses and Designated Standards, *"the St. Croix River has high scenic and aesthetic value and is used for recreation, fishing, hydropower, commercial shipping, stock and wildlife water supply, and waste assimilation. Its water shall meet the standards and requirements for recreational use and fish and aquatic life….. standards for public water supply shall be met downstream of the north line of Polk County."* The two parameters that apply to the suite of water quality characteristics monitored by the Network are dissolved oxygen and pH. NR 102.04(4) states that *"dissolved oxygen may not be lowered to less than 5 mg/L at any time. Dissolved oxygen in classified trout streams…… may not be artificially lowered to less than 6.0 mg/L, nor 7.0 mg/L during spawning….. pH shall be maintained between 6.0 to 9.0 with no change greater than 0.5 units outside estimated neutral seasonal maximum and minimum."*

These standards were met at all monitoring sites in the St. Croix Basin, except for two stations on Lake St. Croix that had low dissolved oxygen levels in the lower water column during summer stratification. The Kinnickinnic River, classified as a Wisconsin Trout Stream, had the highest mean dissolved oxygen concentration (11.23 mg/L) of all sampling sites, with a low of 9.12 mg/L in July.

Federal

The USEPA (EPA) has recommended nutrient water quality criteria for two broad categories of water resources: rivers and streams, and lakes and reservoirs. EPA criteria are stringent, as they are based on the 25th percentile of all data (USEPA 2000a, 2000b, 2000c, 2000d, 2001). Table 9 shows EPA-recommended water quality reference criteria applicable to GLKN monitoring sites in the St. Croix River basin. For the river sites, most nutrient criteria were exceeded throughout the sampling season, except for the monitoring site on the Namekagon at Phipps (SACNb), where nutrient concentrations were frequently below reference levels. As discussed earlier, NO_3+NO_2-N concentrations in the Kinnickinnic River were much higher (4.62 to 5.32 mg/L) than the recommended reference criterion (1.97 mg/L). However, TP concentrations were below (19 to 51 µg/L) the recommended reference criterion (118.13 µg/L). Nutrient reference criterion was also exceeded on most occasions for the lake sites.

Table 9. U.S. Environmental Protection Agency recommended nutrient criteria for sampling sites in the St. Croix River Basin, 2007 (USEPA 2000a, 2000b, 2000c, 2000d, 2001).

Water Resource	Ecoregion	Sub-ecoregion	Site #	TN (mg/L)	NO3+NO2-N (mg/L)	TP (µg/L)
Rivers & Streams	VI	47	10	3.26	1.965	118.13
	VII	51	06	0.71	0.13	28.75
	VIII	50	a, b, 01, 02, 03, 04	0.44	0.03	12
Lakes & Reservoirs	VII	51	07, 08, 09, 11	0.81	0.008	20
	VIII	50	05	0.40	0.003	9.69

Even though EPA-recommended nutrient reference conditions were exceeded at almost all of the monitoring sites throughout the 2007 sampling season, this does not necessarily imply that water quality at the sample locations is nutrient-impaired. However, it has long been recognized that excessive nutrients, especially phosphorus, are having a deleterious effect on Lake St. Croix (Davis 2004). In 2004, the Basin Team recommended a 20% reduction in total phosphorus loading within the St. Croix Basin, with the intent of lowering downstream concentrations of TP in Lake St. Croix to 40 µg/L. Acting on that recommendation, the Minnesota Pollution Control Agency and the Wisconsin Department of Natural Resources signed an agreement in 2006 to support the 20% phosphorus reduction goal (MPCA 2006. www.pca.state.mn.us/publications/ wq-b6-04.pdf).

Although TP concentrations in Lake St. Croix have decreased slightly over the last few decades (Lafrancois et al. *in press*), monitoring in the last decade (1998-2006) indicates that TP exceeds

EPA guidelines for determination of use support for lakes. As a result, Lake St. Croix was added to Minnesota's 2008 303d list of impaired waters for excessive nutrients. Table 10 shows the guidelines used by the MPCA to make a nutrient impairment determination for Lake St. Croix, based on their nutrient guidelines for lakes in Ecoregion VII, subecoregion 51.

Table 10. MPCA guidelines to assess nutrient impairment in lakes.

EPA Section	TP (µg/L)	TP Range (µg/L)	TP (µg/L)
305(b):	Full Support	Partial Support to Potential Non-Support	Partial Support to Potential Non-Support
303(d):	Not Listed	Review	Listed
	<40	40 - 45	>45

The listing is based on a summer (typically May to September) mean TP concentration of 51 µg/L for Lake St. Croix from 1998 to 2006. In comparison, 2007 summer (May to September) mean TP concentrations for sites SACN07, 09, and 11 were 42.8, 40.6, and 31.7 µg/L, respectively. The 2007 summer mean TP concentration across all three monitoring sites was 38.4 µg/L. Although 2007 summer mean TP concentration across all three monitoring sites was less than 45 µg/L, TP over a much longer period (i.e., 1998 to 2006) is more applicable to use for determining impairment as it takes into account natural variability among years. This is particularly true given that TP concentration is typically flow-related, and that 2007 was a generally low-flow year.

Quality Assurance and Quality Control

During each round of sampling we collected a duplicate sample from one site. As mentioned above, duplicates consisted of a single composite sample split into two bottles for laboratory analysis. Network quality assurance criteria stipulate that duplicates should be within 10% of each other for all parameters except nutrients, chlorophyll-*a*, and TSS, which should be within 30% of each other (Ledder and Elias 2007). Most of our duplicates fell within the acceptable criteria (Appendix B). Those that did not meet quality assurance criteria were chlorophyll-*a* (five times) and total phosphorus (once). As discussed earlier, chlorophyll-*a* values were much lower than expected for much of the sampling season and may be unreliable, including values for duplicate samples. The difference in the TP duplicate samples in July may be explained by an uneven distribution of particulate materials in the water. A few small clumps of algae or suspended sediment could account for the difference between the two samples. All other nutrient duplicates in July were well within acceptable criteria. We have used all values in this report, averaging the duplicates even when differences exceeded quality assurance criteria. Values that do not meet our quality assurance criteria will be flagged as such in the National Park Service database NPSTORET.

Summary

Water quality monitoring was conducted at 13 sites at SACN in 2007. The sites were categorized into two general groups, lake sites and river sites, based mainly on hydrology and channel morphology. Alkalinity values at both river and lake sites indicate that waters at SACN are reasonably well-buffered, especially in the lower portion of the basin. The Apple, Willow, and Kinnickinnic Rivers had very high concentrations of nitrate+nitrite-N (NO_3+NO_2-N). The watersheds associated with these tributaries are dominated by agriculture and increasing development, and have coarse-textured highly permeable soils over carbonate bedrock, which makes groundwater more susceptible to NO_3+NO_2-N loading from fertilizer. In addition, most samples collected at the lake sites had TN:TP values greater than 15, which may indicate that primary productivity is being limited by the availability of phosphorus.

Flow conditions throughout the St. Croix River basin were well below average for most of the sampling season, until heavy rains in late summer and the fall caused flow to increase to average or above average conditions. Water temperatures became stratified at three out of the five lake sites in mid-summer, which led to low dissolved oxygen levels, decreasing pH, and higher TP concentrations below the thermocline at two out of three sites. In general, TP and TN (including NO_3+NO_2-N and NH_4-N) concentrations across all sites were highest in the spring, lowest in August or September, and increased throughout the fall. pH values were usually lower in early spring, higher in mid-summer, and lower again in the fall, with seasonal changes most likely due to variability in water temperature and dissolved organic carbon.

Examination of spatial variability among five sites on the mainstem of the St. Croix River revealed that temperature, pH, specific conductivity, TN, alkalinity, cations, and anions typically increased from upstream to downstream. There were no clear patterns among these five sites for DO, TSS, Secchi Depth, TP, DOC, and silica. However, by examining only those sites on Lake St. Croix, concentrations of TSS, TP, DOC, and silica generally decreased from upstream to downstream.

Water quality monitoring revealed that EPA-recommended nutrient reference conditions were exceeded at almost all of the monitoring sites in 2007. However, nutrient impairment may only be occurring at sites farthest downstream on the St. Croix River (i.e., Lake St. Croix) and the Willow River (Lake Mallalieu). Applicable water quality standards as outlined by the States of Minnesota and Wisconsin were met at SACN throughout season, except for low dissolved oxygen concentrations in the lower portion of the water column at two sites on Lake St. Croix in mid-summer.

Future Monitoring

Monitoring of water quality will be conducted at SACN again in 2009. We expect to measure the same variables at the same frequency. Off-year monitoring (2008, 2010, etc.) on a quarterly basis may occur depending on funding assistance.

One recommendation for future monitoring is to move the water quality station at Phipps Landing (SACNb) nine miles upriver to Leonards, Wisconsin to be co-located with the active USGS streamflow gage. This would allow for more accurate nutrient loading calculations in the upper Namekagon River, which would be of more use to the overall interagency monitoring effort in the St. Croix Basin.

We intend to share data with other agencies conducting monitoring in SACN and the surrounding area in order to provide a more complete picture of water quality. After three years of monthly sampling (2007, 2009, 2011), we will analyze the data for potential trends over time and will produce a report that synthesizes our data and those of other monitoring efforts. Trend information will indicate whether the water quality at SACN is improving, declining, or staying the same. After several sampling seasons, we will determine whether all of the NPS monitoring sites are adding value to the GLKN Monitoring program and to the interagency monitoring effort.

Park Support

Park support was crucial during this initial year of sampling at SACN. The park provided a boat and laboratory space for processing samples, maintaining lab and field equipment, and office space for a Network employee. SACN staff assisted with water sampling and processing; the Network paid salaries when staff worked on this project.

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Appendix A. Water quality field data from St. Croix National Scenic Riverway, 2007. Near-surface values used for specific conductance, dissolved oxygen, temperature, and pH. Field data not collected at SACNa and SACNb in April. Transparency tube measurements of >120 were assigned a value of 120 to calculate means, unless all values were >120, where means were reported as >120. Secchi depth of 1.46 m in October for SACN11 was calculated using Secchi Depth (m) = [(1.09*Transparency Tube (cm)) +15.6]/100 (Dahlgren et al. 2004). Dash (-) = not measured or calculated.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
Specific	Apr	130.8	84.6	92	94	106.5	227.3	106.8	294.7	116.9	464.7	145.8	-	-
Conductivity	May	162.6	129.7	142.4	128.8	147.5	274.2	150.8	327	152.9	475.3	166.4	90.2	141.6
(µS/cm)	Jun	156.2	128.9	190.1	138.6	150.9	251	194.5	323.7	183.4	475.1	208	98.4	139.7
	Jul	181.6	158	214.4	179.9	194.4	291.9	230.9	320	229.3	488.6	229.7	91.4	165.2
	Aug	185.3	161.4	228.7	182.1	202.6	295.2	240.3	308.2	242.2	492.4	244.3	88.1	172.8
	Sept	185.1	157	248.8	176.5	196.1	300.1	238.5	352.6	250.7	492.8	261	92.2	170.8
	Oct	133.6	118.3	208.8	122.2	144.7	234.3	192.9	342.4	211.3	493.2	242.6	86.7	126.7
	Nov	156.3	118.8	155.3	133.4	151.9	261.5	163.2	359.1	82.2	489.7	140.4	99.1	140.1
	mean	161.4	132.1	185.1	144.4	161.8	266.9	189.7	328.5	183.6	484.0	204.8	92.3	151.0
Dissolved	Apr	11.04	11.57	12	8.91	9.28	12.99	13.3	10.82	12.49	14.2	10.98	-	-
Oxygen	May	10.09	8.21	8.75	8.86	8.77	9.01	8.7	13.2	9.36	11.81	8.85	9.64	10.84
(mg/L)	Jun	9.75	8.14	9.07	8.58	8.94	9.04	7.39	10.43	7.56	9.9	8.37	9.09	11.53
	Jul	7.2	6.81	9.12	7.45	8.46	7	7.79	9.71	8.61	9.12	9.3	8.04	8.71
	Aug	6.86	6.91	9.76	7.27	9.3	8.4	7.64	12.84	8.64	10.24	7.36	8.65	8.22
	Sept	8.68	8.57	9.73	9.32	9.55	8.99	7.43	10.89	8.03	10.33	6.28	8.78	10.18
	Oct	8.59	9.38	10.75	9.23	8.9	9.55	7.78	8.37	7.94	11.17	7.64	10.12	9.37
	Nov	11.53	12.64	11.72	12.39	11.48	12.1	10.7	11.48	10.04	13.07	9.26	12.79	11.15
	mean	9.22	9.03	10.11	9.00	9.34	9.64	8.84	10.97	9.08	11.23	8.51	9.59	10.00
Temperature	Apr	5.81	4.25	2.2	3.93	4.22	5.03	2.69	5.9	2.77	5.05	4.35	-	-
(°C)	May	13.60	15.51	15.13	15.88	16.48	16.23	16.64	17.2	16.07	15.5	15.07	13.99	12.81
	Jun	17.00	18.15	19.53	19.41	19.58	18.77	22.24	19.94	20.26	17.35	20.78	18.12	14.63
	Jul	22.46	24.45	27.84	25.33	27.37	23.48	25.17	24.8	25.24	14.93	25.19	26.47	18.59
	Aug	20.98	24.1	24.47	25.77	27.32	21.7	27.26	24.24	26.24	15.72	25.54	23.91	16.35
	Sept	14.84	15.24	18.41	15.24	18.12	17.89	22.03	19.44	21.7	10.38	21.5	17.93	11.66
	Oct	13.76	10.82	12.01	11.21	11.6	13.29	15.07	13.95	16.49	9.46	16.83	13.4	11.79
	Nov	5.91	2.91	6.91	3.61	4.36	6.43	6.5	6.45	7.07	4.68	8.67	6.56	5.53
	mean	14.30	14.43	15.81	15.05	16.13	15.35	17.20	16.49	16.98	11.63	17.24	17.20	13.05

Appendix A (continued). Water quality field data from St. Croix National Scenic Riverway, 2007. Near-surface values used for specific conductance, dissolved oxygen, temperature, and pH. Field data not collected at SACNa and SACNb in April. Transparency tube measurements of >120 were assigned a value of 120 to calculate means, unless all values were >120, where means were reported as >120. Secchi depth of 1.46 m in October for SACN11 was calculated using Secchi Depth (m) = [(1.09*Transparency Tube (cm)) +15.6]/100 (Dahlgren et al. 2004). Dash (-) = not measured or calculated.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
pH	Apr	7.95	7.39	6.84	7.15	7.02	7.96	7.04	8.05	7.06	8.25	7.37	-	-
	May	8.16	7.90	7.87	7.93	7.85	8.55	7.88	9.06	8.01	8.66	8.02	7.7	8.45
	Jun	8.12	7.90	8.16	8.03	8.06	7.9	7.81	8.71	7.83	8.07	7.96	8.09	8.53
	Jul	7.83	7.77	8.63	8.14	8.52	7.9	8.21	8.56	8.62	7.93	8.8	8.06	7.81
	Aug	7.81	7.57	8.64	8.05	8.43	7.97	8.36	8.83	8.6	7.79	8.6	8.09	7.58
	Sep	7.53	7.38	8.23	7.83	8.2	7.86	8.07	8.22	7.96	7.65	7.73	7.67	7.42
	Oct	6.54	6.94	7.33	6.94	6.99	7.42	7.42	7.56	7.53	7.55	7.47	6.36	6.62
	Nov	6.79	7.01	6.67	6.77	6.77	7.36	6.89	7.28	7.01	7.85	6.73	6.91	6.5
	mean	7.59	7.48	7.80	7.61	7.73	7.87	7.71	8.28	7.83	7.97	7.84	7.55	7.56
Secchi Depth (m)	Apr	-	-	-	-	0.70	-	0.67	0.31	1.10	-	1.40	-	-
	May	-	-	-	-	1.35	-	1.10	0.85	1.12	-	1.60	-	-
	Jun	-	-	-	-	1.25	-	2.25	0.61	1.30	-	3.28	-	-
	Jul	-	-	-	-	1.23	-	1.00	1.05	1.08	-	1.45	-	-
	Aug	-	-	-	-	2.00	-	1.45	0.35	1.35	-	1.43	-	-
	Sep	-	-	-	-	1.15	-	1.20	0.70	1.48	-	1.77	-	-
	Oct	-	-	-	-	1.05	-	1.38	1.08	1.55	-	1.46	-	-
	Nov	-	-	-	-	1.30	-	1.18	1.30	1.05	-	0.80	-	-
	mean	-	-	-	-	1.25	-	1.28	0.78	1.25	-	1.65	-	-
Transparency Tube (cm)	Apr	>120.00	71.40	88.40	52.20	-	>120.00	-	-	-	>120.00	-	-	-
	May	>120.00	>120.00	>120.00	98.10	-	107.40	-	-	-	>120.00	-	>120.0	>120.0
	Jun	>120.00	88.00	82.50	55.00	-	>120.00	-	-	-	>120.00	-	>120.0	>120.0
	Jul	>120.00	>120.00	90.20	>120.00	-	>120.00	-	-	-	>120.00	-	>120.0	>120.0
	Aug	>120.00	>120.00	62.40	>120.00	-	>120.00	-	-	-	>120.00	-	>120.0	>120.0
	Sep	>120.00	>120.00	80.10	>120.00	-	>120.00	-	-	-	>120.00	-	>120.0	>120.0
	Oct	87.75	87.85	57.65	66.75	-	89.85	-	-	-	>120.00	-	>79.3	>120.0
	Nov	>120.00	>120.00	105.55	>120.00	-	>120.00	-	-	-	>120.00	-	>120.0	>120.0
	mean	115.97	105.91	85.85	94.01	-	114.66	-	-	-	>120.00	-	114.2	>120.0

Appendix B. Laboratory results for sites at St. Croix National Scenic Riverway, 2007. Water samples not collected at SACNa and SACNb in April. Chlorophyll-*a* data should be considered unreliable. Duplicate samples for quality assurance are in parentheses, with the averages reported and used for site means. Duplicates that did not meet our quality assurance criteria (Ledder and Elias 2007) are highlighted in yellow. See notes below this table for explanation of values used to calculate means.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
Alkalinity (mg/L)	Apr	55	35 (34,36)	32	26	37	99	39	118	43	185	58	-	-
	Jul	83	75	99	82	87	133	106	133	104	173	103.5 (101, 106)	44	79
	Oct	55	51	93	55 (54, 56)	59	105	71	142	92	195	103	32	54
	mean	64.33	53.67	74.67	54.33	61.00	112.33	72.00	131.00	79.67	184.33	88.17	38.00	66.50
Chl-*a* (µg/L)	Apr	ND	1.05 (0.7, 1.4)	ND	7.8	8.7	5	ND	ND	3.5	1	ND	-	-
	May	1.4	0.3	2.4	1	3.8	2.1	5.1 (3.7, 6.5)	15.3	7.9	ND	0.5	2.1	ND
	Jun	ND	1.4	0.1	3.8	5.2 (4.5, 5.9)	1.0	1.4	14.8	2.4	ND	1	ND	ND
	Jul	ND	ND	ND	ND	6.5	ND	18.00	9.00	16.70	ND	8.3 (7.6, 9.0)	ND	ND
	Aug	ND	ND (ND, ND)	ND	ND	3.7	0.70	6.90	49.5	13.00	ND	7.4	ND	ND
	Sep	ND	ND	1.6	ND	4.5	ND	5.6	19.2	4.75 (2.4, 7.1)	ND	5.6	ND	ND
	Oct	ND	ND	6.5	3.0 (1.8, 4.2)	ND	ND	6.6	2.1	6.2	0.2	2.1	ND	ND
	Nov	ND	0.2	0.88 (ND, 1.70)	ND	ND	ND	ND	4.5	ND	ND	ND	ND	ND
	mean	0.22	0.39	1.45	1.98	4.06	1.13	5.46	14.31	6.81	0.19	3.13	0.34	ND

Appendix B (continued). Laboratory results for sites at St. Croix National Scenic Riverway, 2007. Water samples not collected at SACNa and SACNb in April. Chlorophyll-*a* data should be considered unreliable. Duplicate samples for quality assurance are in parentheses, with the averages reported and used for site means. Duplicates that did not meet our quality assurance criteria (Ledder and Elias 2007) are highlighted in yellow. See notes below this table for explanation of values used to calculate means.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
TSS (mg/L)	Apr	9	10.5 (10, 11)	5	18	20	4	3	2	3	2	2	-	-
	May	5	6	5	6	5	5	4 (4, 4)	13	4	3	3	2	3
	Jun	7	8	8	11	5 (5, 5)	3	3	15	4	6	2	2	2
	Jul	4	4	6	5	4	4	6	10	7	2	6 (6, 6)	2	2
	Aug	1	2 (2, 2)	9	2	4	3	5	12	4	2	5	ND	2
	Sep	2	2	5	2	6	3	6	14	5 (5, 5)	2	3	ND	2
	Oct	12	8	12	12 (12, 12)	6	10	5	10	6	4	4	14	3
	Nov	3	2	3 (3, 3)	3	3	4	4	6	4	3	3	1	2
	mean	5.38	5.31	6.63	7.38	6.63	4.50	4.50	10.25	4.63	3.00	3.50	3.14	2.29
Ca^{+2} (mg/L)	Apr	18.3	11.1 (11.1, 11.1)	10.6	11.1	12.1	27.7	12.8	30.9	14.4	54.3	17.6	-	-
	Jul	23.0	19.4	27.0	22.8	24.1	32.4	27.7	26.9	27.1	55.0	26.95 (26.6, 27.3)	11.4	23.8
	Oct	17.6	14.6	24.0	16.6 (16.3, 16.9)	17.5	26.1	22.4	35.4	25.4	53.9	27.8	11.0	17.3
	mean	19.63	15.03	20.53	16.83	17.9	28.73	20.97	31.07	22.30	54.40	24.12	11.20	20.55
Cl^- (mg/L)	Apr	3.9	3.1 (3.1, 3.1)	4.8	4.7	5.3	7.9	5.5	12.0	5.8	20.1	4.0	-	-
	Jul	4.2	3.2	5.9	4.9	5.4	8.6	7.5	14.7	7.8	21.1	8.45 (8.4, 8.5)	1.9	2.6
	Oct	4.1	3.7	7.5	4.9 (4.9, 4.9)	4.9	8.0	6.7	13.9	7.4	21.5	8.5	2.7	3.1
	mean	4.07	3.33	6.07	4.83	5.20	8.17	6.57	13.53	7.00	20.90	6.98	2.30	2.85

Appendix B (continued). Laboratory results for sites at St. Croix National Scenic Riverway, 2007. Water samples not collected at SACNa and SACNb in April. Chlorophyll-*a* data should be considered unreliable. Duplicate samples for quality assurance are in parentheses, with the averages reported and used for site means. Duplicates that did not meet our quality assurance criteria (Ledder and Elias 2007) are highlighted in yellow. See notes below this table for explanation of values used to calculate means.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
Mg^{+2} (mg/L)	Apr	5.24	3.64 (3.62, 3.66)	4.23	4.06	4.41	10.6	4.56	15.4	5.28	24.3	6.43	-	-
	Jul	7.46	6.96	10.7	8.01	8.99	16.0	10.8	22.7	11.3	28.2	11.5 (11.5, 11.5)	4.26	7.02
	Oct	5.41	4.98	9.80	6.02 (5.93, 6.10)	6.14	10.9	8.33	18.7	9.62	25.7	11.8	3.54	4.86
	mean	6.04	5.19	8.24	6.03	6.51	12.50	7.90	18.93	8.73	26.07	9.91	3.90	5.94
K^{+} (mg/L)	Apr	1.01	1.50 (1.49, 1.51)	3.28	2.83	2.71	1.82	2.73	3.83	2.57	1.94	2.78	-	-
	Jul	0.70	0.68	1.90	0.97	1.03	1.13	1.21	1.28	1.20	1.42	1.32 (1.31, 1.33)	0.15	0.65
	Oct	1.11	0.98	2.44	1.47 (1.46, 1.48)	1.42	2.27	1.56	3.38	1.48	1.87	1.37	0.89	0.87
	mean	0.94	1.05	2.54	1.76	1.72	1.74	1.83	2.83	1.75	1.74	1.82	0.52	0.76
SiO_2 (mg/L)	Apr	12	8.35 (8.3, 8.4)	6.5	8.0	8.5	14	7.8	14	8.3	13	8.6	-	-
	Jul	5.4	3.4	2.5	3.3	3.5	6.2	6.2	4.9	5.4	6.2	3.8 (3.8, 3.8)	2.8	5.7
	Oct	14	11	14	11.5 (11, 12)	12	17	12	16	11	14	10	10	13
	mean	10.47	7.58	7.67	7.60	8.00	12.40	8.67	11.63	8.23	11.07	7.47	6.40	9.35
Na^{+} (mg/L)	Apr	3.0	2.15 (2.1, 2.2)	2.8	2.8	3.0	4.1	3.0	4.6	3.2	7.3	3.6		
	Jul	3.55	3.28	4.85	4.30	4.49	4.62	5.03	5.34	5.03	7.89	5.04 (5.01, 5.08)	2.53	2.98
	Oct	3.1	2.8	5.0	3.45 (3.4, 3.5)	3.6	4.3	4.6	5.6	4.8	8.0	5.3	2.3	2.6
	mean	3.22	2.74	4.22	3.52	3.70	4.34	4.21	5.18	4.34	7.73	4.65	2.42	2.79

Appendix B (continued). Laboratory results for sites at St. Croix National Scenic Riverway, 2007. Water samples not collected at SACNa and SACNb in April. Chlorophyll-*a* data should be considered unreliable. Duplicate samples for quality assurance are in parentheses, with the averages reported and used for site means. Duplicates that did not meet our quality assurance criteria (Ledder and Elias 2007) are highlighted in yellow. See notes below this table for explanation of values used to calculate means.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
SO_4 (mg/L)	Apr	4.59	5.27 (5.19, 5.35)	5.21	5.24	5.11	5.68	5.73	8.59	5.94	15.3	5.62	-	-
	Jul	4.7	3.9	4.5	4.3	4.6	5.8	5.7	10.6	6.2	18.6	6.9 (6.8, 7.0)	3.6	5.0
	Oct	6.4	7.28	5.79	7.05 (6.38, 7.72)	7.33	5.27	7.00	9.40	6.65	19.3	6.66	9.94	6.29
	mean	5.23	5.48	5.17	5.53	5.68	5.58	6.14	9.53	6.26	17.73	6.39	6.77	5.65
DOC (mg/L)	Apr	8.7	13.5 (13, 14)	16	14	14	4.9	15	7.0	14	2.7	10	-	-
	Jul	3.1	4.9	14	6.4	6.4	3.7	7.2	4.0	7.0	2.4	8.5 (8.4, 8.6)	5.3	2.7
	Oct	18	17	14	17 (17, 17)	16	9.2	10	6.0	7.2	5.0	4.6	18	14
	mean	9.93	11.80	14.67	12.47	12.13	5.93	10.73	5.67	9.4	3.37	7.70	11.65	8.35
NH_4-N (µg/L)	Apr	23	100 (100, 100)	89	154	165	36	121	195	99	8	183	-	-
	May	6	7	38	9	15	21	14 (14, 14)	11	17	12	29	14	11
	Jun	4	9	18	4	4.5 (4, 5)	64	163	36	177	22	52	9	4
	Jul	15	14	17	7	10	88	100	86	16	13	8.5 (8, 9)	14	11
	Aug	5	11 (11, 11)	4	5	7	24	35	12	7	9	16	5	4
	Sep	3	42	6	5	4	13	49	13	31 (30, 32)	5	57	12	4
	Oct	24	19	35	18 (17, 19)	24	32	58	95	59	6	8	19	25
	Nov	10	16	69.5 (69, 70)	23	21	14	47	8	54	6	99	15	8
	mean	11.25	27.25	34.56	28.13	31.31	36.50	73.38	57.00	57.50	10.13	56.56	12.57	9.57

Appendix B (continued). Laboratory results for sites at St. Croix National Scenic Riverway, 2007. Water samples not collected at SACNa and SACNb in April. Chlorophyll-*a* data should be considered unreliable. Duplicate samples for quality assurance are in parentheses, with the averages reported and used for site means. Duplicates that did not meet our quality assurance criteria (Ledder and Elias 2007) are highlighted in yellow. See notes below this table for explanation of values used to calculate means.

Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
NO_3+NO_2-N (µg/L)	Apr	216	279 (279, 279)	251	315	414	813	399	2356	428	4890	496	-	-
	May	56	28	69	39	99	563	113 (112,114)	1685	135	4620	298	22.0	27
	Jun	78	52	162	83	143 (141, 145)	824	139	1540	148	5080	385	10.0	6
	Jul	103	105	367	78	30	1033	176	886	63	4990	267.5 (266, 269)	93.0	10
	Aug	32	9.5 (9, 10)	36	17	6	988	44	647	20	5058	193	0.0	0.0
	Sep	34	78	31	25	59	861	132	1376	219 (218, 220)	5134	306	5.0	11
	Oct	125	88	131	114 (114, 114)	160	415	256	1883	341	4990	608	49.0	110
	Nov	182	122	179.5 (179, 180)	149	233	835	310	2626	346	5320	356	21.0	98
	mean	103.25	95.19	153.31	102.50	143.00	791.50	196.13	1624.88	212.50	5010.25	363.69	28.79	37.64
TN (µg/L)	Apr	678	1191.5 (1179, 1204)	1236	1337	1305	1184	1315	2890	1241	4740	1248	-	-
	May	374	491	954	684	770	933	837 (832, 842)	2230	894	4510	968	590	254
	Jun	475	511	1011	771	794 (782, 806)	1241	904	2208	829	5146	990	406	253
	Jul	372	419	1262	633	704	1580	866	1797	893	5284	1100.5 (1087, 1114)	464	317
	Aug	325	393 (390, 396)	1322	487	568	1352	580	1600	620	5195	899	316	168
	Sep	199	541	929	482	675	1213	675	2091	686 (684,688)	5250	769	258	155

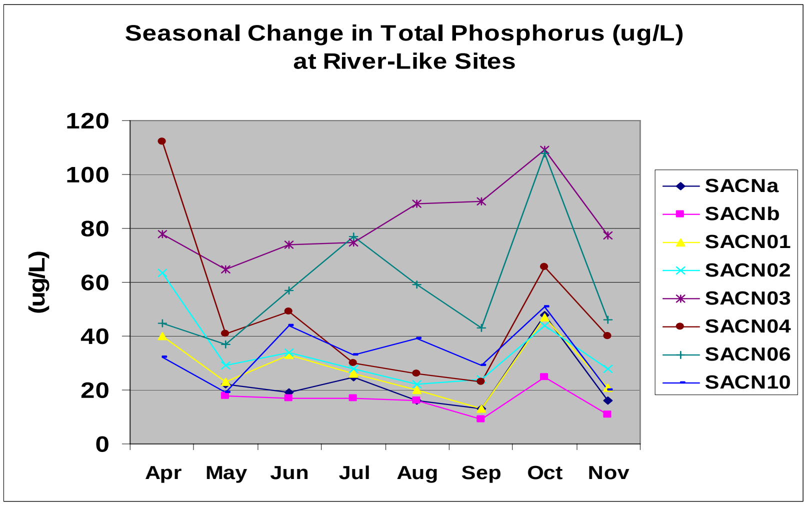
Appendix B (continued). Laboratory results for sites at St. Croix National Scenic Riverway, 2007. Water samples not collected at SACNa and SACNb in April. Chlorophyll-*a* data should be considered unreliable. Duplicate samples for quality assurance are in parentheses, with the averages reported and used for site means. Duplicates that did not meet our quality assurance criteria (Ledder and Elias 2007) are highlighted in yellow. See notes below this table for explanation of values used to calculate means.

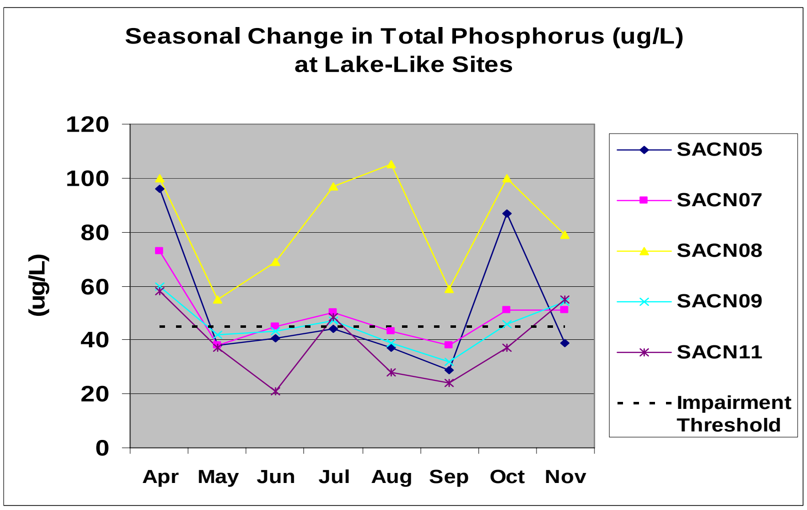
Parameter	Month	SACN01	SACN02	SACN03	SACN04	SACN05	SACN06	SACN07	SACN08	SACN09	SACN10	SACN11	SACNa	SACNb
TN (µg/L) (continued)	Oct	996	957	1185	1084 (1057, 1111)	1050	1186	935	2539	915	5140	945	1022	703
	Nov	509	700	1333.5 (1329, 1338)	847	901	1259	1134	3149	1235	5400	1342	592	337
	mean	491.00	650.44	1154.06	790.63	845.88	1243.50	905.75	2313.00	914.13	5083.13	1032.69	521.14	312.43
TP (µg/L)	Apr	40	63.5 (62, 65)	78	112	96	45	73	100	60	32	58	-	-
	May	23	29	65	41	38	37	38 (36, 40)	55	42	19	37	22	18
	Jun	33	34	74	49	40.5 (40, 41)	57	45	69	43	44	21	19	17
	Jul	26	28	75	30	44	77	50	97	47	33	48.5 (27, 70)	25	17
	Aug	20	22 (21, 23)	89	26	37	59	43	105	39	39	28	16	16
	Sep	13	24	90	23	29	43	38	59	32 (31, 33)	29	24	13	9
	Oct	47	44	109	65.5 (63, 68)	87	108	51	100	46	51	37	48	25
	Nov	21	28	77.5 (77, 78)	40	39	46	51	79	54	20	55	16	11
	mean	27.88	34.06	82.19	48.31	51.31	59.00	48.63	83.00	45.38	33.38	38.56	22.71	16.14

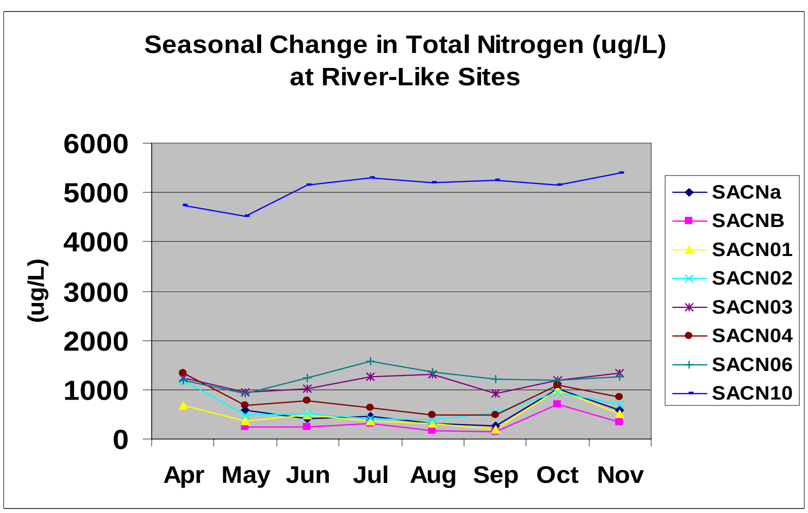
Notes:

1) For Chl-*a*, used 1/2 of lowest reported value that was <MDL (1.0 µg/L) but >0 (0.1 µg/L/2 = 0.05 µg/L) for values reported as non-detects.
2) For NO_2+NO_3-N, used 1/2 of MDL (3.0 ppb/2 = 1.5 ppb) for values reported as 0.
3) For TSS, used ½ OF MDL (1.0 mg/L/2 = 0.5 mg/L) for values reported as non-detects.
4) For all parameters, all reported values > 0 were used to calculate means, including those < method reporting limit or < method detection limit.

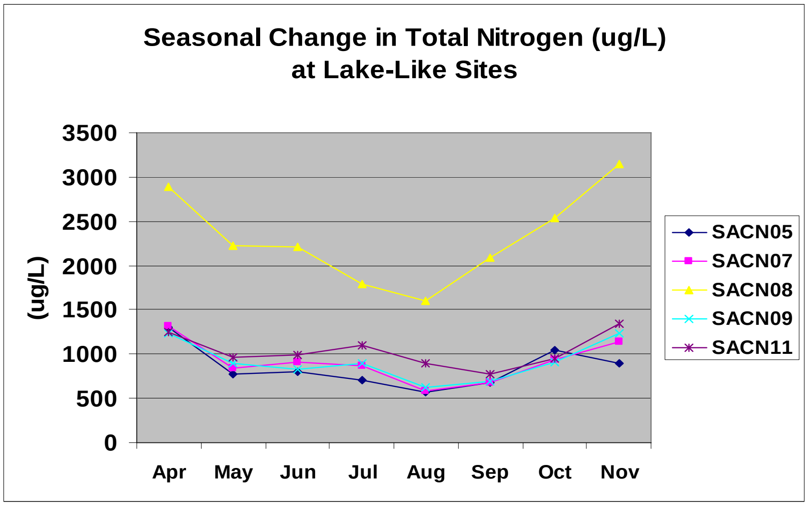
Appendix C. Nutrient concentrations across the sampling season with comparisons among sampling sites for river- and lake-like sites, St. Croix Nation Scenic Riverway, 2007.

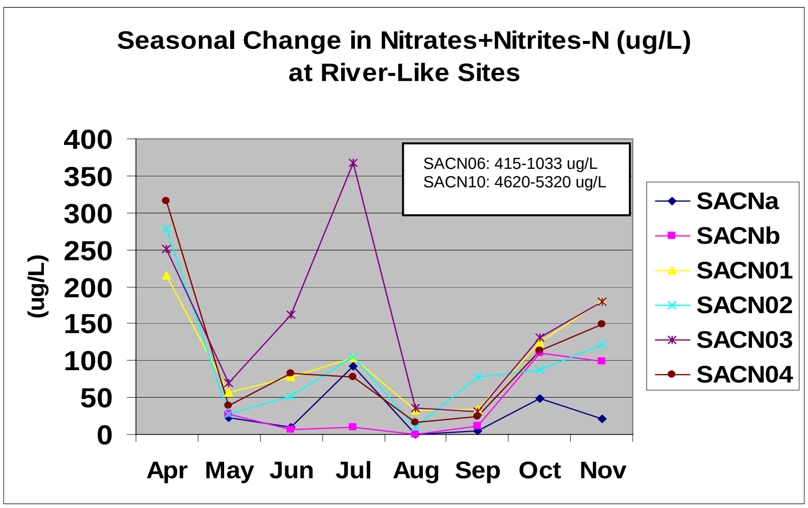


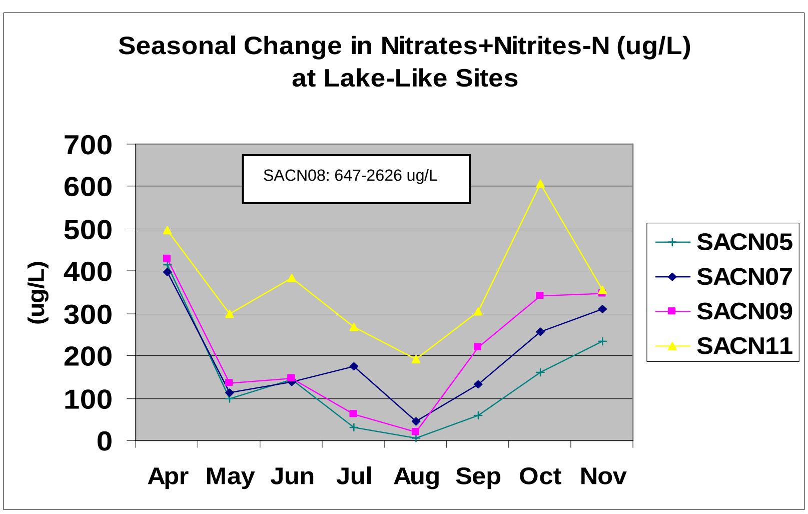




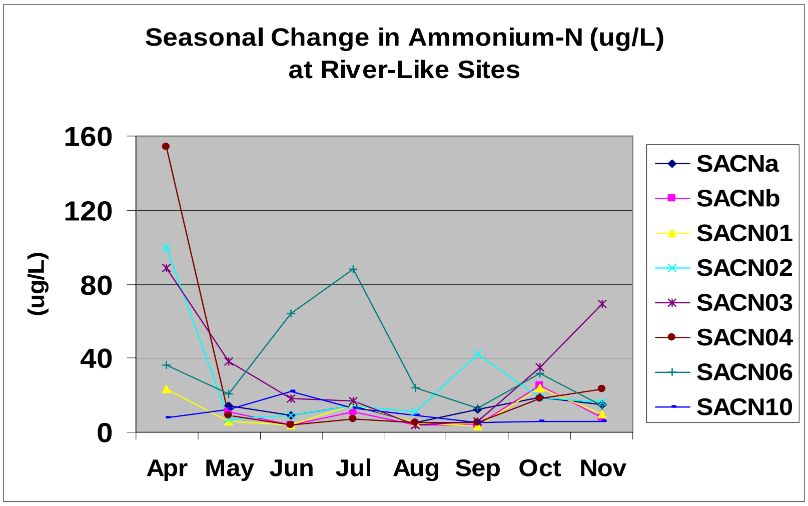
Appendix C (continued). Nutrient concentrations across the sampling season with comparisons among sampling sites for river- and lake-like sites, St. Croix Nation Scenic Riverway, 2007.

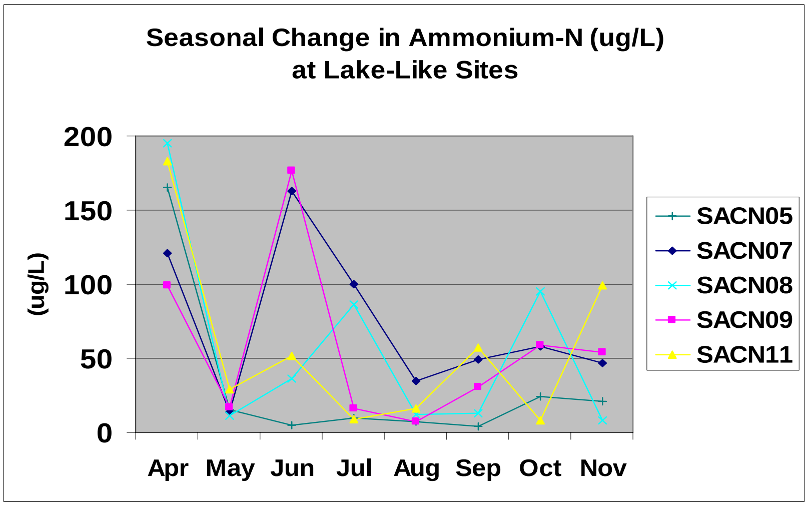






Appendix C (continued). Nutrient concentrations across the sampling season with comparisons among sampling sites for river- and lake-like sites, St. Croix Nation Scenic Riverway, 2007.





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