National Park Service
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Natural Resource Stewardship and Science

Large Rivers Water Quality Monitoring Protocol

Great Lakes Inventory and Monitoring Network (Version 1.1)

Natural Resource Report NPS/GLKN/NRR—2016/1262

ON THE COVER
Top: Barge traffic on the Mississippi River in Mississippi National River and Recreation Area. Photograph by Jennifer Sieracki.
Bottom: Namekagon River, in the St. Croix National Scenic Riverway. Photograph by David VanderMeulen.

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Revision History Log

The following table lists all edits and amendments to this document since the original publication date. Information entered in the log must be complete and concise. Users of this standard operating procedure will promptly notify the project manager and/or the Great Lakes Network (GLKN) data manager about recommended and required changes. The project manager must review and incorporate all changes, complete the revision history log, and change the date and version number on the title page and in the header of the document file. For complete instructions, please refer to Revising the Protocol, SOP #13.

Revision Date	Previous Version #	New Version #	Author (with title and affiliation)	Location in Document and Concise Description of Revision	Reason for Change
4/01/2016	1.0	1.1	David VanderMeulen, Richard Damstra GLKN	Updated the NPS contact author, and added additional author; added details about sampling variables of interest; detailed changes to sampling sites; updated and simplified some tables and graphs; added tables and graphs to clarify sampling regime under previous version of protocol; updated site maps; updated literature cited where appropriate; made some changes to document organization; fixed a handful of grammatical errors throughout.	To clarify and update protocol narrative based on changes that have occurred since Version 1.0 was published in 2007

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List of Acronyms

cfs	cubic feet per second
EPA	Environmental Protection Agency
EMAP	Environmental Monitoring and Assessment Program
GLKN	Great Lakes Inventory and Monitoring Network
MCES	Metropolitan Council Environmental Services
mg/L	milligrams per liter
MISS	Mississippi National River and Recreation Area
MNDNR	Minnesota Department of Natural Resources
MPCA	Minnesota Pollution Control Agency
NAWQA	National Water Quality Assessment Program
NPSTORET	National Park Service Storage and Retrieval Database
SACN	St. Croix National Scenic Riverway
STORET	Storage and Retrieval Database
USGS	United States Geological Survey
WDNR	Wisconsin Department of Natural Resources

1.0 Background and Objectives

1.1 Rationale For Selecting This Resource To Monitor

Large temperate rivers around the world have been historically affected by human activities and face an uncertain future in which water quality may be further threatened by climate change, urban development, agriculture, exotic species, recreation, and transportation uses (Meybeck and Helmer 1989; Zhang et al. 1999). In addition, large rivers can transfer water quality pollutants from land to sea, such as agricultural nitrogen in the Mississippi River causing hypoxia in the Gulf of Mexico (Burkart and James 1999).

Early in the Great Lakes Network's (hereafter, GLKN or the Network) development of a long-term monitoring plan (Route and Elias 2006), large rivers were recognized as one of the important ecosystems within Network parks. The National Park units in the Network that are based on large, non-wadeable rivers are the Mississippi National River and Recreation Area (MISS) and the St. Croix National Scenic Riverway (SACN). Key water quality concerns of these parks include: (1) excess nutrients (particularly nitrogen and phosphorus) from urban and agricultural runoff and wastewater treatment facilities; (2) fluctuations in flow regime caused by climate change, farming drainage, impervious-surfaced urban growth, or channel engineering; (3) sediment loading from stream-bank and agricultural-field erosion causing increased turbidity; (4) invasion of exotic species such as Asian and common carp (*Hypophthalmichthys* spp., *Cyprinus carpio*) as well as zebra/quagga mussels (*Dreissena polymorpha*, *Dreissena bugenesis*); and (5) environmental contaminants of emerging concern, including polybrominated diphenyl ether (PDBE) flame-retardants, mercury, and endocrine disrupters.

1.2 Key Variables of Interest

In scoping workshops held by the Great Lakes Network, the core suite of water quality variables (temperature, pH, specific conductance, dissolved oxygen, and flow) was ranked as the highest priority among potential vital signs (Route 2004). In addition, the advanced water quality suite (turbidity, nutrients, ions) and water level fluctuations were ranked among the top-priority vital signs. A large rivers conceptual model (Lubinski 2004) identified key attributes as water flow and basic water quality variables, including nutrients, dissolved oxygen, turbidity, and temperature. These variables will be the focus of the large rivers protocol.

The five core water quality variables (temperature, pH, specific conductance, dissolved oxygen, and flow/water level) were established by a national review panel assembled by the National Park Service-Water Resources Division (NPS-WRD). The panel recommended this suite be measured across all NPS monitoring networks (NPS 2002). Although the core suite was ranked highest among potential vital signs for aquatic systems of GLKN parks, it was recognized that these measurements were less diagnostic of water quality degradation than biotic communities and other water quality variables, such as turbidity, nutrients and chlorophyll-*a*, and ions. Therefore, these variables were included for monitoring along with the five core water quality variables.

1.2.1 Temperature

Water temperature exerts a major influence on the activity, growth, distribution, and survival of aquatic biota. Fish, insects, zooplankton, phytoplankton, and other aquatic organisms all have preferred temperature ranges for optimal health and reproduction. Temperature is also important because of its influence on water chemistry and physical processes, such as evaporation, oxygen (and other gas) diffusion rates, chemical reaction rates, particle settling velocities (via viscosity), and the stability of thermal stratification. Temperature, via its effect on water density, also acts to structure deeper lake-like areas of rivers into distinct layers with profound physical and chemical differences that create a diversity of habitats for organisms (e.g., Wetzel 2001).

1.2.2 pH

The pH value is the negative logarithm of the hydrogen ion (H^+) activity in the water. At higher pH levels, fewer free hydrogen ions are present; a change of one pH unit (e.g., pH 7 to pH 8) reflects a tenfold change in the concentrations of the hydrogen ion. A closely related parameter is the alkalinity or acid-neutralizing capacity (ANC,) which is a measure of the buffering capacity of the water. The pH of water determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (e.g., lead, copper, cadmium). pH is generally used to set water quality criteria for lakes and streams because of its potential impacts to the life cycle stages of aquatic macroinvertebrates and certain salmonids that can be adversely affected when pH levels are above 9.0 or below 6.5 (Stednick and Gilbert 1998). The mobility of many metals is also enhanced by low pH and can be important in assessing mining impacts. Estimating the toxicity of ammonia, aluminum, and some other contaminants requires accurate pH values. Daily and seasonal variability in pH is associated with natural changes in biological photosynthesis and respiration, as well as inputs from runoff and atmospheric deposition (e.g., Schindler 1988, Schindler et al. 1985). When nutrient pollution results in higher algal and plant growth (e.g., from increased temperature or excess nutrients), pH levels may increase, as allowed by the buffering capacity of the lake or stream. Although these small changes in pH are not likely to have a direct impact on aquatic life, they greatly influence the availability and solubility of all chemical forms in the river and may aggravate nutrient problems.

1.2.3 Specific Electrical Conductivity (EC25 or SC25)

Electrical conductivity is a measure of the capacity of water to conduct an electrical current. Specific conductivity (called EC25 or SC25) is the “raw” conductivity normalized to unit length and cross-section at 25ºC. This normalization eliminates its temperature dependent variability and makes it a good estimator and surrogate measure of the concentration of total dissolved ions in the water. The magnitude of SC25 is controlled largely by geology (rock types) in the watershed, which determines the chemistry of the watershed soil and ultimately the rivers and lakes. Increased SC25 may indicate a number of sources of pollutants, such as wastewater from sewage treatment plants or on-site septic systems, urban runoff from roads (especially road salt), agricultural runoff, and atmospheric deposition. Increased conductivity from runoff into soft waters can be a major stressor to salmonids and other aquatic organisms. Conductivity is an important indicator of polluted runoff that may contain excess nutrients, organic matter, pathogenic microbes, heavy metals, and organic contaminants. SC25 increases naturally due to evaporative salt concentration and respiration, which

increases bicarbonate and carbonate concentrations. It is also an excellent 'tracer' to help identify tributary and groundwater inflows.

1.2.4 Dissolved Oxygen (Concentration and % Saturation)

Dissolved oxygen (DO) is a measure of the amount of oxygen in solution. Oxygen solubility is controlled largely by water temperature and the partial pressure of oxygen within gasses in contact with the solution. The largest source of O_2 is the atmosphere, and as a result, turbulent streams often have DO at or above saturation. In larger, slower streams, phytoplankton and macrophyte photosynthesis produce O_2 during daylight hours. In large, lake-like sections of rivers (e.g., Lake St. Croix at SACN) stratification can occur similar to a lacustrine system, which can result in large seasonal differences in DO between the turbulent, wind and flow-mixed upper layer (epilimnion) and in the deeper relatively static hypolimnion. The major sink for DO is respiration by animals, plants, and microbes. Because photosynthesis is light dependent, and surface mixing is largely dependent on wind energy, water velocity, and morphometry (in the sense of wave height and fetch), DO levels can vary throughout the day and/or season.

A DO level >1 mg/L is generally accepted as a chronic minimum for most aquatic animals; 5 mg/L is a chronic minimum for the maintenance and survival of most aquatic organisms and is a common regulatory criterion for supporting a cold water fishery. As water becomes warmer it can hold less DO. If the water becomes too warm, even if 100% saturated, DO levels may be suboptimal for many species dependent in higher levels of oxygen, such as trout.

1.2.5 Flow

Flow is a key parameter for physical conditions in rivers; it is needed to interpret concentration data and calculate water quality loadings. Although part of the core water quality suite, it is singled out here because flow measurement is operationally different from other water quality monitoring. Flow regimes have been historically altered by land-use changes and may continue to be impacted by shifting agricultural practices, expanding urbanization, and climate change driven by greenhouse warming (Lenz 2004). The U.S. Geologic Survey (USGS) is the only agency with a long-term program to record flow in streams and rivers within GLKN's service area. The historical and ongoing data from these gaging stations are absolutely critical for the analysis of water quality trends and loading, and land use and climate changes.

1.2.6 Turbidity

Turbidity is a visual property of water and implies a reduction or lack of clarity resulting mainly from suspended organic and inorganic particles. Organic particles typically are from suspended algae, microcrustaceans, and bacteria, while inorganic geologically-derived particles are from soils made up of silicate minerals and aluminum and iron oxides. Water turbidity is commonly assessed through analysis of total suspended solids (TSS), which is the amount of material left on a filter after filtering a measured volume of water. High TSS levels can impair lakes and rivers by preventing sunlight from penetrating deep enough into the water column to support growth of submerged aquatic vegetation, as well as inhibiting fish and mussel populations, and reducing overall aesthetics for recreational uses.

1.2.7 Nutrients (Total Phosphorus [TP], Total Nitrogen [TN], Nitrate+Nitrite-N [NO_3+NO_2-N], and Ammonium-N [NH_4-N])

Nitrogen and phosphorus, the two most influential nutrients in terms of regulating phytoplankton and aquatic macrophyte growth, will be included in this monitoring protocol. Excessive inputs of nutrients can lead to excessive algal growth and eutrophication (Wetzel 2001, Horne and Goldman 1994). Their effects on biological communities and recreational uses are among the most serious threats to large river systems.

Nutrients are carried into rivers primarily through surface runoff. Bioavailable forms of phosphorus and nitrogen (dissolved phosphate, nitrate, and ammonium) are typically highest following runoff events and immediately downstream of point sources such as wastewater treatment plants. Expanding urbanization, agricultural intensification, encroachment of exotic species, and management efforts to mitigate these impacts are likely to change nutrient levels in these riverine parks. Nutrients are also introduced to rivers through atmospheric deposition, although typically at much lower levels than other anthropogenic sources.

*1.2.8 Chlorophyll-*a

The concentration of chlorophyll-*a*, the primary photosynthetic pigment in all green plants including phytoplankton, is a nearly universally accepted measure of phytoplankton biomass (e.g., Wetzel 2001, Wetzel and Likens 2000). Chlorophyll-*a* concentrations are expected to be dynamic, reflecting changes in algal abundance through the growing season.

1.2.9 Major Ions

- Cations—calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^{+}), and potassium (K^{+})
- Anions—SO_4^{-2}, Chloride (Cl^{-}), and alkalinity ($CaCO_3$)

The chemical composition stream water is a function of land use, climate, and basin geology. Each waterbody has an ion balance of the three major anions and four major cations (Table 1). The ionic concentrations influence a river's ability to assimilate pollutants (e.g., acidification) and maintain nutrients in solution. For example, high Ca^{+2} and Mg^{+2} directly reduce the bioavailability and toxicity of many heavy metals, and indirectly affect mercury cycling (e.g., Horne and Goldman 1994, Driscoll et al. 1994, Driscoll et al. 1995).

Table 1. Ion balance typical for fresh water in the upper Midwest (Wetzel 2001, Horne and Goldman 1994).

Cations	Percent	Anions	Percent
Ca^{+2}	63%	HCO_3^{-}	73%
Mg^{+2}	17%	SO_4^{-2}	16%
Na^{+}	15%	Cl^{-}	10%
K^{+}	4%	--	--
Other	<1%	other	<1%

Bicarbonate and carbonate ions, which are estimated by alkalinity, dominate the major anions. Alkalinity directly estimates the majority of the buffering capacity of the water and is used to estimate sensitivity to acid precipitation. Sulfate concentrations provide a measure of the potential accumulation of sulfur due to acidic deposition of SO_x compounds and are important for assessing acid deposition effects. Sulfate is also a critical parameter for understanding and modeling mercury cycling because sulfate-reducing bacteria in anoxic environments are the primary source of methyl mercury, the major fraction involved in the bioaccumulation of mercury in food webs (e.g., Driscoll et al. 1994). Chloride (Cl^-) is a particularly good indicator of wastewater plumes as well as inputs and accumulation of road salt. It may be used as a tracer, as it moves through soil without significant absorption or adsorption.

1.2.10 Dissolved Silica (SiO_2)

Silica is considered an essential micronutrient for microorganisms and diatom algae. These organisms use silica to form shells and other protective structures. Diatoms are capable of using large amounts of silica, and may be growth-limited when silica is in short supply.

1.2.11 Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) is usually the largest fraction of organic material in the open waters of lakes and rivers, except during intense algal blooms or when an abundance of aquatic plants die off during fall senescence, causing a surge in particulate organic carbon. DOC is derived primarily from decomposing material in the watershed that is leached into stream and groundwater inputs and washed in from wetlands with abundant sphagnum mosses (Wetzel 2001, Schindler and Curtis 1997). Typically, a lesser amount is contributed by algae, both from extracellular leakage and via decomposition; concentrations may be high following intense algae blooms. DOC plays important roles in freshwater ecosystems , including 1) affecting acid-base chemistry and metal cycling (e.g., copper, mercury, aluminum), and potential toxicity; 2) acting as a source of energy and nutrients to the microbial food chain, thereby influencing nutrient availability; 3) attenuating UV-B radiation; 4) attenuating PAR (photosynthetically active radiation) and thereby regulating primary production; and 5) influencing the heat budget of rivers and lakes by absorbing sunlight (Gergel et al. 1999, Schindler and Curtis 1997). Anthropogenic stressors, such as global warming, ozone losses, acidification, and intensive logging are cause for concern as they may be altering the concentration and distribution of DOC, resulting in adverse effects on lakes and rivers.

1.2.12 Water Clarity

Although not mandated, GLKN has included a measure of water clarity (transparency tube depth on all sites and Secchi depth on lake-like sites), which is also closely linked to turbidity (*see section 1.2.6*). Water clarity is in the core suite of parameters because of its fundamental importance to stream ecology, ease of measurement, and the fact that it will always be measured along with core suite profiles. Light penetration, for which water clarity and TSS are surrogates, is an important regulator of rate of primary production and plant species composition. Water clarity provides a visual measurement that relates directly to the aesthetic perceptions of the general public. Transparency tube and Secchi depth can be an effective indicator of non-algal suspended sediment loading from agricultural and urban runoff and from shoreline erosion (Swift et al. 2006, Holdren et al. 2001, Preisendorfer 1986). Additionally, Secchi depth transparency has a long history of use as an excellent

indicator of trends in phytoplankton biomass (e.g., WOW 2005, Goldman 1988), and is an integral component of upper Great Lakes States Monitoring programs (e.g., WDNR 2005; MPCA 2005a, 2004c; MDEQ 2004, 2001).

1.2.13 Limitations of this Protocol

NPS-WRD has advised that monitoring protocols include the water quality variables that have caused resource waters to be designated as impaired on the 303(d) list. All or portions of the Mississippi River within MISS are on the 303(d) list of impaired waters for aquatic life due to turbidity, aquatic consumption due to mercury and polychlorinated biphenyl (PCB), and aquatic recreation due to fecal coliform bacteria (Ledder 2003). Although most of the exceedances occurred prior to the 1990s (National Park Service 1995b), the St. Croix River below St. Croix Falls is on Wisconsin's Section 303(d) list for aquatic consumption due to PCBs (Ledder 2003). The entire section of the St. Croix River within Minnesota is on the state's 303(d) list for aquatic consumption due to mercury. Because regional and state regulatory agencies monitor regularly (Tables 3 and 5) for the listed water quality variables, GLKN has chosen to not conduct duplicate monitoring for these variables under this protocol. However, through separate bioaccumulative toxics protocols GLKN will monitor levels of PCBs, mercury, and other organic contaminants in tissues of bald eagles (Route et al. 2009) and in fish, and dragonfly larvae (Wiener et al. 2009).

In addition, separate protocols for monitoring aquatic biological parameters (algae, macroinvertebrates, fish species, etc.) in rivers may be developed in the future, as needed. Therefore, although additional variables may be monitored opportunistically, the measurement variables routinely monitored for this large river water quality protocol are limited to the primarily physical and chemical parameters shown in Sections 1.2.1–1.2.12.

1.3 Background and History; Description of Resource

This protocol is designed to guide monitoring of the physical and chemical water quality of large non-wadeable rivers in park units of the Great Lakes Inventory and Monitoring Network. Monitoring will focus on that portion of the mainstem of the Mississippi River, which occurs within the Mississippi National River and Recreation Area (MISS), and the mainstems of the St. Croix and Namekagon Rivers, which occur in the St. Croix National Scenic Riverway (SACN).

Neither MISS nor SACN currently has a water quality monitoring program of its own, but until the onset of GLKN monitoring in 2006 (MISS) and 2007 (SACN) they relied solely on data collected by other agencies and institutions. The NPS-WRD retrieved data from several EPA databases, including STOrage and RETrieval System (STORET), and summarized these data for national park units (NPS 1995a, 1995b). Monitoring programs administered by federal, state, and regional agencies have collected flow and water quality data within MISS and SACN park boundaries since the 1920s. Many of these monitoring programs are on-going at present, and offer the potential for sharing data with the NPS monitoring network. By sharing data among agencies, sampling costs will be minimized and sampling records will be maximized.

1.3.1 MISS – Mississippi River

Flowing through the Twin Cities metropolitan area of Minneapolis-St. Paul, 123 km of the Mississippi River is included within the MISS park boundaries (Figure 1). The southern boundary of MISS is immediately downstream of the confluence between the Mississippi and St. Croix Rivers, that is, downstream of SACN. Table 2 lists Mississippi River locations that have been monitored by other government agencies for at least five years and that are still active, including four USGS streamflow gages within MISS boundaries. Monitoring sites for major tributaries to the Mississippi River within park boundaries are shown in version 1.0 of this protocol (Magdalene et al. 2008).

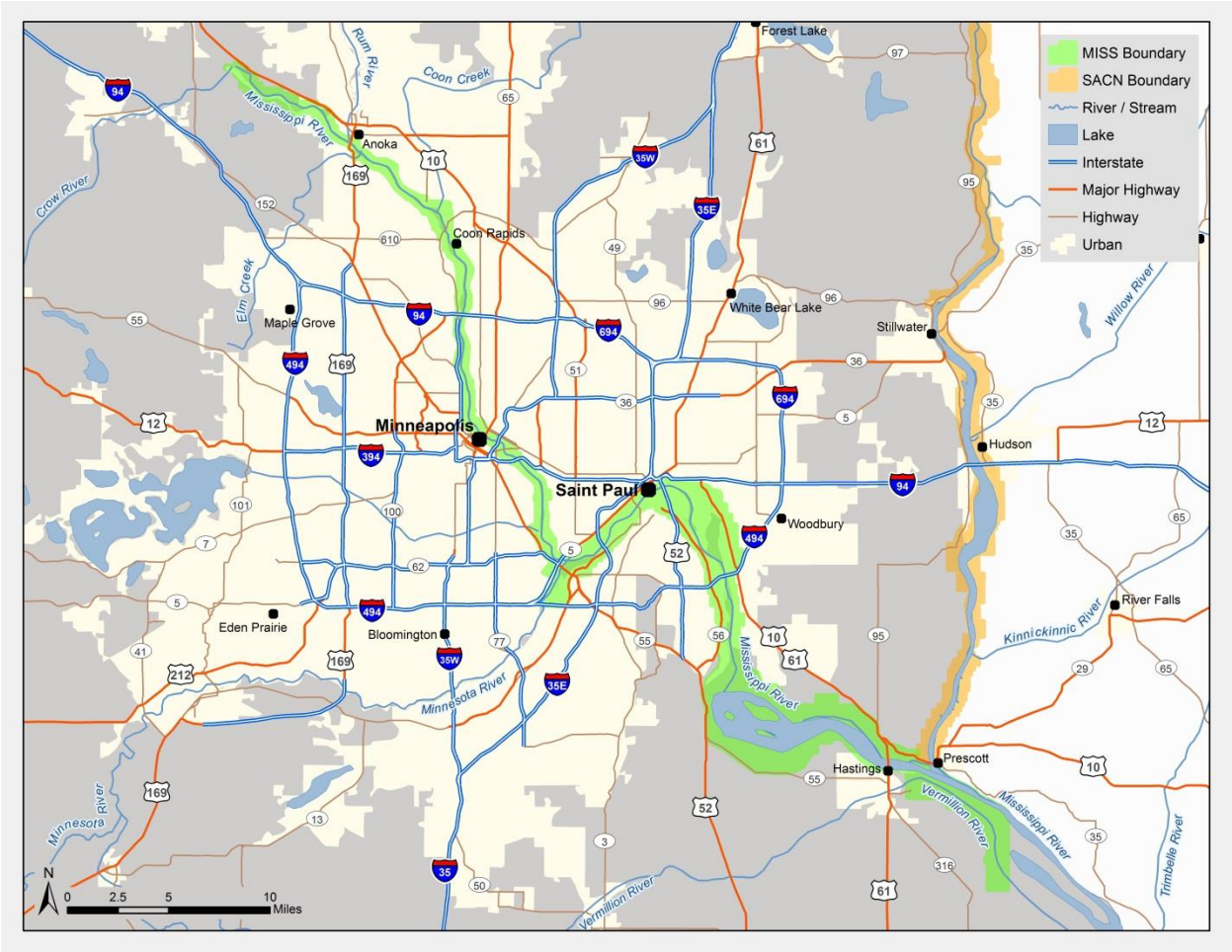


Figure 1. Map showing the location of the Mississippi National River and Recreation Area (MISS) and Lake St. Croix within the St. Croix National Scenic Riverway (SACN).

MISS receives heavy urban and suburban pressures, including industrial and municipal wastewater discharge, recreational use, and stormwater runoff. Although numerous water quality parameters have exceeded EPA criteria for protection of aquatic life and for drinking water in this stretch of the river (National Park Service 1995a), the river remains a source of drinking water for the Twin Cities. The NPS-WRD summary of water quality for MISS included data from 184 stations within park boundaries, 59 of which had exceedances recorded during the period of record 1926–1994 (National

Park Service 1995a). Most of the documented problem parameters fall under the categories of dissolved oxygen, metals, or indicator bacteria (Table 3; Ledder 2003). Outside of park boundaries, the headwaters of the river are designated as an Outstanding Resource Value Water (ORVW) by the state of Minnesota.

Table 2. Long-term Mississippi River water quality (WQ) monitoring stations established by other agencies within MISS boundaries. Parameters monitored and monitoring frequency varies widely among agencies. USGS=United States Geologic Survey, MPCA=Minnesota Pollution Control Agency, WDNR=Wisconsin Department of Natural Resources, MCES=Metropolitan Council Environmental Services, MWMO=Mississippi Watershed Management Organization. ¥=active USGS streamflow gauging station.

Agency	Station Location (Station ID)	WQ Period of Record	Flow Period of Record
USGS	MissR @ Anoka (05283500)	1973–1998	1905–1913
	MissR @ Brooklyn Park (05288500) ¥	1960–2006	1931–present
	MissR @ Robt. Street (05331001)	1938–1972	1938–1972
	MissR @ St. Paul (05331000) ¥	1967–1981	1892–present
	MissR @ Hastings (05331580) ¥	1936–present	1995–present
	MissR @ Prescott (05344500) ¥	none	1928–present
MPCA	MissR @ Anoka (S-25)	1953–2002	--
	MissR @ Mpls Intake (S-24, UM-859)	1953–present	--
	MissR @ Coal flats (S1-303)	1998–2004	--
	MissR @ Wab. Br. (S-266, UM-840)	1973–present	--
	MissR @ S. of StP (S-133)	1967–1978	--
	MissR @ Grey Cloud Is. (S-339, UM-826)	1975–present	--
	MissR @ Hastings (S-68, UM-815)	1958–present	--
WDNR	MissR @ Hastings (483026)	1977–1994	--
MCES	MissR @ Anoka (UM-871.6)	1976–present	--
	MissR @ Fridley (UM-862.8)	1978–present	--
	MissR @ L&D#1 (UM-847.7)	1976–present	--
	MissR @ Lamberts Landing (UM-839.1)	1976–present	--
	MissR @ Newport (UM-831.0)	1980–present	--
	MissR @ Grey Cloud (UM-826.7)	1976–present	--
	MissR @ Spring Lake (UM-821.8)	1982–1991	--
	MissR @ Hastings L&D#2 (UM-815.6)	1976–present	--
	MissR @ Hastings Hwy (UM-813.9)	1976–2000	--

Table 2 (continued). Long-term Mississippi River water quality (WQ) monitoring stations established by other agencies within MISS boundaries. Parameters monitored and monitoring frequency varies widely among agencies. USGS=United States Geologic Survey, MPCA=Minnesota Pollution Control Agency, WDNR=Wisconsin Department of Natural Resources, MCES=Metropolitan Council Environmental Services, MWMO=Mississippi Watershed Management Organization. ¥=active USGS streamflow gauging station.

Agency	Station Location (Station ID)	WQ Period of Record	Flow Period of Record
MCES	MissR @ Hastings RR (UM-812.8)	1977–1991	--
MWMO	MissR @ Camden, UM-859.1 (MS-1)	2005–present	--
	MissR @ Mississippi Park, UM-857.8 (MS-2)	2005–present	--
	MissR @ North Loop, UM-854.9 (MS-3.1)	2005–present	--
	MissR @ Univ. of MN, UM-852.2 (MS-4)	2005–present	--
	MissR @ Lake St. Br., UM-849.9 (MS-5)	2005–present	--
	MissR @ W. River Pkwy., UM-848.2 (MS-6.1)	2005–present	--

Table 3. Water quality variables and locations of Minnesota 303(d) impaired waters listings within MISS, the agency or organization that monitors that variable, and monitoring frequency. MPCA=Minnesota Pollution Control Agency, MNDNR=Minnesota Department of Natural Resources, MCES=Metropolitan Council Environmental Services, MWMO=Mississippi Watershed Management Organization. FCA=fish consumption advisory, L&D=lock and dam, PCB=polychlorinated biphenyls.

Listed Variable	Mississippi River Segment (in river miles)	Agency / Organization	Monitoring Frequency
Fecal coliform	Crow R. to Rum R. (879-871.6)	MCES	weekly
	Lower St. Anthony Dam to L&D#1 (853-848)	MCES	weekly
	Minnesota R. to Metro WWTP (844-835)	MCES	weekly
	Camden to West River Parkway (859.1-848.2)	MWMO	Weekly to bi-monthly
PCB FCA	Crow R. to Lower St. Anthony Dam (879-853)	MNDNR	annually
	L&D#1 to St. Croix R. (848-811)	MNDNR	annually
Mercury FCA	Crow R. to St. Croix R. (879-811)	MNDNR	annually
Mercury in water	Minnesota R. to L&D#2 (844-815)	MCES	annually
Turbidity	Minnesota R. to St. Croix R.	MCES	weekly

Analyses of the data collected by federal, state, and regional agencies and by many independent research projects are discussed in a comprehensive review by Lafrancois and Glase (2005). A summary of key information relating to MISS follows:

> Ayers et al. (1985) determined that the seasonal rainfall pattern was the most significant factor controlling runoff loads in urban, sewered watersheds, while spring snowmelt carried

> the greatest runoff loads in rural watersheds within the larger Twin Cities area. Kroening and Andrews (1997) found that nitrogen runoff varied with land use and season: in agricultural watersheds runoff peaked in spring and summer, while peak runoff in forested watersheds occurred in winter. Kroening (1998) found that nonpoint sources of nutrients dominated all sub-basins of the Upper Mississippi River. Highest nutrient and sediment loads were found below the confluence of the Minnesota River with the Mississippi River (Kroening et al. 2002). Kloiber (2004) found that nitrate-nitrite concentrations have increased in the Upper Mississippi, according to data collected by the Metropolitan Council Environmental Services (MCES) from 1976 to 2002. In contrast, Kloiber (2004) identified declines in biological oxygen demand, ammonium, total phosphorus, total suspended solids, and turbidity.

Since the review by Lafrancois and Glase (2005) was published, the status and trends of key water quality variables have recently been assessed by Russel and Weller (2013) and by Kraft et al. (2015a). The status and trends reports include information from studies identified in Lafrancois and Glase (2005) as well as that published since (e.g., Lafrancois et al. 2013). A summary of key information from the status and trends reports follows:

> The current status of Mississippi river flow within MISS, expressed as mean annual discharge, was categorized as of moderate concern with a deteriorating trend, as when compared to the historic flow regime present before the onset of dredging and alterations beginning in 1866, flow has significantly increased in the Mississippi and Minnesota Rivers since 1950 and 1976, respectively. Phosphorus, the primary nutrient controlling algal growth, and when overabundant can lead to eutrophication, is described as of significant concern but with an improving trend, when data from Network and MCES monitoring efforts are compared to draft river nutrient criteria described in Heiskary and Wasley (2012) and Heiskary et al. (2013). The status of total nitrogen was categorized as of significant concern with a stable trend, using the same Network and MCES data sources, and draft criteria described in Heiskary and Wasley (2012) and Heiskary et al. (2013). Nitrate concentrations were described as of significant concern but with a stable trend, by comparing trend analyses from a number of studies with draft chronic (Monson 2010) and U.S. Environmental Protection Agency reference (USEPA 2000) criteria. The status of total suspended solids (also referred to as total suspended sediment) was rated as of significant concern but with an improving trend, when compared to reach-specific draft TSS standards (MPCA 2012, Heiskary and Bouchard 2015).

1.3.2 SACN – St. Croix and Namekagon Rivers

Stretching from northwest Wisconsin south to the Twin Cities, SACN includes 248 km of the St. Croix River and 172 km of the Namekagon River (Figure 2). The upper reaches of the Riverway flow through a largely rural landscape consisting of forests and wetlands. Agricultural land use increases as one travels south through the watershed. Urban and suburban development also increases southward, until the St. Croix River joins the Mississippi River at Prescott, Wisconsin. The lower 41 km of the river, known as Lake St. Croix, function as a lake with a retention time of approximately 20 days (Triplett et al. 2003), due to a glacial-age delta at the confluence of the two

rivers. Lake St. Croix is composed of four distinct pools (Pool 1 is near Stillwater, Minnesota and Pool 4 is near Prescott, Wisconsin) caused by narrows or constrictions in the river mainstem. Table 4 shows St. Croix or Namekagon river locations that have been monitored by other government agencies for at least five years, including six active USGS streamflow gages within SACN boundaries.

Pressures potentially affecting water quality of the Namekagon and St. Croix Rivers include industrial and wastewater discharge; storm water and agricultural runoff; nutrient loading from tributaries, agriculture, forestry; and recreational use (Ledder 2003; Lafrancois and Glase 2005). The NPS-WRD summary of water quality for SACN covered the period of record from 1926 to 1995 (National Park Service 1995b). The summary includes data from 469 monitoring stations in the study area, of which 107 are within park boundaries. Measured values for 14 parameters have exceeded EPA criteria at least once for freshwater aquatic life or drinking water at 22 stations within park boundaries.

Despite the 303(d) listings (Table 5), the State of Wisconsin has designated the Namekagon River and the majority of the St. Croix River as outstanding resource waters (ORW). Further, the St. Croix River at St. Croix Falls and from Hudson to Prescott, is designated as exceptional resource waters (ERW; high quality resource subject to point source pollution) by the State of Wisconsin. The State of Minnesota has designated the entire section of the St. Croix River within state boundaries as outstanding resource value waters (ORVW).

Analyses of the data collected by federal, state, and regional agencies, and by many independent research projects, are discussed in a comprehensive review by Lafrancois and Glase (2005). A summary of key information relating to SACN follows:

> Lenz (2004) analyzed St. Croix River flow data from USGS gages at Danbury (1914–2003) and St. Croix Falls (1902–2003), noting increasing stream flows at both sites over the past century. Agricultural streams carried much more nitrogen and phosphorus than did forested or urban streams in the St. Croix basin (Fallon and McNellis 2000). Phosphorus loading in the St. Croix River has decreased slightly over the last 30 years, but current conditions far exceed EPA Ecoregion VII reference conditions (Lafrancois et al. 2004). About 90% of the phosphorus loading appears to derive from nonpoint sources, while nitrate levels have increased over the last 30 years (Lenz et al. 2003). Kloiber (2004) found that dissolved oxygen and nitrate-nitrite concentrations have increased in the Lower St. Croix, according to data collected by the Metropolitan Council Environmental Services (MCES) from 1976 to 2002. In contrast, Kloiber (2004) identified declines in biological oxygen demand, ammonium, total Kjeldahl nitrogen, fecal coliform bacteria, total suspended solids, and turbidity.

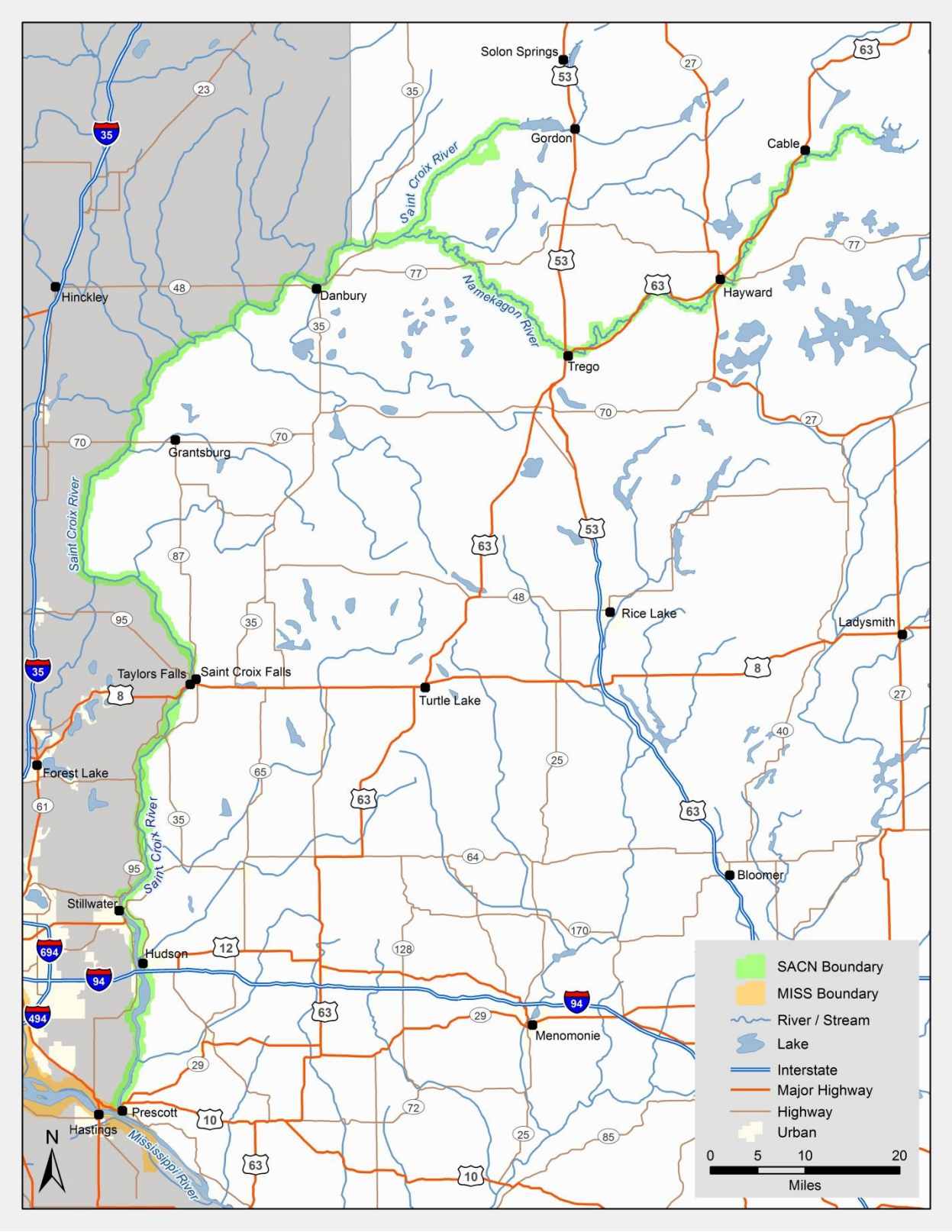


Figure 2. The St. Croix National Scenic Riverway (SACN) is composed of 248 km of the St. Croix River and 172 km of the Namekagon River.

Table 4. Long-term St. Croix or Namekagon river water quality (WQ) monitoring stations established by other agencies that are within SACN boundaries. Parameters monitored and monitoring frequency varies widely among agencies. USGS=United States Geologic Survey, MPCA=Minnesota Pollution Control Agency, WDNR=Wisconsin Department of Natural Resources, MCES=Metropolitan Council Environmental Services. ¥=active USGS streamflow gauging station.

Agency	Station Location (Station ID)	WQ Period of Record	Flow Period of Record
USGS	Namekagon @ Leonards (05331833) ¥	1995–2002, 2005–present	1995–2002, 2005–present
	Namekagon @ Hayward (05331855)	1975–1985	1975–1985
	Namekagon nr Trego (05332500) ¥	1966–present	1927–present
	St. Croix R. @ Danbury (05333500) ¥	1964–present	1914–present
	St. Croix R. nr Grantsburg (05336000)	2008–2010	1923–2011
	St. Croix R. @ SCFalls (05340500) ¥	1902–present	1902–present
	St. Croix R. @ Stillwater (05341550) ¥	1974–1981, 2011–present	1974–1981, 2011–present
	St. Croix R. @ Prescott (05344490) ¥	2007–present	2007–present
MPCA	St. Croix R. nr Danbury (S-56, SC-111)	1957–present	--
	St. Croix R. @ Osceola (S-57)	1957–1965	--
	St. Croix R. @ Stillwater (S-19, SC-23)	1953–present	--
	St. Croix R. @ Hudson (S-126, SC-17)	1967–present	--
	St. Croix R. @ Afton (S-918)	1982–1999	--
	St. Croix R. @ Pt. Douglas (S-18)	1953–1965	--
WDNR	Namekagon R. nr Trego	2003–present	--
	St. Croix R. nr Danbury	2003–present	--
	St. Croix R. @ Interstate (nr SCFalls)	2003–present	--
MCES	St. Croix R. @ Stillwater (SC 23.3)	1976–present	--
	St. Croix R. @ Prescott (SC 0.3)	1976–present	--

Table 5. Water quality variables and locations of Minnesota (MN) and Wisconsin (WI) 303(d) impaired waters listings within SACN, the agency that monitors the variable, and monitoring frequency. MNDNR=Minnesota Department of Natural Resources, WDNR=Wisconsin Department of Natural Resources. FCA=fish consumption advisory, PCB=polychlorinated biphenyls.

State	Listed Variable	St. Croix River Segment (in river miles)	Agency	Monitoring Frequency
MN	Mercury FCA	MN/WI border to Prescott (127-0)	MNDNR	annually
WI	PCB FCA	St. Croix Falls to Prescott (52-0)	WDNR/MNDNR	annually
MN/WI	Total phosphorous	Stillwater, MN to Prescott (25–0)	WDNR/MNDNR	annually

Lafrancois et al. (2009) have analyzed the trends in concentrations and loadings from 29 years of monitoring data for Lake St. Croix (St. Croix River between Stillwater, Minnesota, and Prescott, Wisconsin), within SACN, and for Lake Pepin, which is immediately downstream of both MISS and SACN. Total phosphorus (TP), orthophosphate, ammonia-N, and sediment concentrations and loads have decreased since the 1970s, but nitrate+nitrite-nitrogen and total nitrogen have increased over the same period. Although TP concentrations in Lake St. Croix have decreased slightly over the last few decades, monitoring in the last decade (1998-2006) indicated that TP exceeds EPA guidelines for determination of use support for lakes. As a result, both Minnesota and Wisconsin added Lake St. Croix to their 2008 303(d) lists for excessive nutrients (MPCA and WDNR 2012).

The status of key water quality variables have recently been assessed by Kraft et al. (2015b), and includes information from studies identified in Lafrancois and Glase (2005) as well as that published since (Lafrancois et al. 2009, MPCA and WDNR 2012). Trends are not analyzed for most water quality variables by Kraft et al. (2015) due to the lack of long-term datasets. A summary of key information from Kraft et al. (2015) follows:

> The current status of St. Croix River flow was not addressed in Kraft et al. (2015), but the authors reference the previously-mentioned study by Lenz (2004) who noted an increase in river flow at Danbury, Wisconsin, and St. Croix Falls, Wisconsin, over the past century. Phosphorus, the primary nutrient controlling algal growth, is described as of significant concern for Lake St. Croix, and is the focus of a multi-state Total Maximum Daily Load Plan (TMDL; MPCA and WDNR 2012). In contrast, phosphorus levels for mainstem monitoring sites upstream of St. Croix Falls, WI easily meet State of Minnesota and Wisconsin nutrient standards (Heiskary and Bouchard 2015, WDNR 2010) and at the uppermost sites frequently meet USEPA nutrient reference criteria (USEPA 2001). The status of total nitrogen was categorized as of moderate concern, when total nitrogen data from a variety of sources was compared with USEPA reference criteria. Trends in total nitrogen were not assessed, but stable, increasing, and decreasing trends have been identified in other studies, depending on the specific monitoring site and period of record (Lorenz et al. 2009, Lafrancois et al. 2009). Although not assessed by Kraft et al. (2015b), in comparison to that found for Mississippi River sites within MISS, nitrate and total suspended solids concentrations found at mainstem monitoring sites on the St. Croix River are good and not of concern (VanderMeulen 2012).

1.4 Objectives and Monitoring Questions

Our overall goal is to develop a protocol for monitoring water quality in large rivers that will contribute to an understanding of the ecological integrity of park units of the Great Lakes Network. Specifically, this protocol is designed to document river water quality status and trends for individual stations, on a longitudinal (downstream) basis, and a park-wide basis. The protocol includes historical analysis, sample design, field and laboratory methods, data analysis and reporting, and training and operational requirements.

1.4.1 Objectives

1) Monitor mean annual concentrations of core and advanced suite parameters in MISS and SACN, accounting for seasonality in water quality conditions.

2) Relate current water quality conditions to known historical conditions.

3) 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).

4) Gather flow data from other agencies for the St. Croix, and Namekagon, and Mississippi Rivers to determine changes in mean monthly and mean annual flows.

1.4.2 Monitoring Questions

1) What are the current status and long-term spatial and temporal trends in select water quality variables, including temperature, pH, specific conductance, dissolved oxygen, water clarity, sediment, alkalinity, major ions, and nutrients?

2) Are changes in water quality parameters correlated with tributary influences or changes in other aspects of the ecosystem, such as measures of biotic communities, exotic species, land use or land cover, weather and climate, or atmospheric deposition?

3) What are the current status and long-term trends in systematic flow regime?

1.5 Quality Assurance and Quality Control

Quality control is the planned and systematic pattern of all actions, or controls, necessary to provide adequate confidence that a project outcome optimally fulfills expectations. Quality assurance is a program for the systematic monitoring and evaluation of the various aspects of a project to ensure that standards of quality are being met. Together, quality assurance/quality control (QA/QC) is a significant part of any monitoring program. It is a broad management concept of maintaining the ability to provide reliable information, requiring the complete integration of field and laboratory systems of sample collection and analysis. QA/QC incorporates peripheral but essential operations such as survey design, equipment preparation, maintenance tasks, data handling, and personnel training. The objective of QA/QC is to ensure that the data generated by a project are meaningful, representative, complete, precise, accurate, comparable, and scientifically defensible (O'Ney 2005).

This protocol includes QA/QC procedures that must be followed, beginning with field preparations, through the collection of data, to the final analyses and reporting of results. See standard operating procedure (SOP) #12 for QA/QC details.

2.0 Sample Design

2.1 Rationale for Selecting This Sampling Design

The GLKN large rivers monitoring protocol strives to integrate two existing protocols: the USGS National Water-Quality Assessment (NAWQA) program (Gilliom et al. 1995) and the EPA Environmental Monitoring and Assessment Program-Aquatic Resource Monitoring (EMAP-ARM) (McDonald and Geissler 2004). Both protocols use different site-selection methods (random versus non-random), and have different goals (assessment of long-term trends versus current conditions). Our goal is to combine the strengths of both programs for monitoring water quality of lotic systems in the NPS Great Lakes Network.

2.1.2 USGS NAWQA Program Site-Selection Method

The USGS National Water-Quality Assessment (NAWQA) program is designed to assess the current status and long-term trends of the water quality of the nation's water resources. The study units (each about 10,000 km^2) cover a major portion of the nation, and research focuses on hydrologic and ecologic resources that are under agricultural and urban influences. The status of water quality conditions is assessed in two- to three-year intensive studies, while long-term trends in water quality are assessed by repeated intensive studies every 10 years.

Gilliom et al. (1995) summarized the NAWQA design and site-selection method as follows. Water-quality sampling is conducted at two types of fixed sites: integrator and indicator. Integrator sites, located at major intersections in the drainage network, are chosen to represent water-quality conditions in heterogeneous, large basins that are often affected by complex combinations of land-use settings, point sources, and natural influences. Indicator sites, in contrast, are chosen to represent water-quality conditions in relatively homogeneous smaller basins (50–500 km^2) associated with specific individual environmental settings. Each study unit typically contains three-to-five integrator sites and four-to-eight indicator sites (Figure 3). Depending on the water quality variable, sampling occurs on a continuous, fixed-interval (usually monthly), or extreme-flow basis.

In addition to the fixed-site locations, NAWQA study units may contain synoptic sites designed to increase the spatial resolution of data for the highest-priority water-quality issues. Sites are located to provide balanced spatial coverage at the desired resolution in the target geographic area and near stream junctions to facilitate mass-balance analysis for the sampling period.

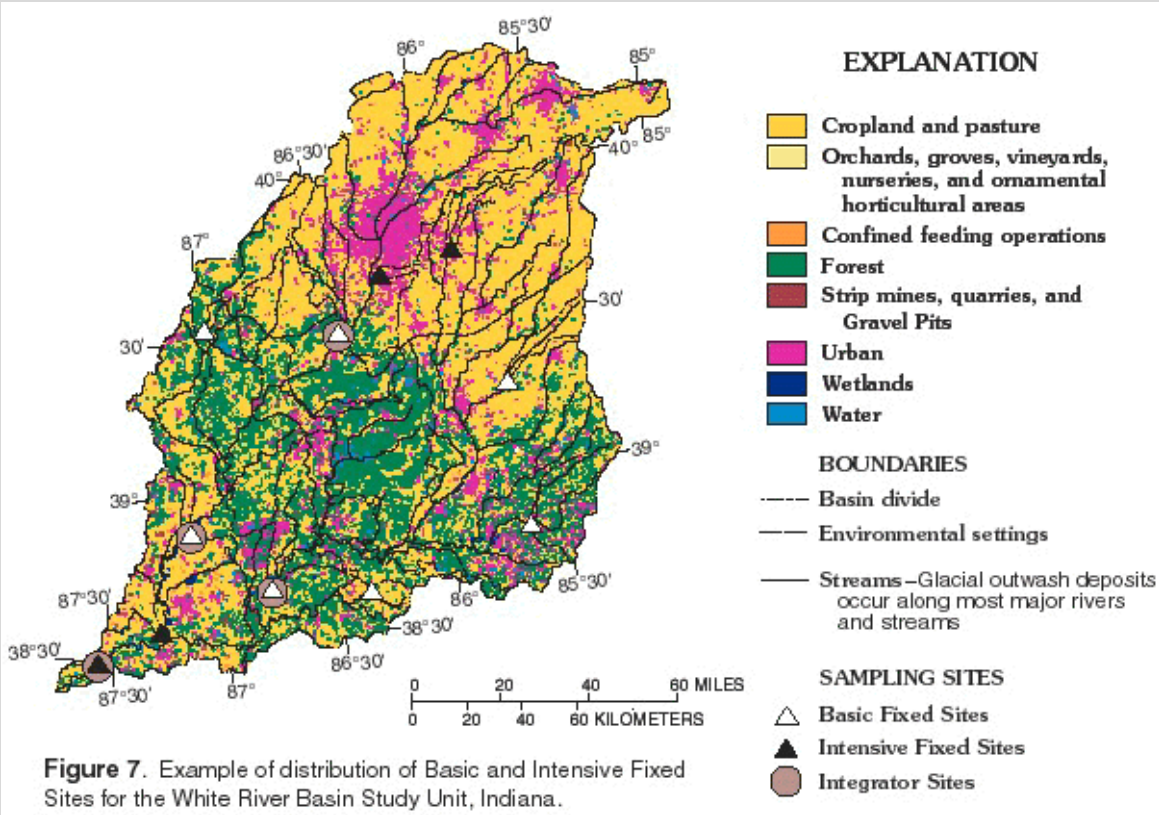


Figure 3. Geographic distribution of environmental settings and sampling sites within a NAWQA study unit (White River Basin, Indiana) (from Fenelon 1998).

2.1.3 EPA EMAP-ARM Site-Selection Methods

In theory one could design a comprehensive monitoring program that directly measured the current and changing conditions of river water quality. However, such a census of the entire 'population' of water quality samples would be cost-prohibitive. McDonald and Geissler (2004) posit that judgment sampling, or using 'representative' sites selected by experts, is inappropriate for long-term monitoring projects because this method of sample design can produce biased information. Statistical sampling methods are efficient for broad spatial domains because they require sampling fewer locations to make valid scientific statements about conditions across large areas. In addition, the statistical design of a project should precede data collection to maximize budget and minimize bias (Ward et al. 1990).

All streamwater within a watershed at a given moment in time represents a statistical population. Random sampling from the population allows for scientifically valid inferences to be made about the current and changing conditions of the watershed. The larger watershed can be stratified into subwatersheds (stratum). Random sampling within each stratum allows statistical inferences to be made about each stratum. For example, sampling from particular tributaries could make it possible to monitor the effect of distinct land uses within those subwatershed areas. Generally, stratification seeks to minimize within-stratum variability by maximizing variability among pre-defined groups.

McDonald et al. (2002) summarize the site-selection method of EMAP as follows. The method proceeds from a generalized random tessellation stratified (GRTS) design (Stevens and Olsen 2004). Stream networks are identified on 1:100,000 scale maps, including the length and stream order of each stream segment. If equal numbers of samples from each stream order are desired, then differential weighting by size may be necessary, due to the predominance of lower-order streams. For example, weighting factors of 1, 2, and 4 could be used to produce similar-sized statistical samples for first-, second-, and third-order streams, respectively.

Using this weighting scheme, the inclusion probability for a stream segment is proportional to its segment length times the weight of its stream order. Segment lengths are multiplied by their weight, sorted randomly, and organized in a single continuous line (Figure 4). The minimum number of water samples that need to be collected from a population or stratum are determined by the analytical precision required to identify changes in water quality (see Section 2.4). The selection length is determined by dividing the length of the randomly-sorted line by the number of samples needed. The selection of sites begins with a random point on the first segment, and proceeds by measuring off the selection length along the randomly-sorted line. In this way, the site-selection method not only identifies which stream segments are to be sampled, but at what point on the segment the sample is to be located.

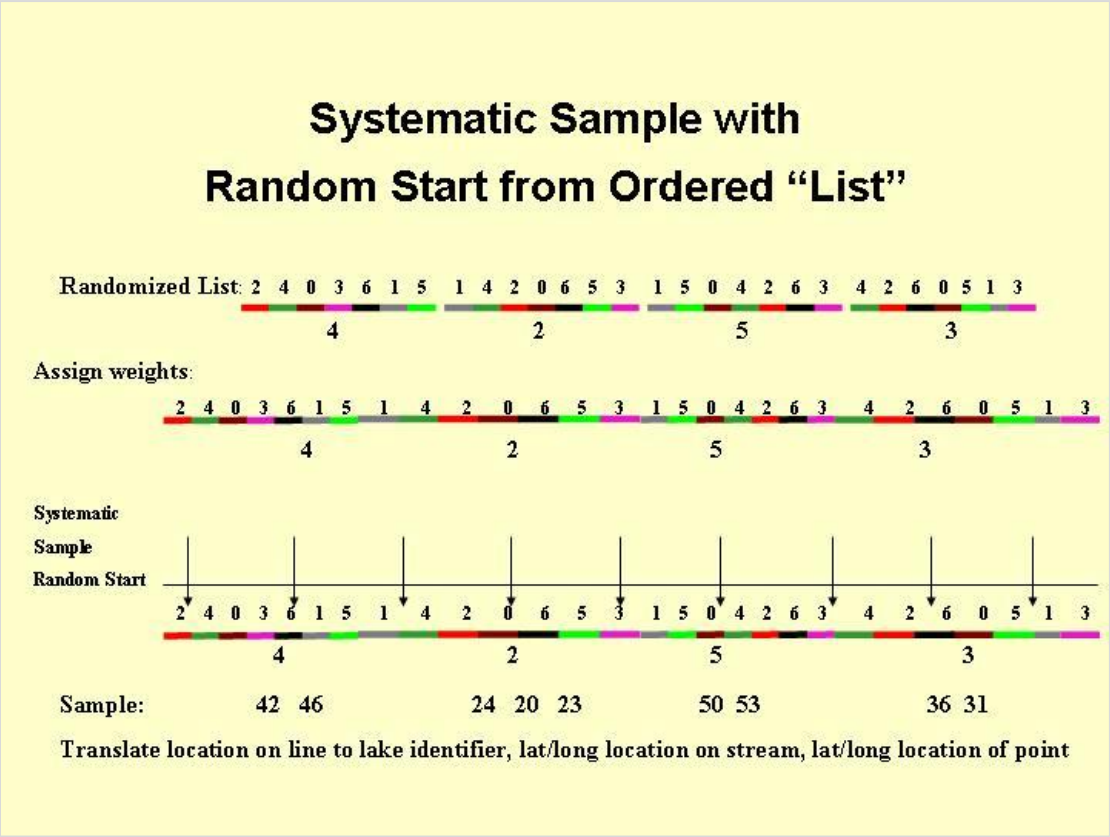


Figure 4. Example of a random statistical sample selection process for stream networks (from Olsen 2002).

2.1.4 General Great Lakes Network Design

This program is designed to monitor the water quality of the Mississippi, St. Croix, and Namekagon Rivers within the boundaries of MISS and SACN. Unlike the USGS and EPA study units, these NPS parks do not include the entire watershed but rather are linear features containing sections of the mainstem river, riparian lands, and the mouths of tributaries. Geographic stratification of the population by sub-watersheds and stream-order weighting do not apply in this case.

Random versus Nonrandom Site-Selection: The monitoring objectives drive the site-selection process. The objective to determine population statistics, such as mean annual concentrations, requires randomly-selected sites. The objective to track the influence of individual tributaries (and land uses) requires non-randomly-selected sites. As discussed earlier, we aim to incorporate the practical strengths of the USGS and EPA designs into the monitoring design of the Great Lakes Network's river water quality program. Specifically, we plan to employ a random site-selection similar to the EPA method, and make use of nonrandom site-selection similar to the USGS method.

Random site-selection along the mainstem using statistical methods can ensure scientifically-valid assessments of mainstem river water quality. Therefore, a set of randomly-selected monitoring sites is needed to define the population characteristics, in spite of existing efforts of other agencies to monitor long-term mainstem water quality at particular locations (*see Section 1.3*). Installation of a new set of random sites, independent of another agency's monitoring budget, will help to ensure GLKN collects a consistent dataset with which to assess long-term water quality trends.

Nonrandom site-selection can help to identify water quality trends at locations of high interest. Tributaries often influence water quality within the mainstem (e.g., the influence of the Minnesota River on the upper Mississippi), and it will be important to monitor the contributions of tributaries. In addition, particular mainstem locations may be deemed important monitoring sites. For example, no monitoring program has ever monitored the downstream end of the MISS park unit, where mixing of the St. Croix and Mississippi Rivers occurs.

This program will include both randomly-selected and non-randomly-selected sites. All sites will be analyzed on an individual basis, to determine water quality trends at each location. Only the randomly-selected sites will be grouped for analysis of population statistics and trends.

Stratification to Reduce Population Variability: Stratification is employed to reduce the variability in a selected population. Although this water quality monitoring program will not cover entire subwatersheds, the method of stratification described previously is still desirable for the two large river parks in the Network, as they have distinctive geographic features within the parks that serve to increase the variability of water quality data.

SACN: The St. Croix River is known to have a gradient of decreasing water quality as one travels downstream, due in part to distinctly different land uses and land covers in the upper and lower portions of the watershed. Forests and wetlands cover the upper portion of the St. Croix watershed, and streams are rocky and dynamic, whereas agricultural and urban lands dominate the lower portion, and the river widens to form a riverine lake (Figure 5). However, the geographic distribution

of these land uses has and will continue to change with time. Consistent characterization of an ecological resource requires that it be stratified based on a feature that will not change with time (Stevens and Olsen 1991). Therefore, we stratified the river based on hydrological processes rather than land use. Our stratification was between the mainstem of the St. Croix River above Stillwater, Minnesota, and the riverine lake (St. Croix River below Stillwater, known as Lake St. Croix). Fundamental differences exist in the hydrological processes of these two portions of the river; the slower residence time of Lake St. Croix makes it behave more like a lake, very differently than classic mainstem river flow. This difference in flow behavior leads to different outcomes in water quality, detailed below, in the discussion on power analysis.

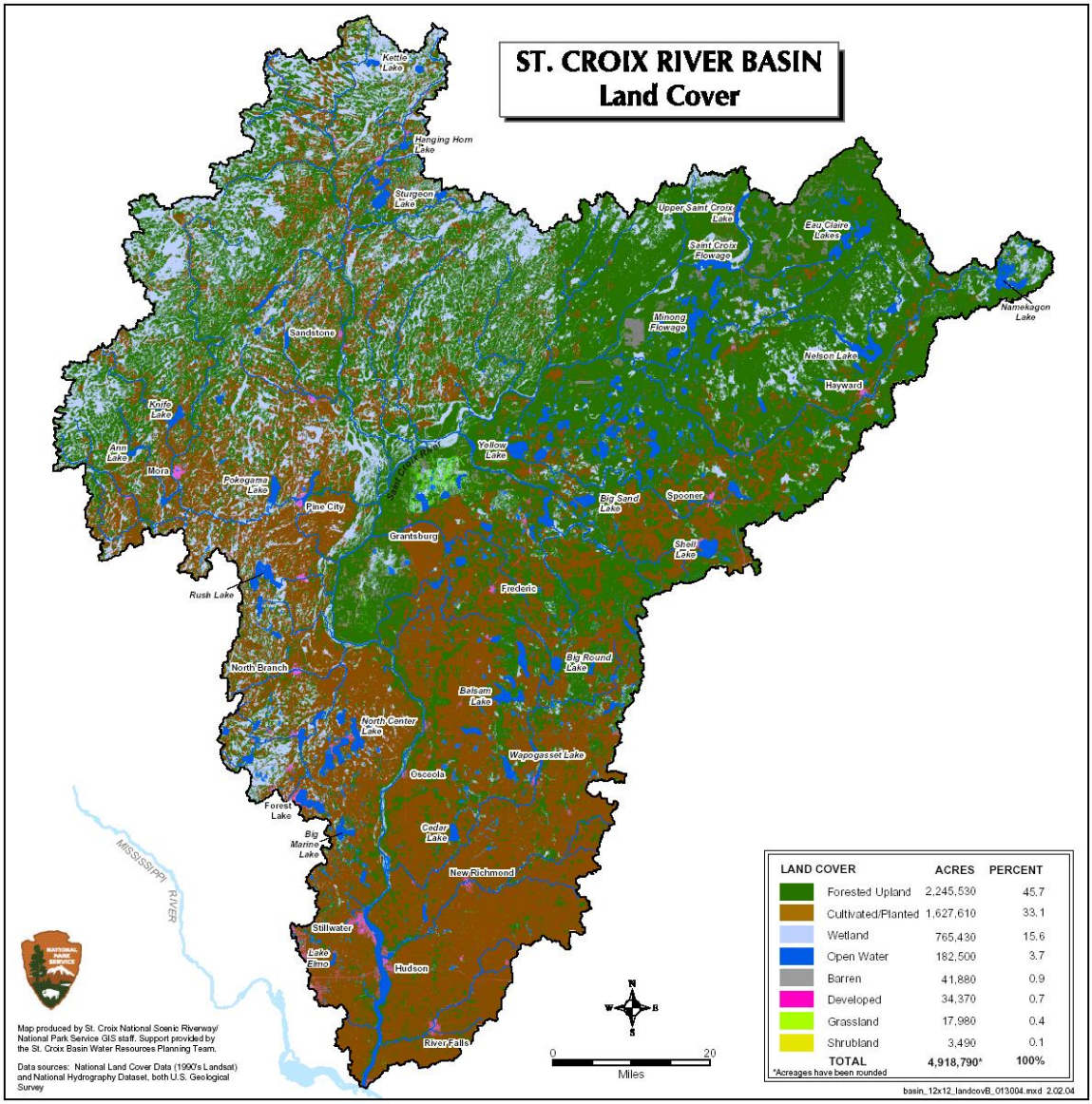


Figure 5. Land cover of the St. Croix River basin.

MISS: We stratified the Mississippi River within park boundaries into four segments (listed by river mile): UM-878 to UM-845, UM-845 to UM-836, UM-836 to UM-813, and UM-813 to UM-807. These segments are delineated by three major features within the river corridor that are known to have strong influence on the water quality of the Mississippi River: 1) the confluence of the Minnesota River (at river mile UM-845), which is the single largest point source of sediments and nutrients to the Upper Mississippi River; 2) the Twin Cities metropolitan wastewater treatment facility, which discharges phosphorus and nitrogen to the Mississippi River below St. Paul, Minnesota (at river mile UM-836); and 3) the confluence of the St. Croix River (at river mile UM-813), which exerts dilution on Mississippi River water quality. Each of these long-term features fundamentally changes the hydrology of the Mississippi River.

2.1.5 Great Lakes Network Design Changes Since Protocol Implementation

This protocol was first implemented at MISS in 2006 and at SACN in 2007, with monitoring alternating between parks in subsequent years. Therefore, monitoring at MISS was carried out in 2006, 2008, 2010, and 2012 (Elias and Sieracki 2007; VanderMeulen 2009, 2011, 2013) and at SACN in 2007, 2009, and 2011. Additional monitoring at select sites and at a reduced frequency took place at SACN in 2008, 2010, and 2012 (VanderMeulen 2008, 2011, 2012).

MISS: Monitoring at MISS was suspended in 2014 after it was determined that water quality monitoring by MCES and other agencies was adequately characterizing water quality conditions throughout MISS (Lafrancois et al. 2013, VanderMeulen 2013). Many GLKN sites are in reasonable proximity to sites already being monitored. Additionally, MCES and other agencies typically monitor water quality at their respective sites more frequently than GLKN (i.e., weekly vs. monthly. As a result, GLKN data collection at MISS was not contributing to the ability to detect ecosystem change more than MCES data alone. Nor did GLKN data substantially enhance the ability to develop pool-specific TMDLs in the park. GLKN water quality monitoring at MISS could resume if monitoring efforts by other agencies are discontinued. Despite the suspension of monitoring, information about how individual sites at MISS were selected, and general references to monitoring at MISS are retained in this protocol, to both provide context for past monitoring and as a guide for future monitoring should it be re-initiated. Last, aquatic-related sampling by GLKN may occur at MISS on a project-by-project basis.

SACN: As a consequence of suspending monitoring at MISS, work at SACN was expanded to annual monitoring, beginning in 2014 and continuing to present. However, from 2011 to 2013 a number of sites were dropped and added; a full explanation of these changes is discussed in Section 2.4.2.

2.2 Site-Selection

2.2.1 Procedures for Random Site-Selection

(Modified from: http://archive.epa.gov/nheerl/arm/web/html/.)

1) Determine the minimum number of random sites required to achieve the desired level of precision (*see Section 2.4 below*). Double the size of the selection pool to accommodate oversampling (enabling the ability to eliminate inaccessible sites, or adding future sites, etc.).

2) Measure the length of mainstem river within the park unit to be sampled.

3) Calculate selection length by dividing river length by the number of sites in the selection pool.

4) Identify the individual reaches of the river and re-order the reaches into a randomly-sorted line.

5) Randomly select a site within the first reach in the line.

6) Proceed along the randomly-sorted line, selecting sites spaced one selection length from each other.

7) From the resulting selection pool, randomly select half of the stations; these are the randomly-selected monitoring sites.

8) If one of the randomly-selected locations is physically inaccessible, choose the next location from the selection pool.

Additional considerations (Stednick and Gilbert 1998): sampling locations on the mainstem should be located a distance of five stream widths below the influence of a tributary to ensure adequate mixing; stations with continuous flow monitoring are preferred; if this is not possible, stations should be located along a straight and narrow reach with minimal channel complexity.

2.2.2 Criteria for Nonrandom Site-Selection

In general, the goal of nonrandom site-selection for MISS and SACN is to fill spatial gaps for areas not currently being monitoring by other agencies, especially at locations that have historical monitoring data, in order to improve overall monitoring coverage across both parks. On both rivers, resources exist to understand where other agencies are sampling and where gaps in sampling exist, to help choose where non-random sites should be added.

The St. Croix Basin Water Resources Planning Team (hereafter called the Basin Team), composed of federal, state (Minnesota and Wisconsin), and regional water resources professionals who are actively involved in management of the St. Croix River basin, has developed a comprehensive monitoring plan for the St. Croix River that identifies existing monitoring efforts of various agencies and provides additional monitoring needs (VanderMeulen et al. 2010). Taking into account current monitoring by other agencies (Table 4) and monitoring gaps identified in the most recent version of the St. Croix River Monitoring Plan, additional needs include:

1) Adding monitoring stations along the mainstem of the St. Croix River, particularly in underrepresented areas.

2) Some existing monitoring stations (e.g., USGS gaging stations) are monitored for water quality on a quarterly basis or not at all; supplement monitoring at these locations with a higher frequency of sampling.

3) Resuming monitoring at the mouth of tributaries that have a history of previous monitoring, particularly if the tributary has a nearby upstream gaging station.

4) Targeting tributaries without a monitoring history if significant water quality changes are occurring or are expected to occur in the future.

Unlike SACN, MISS does not have a multi-agency team of water quality professionals through which water quality monitoring efforts are formerly coordinated. However, MISS hosts a bimonthly Mississippi River Forum that seeks to increase coordination between a multidisciplinary group of water resources practitioners and decision-makers, and is an opportunity for water quality professionals to coordinate monitoring and connect their work to those in different fields who also impact the quality of the river.

2.3 Historical Variability and Statistical Power Analysis

Large rivers often exhibit variations in flow and subsequent variations in water quality due to climate seasonality, geology, geography, dominant vegetation, and land use. All of these factors contribute to the storm water runoff and baseflow characteristics of sub-watersheds. As a rule, river systems respond more dynamically to fluctuating runoff than do lake systems. By virtue of their longer residence times, lakes tend to modulate the effects of water quality variability in runoff; collecting relatively few samples during a year can be sufficient to define the average water quality conditions for that year. In contrast, a river drainage network is a flow-through system, efficiently delivering dynamic pulses of runoff from the land surface to waterways. In addition, river water quality will reflect the seasonal fluctuations in runoff water quality. As a result, large rivers require a much higher sampling frequency than lakes in order to define the average water quality conditions.

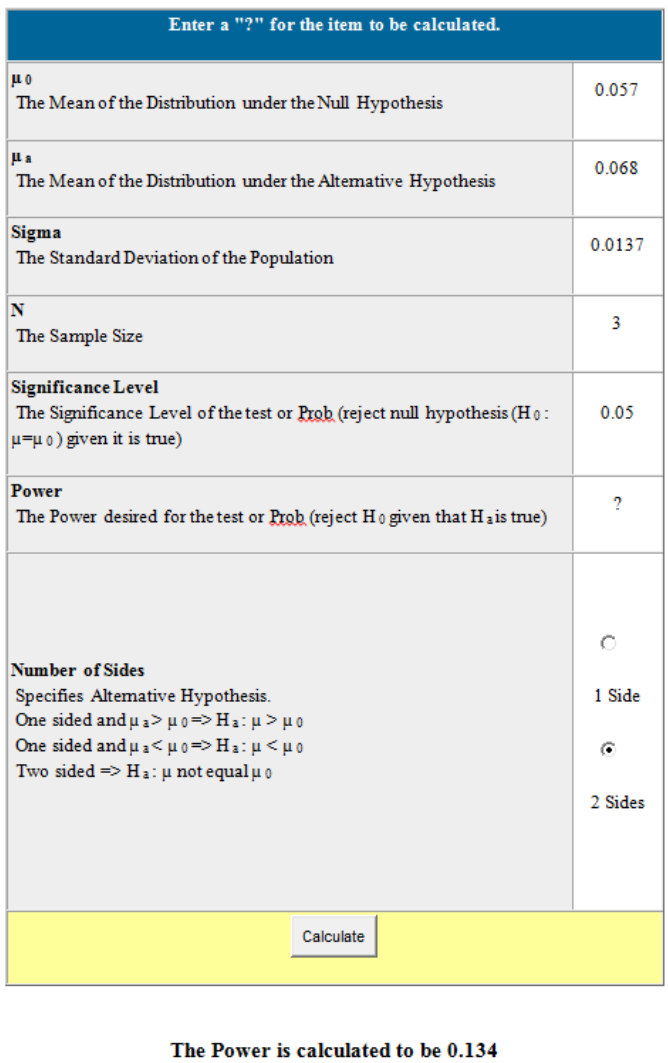
The variations in historical sampling frequencies make it challenging to determine if water quality changes have occurred with time. Statistical power analysis assesses the ability of a hypothesis test to detect a change, given that change actually exists. We conducted statistical power analysis on St. Croix River historical data to test the power of the historical monitoring efforts to detect a 20% change, using an online calculator (http://www.ats.ucla.edu/stat/gpower/) shown in Figure 6. This calculator has been found to match the results of the Zar (1999) equations. However, these types of calculators assume a normal distribution to the data and tend to overestimate the power and underestimate the sample size of skewed data. Statistical power ($1-\beta$) increases as sample size (n), minimum detectable change or effect size (d), or specified significance-level (α) increases, and declines as the population variance (σ) increases. Effect size (e.g., 20% change), often called minimum detectable difference (MDD), is the difference between the null and alternative hypotheses (μ_o and μ_a), and can be measured either using raw or standardized values. Raw measures, such as the difference between means (μ_a - μ_o) or slope in a regression analysis, are closer to the measurements that researchers take and hence are easier to visualize and interpret (Thomas and Krebs 1997). Thus,

statistical calculators of this type require the input of five parameters (n, α, 1-β, μ_o, σ, or μ_a) in order to solve the sixth.

We evaluated the possibility of reducing variability by limiting sampling to narrow index times of the year. Using the historical data, we conducted power analysis on monthly and quarterly means of selected water quality variables. Across sites and parameters, there were no consistently 'better' periods of the year for reducing variability in the sampled data. In addition, this large rivers protocol is designed for analysis of long-term trends in annual means, rather than the trend in a small portion of the year (for example, only sampling in August). As a natural resource, large rivers are highly variable, and it is important to observe their behavior throughout the entire year.

Normal Power Calculations

Normal Distribution 1-Sample



Enter a "?" for the item to be calculated.	
μ_0 The Mean of the Distribution under the Null Hypothesis	0.057
μ_a The Mean of the Distribution under the Alternative Hypothesis	0.068
Sigma The Standard Deviation of the Population	0.0137
N The Sample Size	3
Significance Level The Significance Level of the test or Prob (reject null hypothesis (H_0: $\mu=\mu_0$) given it is true)	0.05
Power The Power desired for the test or Prob (reject H_0 given that H_a is true)	?
Number of Sides Specifies Alternative Hypothesis. One sided and $\mu_a > \mu_0 \Rightarrow H_a: \mu > \mu_0$ One sided and $\mu_a < \mu_0 \Rightarrow H_a: \mu < \mu_0$ Two sided $\Rightarrow H_a: \mu$ not equal μ_0	○ 1 Side ◉ 2 Sides
Calculate	

The Power is calculated to be 0.134

Figure 6. Screen shot of online statistical power calculator (http://www.ats.ucla.edu/stat/gpower/). Alternative hypothesis was defined as 20% change from population mean.

2.3.1 SACN

The historical data were stratified between three stations in the upper St. Croix basin (Trego, Danbury, and St. Croix Falls) and three stations in the lower St. Croix basin (Stillwater, Hudson, and Prescott). Three water quality variables (pH, dissolved oxygen, and total phosphorus) were chosen to represent low, moderate, and high variability data, respectively. Based on the 30-year mean values, DO concentration was greater and pH and TP levels were lower in the Upper St. Croix than in the Lower St. Croix.

Annual means were calculated from all available data for each parameter for each of 30 years (1974-2003) for each station. The individual annual means for each group of three stations were used to calculate 30 annual means and coefficients of variation (CVs) for the upper and lower portions of the basin. Because each of the annual statistics was derived from one value per station, the result is a measure of the range of variability among stations, providing the valid basis from which to calculate sample size. To gage the range of variability, the 30-year minimum, mean, and maximum values of the annual statistics were evaluated in the power analysis. Table 6 lists the minimum, mean, and maximum of the annual mean and CVs in the upper and lower portions of the basin, and the power of previous monitoring efforts to detect change. Over the range of variation observed in pH and dissolved oxygen, the sampling frequency of historical monitoring was sufficient to achieve the goal of 70-80% power of detecting 20% change. In contrast, the historical monitoring efforts had very low power to detect change in total phosphorus, due to the higher observed variation for this water quality variable.

Table 6. Within the upper and lower portions of the SACN park unit, the 30-year minimum, mean, and maximum values of the annual mean and coefficient of variation (CV, %), and the statistical power (%) of historical monitoring efforts to detect a 20% change (n=3), based on the annual means (1974–2003) of three water quality variables: pH (standard units), dissolved oxygen (DO, mg/L), and total phosphorus (TP, mg/L). Two-tailed significance level α_2=5%.

		Upper St. Croix			Lower St. Croix		
Value Type	**Statistic**	***pH***	***DO***	***TP***	***pH***	***DO***	***TP***
Min Value	Annual Mean	6.85	8.32	0.018	7.42	8.45	0.036
	CV (%)	0.2	1	3	0.04	2	1
	Power (%)	100	100	91	100	100	100
Mean Value	Annual Mean	7.55	9.55	0.041	7.70	9.48	0.057
	CV (%)	2	5	34	0.6	7	24
	Power (%)	100	90	9	100	75	13
Max Value	Annual Mean	8.20	11.33	0.071	8.14	11.77	0.094
	CV (%)	9	12	95	3	21	98
	Power (%)	53	35	4	100	16	4

2.3.2 MISS

Six historical water quality monitoring stations administered by other agencies are located within the first three of the four Mississippi River segments. These six stations have historical records of pH, dissolved oxygen, total phosphorus, and nitrate-nitrogen data since 1980 (Table 2). Unfortunately, no agency has ever monitored along the fourth segment, so the historic mean and variability of water quality at the downstream end of the park unit are unknown. Based on mean values from 1980 to 2006 for the first three segments, the downstream spatial trend of water quality through the MISS corridor is one of decreasing pH and DO, and increasing TP and nitrogen-oxides (NO_x-N).

Annual means and standard deviations of the four variables were used to derive 26-year means and standard deviations. Care was taken to ensure that the calculated standard deviations were a measure of the variability among stations. Power analysis was conducted 1) on the entire dataset (n=6) representing historical water quality in the entire park unit corridor, and 2) on two subsets (n=2 and n=3) representing the water quality in two segments of the park unit corridor (Table 7). Power analysis, which requires a measure of population variability, was not conducted on one of the segments because it contained only one historical monitoring station.

Table 7. The 26-year mean values of annual mean and coefficient of variation (CV, %) for monitored portions of the MISS park unit, and the statistical power (%) of historical monitoring efforts to detect a 20% change, based on the annual means (1980–2005) of four water quality variables: pH (standard units), dissolved oxygen (DO, mg/L), total phosphorus (TP, mg/L), and nitrogen oxides (NO_x-N, mg/L). (-- = data not available.)

River Segment	Statistic	pH	DO	TP	NO_x-N
MISS 878-845 (n=2)	Mean	8.06	10.50	0.103	0.73
	CV (%)	0.7	7	13	25
	Power (%)	99.7	25	12	7
MISS 845-836 (n=1)	Mean	8.03	10.08	0.157	1.98
	--	--	--	--	--
MISS 836-813 (n=3)	Mean	7.97	9.78	0.228	2.28
	CV (%)	0.5	3	8	4
	Power (%)	100	100	56	98
MISS 813-807 (n=0)	--	--	--	--	--
	--	--	--	--	--
MISS 878-807 (n=6)	Mean	8.01	10.07	0.175	1.71
	CV (%)	0.9	6	38	47
	Power (%)	100	100	20	14

Three pieces of evidence point to the existence of separate populations of water quality along the MISS corridor. First, two-sample comparisons (http://www.ats.ucla.edu/stat/gpower/) of the first

three segments revealed three distinct populations of water quality; p-values were generally small (Table 8). Second, for each segment, the variability among stations is less than the variability among years. Third, stratification into separate subpopulations (n=2 and n=3) appears to decrease the variability observed in the entire (n=6) set of monitoring data (Table 8).

In summary, the information goals and statistical requirements determine the sampling frequency. To identify the long-term trends in a stream or river, the sampling frequency should be sufficient to identify a statistical trend beyond the background variability of a dynamic flow system. Therefore, it is essential to evaluate existing data prior to establishing 1) the number of sites and 2) the frequency of sampling. Statistical power analysis based on the power to detect change will guide the selection of these two parameters, using calculations of statistical sample size and analysis of sensitivity to sampling frequency, respectively.

Table 8. Two-sample comparisons based on 26 annual means for pH (standard units), dissolved oxygen (DO, mg/L), total phosphorus (TP, mg/L), and nitrogen oxides (NO_x-N, mg/L).

Comparison	Statistic	pH	DO	TP	NO_x-N
Segment 1(879-845) vs. Segment 2 (845-836)	T-stat	0.68	2.68	-6.43	-6.48
	P-value	0.499	0.011	<1E-6	1E-6
Segment 2(845-836) vs. Segment 3 (836-813)	T-stat	1.98	1.82	-6.37	-1.28
	P-value	0.053	0.076	<1E-6	0.207
Segment 1(879-845) vs. Segment 3 (836-813)	T-stat	2.50	6.43	-13.2	-9.47
	P-value	0.016	<1E-6	<1E-6	<1E-6

2.4 Number and Location of Monitoring Stations

The National Park Service-Water Resources Division (NPS-WRD) has recommended that roughly two-thirds of selected sites should be located within either Section 303(d)-impaired waters or pristine waters that the park seeks to preserve (Irwin 2004). All of the St. Croix and Namekagon Rivers within SACN have been designated as outstanding or exceptional waters by Minnesota and Wisconsin (see Section 1.3.2). A portion of the St. Croix River, from where it enters Minnesota down to Prescott, is on the 303(d) list. In addition, a majority of the tributary mouths that might potentially be monitored as part of the non-randomly-selected sites are either pristine or impaired. All of the Mississippi River within MISS is on the 303(d) list, and none of it is designated as outstanding waters by Minnesota (see Section 1.2.1). Therefore, we expect that 1) all of the randomly-selected sites for SACN, 2) the majority of the non-randomly-selected sites for SACN, and 3) all of the sites selected for MISS, will be located within pristine or impaired waters.

2.4.1 Randomly-Selected Stations Within SACN

When planning a study, statistical power analysis is most useful to: 1) explore the relationships between the range of statistical sample sizes that are deemed feasible, 2) determine the effect size, or minimum detectable change thought to be biologically important, 3) calculate levels of variance that

could exist in the population, and 4) establish desired levels of error risks (α and β) (Thomas and Krebs 1997). The outcome of such analysis is a decision about statistical sample size and target effect size, or conversely, whether a study is worth pursuing based on an expected sample size limit. NPS-WRD recommends conducting sample size analysis using a multi-step approach, and to "consider throwing out variables where the variability in pristine sites is so high that one would never find a trend or effect size of biological concern given funding limitations" (Irwin 2004).

Estimation of the number of sites needed, or statistical sample size analysis, was conducted using the observed variation in the historical monitoring data for the St. Croix River. The on-line statistical sample size calculator (http://www.ats.ucla.edu/stat/gpower/) was used to determine the number of sites needed to detect 20% change at 80% power and 5% significance (Table 9). For pH and dissolved oxygen, the range of observed variation is small enough to require relatively few monitoring sites. In contrast, the mean CV of total phosphorus requires 40 monitoring sites in the St. Croix basin—far more than the GLKN monitoring budget allows.

Based on the historical data, it is not possible to monitor total phosphorus to detect 20% change. Therefore, we have made the decision that the GLKN large rivers monitoring program will seek to detect 20% change in low to moderate variability parameters of the St. Croix River. Accordingly, the sample size analysis (Table 9) indicates that three stations in each of the upper and lower portions of the St. Croix basin should be sufficient to monitor the long-term average water quality conditions. Thus, there will be six randomly-selected monitoring sites within SACN.

Table 9. Within the upper and lower portions of the SACN park unit, the 30-year minimum, mean, and maximum values of the annual mean and coefficient of variation (CV, %), and the predicted sample size (number of sites) required to detect a 20% change at 80% power, based on the annual means (1974–2003) of three water quality variables: pH (standard units), dissolved oxygen (DO, mg/L), and total phosphorus (TP, mg/L). Two-tailed significance level α_2=5%.

		Upper St. Croix			Lower St. Croix		
Value Type	**Statistic**	***pH***	***DO***	***TP***	***pH***	***DO***	***TP***
Min Value	Mean	6.85	8.32	0.018	7.42	8.45	0.036
	CV (%)	0.2	1	3	0.04	2	1
	Sample size	1	1	1	1	2	4
Mean Value	Mean	7.55	9.55	0.041	7.7	9.48	0.057
	CV (%)	2	5	34	0.6	7	24
	Sample size	2	3	26	1	3	14
Max Value	Mean	8.20	11.33	0.071	8.14	11.77	0.094
	CV (%)	9	12	95	3	21	98
	Sample size	4	5	187	2	11	190

The random site-selection process resulted in three upper SACN stations (Namekagon River near Earl, Wisconsin, St. Croix River near Norway Point, and St. Croix River near 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). Although the three lower SACN stations substantially overlap with long-term monitoring sites by MCES (Pools 1 and 4 in Stillwater, Minnesota, and Prescott, Wisconsin, respectively (Table 4) and MCES volunteers (Pool 2 in Hudson, Minnesota (unpublished data), because they were randomly selected they were retained. The random site-selection process included oversampling (*see Section 2.2.1*), so that if any of the stations are deemed as inappropriate monitoring sites, there are more locations from which to choose. The oversampled sites are in the upper SACN (Namekagon River at Leonard School Road Bridge, Namekagon River at Groat Landing, and St. Croix River at Stillwater, Minnesota) and the lower SACN on the St. Croix River (Pool 1 near Stillwater, Minnesota, Pool 3 near Afton, Minnesota, and Pool 4 below the confluence with the Kinnickinnic River).

2.4.2 Non-randomly-Selected Stations Within SACN

The Network will include four to seven additional non-randomly-selected sites within SACN, with the exact number dependent on the annual budget. Potential locations, given as river miles on the Namekagon (NAM) or St. Croix (SC) rivers, of non-randomly-selected monitoring stations are listed below, including the reason for possible inclusion (sites with an asterisk [*] are deemed to be a high priority by the Monitoring and Assessment subcommittee of the St. Croix Basin Team]:

1) NAM 98 – Nearest of headwaters of SACN, at Namekagon Dam
2) NAM 35 – USGS gaging station at Trego (*)
3) NAM 4.5 – Namekagon Trail Bridge — integrates upstream conditions
4) SC 96 – Mouth of Kettle R., downstream from active USGS gage
5) SC 92 – Mouth of Snake R., downstream from active USGS gage
6) SC 89.7 – Hwy. 70 Bridge — fills spatial gap in monitoring
7) SC 70.5 – Mouth of Sunrise R., MPCA samples only 2 of 5 yrs (*)
8) SC 52 – St. Croix Falls, active USGS gaging station not monitored (*)
9) SC 30 – Mouth of Apple R., downstream from active USGS gage (*)
10) SC 17 – Mouth of Willow R., downstream from active USGS gage (*)
11) SC 13 – Pool 2 of Lake St. Croix — supports modeling efforts
12) SC 8 – Pool 3 of Lake St. Croix — supports modeling efforts
13) SC 6 – Mouth of Kinnickinnic R., downstream from active USGS gage (*)

In April 2007 monitoring was implemented at the six randomly-selected sites, four out of six sites (SC 52, 30, 17, and 6) noted as high priority by the St. Croix Basin Team, and on the Snake River (SC 92) just upstream of the confluence with the St. Croix River. In May 2007 two additional sites of particular interest to SACN staff were added: one on the Namekagon River at Phipps Landing (NAM 74.5) downstream from a cranberry farm and the other on the upper St. Croix River (SC 138.9) that reflects upper St. Croix River water quality conditions just above the rivers confluence with the Namekagon River (Figures 7, 8, and 9; Table 10) (Magdalene et al. 2008).

Table 10. Years and sites monitored ("x") at St. Croix National Scenic Riverway during open-water months (typically April-November), 2007–2015. Site IDs are those used to identify site locations in Network database, with river (SC=St. Croix; NAM=Namekagon) and river mile shown in parenthesis. Core suite of parameters monitored each visit, with advanced suite of parameters also monitored quarterly in April, July, and October. Off-year monitoring in 2008, 2010, and 2012 quarterly only. Annual monitoring initiated in 2014. Dash (-) indicates no monitoring.

Site ID	2007	2008	2009	2010	2011	2012	2013	2014	2015
SACNa (SC 138.9)	x	x	x	-	x	-	x	x	x
SACNb (NAM 74.5)	x	x	x	-	x	-	x	x	x
SACN01 (NAM 41.3)	x	x	x	x	x	x	x	x	x
NAKA 4.8 (NAM 4.8)	-	-	-	-	-	-	x	x	x
SACN02 (SC 104.0)	x	x	x	x	x	x	x	x	x
SACN03 (SC 92)	x	x	x	-	x	-		-	-
STCR89.7 (SC 89.7)	-	-	-	-	-	-	x	x	x
SACN04 (SC 63.8)	x	x	x	x	x	x	x	x	x
SACN05 (SC 52)	x	x	x	-	x	-		-	-
SACN06 (SC 30)	x	x	x	-	x	-	x	-	-
SACN07 (SC 20.0)	x	x	x	x	x	x	x	x	x
SACN08 (SC 17)	x	x	x	-	x	-	x	-	-
SACN09 (SC 15.8)	x	x	x	x	x	x	x	x	x
SACN10 (SC 6)	x	x	x	-	x	-	x	-	-
SACN11 (SC 2.0)	x	x	x	x	x	x	x	x	x

With the passage of the State of Minnesota's Clean Water, Land and Legacy Amendment in 2008, the Minnesota Pollution Control Agency and their partners significantly increased their water quality monitoring efforts, to be able to better protect, enhance, and restore water quality in lakes, rivers, streams, and groundwater (MPCA 2011). Specific to SACN, in 2009 the MPCA began intensive (30–35 visits per year) long-term monitoring on the St. Croix River at the two USGS gauging sites in St. Croix Falls and Danbury, Wisconsin, and on major Minnesota tributaries to the St. Croix River,

including the Kettle, Snake, and Sunrise Rivers. Therefore, to avoid duplication of effort, Network monitoring was dropped at St. Croix Falls (SACN05) and on the Snake River (SACN03) after 2011.

After 2013, Network monitoring was also discontinued at the Apple River (SACN06), the Willow River at Lake Malleau (SACN08), and the Kinnickinnic River (SACN10). These sites were initially included in Network monitoring to fill data gaps identified by the St. Croix Basin Team pursuant to the calculation of TMDLs. However, because of the sampling frequency (monthly, April–November) and the lack of monitoring storm events that are critical for calculating pollutant loads, it was determined that Network monitoring at these sites was not adequate for this purpose. Additionally, staff from the USGS Wisconsin Science Center began an intensive monitoring project at or near these sites in 2013 in order to derive nutrient loads, which at least from a nutrient monitoring perspective would have represented a duplication of effort with planned Network monitoring.

Through a re-examination of long-term mainstem monitoring efforts by the Network and other agencies, we concluded that in general, most of the monitoring was focused on Lake St. Croix, and that portions of SACN upstream of St. Croix Falls were underrepresented. Therefore, at the same time Network monitoring was dropped at the Apple, Willow, and Kinnickinnic Rivers we added mainstem river sites on the St. Croix River at the Highway 70 Bridge near Grantsburg, Wisconsin, (STCR89.7) and on the Namekagon River a few miles upstream from its confluence with the upper St. Croix River (NAKA4.8). The site at Highway 70 fills a large spatial gap between two other Network monitoring sites (SACN02 and SACN04), represents an area of the river previously impacted by a hydraulic fracturing (“frac”) sand mine operation, and integrates all upstream conditions. Located 4.8 river miles upstream of the confluence with the upper St. Croix River, the new site on the Namekagon River at the Namekagon Trail Bridge also integrates all upstream conditions. No Network monitoring sites have been added or dropped since 2014; all locations are shown in Figures 7, 8, and 9.

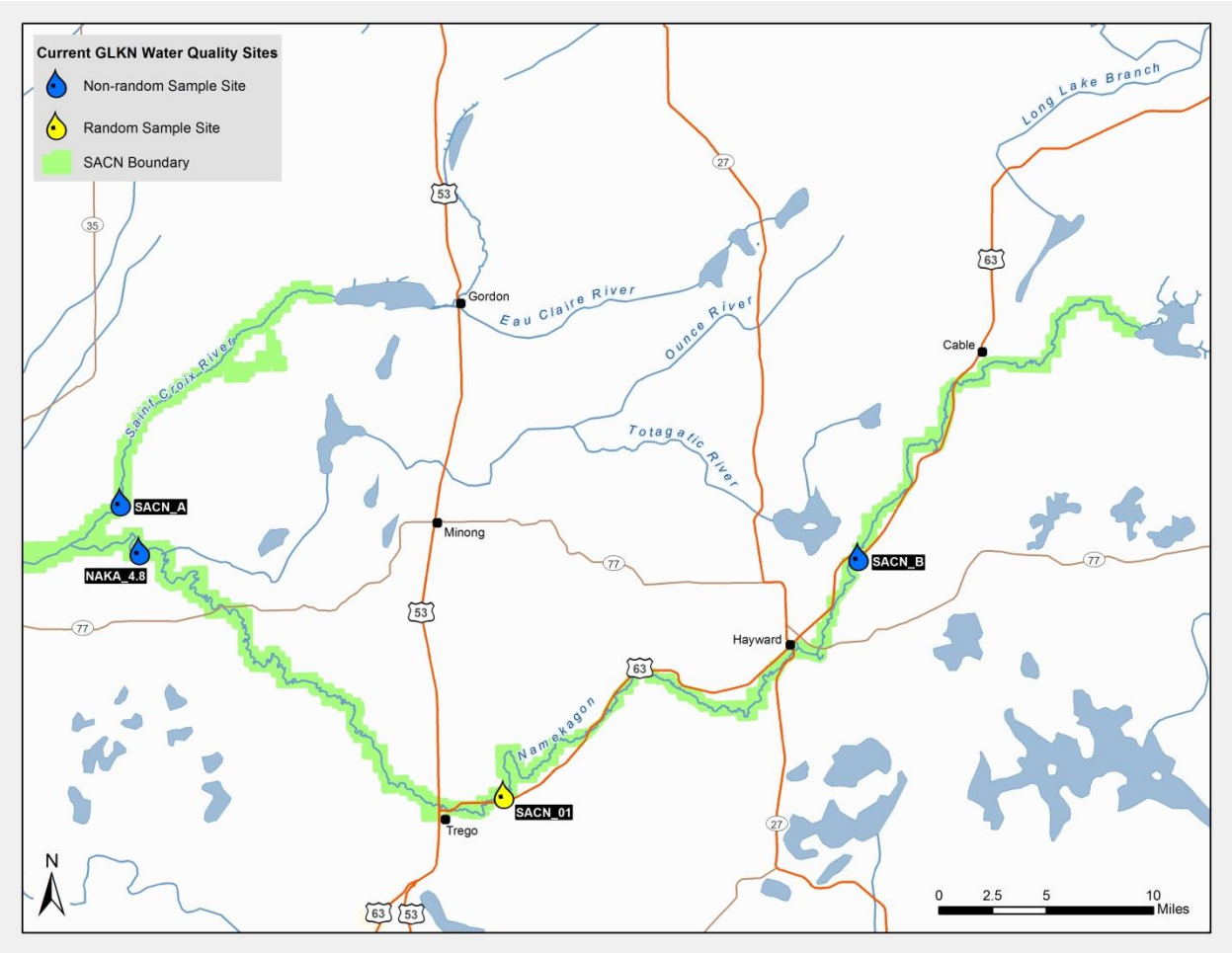


Figure 7. Great Lakes Inventory and Monitoring Network (GLKN) monitoring sites upstream of the confluence of the upper St. Croix and Namekagon Rivers within the St. Croix National Scenic Riverway (SACN).

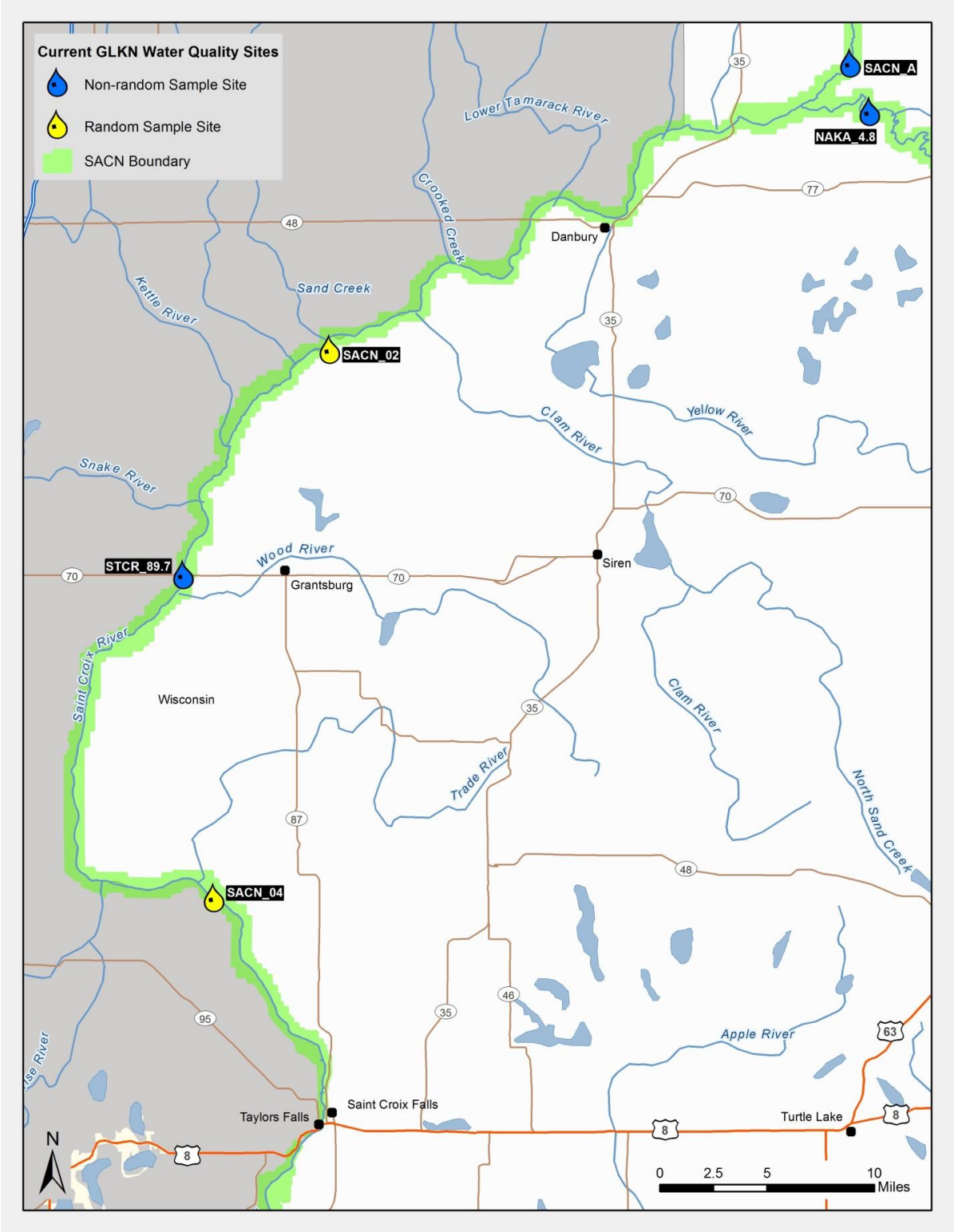


Figure 8. Great Lakes Inventory and Monitoring Network (GLKN) monitoring sites upstream of St. Croix Falls, Wisconsin, to the confluence of the upper St. Croix and Namekagon Rivers within the St. Croix National Scenic Riverway (SACN).

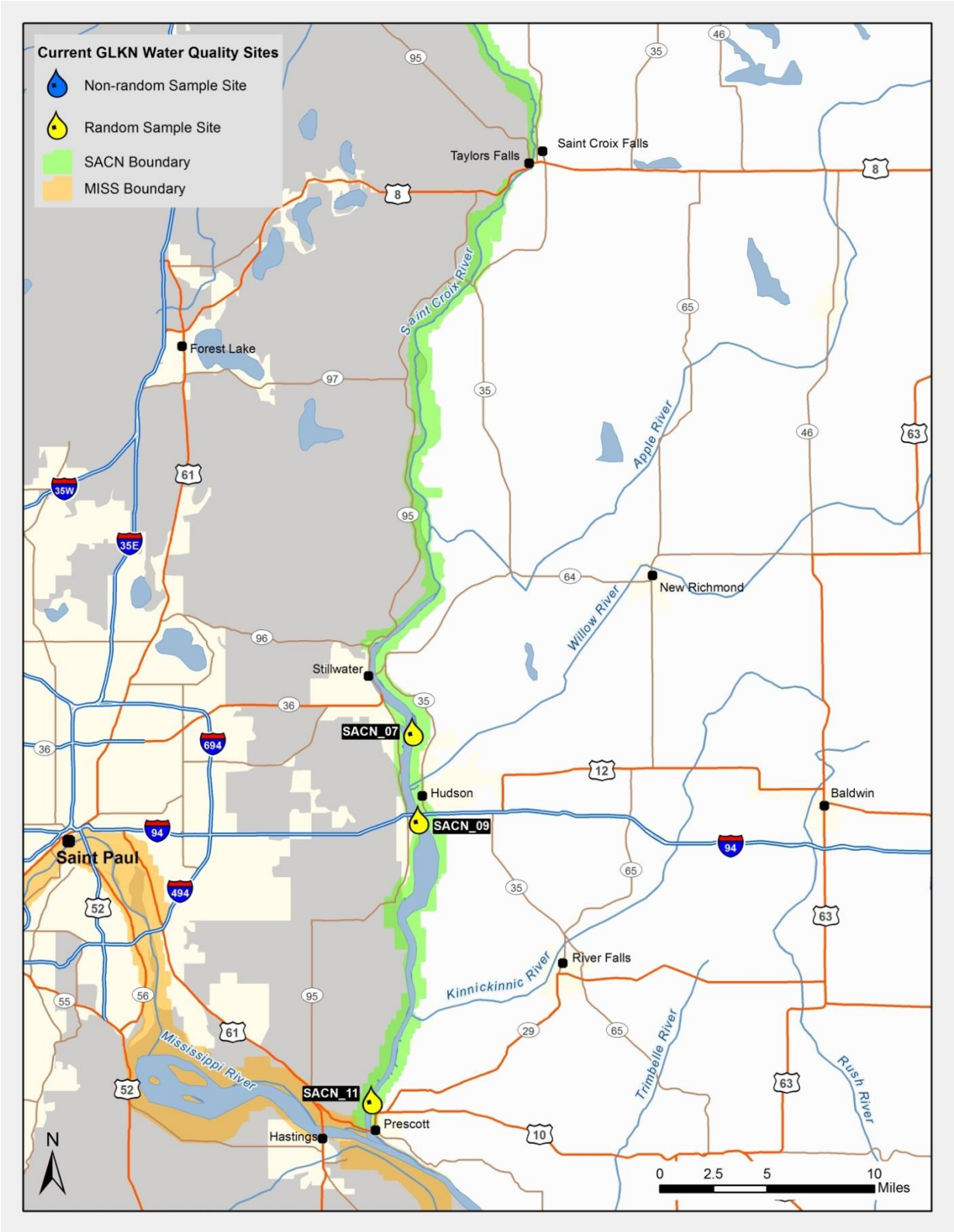


Figure 9. Great Lakes Inventory and Monitoring Network (GLKN) monitoring sites on the St. Croix River upstream of the confluence with the Mississippi River at Prescott, Wisconsin, to St. Croix Falls, Wisconsin, within the St. Croix National Scenic Riverway (SACN).

2.4.3 Stations Selected Within MISS

MISS lies within an urban metropolitan area and therefore is heavily monitored by regulatory agencies. As discussed earlier, after four seasons of monitoring at MISS we suspended our work in 2014. If other agencies suspend or discontinue their water quality monitoring we may re-initiate our work. The remainder of this section outlines how the number and locations of Network sites were derived prior to the onset of monitoring at MISS in 2006, which is purposefully retained in the event that monitoring is re-initiated at the park.

Statistical power analysis was conducted to determine the sample size (number of random sites) needed to detect 20% change at 80% power (Table 11). Based on the sample size analysis of two out of four segments of MISS, as many as 1–16 sites/segment (4–64 total) would be required to detect 20% change within each segment. These high numbers are not feasible; NPS-GLKN cannot afford to monitor the MISS park unit with randomly-selected sites in each segment. However, non-randomly-selected sites could be useful within MISS to fill spatial gaps in the existing monitoring of other agencies. The Great Lakes Network has determined that adding five monitoring stations to these on-going efforts will substantially close gaps in the existing monitoring programs. Individual stations will be analyzed for temporal trends; although this method is not as valid as that determined from a population trend, a consistent pattern in the trends could suggest a temporal trend for the entire corridor. In addition, the downstream sequence of stations will be analyzed for spatial trends.

Table 11. Within MISS, the 26-year mean values of the annual mean and coefficient of variation (CV, %), and the predicted sample size (number of sites) required to detect a 20% change at 80% power, based on the annual means (1980–2005) of four water quality variables: pH (standard units), dissolved oxygen (DO, mg/L), total phosphorus (TP, mg/L), and nitrogen oxides (NOx-N, mg/L). Two-tailed significance level α_2=5%.

River Segment	Statistic	pH	DO	TP	NO_X-N
MISS 878-845 (n=2)	Mean	8.06	10.50	0.103	0.73
	CV (%)	0.7	7	13	25
	Sample size	1	4	7	16
MISS 836-813 (n=3)	Mean	7.97	9.78	0.228	2.28
	CV (%)	0.5	3	8	4
	Sample size	1	3	4	3
MISS 878-807 (n=6)	Mean	8.01	10.07	0.175	1.71
	CV (%)	0.9	6	38	47
	Sample size	1	3	28	42

One possible monitoring approach could include monitoring sites at the upstream and downstream ends of MISS, to assess the water quality inputs to and outputs from the park unit. The upstream end of MISS is located at the confluence of the Mississippi River with the Crow River, and a monitoring station could be sited within the Mississippi River immediately above the confluence. However, the

downstream end of MISS is below the confluence of the Mississippi and St. Croix Rivers, both of which are major drainage basins, and it requires several river miles before these two waters are adequately mixed. Attempting to sample at the downstream end of MISS would require a complex sampling method, where samples collected from the river's cross-section would be weighted according to the flow volume of the cross-section. In the long run, the results would be a function of the relative flow volumes of the St. Croix and Mississippi Rivers. This information could more readily, and perhaps accurately, be acquired by analyzing St. Croix and Mississippi river water quality data using geochemical mixing software.

In addition to a new monitoring site at the upstream end of MISS, sites could be added to fill spatial gaps between the monitoring stations of other agencies. In particular, 1) Spring Lake, between river mile 820 and 825, which has historical monitoring data, 2) the portion of MISS above river mile 848, along which significant water quality changes occur from undetermined sources (Johnson and Schellhaass, MCES, personal communication). By filling these spatial gaps in existing monitoring networks, GLKN will achieve a more accurate assessment of the water quality trends within the park unit. Potential locations of non-randomly-selected monitoring stations are listed below, including the reason for possible inclusion.

Selected MISS monitoring locations (Figure 10), given as river miles on the upper Mississippi (UM) River, and reason for inclusion:

1) UM880 — Top of MISS, above confluence with Crow River, to assess incoming water quality.

2) UM868 — Above Coon Rapids Dam (easy access), incorporates upstream point sources, coordinates with riverine diatom monitoring.

3) UM862 — Metropolitan Council Environmental Services monitors weekly for limited variables; will monitor for additional variables.

4) UM852 — Top of Pool 1, above Lock & Dam #1, incorporates upstream point sources, coordinates with riverine diatom monitoring.

5) UM822 — Spring Lake, historically monitored, coordinates with riverine diatom monitoring.

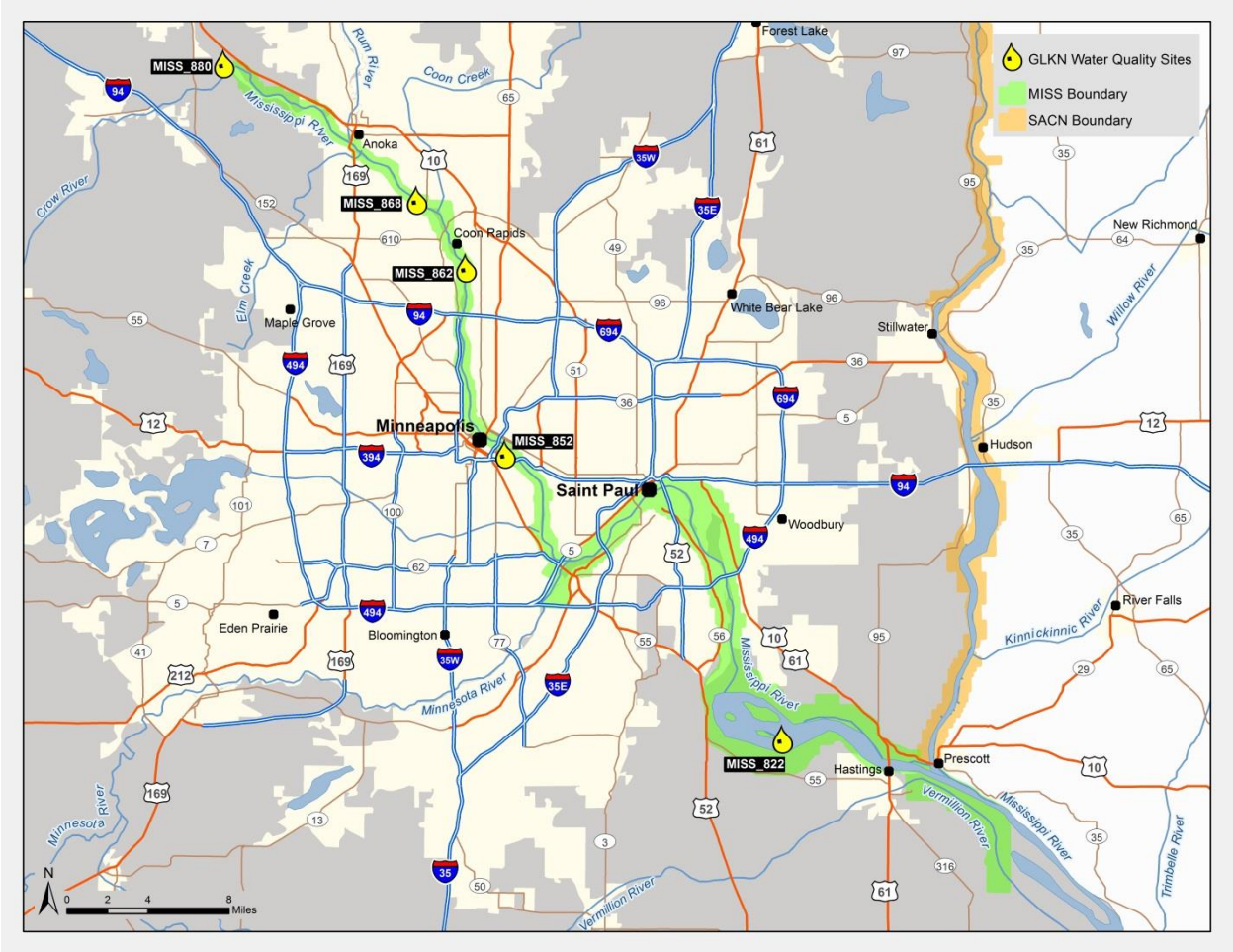


Figure 10. Great Lakes Inventory and Monitoring Network (GLKN) monitoring site locations within the Mississippi National River and Recreation Area (MISS). Lake St. Croix within the St. Croix National Scenic Riverway (SACN) is also shown.

2.5 Frequency and Timing of Sampling

River systems respond dynamically to runoff and require more frequent sampling than lakes to define the average water quality conditions for a given year. However, autocorrelation can become important at high monitoring frequencies (e.g., weekly or more frequent). For most lotic water quality monitoring programs, year-to-year variations in the mean are assumed to be serially independent.

The spreadsheet-based power analysis software LRSD-1.0 (Walker 1988) includes sensitivity analysis of sampling frequency. The effects of serial correlation (date-to-date within a given year) on the precision of annual and long-term means are considered using the "effective number of samples" concept. Autocorrelation reduces the effective number of samples for calculating the annual mean. The results of the sampling frequency sensitivity analysis based on a nine-month sampling season, using LRSD-1.0, for dissolved oxygen and total phosphorus are shown in Table 12, listed in terms of the number of monitoring years required to detect 20% change at 80% power. The higher sampling frequencies require fewer monitoring years to detect a given level of change. The most cost-effective

sampling frequency is biweekly (i.e., every other week) sampling; however, monthly sampling has been selected at half the budget cost. This sampling frequency would not be sufficient to, for example, conduct pollutant (e.g., nutrients) loading analysis, but is sufficient to meet the goal of the protocol to determine mean annual concentrations.

Table 12. Sampling frequency sensitivity analysis: number of monitoring years required to detect 20% change at 80% power. LRSD-1.0 power analysis based on historical variability of dissolved oxygen and total phosphorus at two locations: on the upper St. Croix River (Danbury, WI) and the lower St. Croix River (Hudson, WI).

Sampling Frequency	*Dissolved Oxygen*		*Total Phosphorous*	
	Danbury, WI	*Hudson, WI*	*Danbury, WI*	*Hudson, WI*
Annual	10	25	>100	>100
Bimonthly	2	3	>100	100
Monthly	1	2	50	20
Biweekly	1	2	25	10
Weekly	1	1	20	10
Semi-weekly	1	1	20	10

In the upper Midwestern United States, larger rivers may freeze over during the winter months. Flow rates under the ice are low and water chemistry changes less than during other times of the year, although low oxygen levels can occur in rivers sealed by ice. Sampling an ice-covered river can be difficult and dangerous where there is no bridge crossing over the monitoring station.

Therefore, samples will be collected monthly only during the open water season, which is usually March/April through November, monitoring water quality conditions from shortly after ice out in early spring to just before ice on in late fall. The core water quality suite (dissolved oxygen, temperature, specific conductance, pH, flow, and clarity), nutrients (total phosphorus, total nitrogen, nitrate+nitrite-nitrogen, ammonium-nitrogen), total chlorophyll-*a*, and total suspended solids will be monitored monthly, while alkalinity, major ions (chloride, sulfate, calcium, sodium, potassium, and magnesium), dissolved organic carbon, and dissolved silica, which generally tend to be less variable, will be monitored quarterly (Table 10). Randomly-selected and non-randomly-selected stations will be sampled at the same frequency, that is, during each sampling period.

2.6 Level of Change That Can Be Detected By The Proposed Sampling Design

2.6.1 Minimum Detectable Change

Using the parameter values of the proposed randomly-selected sampling design for SACN (given mean and standard deviation, n=3, α=5%, 1-β=80%) the online statistical power calculator (http://www.ats.ucla.edu/stat/gpower/) resulted in the smallest value of the mean under the alternative hypothesis, μ_A, that would not reject the null hypothesis. In other words, it yielded the

value of the minimum detectable change, or effect size, of the proposed sampling design (Table 13). The mean effect size is expected to be less than 10% for pH, less than 20% for dissolved oxygen, and about 100% for total phosphorus. Of the three water quality variables, only total phosphorus exceeded the goal of 20% minimum detectable change.

Table 13. Within the upper and lower portions of the SACN park unit: the 30-year minimum, mean, and maximum values of the annual mean and coefficient of variation (CV, %), and minimum detectable change (effect size, %) for proposed sampling design (n=3) at 80% power, based on the annual means (1974–2003) of three water quality variables: pH (standard units), dissolved oxygen (DO, mg/L), and total phosphorus (TP, mg/L). Two-tailed significance level α_2=5%.

Value Type	Statistic	Upper St. Croix			Lower St. Croix		
		pH	DO	TP	pH	DO	TP
Min Value	Mean	6.85	8.32	0.018	7.42	8.45	0.036
	CV (%)	0.2	1	3	0.04	2	1
	Effect size (%)	1	3	15	1	7	3
Mean Value	Mean	7.55	9.55	0.041	7.7	9.48	0.057
	CV (%)	2	5	34	0.6	7	24
	Effect size (%)	7	16	104	2	21	74
Max Value	Mean	8.20	11.33	0.071	8.14	11.77	0.094
	CV (%)	9	12	95	3	21	98
	Effect size (%)	28	38	296	8	66	300

2.6.2 Minimum Duration of Monitoring Effort

The software program TRENDS is designed to carry out a power analysis of linear regression, particularly in the context of monitoring populations in wildlife studies (Gerrodette 1987). TRENDS summarizes the power analysis in 5 parameters: duration of study, rate of change, precision of estimates (coefficient of variation), alpha (type 1 error rate), and power (1-β, where β is the type 2 error rate) (Figure 11). Based on the observed variation in historical monitoring data for the St. Croix River, TRENDS was used to determine the minimum number of monitoring years required to detect 20% change at 80% power (Table 14). The program would not accept CV <0.01 (duration = 4 years) or CV > 0.13 (duration = 44 years). Therefore, all the values in Table 14 fall between 4 and 44 years minimum duration of monitoring to detect 20% change. Of the three water quality variables, pH required only one or two monitoring years, dissolved oxygen fell within the range of 5–15 monitoring years, and the variations observed in total phosphorus were beyond the ability of TRENDS to estimate minimum duration of monitoring.

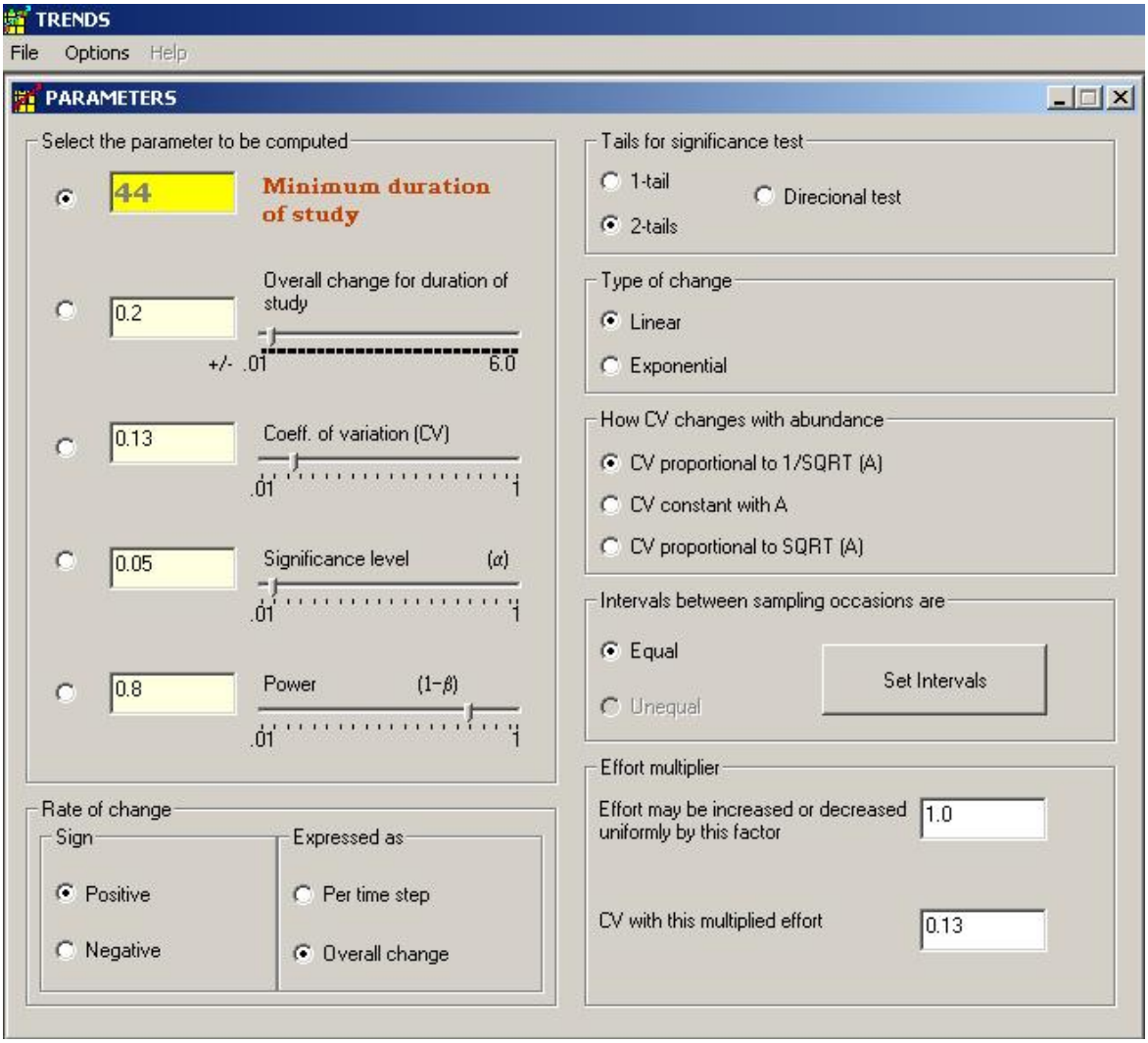


Figure 11. Screen shot of TRENDS statistical power analysis software.

2.4.3 Expectation of Improvement in Post-Hoc Statistical Power

It is expected that the post-hoc statistical power of the proposed sampling design, after several years of sampling for the large rivers protocol, will show substantial improvement over the results from the power analysis of the available historical data. The primary reason for this expectation is protocol consistency—in the sampling time of day and collection methods, in the processing methods, and in the analytical laboratory and laboratory methods. In a post-hoc analysis, the numbers given in the preceding power analysis tables of this chapter should be improved, but the degree of improvement cannot be anticipated.

Table 14. Within the upper and lower portions of the SACN park unit: the 30-year minimum, mean, and maximum values of the annual mean and coefficient of variation (CV, %), and number of years required to detect 20% change at 80% power, based on the annual means (1974–2003) of three water quality variables: pH (standard units), dissolved oxygen (DO, mg/L), and total phosphorus (TP, mg/L). Two-tailed significance level α_2=5%.

		Upper St. Croix			Lower St. Croix		
Value Type	**Statistic**	**pH**	**DO**	**TP**	**pH**	**DO**	**TP**
Min Value	Mean	6.85	8.32	0.018	7.42	8.45	0.036
	CV (%)	0.2	1	3	0.04	2	1
	Years	<4	4	5	<4	4	5
Mean Value	Mean	7.55	9.55	0.041	7.7	9.48	0.057
	CV (%)	2	5	34	0.6	7	24
	Years	4	8	>44	<4	13	>44
Max Value	Mean	8.20	11.33	0.071	8.14	11.77	0.094
	CV (%)	9	12	95	3	21	98
	Years	5	>44	>44	5	>44	>44

3.0 Sampling Methods

This section summarizes the information presented in greater detail in the standard operating procedures (SOPs) #1 (Pre-Season Preparation), #6 (Field Measurements and Water Sample Collection), #7 (Processing Water Samples and Analytical Laboratory Requirements), and #11 (Post-Season Procedures). The section ends with an overview of quality assurance and quality control (QA/QC) procedures, which pertain to all aspects of sampling. The details of QA/QC are presented in SOP #12.

3.1 Field Season Preparations and Equipment Setup

(Summary of SOP #1: Pre-Season Preparation)

All details of field work need to be planned well in advance. Checklists help ensure that personnel, equipment, and supplies will be prepared in a timely and orderly manner.

Table 15 summarizes which of the SOPs contain key checklists of equipment and supplies for water sampling. Field personnel should check the inventory of equipment and supplies against these lists to verify that no necessary equipment or supply is missing. All equipment, meters, and probes should be checked to verify that they are functioning properly. If needed, replacement equipment or supplies should be ordered well in advance of the onset of sampling, to allow time for inspection, pilot-testing, and calibration of replacements.

Table 15. Water quality monitoring checklists for equipment and supplies.

Checklist	Location
Safety equipment and supplies	SOP #2
Decontamination equipment and supplies	SOP #5
Field equipment and supplies	SOP #6
Laboratory equipment and supplies	SOP #7

Table 16 provides general guidance for activities conducted prior to the field season. Additional considerations are as follows:

1) Copies of field information on waterproof paper should be kept in two types of three-ring binders: a project binder and a site binder. The project binder should contain reference information relevant to general field sampling procedures with tabs identifying each procedure for easy access during field work, including QA/QC reminders, copies of all SOPs relating to safety, decontamination, sample collection and processing, copies of equipment instructions and troubleshooting, calibration logs (may be a separate binder), extra field forms, safety data sheets (SDSs) for field supplies that contain hazardous chemicals or materials, and analytical service request and chain-of-custody forms. Site binders should contain reference information specific to each sampling station, including a complete

description of and directions to the monitoring site, location coordinates, maps, and photos, copies of previous field forms, and data tables summarizing all previous measurements of field variables and analytical laboratory results. Both project and site binders should be taken along on each sampling trip, and thoroughly reviewed beforehand.

2) Field personnel should be adequately experienced or trained in using field and water quality sampling equipment. This experience is best obtained through a combination of classroom and hands-on training while pilot-testing equipment at a nearby waterbody. Personnel should be familiar with the instruction manuals, particularly with regard to calibration, maintenance, and troubleshooting procedures.

3) Meters, probes, and sensors should undergo appropriate annual, weekly, and daily calibration.

4) Conduct field reconnaissance, if necessary.

5) Pack all field gear to minimize shock and vibration during transport. Pack gear into organized and labeled boxes or cartons, to facilitate inventory and management of supplies.

6) Inspect motorized field vehicles to verify that they are tuned up and working properly. Ensure that vehicles meet space, power, and towing requirements.

Table 16. Checklist of activities to be conducted prior to sampling large rivers.

✓	Activity	Approximate Date	Responsible Person
	Prepare calendar of planned field trips	Before Feb. 1	Project manager
	Review sampling methods	Jan.–Feb.	Project manager
	Review checklists of equipment and supplies	Jan.–Feb.	Project manager or crew leader
	Charge/replace batteries	Feb. and prior to each sampling day	Field personnel
	Clean and test equipment, repair or replace as needed	Jan.–Feb. and prior to each sampling day	Project manager or crew leader
	Prepare equipment blanks	Feb.	Project manager or crew leader
	Check expiration dates of reagents and calibration standards	Feb.	Crew leader
	Contract for lab analyses	Jan.–Feb.	Project manager
	Prepare list of items to be ordered; order supplies	Jan.–Feb .	Crew leader
	Train field personnel	Jan.–Feb.	Project manager
	Obtain permission for site access, if necessary	Feb.	Project manager or crew leader
	Confirm current research and collection permits	Jan.–Feb.	Project manager
	Check field vehicle for safety equipment and supplies	Feb. and prior to each sampling day	Crew leader
	Update site binders	Jan.–Feb.	Project manager or crew leader
	Prepare headers on field data forms, chain of custody forms, analytical service request forms; bottle labels	Prior to each sampling round	Crew leader or crew personnel
	Review sample collection, processing and documentation information	Feb. (Refer to SOPs #6 and #7)	Project manager and all crew personnel
	Notify contract analytical laboratory of planned sample shipments	Prior to each sampling round and day of shipment	Crew leader
	Make travel reservations and arrangements as needed	Feb. and prior to each sampling round	Project manager and crew leader
	Provide supervisor with field trip and check-in schedule	Prior to each sampling round	Crew leader

3.2 Details of Taking Field Measurements and Collecting Samples

(Summary of SOP #6: Field Measurements and Water Sample Collection)

3.2.1 Sequence of Activities During Field Workday

This subsection provides a general overview of all sampling tasks, while the next subsections contain more detailed descriptions of particular tasks. Following is the sequence of activities during any given field day:

1) Review the checklist of field gear.

2) Create a new field form for each monitoring station, printed on waterproof paper.

3) Sample bottles and labels should be prepared in advance and placed in a cooler.

4) Conduct daily calibration of appropriate meters and probes.

5) Inspect motorized field vehicles at the beginning of every field day, including all safety and directional lights, oil, gasoline, and tire air pressure levels.

6) Drive to boat landing or sampling site. If sampling from a boat, load boat with sampling gear, launch boat, and navigate to monitoring site. Set up a clean work space on the boat for sampling. If sampling from a bridge deck, set up a controlled workspace by deploying traffic cones around where you will be sampling. If sampling by wading, establish as clean an area for sampling as possible on the streambank.

7) Refer to description of monitoring station location, directions, and photo to verify correct location. Verify coordinates on GPS unit. Take photos downstream, upstream and each side of the river from the sample site. Note how many photos were taken on the field sheet.

8) Measure field water quality variables, conduct sampling, and/or deploy sensors per SOP #6. Collect water sample from the highest nutrient depth last, which is usually the bottom sample. On bridge sites, record water level.

9) Be sure that all samples are correctly labeled and preserved on ice.

10) Verify that the field form is completely filled out, and initial the form.

11) If sampling from more than one monitoring station in a day, go back to step 7.

12) Upon return to shore, inspect boat, trailer, and all equipment that has come into contact with the water for invasive species. Follow procedures for decontamination of equipment per SOP #5.

13) After returning to the office or lab, clean sampling equipment per SOP #6. Rinse sensors with deionized water and perform calibration re-checks, as detailed in SOPs #6 and #12.

14) Conduct sample processing per SOP #7. Refrigerate or freeze samples, as required. Conduct in-house laboratory work and package samples for sending to contract analytical laboratory.

15) Enter or import data into NPSTORET or Aquarius as soon as possible after collecting field data and receiving results of laboratory analyses.

3.2.2 Arrival at Monitoring Site - Recording Field Information

Waterproof field forms should be prepared ahead of time, labeled with the project and station IDs. Field sampling information forms are used to record the physical and chemical water quality

variables measured at the time of sample collection. Field forms should be utilized for both routine and non-routine monitoring (e.g., if only a subset of data is collected, or if additional monitoring occurs beyond the typical number of visits per season). In addition to recording the field variables, any samples collected for laboratory analyses must be so indicated. Documentation should include calibration data for each instrument, field conditions at the time of sample collection, visual observations, and other information that might prove useful in interpreting these data in the future.

Upon arrival at the sampling station, record general observations of the appearance of the water (e.g., water color and odor) and other information related to water quality and water use (e.g., fishing and swimming).

General observations should include information that will be useful in interpreting water quality information, such as:

- *Water appearance*. General observations on water may include color, unusual amount of suspended matter, debris, or foam.
- *Water level*. Observations related to relative water level, stage, and/or flow, especially high or low flow events that may have influenced water quality measurements.
- *Weather*. Recent meteorological events that may have impacted water levels and/or quality include precipitation, cold fronts, high temperatures, or high winds.
- *Biological activity*. Excessive macrophyte, phytoplankton, or periphyton growth. The observation of water color and excessive algal growth is important in explaining high chlorophyll-*a* values. Other observations to note include fish, birds, or spawning fish.
- *Unusual odors*. Examples include hydrogen sulfide, mustiness, sewage, petroleum, chemicals, or chlorine.
- *Watershed or observed activities*. Changes to riparian areas, or drainage-basin activities or events such as bridge construction or other construction, dredging, erosion events, shoreline mowing, high densities of fast moving boats or personal watercraft.
- *Other items related to water quality and uses for human activity*. If the water quality conditions are exceptionally poor, note that standards are not met in the observations (for example, dissolved oxygen is below minimum criteria). Uses may include swimming, wading, boating, fishing, irrigation pumps, or navigation. This type of information may be used in evaluating standards compliance.

While at each monitoring site, the information recorded on field data sheets should include:

- Date
- Time of arrival

- Names of field team members
- GPS coordinates, to verify location
- Current weather (air temperature, wind speed and direction, wave height) and relevant notes about recent weather (storms or drought)
- Observations of water quality conditions
- Description of any photographs taken
- Multiprobe (model), calibration date, and field measurements of core suite variables
- List of samples collected and collection times for advanced suite variables or quality assurance samples and method of collection (e.g., integrating tube or grab)
- Whether any samples were not collected, and reason
- Water level measurement (where applicable)
- Any other required metadata for NPSTORET or Aquarius data entry
- Time of departure

All entries should be made clearly. If an incorrect entry is made, a single heavy line should be drawn through the incorrect entry and the correction made. All corrections should be initialed and dated. The completed field forms will be maintained in chronological order by station, copied into project binders and the originals maintained on file indefinitely. Field data are reviewed annually by network personnel (see SOP #8, Data Entry and Management, for details).

3.2.3 Measurement of Field Parameters

Field measurements must be collected from an undisturbed area, and multiprobe instruments must be allowed to stabilize (Table 17). Take a replicate reading for every 10 readings; values should agree within 10% or the acceptance criteria in Table 17, whichever is larger. Use a Secchi disk and/or transparency tube to measure the water clarity. Deploy, retrieve, and/or download data from the thermal array, if applicable.

Table 17. Typical sensor performance specifications (Penoyer 2003).

Sensor	Expected Range	Reporting Resolution*	Estimated Bias	Stabilization Criteria
Temperature	-5ºC to 45ºC	0.01ºC	±0.15ºC	Thermistor: ±0.2ºC Glass: ±0.5ºC
Specific Conductivity (SC25)	0 to 2000 µS/cm	µS/cm (range dependent)	±0.5% of reading + 1 µS/cm	≤100 µS/cm: ±5% >100 µS/cm: ±3%
pH	1 to 14 units	0.01 unit	±0.2 units	±0.1 standard unit
Dissolved Oxygen (concentration)	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L: ±0.2 mg/L 20 to 50 mg/L: ±0.6 mg/L	±0.3 mg/L
Dissolved Oxygen (% saturation)	0%–200%	0.1%	ca. ±2%	±2%
Depth–Z (pressure sensor)	0 – >100 m	0.1 m	ca. 0.1 m	0.1 m

* Resolution specifications are supplied by the manufacturers of the measuring meters. They are not necessarily closely related to real-world (outdoor) precision or bias, and are sometimes more related to the number of significant figures reported rather than how accurate the extra significant figures are. This is why we will control measurement sensitivity in the actual outdoor measuring environment at least once a year by calculating alternative measurement sensitivity (AMS; see Irwin 2008 for more details on AMS).

3.2.4 Collection of Water Samples

Collect water sample(s) with an integrated sampling tube in lake-like areas, or with a grab sample in moving waters for 0–2 m samples and Van Dorn for near-bottom samples. In the field log book and on the field data sheet, record information related to the sample collection, including:

1) Site name and site identification code.
2) Sample date, time, and depth.
3) The amount of sample collected.
4) Whether duplicate samples for quality control were collected at this site.
5) Any additional notes or observations pertinent to this sample or location for this sampling period.

Always keep the following in mind:

- Sample containers should be labeled in indelible ink with, at a minimum, the station name, date and time of collection, and preservation method, if applicable.
- To ensure the integrity of the sample, be aware of possible sources of contamination. Contamination introduced during each phase of sample collection and processing is additive and usually is substantially greater than contamination introduced elsewhere in the sample handling and analysis process.

Use appropriate procedures and quality-assurance measures that ensure sample representativeness and integrity and that meet study criteria. The degree to which a sample can be considered representative of a waterbody depends on many interrelated factors including temporal and spatial homogeneity of the waterbody, sample size, and the method and manner of sample collection.

3.3 Post-Collection Sample Processing

(Summary of SOP #7: Processing Water Samples and Analytical Laboratory Requirements)

Upon return to the office or home base, conduct in-house laboratory work, prepare and ship sample bottles, clean and prepare equipment for storage, and enter or import data from field forms into NPSTORET.

3.3.1 In-house Laboratory Work

Upon return from the field, keep sample bottles refrigerated prior to processing or analysis.

Process samples according to SOP #7 and specific laboratory instructions. If any of the water quality analyses are done in-house (for example, alkalinity titrations), conduct these procedures as soon as possible after returning from field work, ensuring that the maximum holding times for these variables are not exceeded. Store processed samples in the refrigerator or freezer, as appropriate, until shipping to the contract laboratory.

3.3.2 Shipping Samples to Contract Laboratory

Prior to shipping samples, notify the laboratory of how many samples of what type and when to expect shipment. Ensure that laboratory personnel will be available to receive the shipment. Check that the sample bottles are correctly labeled according to the protocols of the contract laboratory and that caps are securely tightened. Complete the analytical services request and chain-of-custody forms provided by the laboratory. Pack samples carefully in the shipping container according to laboratory protocols, to prevent bottle breakage, shipping container leakage, and sample degradation.

Table 18 summarizes the variety of methods, detection limits, preservation techniques, and holding times for water samples addressed by this protocol. Methods conform to those used by Minnesota, Wisconsin, and Michigan for state certification of environmental laboratories involved in Clean Water Act or drinking water sample analysis (MDH 2005, WSLH 2003, MDEQ 2005). They are also used by EPA-funded research projects of natural waters in the upper Midwestern United States. Refer to SOP #6 for additional details regarding sample collection and preservation.

The selection of a contract laboratory will include criteria regarding the laboratory's ability to provide method limits of quantitation (ML) adequate for the dilute, oligotrophic lakes included in this monitoring protocol. Desired MLs and method detection limits (MDL) for water chemistry parameters are based on examination of historical data, the occurrence of low nutrient lakes in several of the parks, and the MDLs achievable using the standard water chemistry methods that research limnologists currently use. See SOP #12 for details regarding analytical detection levels required for GLKN water quality monitoring.

3.3.3 Equipment Cleaning and Storage

Clean all sample collection and storage containers and labware in a 0.1N HCl acid bath followed by deionized water rinses per SOP #7. Monitoring equipment should be cleaned and packed for storage. Keep equipment and supplies properly organized and labeled so they can easily be inventoried using the checklists.

3.3.4 Data Entry and Management

Download, enter, or import field and laboratory data into appropriate spreadsheets and databases as soon as possible to minimize error, per SOP #8. Refer to the instrument manufacturer's instruction manual for details on downloading data from field data loggers.

Table 18. Example range of analytical methods, method detection limits (MDLs), containers, preservation methods, and holding times.

Analyte	Analytical (*Note 1*)	Method #	Det. Limit	Vol. (ml)	Filter	Preservation	Sample Bottle (*Note 2*)	Hold Time
Alkalinity	Titrimetry	310.1 EPA-NERL	10 mg/L	--	--	4ºC	--	14 days
	Spec. auto.	310.2 EPA-NERL	10 mg/L	--	--	4ºC	--	14 days
	Titrimetry	NFM USGS-OWQ	0.01 meg/L	--	*Note 4*	None	--	none
Ca^{+2}	ICP	3120B APHA	10 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
	Titrimetry	215.2 EPA-NERL	0.5 mg/L	--	*Note 3*	4ºC	--	6 mos
	FAA	I-3152 USGS-NWQL	0.1 mg/L	250 mL	*Note 3*	pH<2 HNO_3	P	180 days
Cl^-	IC	300.0 EPA-NERL	0.02 mg/L	--	--	4ºC	P or G	28 days
	Colorimetry	325.2 EPA-NERL	1 mg/L	--	--	4ºC	--	28 days
	Titrimetry	4500-Cl APHA	0.15 mg/L	100 mL	--	4ºC	P or G	28 days
Chlorophyll-*a*	Spect.	10200 APHA	2 ug/L	≤1 L	*Note 4*	Freeze filter	P	30 days
DOC	Spect.	415.3 EPA	0.018 mg/L	125	*Note 3*	pH<4 H_2SO_4	G	28 days
	Spect.	0-1122-92 USGS	0.1 mg/L			4ºC	AG	--

Source: National Environmental Methods Index website (https://www.nemi.gov/home/)

This list is not an endorsement of any particular method or laboratory for any particular analyte. Rather it is to be used as a reference for the range of analytical methods available for each analyte. There are surface water conditions (pH, turbidity, other elements) that make a particular method unsuitable for a particular situation. As GLKN is monitoring surface water, the methods listed were chosen as representative of the lower range of detection limits.

APHA= Clesceri et al. (1998).

Note 1. CIE-UV= capillary ion electrophoresis with UV detection, FAA = flame atomic absorption, FIA = flow injection analysis, IC= ion chromatography, ICP = inductively coupled plasma, Spec. auto = spectroscopy with autoanalyzer

Note 2. P = plastic (polypropylene), G=glass, AG=amber glass

Note 3. 0.45 µm membrane filter. Pre-filter for dissolved portion analysis.

Note 4. 0.45 µm glass fiber filter.

Note 5. USGS 2003= Patton and Kryskalla (2003).

Table 18 (continued). Example range of analytical methods, method detection limits (MDLs), containers, preservation methods, and holding times.

Analyte	Analytical (*Note 1*)	Method #	Det. Limit	Vol. (ml)	Filter	Preservation	Sample Bottle (*Note 2*)	Hold Time
K^+	ICP	3120B APHA	0.3 mg/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
	FAA	3111B APHA	5 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
Mg^{+2}	ICP	3120B APHA	20 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
	FAA	3111B APHA	0.5 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
Na^+	ICP	3120B APHA	30 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
	FAA	3111B APHA	2 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
NH_4-N	Selective elec.	4500-NH_3E	0.08 mg/L	--	--	4ºC/pH2,0ºC	--	24 h/28 d
	Colorimetry	350.2 EPA-NERL	0.08 mg/L	--	--	pH<4 H_2SO_4	--	28 days
	Titrimetry	4500-NH_3 APHA	5 mg/L	--	--	4ºC/pH2,0ºC	--	24 h/28 d

Source: National Environmental Methods Index website (https://www.nemi.gov/home/)

This list is not an endorsement of any particular method or laboratory for any particular analyte. Rather it is to be used as a reference for the range of analytical methods available for each analyte. There are surface water conditions (pH, turbidity, other elements) that make a particular method unsuitable for a particular situation. As GLKN is monitoring surface water, the methods listed were chosen as representative of the lower range of detection limits.

APHA= Clesceri et al. (1998).

Note 1. CIE-UV= capillary ion electrophoresis with UV detection, FAA = flame atomic absorption, FIA = flow injection analysis, IC= ion chromatography, ICP = inductively coupled plasma, Spec. auto = spectroscopy with autoanalyzer

Note 2. P = plastic (polypropylene), G=glass, AG=amber glass

Note 3. 0.45 µm membrane filter. Pre-filter for dissolved portion analysis.

Note 4. 0.45 µm glass fiber filter.

Note 5. USGS 2003= Patton and Kryskalla (2003).

Table 18 (continued). Example range of analytical methods, method detection limits (MDLs), containers, preservation methods, and holding times.

Analyte	Analytical (*Note 1*)	Method #	Det. Limit	Vol. (ml)	Filter	Preservation	Sample Bottle (*Note 2*)	Hold Time
SiO_2	ICP	3120B APHA	20 ug/L	--	*Note 3*	pH<2 HNO_3	P or G	6 mos
	Spect.	4500- SiO_2 D APHA	0.04 mg/L	--	*Note 3*	No, 4ºC	P	28 days
	FIA-Spect.	4500- SiO_2 F APHA	0.78 ug/L	--	*Note 3*	No, 4ºC	P	28 days
SO_4^{-2}	IC	4110C APHA	75 ug/L	--	*Note 3*	pH<4 H_2SO_4	P or G	
	CIE-UV	D6508 ASTM	0.1 mg/L	--	*Note 3*	pH<4 H_2SO_4	--	ASAP
	Spect.	37512 EPA-NERL	0.5 mg/L	--	*Note 3*	pH<4 H_2SO_4	P or G	28 days
TP	Spect.	I-2606 USGS-NWQL	0.001 mg/L	125 mL	--	MgCl 4ºC	BrownP	30 days
	Alkaline P	USGS 2003	0.01 mg/L	120 ml	*Note 5*	4ºC /H_2SO_4	--	48 h/30 d
	ICP	200.7 EPA-NERL	60 ug/L	--	--	pH<2 HNO_3	P	6 mos
TN	Alkaline P	USGS 2003	0.03 mg/L	120 ml	*Note 5*	4ºC /H_2SO_4	--	48 h/30 d
	Titrimetry	4500-N	0–100 mg/L	--	--	4ºC	AG	7 days
	Combustion	440.0 EPA-NERL	0.1 mg/L	--	--	Filter	--	100 days

Source: National Environmental Methods Index website (https://www.nemi.gov/home/)

This list is not an endorsement of any particular method or laboratory for any particular analyte. Rather it is to be used as a reference for the range of analytical methods available for each analyte. There are surface water conditions (pH, turbidity, other elements) that make a particular method unsuitable for a particular situation. As GLKN is monitoring surface water, the methods listed were chosen as representative of the lower range of detection limits.

APHA= Clesceri et al. (1998).

Note 1. CIE-UV= capillary ion electrophoresis with UV detection, FAA = flame atomic absorption, FIA = flow injection analysis, IC= ion chromatography, ICP = inductively coupled plasma, Spec. auto = spectroscopy with autoanalyzer

Note 2. P = plastic (polypropylene), G=glass, AG=amber glass

Note 3. 0.45 µm membrane filter. Pre-filter for dissolved portion analysis.

Note 4. 0.45 µm glass fiber filter.

Note 5. USGS 2003= Patton and Kryskalla (2003).

3.4 End of Field Season Procedures

(Summary of SOP # 11: Post-Field Season Procedures)

When sensor probes are to be stored for extended periods of time, thoroughly clean sensors, remove batteries, and store the sonde according to specific instructions in SOP #11 and the manufacturer's manual. Store calibration standards and electrolyte solutions in a temperature-controlled environment. Ensure that containers are dated upon receipt and upon opening; observe expiration dates.

3.5 Quality Assurance/Quality Control

The objective of quality assurance/quality control (QA/QC) is to ensure that the data collected for a project are meaningful, representative, complete, precise, accurate, comparable, and scientifically defensible (O'Ney 2005a). It is a broad management concept requiring the complete integration of field and laboratory systems of sample collection and analysis. The QA/QC procedures that pertain to sample collection and processing are focused on: 1) ensuring that any given field or laboratory measurement accurately represents the water resource at the time the sample was collected, 2) ensuring that water quality data are comparable across all sampling dates, and 3) verifying that no contamination has been introduced to the sample at any time. These activities range from instrument calibration, to specification of field methods and laboratory detection limits, to analysis of sample blanks and spikes. The QA/QC procedures pertaining to sampling methods that will be followed in this protocol are summarized in Table 19.

One important aspect in the accuracy and precision of a water quality monitoring program is the correct selection of probes for measuring field variables and their subsequent calibration and maintenance schedule. Table 17 (above) lists typical field sensor performance specifications that should be expected from monitoring equipment for this protocol. Table 20 summarizes the ideal calibration frequency and minimum acceptance criteria for these sensor probes. The reality of logistical constraints at back country sites may preclude calibration and checks of calibration at the ideal frequency. Calibration logs for multi-parameter sondes will be maintained and will document the frequency of calibration and calibration checks. Ensure calibration standards are not used beyond expiration dates. Refer to SOP #6 for guidelines on potential field measurement problems.

The detection limits for water quality variables specified in Table 18 are based on examination of historical data and the occurrence of dilute concentrations of water quality variables in natural waters. Many commercial laboratories do not routinely analyze samples using these lower detection limits, even if they have the proper instrumentation, because their primary work load is wastewater-related with much higher concentrations. Therefore, the process of selecting a contract analytical laboratory will include consideration of whether the lab has experience analyzing naturally dilute waters.

Quality Control (QC) involves specific tasks undertaken to determine the reliability of field and laboratory data. It is accomplished internally by routine analysis of blanks, duplicates, and spikes in the day-to-day operation of a laboratory, or externally by incorporating field-originated blanks,

duplicates, and spikes into the set of the samples collected during a water quality survey. We will include the following QA/QC routines:

1) Equipment blanks prior to the field sampling, to ensure no extraneous sources of contamination are introduced into the samples.

2) Submit duplicate water samples, at the rate of approximately 10%, so that the reported data are precise, or the results of analyses are reproducible.

3) Document the sensitivity of multiprobes through an estimation of the limits of detection known as alternative measurement sensitivity (AMS).

4) Replicate multiprobe field measurements at the rate of approximately 10%. Calculate the relative percent difference to document precision of the multiprobe.

Table 19. Summary of QA/QC procedures pertaining to sampling methods.

Procedure	Description/reason
Instrument calibration logs	Each instrument must have a calibration log. Calibration schedule must be observed, using fresh calibration standards.
Project binder	Containing: checklist of QA/QC reminders, copies of decontamination, sample collection and processing SOPs, copies of equipment calibration and troubleshooting instructions, ASR and COC forms, blank field forms.
Site binders	Containing: GPS coordinates for verification of correct sampling location, table of previous field measurements to compare with new measurements, map and directions to site.
Field forms	Field forms are the only written record of field measurements, so copies are placed in project binders and originals must be kept on file indefinitely.
Field instrument methods	Require consistent measurement methods and detection limits
Sample preservation and minimum holding time	Water samples are maintained as close to sampling conditions as possible.
Chain-of-custody	A chain-of-custody includes not only the form, but all references to the sample, including information that allows tracing the sample back to its collection and documents the possession of the samples from the time they were collected until the sample analytical results are received.
Laboratory methods	Require consistent analytical methods and detection limits

Table 20. Ideal calibration frequencies and acceptance criteria for field instruments.

Parameter	USEPA Method	Minimum Calibration Frequency and QC Checks	Acceptance Criteria	Corrective Actions
Temperature: thermometer	170.1	Annually, 2-point check with NIST thermometer	±1.0ºC	Re-test with a different thermometer; repeat measurement
Temperature: thermistor	170.1	Annually, 2-point check with NIST thermometer.	±1.0ºC	Re-test with a different thermometer; repeat measurement
Specific Conductance (SC25)	120.1	Daily, prior to field mobilization; calibration check prior to each round of sampling; 10% of the readings taken each day must be duplicated or a minimum of 1 reading if fewer than 10 samples are read.	±5% RPD 10%	Re-test; check low battery indicator; use a different meter; use different standards; repeat measurement
pH	150.1	Daily, prior to field mobilization (two buffers should be selected that bracket the anticipated pH of the water body to be sampled with an independent third buffer selected to check instrument performance in that range);	±0.05 pH unit	Re-test; check low battery indicator; use different standards; repeat measurement; don't move cords or cause friction/static
	--	Calibration check w/ third buffer prior to each round of sampling.	±0.1 pH unit	--
	--	10% of the readings taken each day must be duplicated or a minimum of 1 reading if fewer than 10 samples are read.	RPD 10%	--
Dissolved Oxygen	360.1	Daily, prior to field mobilization; check at the field site if elevation or barometric pressure changed since calibration.	0.2 mg/L concentration or ±10% saturation	Re-enter altitude; re-test; check low battery indicator; check membrane for wrinkles, tears or air bubbles; replace membrane; use a different meter; repeat measurement; allow more time for stabilization
Depth	--	Daily, prior to field mobilization, check at the field site. Check annually against commercially purchased brass sash chain labeled every 0.5 m to ensure that it reads zero at the surface and varies <0.3 m for depths <10 m and no more than 2% for greater depths.	±0.1 m	Retest, check low battery indicator; repeat measurement; use with accurately calibrated line

Table 20 (continued). Ideal calibration frequencies and acceptance criteria for field instruments.

Parameter	USEPA Method	Minimum Calibration Frequency and QC Checks	Acceptance Criteria	Corrective Actions
Transparency Tube	--	Transparency tubes have a 100- or 120-cm scale; ensure tube is clean.	±1.0 cm for transparency tube	Transparency tube
Marked Lines (e.g., Secchi, Van Dorn)	--	Check markings annually against brass sash chain. If lines are heated (for decontamination) check prior to each round of sampling.	±1%, 0–10 m ±2%, >10 m	Re-mark line.

4.0 Data Handling, Analysis, and Reporting

4.1 Metadata Procedures

Metadata allows potential data users to evaluate the quality and usefulness of the data based on an understanding of the complete process under which it was collected and maintained. In this respect, all of the protocol documentation, including standard operating procedures (SOPs), is part of a dataset's metadata. A reference to the appropriate version of these documents is part of the metadata for any particular element of a dataset. Although perhaps obvious, all data must have an associated value for the date and time they were collected.

Most of the remaining metadata will be recorded directly in the protocol-specific databases and tables. We will enter or import all required metadata for NPSTORET and Aquatic Informatics' Aquarius database; the data and metadata will ultimately be moved to the EPA STORET database or for Aquarius maintained by NPS-WRD staff in Ft. Collins, Colorado.

For metadata associated with geospatial data, we will abide by Executive Order 12906, which mandates that every federal agency document all new geospatial data it collects or produces using the Federal Geographic Data Committee (FGDC) Content Standard for Digital Geospatial Metadata (CSDGM; www.fgdc.gov/metadata/contstan.html). All GIS data layers will be documented with applicable FGDC and NPS metadata standards. The Network will also generate FGDC-style metadata for non-spatial datasets that meet this standard, absent only the geospatial-specific elements.

Though it is not required, we will make every effort to complete Biological Data Profiles (www.fgdc.gov/standards/status/sub5_2.html) for appropriate datasets and add associated metadata to the National Biological Information Infrastructure (NBII) Clearinghouse (www.nbii.gov/datainfo/metadata).

For more details on the Great Lakes Network's overall strategy for metadata generation, management, and distribution see chapter 8, Data Documentation, of GLKN's Data Management Plan (Hart and Gafvert 2006) and the appendices of that document.

4.2 Overview of Database Design

The NPS-WRD has established a policy that all I&M water quality monitoring data will be made compatible with, and be uploaded to, the EPA's STORET database. The WRD developed a Microsoft Access database tool, NPSTORET, which duplicates most of the EPA data and table structures in, to facilitate easier movement of I&M Networks' water quality data into EPA Water Quality Exchange (WQX) framework. We will use NPSTORET as the primary data entry tool and data transfer mechanism to WRD. In addition, GLKN uses Aquatic Informatics' Aquarius system for storage and visualization of continuously monitored water quality data from automated loggers (i.e., water temperature data from thermal arrays).

The Network will maintain one master copy of NPSTORET at the Ashland office on a central server. This is the only copy of NPSTORET that can be used to export data to other locations (WRD).

Additional copies of NPSTORET can be used by Network staff or cooperators, but they can only be used as a conduit for data entry and the importation of data to GLKN's master version of NPSTORET. For analysis, the data from the master copy of NPSTORET must be used. The Network will continue to improve tools for automating analysis and visualization of the information contained in the NPSTORET and Aquarius datasets.

4.3 Data Entry, Verification, Certification, and Editing

Detailed instructions for the data entry procedures for this protocol are given in SOP #8, Data Entry and Management. As described above (Section 3, Sampling Methods), three general classes of water quality data are collected. The first is field observations and measurements that are recorded on data sheets in the field. These field sheets will be entered into a digital file. The second class of data is the results of testing performed by contract analytical laboratories. The last class of water quality data is digital data that have been collected by multiprobe sondes and other field data loggers. GLKN will develop formatting routines to be applied to the digital files prior to importation of data into NPSTORET or Aquarius.

Data verification starts with the QA/QC steps that are outlined in the SOPs associated with this protocol. If data being imported into NPSTORET do not pass a QA/QC test, NPSTORET prompts the user to make corrections and re-import the data. Data that are outside the expected rate of change for a parameter based on previous records for that parameter will be flagged for further review by an expert.

Quality assurance/quality control checks are performed as data are imported into NPSTORET or Aquarius and again when the data are transferred to WRD. The Network's water quality data records are regarded as being in provisional status until they are returned to GLKN from WRD, or are accepted by WRD without changes after the final QA/QC steps. Once returned to GLKN by WRD, and after appropriate documentation is completed, the dataset is officially considered certified. Only qualified users who have been trained and given edit permissions are allowed to edit data in NPSTORET or Aquarius. These procedures protect the integrity of the data and allow the history of each data record to be traced.

4.4 Data Archival Procedures

Data archiving serves two primary functions: it provides a source to retrieve a copy of any dataset when the primary dataset is lost or destroyed, and it provides a data record that is an essential part of the QA/QC process. The unedited files are the original data for digital data. The archival of the printed data forms for this protocol is described in SOP #8.

The Network will create duplicate files of all digital data at the earliest opportunity. At least two complete copies of any water quality dataset are required by WRD, including digital replicas (scanned versions) of hard copy data sheets. Digital field data that are entered directly into a field computer or collected from a data logger will be backed up to a second medium at the earliest possibility. The data files on field computers and loggers must not be erased until the integrity of these data files are verified on the duplicate storage medium.

The Network's master version of NPSTORET is maintained on a central server in the Ashland Office that is backed up daily, and backed up off-site weekly. Complete details of the GLKN Server archiving procedure are found the Infrastructure chapter of GLKN's Data Management Plan (Hart and Gafvert 2006); the general strategy for data archiving is also described in this plan and its appendices.

4.5 Quality Assurance and Quality Control Pertaining to Data Entry and Management

Quality assurance and quality control procedures are crucial during every step of data entry and data management. Details of such QA/QC regarding data management are provided in SOP #8 and are summarized below in Table 21.

Table 21. Summary of QA/QC procedures pertaining to data management.

Procedure	Description
Instrument calibration logs	Each instrument must have a calibration log.
Field forms	Field forms are the only written record of field measurements, so copies are placed in project binders and originals must be kept on file indefinitely.
Estimating precision	The precision measurement is calculated using the Relative Percent Difference (RPD) between duplicate sample results per analyte. Precision estimates should be performed within 7 days of receipt of laboratory results.
Electronic data entry	Approximately 10% of electronic data entries should be spot checked on a random basis for errors. If errors are found, another 10% are spot checked.
Data archiving	Program sampling data and associated records are archived in boxes and stored at the GLKN Ashland office. Boxes are numbered consecutively by year, project, and station number.
Data validation	Data validation is the process that determines whether data collection quality control objectives were met.
Data validation reports	Data validation reports provide a narrative that discusses any deviations from QA/QC procedures and the impacts of those deviations.
Data verification	Data verification demonstrates that a data set will qualify as credible data.
Data certification	Data certification demonstrates that data are complete for the period of record; 2) they have undergone and passed the quality assurance checks; and 3) that they are appropriately documented and in a condition for archiving, posting and distribution as appropriate.
Data verification reports	Data verification reports document the results of the data verification procedure.
Data qualification codes	Data must be fully qualified before uploading to the Water Resources Division.

4.6 Routine Data Summaries

Brief characterizations of the data from each site, across SACN will be performed following each sampling year after all QA/QC procedures have been completed. For each water quality variable, these descriptive statistics may include mean, median, maximum, and minimum values by site; and these same values with the addition of skew, kurtosis, and measures of variability (e.g., coefficient of variation, standard error, 95% confidence intervals) among sites. These broader-extent analyses can

inform managers whether anomalous values recorded from a given sites (or even across all site within the riverway) were also observed at broader spatial extents that year (e.g., the watershed and within adjacent watersheds). Given the relevant legislation (e.g., Clean Water Act of 1972), it may be of interest to the park and to other entities to assess the proportion of measurements during a time period or across a domain (at a single point in time) that exceed specific water quality standards or pre-determined thresholds. As with nearly all percentage data, arcsine transformations must be performed on those percentage data before statistical analyses can be performed. However, back-transformed values will be used for graphical presentation and other reporting.

In addition to these descriptive statistics, analytical approaches may also include estimation of interannual change, graphic approaches (e.g., comparison of mean and variability in a parameter in the current year versus past years), and occasionally qualitative analysis (Guthery et al. 2001), as well as modeling, correlational analyses, and various parametric and nonparametric analyses.

4.7 Methods for Long-Term Trend Analysis

After at least three sampling seasons of monitoring data are collected at a given site, more intensive analyses of change may be performed for each site. In addition to repeated-measures, time-series, regression, and non-parametric equivalents of various methods such as Mann-Kendall, monitoring data may also be evaluated through Monte Carlo simulation analyses, Bayesian analyses, and comparisons of period means. For the latter-most approach, one is often interested in comparing values before and after an important event (e.g., change in management policy, remarkable anthropogenic disturbance, natural catastrophe, drought), and considers years within each of the two periods as replicates. The seasonal Kendall test is one of several preferred nonparametric tests for evaluating interannual trends in water quality (Hirsch et al. 1991). The test, which accounts for intra-annual variability, has been used widely for more than 15 years, and usually requires five to ten years of data. In the test, one can define “seasons” as months, quarters, ice-on/off periods, by limnological stratification, or by any other criterion. The examination of interannual change is subsequently performed on each of the seasons; the average of all the seasons’ slopes becomes the final trend line. Trends in parameters that are analyzed with respect to biotic and abiotic covariates that may affect water quality will be examined, although cause-effect relationships may be investigated more thoroughly by NPS partners and collaborators (e.g., USGS-WRD, university investigators).

In addition to analyzing each variable separately, several abiotic indicators of water quality that are not correlated and that naturally could be considered a homogeneous group of parameters could be analyzed collectively through multivariate ordinations (e.g., nonmetric multi-dimensional scaling) of resource conditions through time, following West and Yorks (2002). This approach effectively integrates information across many indicators, and can suggest whether water quality at individual site is moving in the same direction in multidimensional ordination space. Furthermore, joint plots can be overlaid on the ordination, and can suggest which variables correlate most strongly to the direction of changes. Multivariate analyses can help suggest cause-and-effect relationships and are useful as hypothesis-generating tools. Multivariate ordinations are also useful for relating water-quality conditions with abundance or presence data from many species (e.g., diatoms) (McCune and Grace 2002).

See SOP #9 for additional details on data summaries and analyses.

4.8 Reporting Schedule

One of the Network's main goals is to ensure that the results and knowledge acquired through the water quality monitoring program are shared with all appropriate parties, especially the parks and their natural resource managers. We will strive to provide park managers with clear, meaningful products in a timely manner to convey our findings. Because our monitoring data will be of interest to a broader community, we will also provide our reports to the states, the NPS I&M Division, and when appropriate, submit them to peer-reviewed journals for publication. We will also present our findings orally and in poster format at regional meetings, such as the Western Great Lakes Research Conference, or the St. Croix River Research Rendezvous.

As mentioned above, routine data summaries will be conducted annually for sites and parks that are sampled within that year. The summaries will be compiled from data that has been uploaded to the EPA's STORET database or the Aquarius database by NPS-WRD. Hard copy or web-based summary reports will be produced periodically, after the data is certified, with the primary audience being the parks.

More comprehensive reports, with analyses of trends, will occur after three or more seasons of sampling. For stations that are located where no previous monitoring has occurred, three sampling periods are the minimum needed to establish a time series sufficiently powerful to detect meaningful levels of change (e.g., 20%) through time.

The target audience of the analysis and synthesis reports will be the parks, the Network, both regional and Servicewide I&M, and the broader scientific community. Drafts of these reports will be reviewed internally and sent to the parks, and possibly outside sources, for further review. The extent of review will depend on how analytically complicated the methods are and the gravity of inference and recommendations.

4.9 Report Format with Examples of Summary Tables and Figures

Both annual summaries and reports that include detailed analyses on trends should adhere to Servicewide I&M reporting guidelines for Natural Resource Data Summary reports (for annual summaries) and Natural Resource Reports (for detailed analysis reports). Refer to the Natural Resource Publications Management website for the most up-to-date guidelines and formats (http://www.nature.nps.gov/publications/NRPM/index.cfm). Reports should include tables and figures appropriate for the data and for the intended audience.

5.0 Personnel Requirements and Training

5.1 Roles and Responsibilities

The water quality monitoring program at the Network is staffed by a project manager (GLKN aquatic ecologist, GS/11) and two assistant project managers (GLKN aquatic ecologists, GS/9s). The project manager and the assistant project managers are permanent full time employees. The assistant project managers primarily focus on leading fieldwork for separate water quality monitoring protocols (inland lakes or large rivers) during the field season, but also have many overlapping responsibilities throughout the year. The assistant project managers will each supervise at least one seasonal crew member at the GS/4 or GS/5 level, and along with the crew members may be stationed at one of the parks.

The field crews will work on this water quality monitoring project for a limited number of pay periods per year, and may spend the remaining part of their time on other Network or park projects. The Network will explore the possibility of sharing seasonal positions with the parks. When a park has an aquatic person on staff, the Network will make use of such existing staff expertise on the crew when possible, paying for the time spent on I&M monitoring activities, and will provide the same training to the park person as to the rest of the crew members. The field crews will monitor water quality in both rivers and lakes; the responsibilities, training, and qualifications of the crew are essentially the same for both protocols.

5.1.1 Project Manager

The role of the project manager is to serve as a liaison among other related water quality monitoring projects conducted by partners (e.g., state monitoring programs), park staff, other Network staff (field personnel, data manager), contracted analytical laboratories, and other GLKN project managers. The individual will coordinate with resource management staff at the parks to ensure parks are informed of monitoring activities. Specific responsibilities of the project manager include the following:

- Coordinate field schedules and availability of supplies with field personnel.
- Develop a training program for field personnel.
- Develop, document, and oversee the implementation of standard procedures for field data collection and data handling.
- Coordinate logistics with park staff.
- Develop QA/QC measures for the project, supervise staff training, and conduct quality assurance checks of field sampling techniques at least once, mid-season, with each field crew.
- Contract with analytical laboratories for analysis of water samples; ensure lab results meet program needs (e.g., QA/QC procedures, meaningful minimum detection limits for dilute waters, adequate reproducibility of replicate samples).

- Supervise or perform data entry, verification, and validation.
- Summarize data and analyze data, prepare reports.
- Serve as the main point of contact concerning data content.

The project manager will also work closely with the data manager in the following capacities:

- Complete project documentation (i.e., metadata) in appropriate databases.
- Develop data verification and validation measures for quality assurance.
- Establish and implement a procedure to officially certify water quality datasets.
- Ensure staff are trained in the use of database software and quality assurance procedures.
- Coordinate changes to the field data forms and the user interface for the project database.
- Identify sensitive information that requires special consideration prior to distribution.
- Manage the archival process to ensure regular archival of project documentation, original field data, databases, reports and summaries, and other products from the project.
- Define how project data will be transformed from raw data into meaningful information and create data summary procedures to automate and standardize this process.
- Establish meaningful liaisons with state counterparts to promote sharing of data on a timely basis.

5.1.2 Assistant Project Managers

Assistant project managers are largely responsible for implementing the inland lakes and large rivers water quality monitoring protocols. Specific responsibilities include:

- Assist with coordination of field schedules and supplies.
- Supervising and training field personnel.
- Coordinate logistics with park staff.
- Help ensure all aspects of QA/QC are met.
- Perform data entry, verification, and validation.
- Train other staff in the use of database software.
- Assist with data analysis and report writing.

5.1.3 Field Personnel (Field Crew Member/Leader)

The role of field personnel is to conduct all field work related to the monitoring project. Field personnel will include both a crew leader and a crew member. The crew leader is responsible for contacting the parks prior to each sampling event to ensure logistical requirements will be met. Crew leaders and crew members may be park staff that coordinate with their respective parks and the Network project manager. Responsibilities for Network or park crew leaders and crew members include the following:

- Complete all training for field sampling, sample handling, and boat operation, if required by park.
- Complete all phases of field season preparation.
- Collect data and samples according to developed protocols.
- Pack and ship samples to analytical laboratory.
- Maintain accurate field and office notes.
- Ensure that all QA/QC procedures are implemented.
- Maintain and calibrate equipment according to protocols and manufacturers' directions.
- Communicate progress and accomplishments with the project manager during and after sampling at each park unit, and report any deviations from sampling protocols.
- Download, enter, and verify data into databases as required.
- Maintain documentation of important details of each field data collection period, including explanations of all deviations from standard procedures.
- Maintain hard copies of data forms and send original data forms to archive on a regular basis.
- Represent the National Park Service and the Network in a professional manner, and assist in maintaining positive communication among the Network, park staff, and the public.

5.1.4 Data Manager

The data management aspect of the monitoring effort is the shared responsibility of the data collectors first, then the project manager, and finally the network data manager. Typically, field personnel are responsible for data collection, data entry, data verification, and validation. The data manager is responsible for data archiving, data security, dissemination, and database design. The data manager, in collaboration with the project manager, also develops data entry forms and other database features (as part of quality assurance) and automates report generation.

5.2 Crew Qualifications

The crew leader must have a bachelor's or advanced degree in biology, chemistry, or other related physical or biological science. Field experience is mandatory and laboratory experience is preferred.

Prior leadership experience and good decision-making skills are highly desirable, as is experience with boats, motors, and canoes.

Crew members should have a background in biology, chemistry, or other related physical or biological science, although an undergraduate degree is not required. Prior field experience, including that with boats, motors, and canoes, is highly desirable and laboratory experience is preferred.

All crew members must be physically fit, able to work long hours in inclement weather, and able to carry heavy loads.

5.3 Training Procedures

Prior to data collection, field personnel must become familiar with the use, calibration, and maintenance of all meters and probes planned for use in the monitoring project. A combination of classroom and field training will be required prior to each field season. Personnel who were previously trained for this monitoring project will participate in a review of all methods and techniques. Specific details of the training procedures are covered in SOP #2 and will include:

- Basic limnological concepts and field sampling techniques.
- Review of all SOPs for the project.
- Calibration, operation, and maintenance of all field and laboratory meters and probes used in the project.
- Methods for sample collection.
- Methods for cleaning equipment.
- Methods for handling and preserving samples.
- Completion of field data forms, sample labels, chain of custody forms, analytical service request forms.
- Data entry procedures.
- Completion of field and calibration logbooks.
- Use of GPS equipment.
- Park-specific training requirements (e.g., boat operation, navigation, radios).
- NPS-specific training (e.g., computer use, credit card, travel).

6.0 Operational Requirements

6.1 Annual Workload and Field Schedule

The annual workload and schedule for the monitoring of water quality at large rivers must be viewed within the context of the other planned water quality monitoring activities. We prepared the estimated workload and schedule for monitoring of large rivers and inland lakes together, but anticipate additional related protocols in the future (e.g., wadeable streams). As these additional protocols become part of the GLKN monitoring program, the workloads are likely to change.

Parks with large rivers are SACN and MISS. Due to extensive long-term monitoring by other agencies, we are not currently sampling at MISS, but may re-initiate monitoring if other agencies discontinue their work. We will monitor water quality eight times annually at SACN during the ice-free season (April-November). The time it takes to conduct field work is dependent on weather, flow conditions and logistics, but typically we expect sampling at SACN to take three days per month, including travel time, assuming no weather or logistical difficulties.

6.2 Facility and Equipment Needs

At the park, the field crew will need a facility with a sink and counter-top space where they can calibrate instruments, clean and store equipment, and process samples. They will also need a refrigerator and freezer for storing samples prior to shipment to an analytical laboratory, and secure space for storing a boat, motor and gasoline, as well as other field equipment. Availability of needed space is currently met at SACN by the schoolhouse lab and garage facility on County Highway S near Dresser, WI.

6.3 Budget Considerations

6.3.1 Equipment and Supplies

Costs associated with purchase of equipment and supplies related to fieldwork and laboratory activities are now associated with replacing equipment as it wears out or becomes obsolete, or when supplies need to be replenished. The Network owns one Jon boat, with motor, trailer, and other necessary equipment, dedicated for use at the two large river parks. The Network purchases supplies related monitoring under this protocol. Annual expenses related to equipment, supplies, and fuel expenses typically range from $10,000 to $15,000, which takes into account all water quality monitoring across seven out of nine Network parks and three monitoring protocols (Large Rivers, Inland Lakes, and Diatoms). Because monitoring logistics and associated expenses for these three protocols are intertwined it is not feasible to split out annual expenses for equipment, supplies, and fuel for just one or two parks (i.e., only MISS and SACN).

6.3.2 Staff Salaries

From 2013 to 2015 annual salary expenses related to large river water quality monitoring ranged between $160,000 and $180,000 taking into account the following:

- Annual salaries for the Network project manager (Senior Aquatic Ecologist) and assistant project manager (i.e., Network Large Rivers Aquatic Ecologist),

- Four pay periods for a SACN water quality biological technician.

The project manager's annual salary is divided between the I&M Division and WRD, with the majority of salary typically assigned to WRD. The Network data manager's salary is covered entirely by the I&M Division and is not reflected in the annual salary expenses above. The salary estimates include staff time for project management, training, pre-season preparation, sampling, processing samples, packing and shipping samples, data entry, analysis, reporting, and other various tasks associated with the monitoring effort.

6.3.3 Vehicles and Travel

We expect travel expenses to be approximately $7,500 annually. This estimate includes a GSA vehicle and travel (lodging and per diem), and is based on the following assumptions:

1) GSA vehicles will be shared with other Network monitoring projects, when possible.

2) The program manager will travel to Network parks on a rotational basis to assist with monitoring activities and provide oversight on water quality monitoring activities for the Network.

6.3.4 Analytical Laboratory Costs

Monitoring guidelines established by WRD include strong recommendations for selecting an analytical laboratory that has been accredited by the federal National Environmental Laboratory Accreditation Program (NELAP). The Network will assess the differences in detection and reporting limits among NELAP-approved, state accredited, and research laboratories, along with other criteria, prior to selecting a contract laboratory. The laboratory selected by GLKN must be able to detect and report concentrations appropriately low such that changes in water quality variables can be detected early in the naturally dilute waters occurring throughout the Network. The laboratory selected must meet the detection limits outlined in SOP #12 and have a rigorous QA/QC plan.

For the purpose of estimating a budget for monitoring water quality of inland lakes, we use the costs quoted by CT Laboratories and the St. Croix Watershed Research Station, which are the two analytical laboratories that currently process Network water samples (Table 22). The estimates from the other laboratories are included as examples of what our costs might be if we selected one of them instead.

Table 22. Estimates of laboratory costs for analysis of water quality parameters.

Parameter	CT Laboratories	Natural Resources Research Institute	St. Croix Watershed Research Station	Central Michigan University
Alkalinity	**$10***	$12	$4	$6
DOC	**$18***	$18	$15	--
Cl	**$8***	$23 (Cl w/ SO_4)	$10	$5
SO_4	**$8***	$23 (Cl w/ SO_4)	$10	$7

Table 22 (continued). Estimates of laboratory costs for analysis of water quality parameters.

Parameter	CT Laboratories	Natural Resources Research Institute	St. Croix Watershed Research Station	Central Michigan University
Na, K, Mg, Ca	**$32***	$23	NA	--
TP	$18	$28 (dual TP and TN)	**$32*** (dual TP and TN)	$7
TN	$18 (as TKN)	$28 (dual TP and TN	**$32*** (dual TP and TN)	--
NH_4-N	$12	$11	**$32*** (dual NH_4-N w/ NO_3/NO_2-N)	$1
No_3+No_2-N	$12	$12	**$32*** (dual NH_4-N w/ NO_3/NO_2-N)	$10.50
Chlorophyll-*a*	$27	$34	**$16***	$13
SiO_2	**$9***	--	$10	--

* Costs reflect per sample prices for 2015 (also in bold font).

We expect to measure nutrients (TP, TN, NO_3+NO_2-N, NH_4-N) and chlorophyll-*a* each sampling visit, or eight times per survey-year, one near-bottom TP sample per year, and the remaining parameters three times per survey-year (quarterly). Annual estimated laboratory analysis costs associated with large rivers monitoring (samples, duplicates, and equipment blanks) are typically about $12,500 but may be higher if funding is available and additional sites are monitored.

6.3.5 Total Estimated Annual Costs

Annual monitoring costs ($190,000–$215,000; Table 23) for monitoring at Network large rivers parks are high—more than the Network receives from WRD (approximately $150,000). Monitoring water quality of lakes (Elias et al. 2015), diatoms (Ramstack et al. 2008), and wadeable streams (protocol in preparation) are only partially included in these estimates, putting the total cost of monitoring water quality well beyond the funding WRD provides. Because of the importance of water quality to GLKN parks, the Network is contributing substantial I&M funds to implement these water quality monitoring protocols.

Table 23. Total estimated annual costs for monitoring water quality at SACN.

Item	Cost
Annual equipment and supplies	$10,000–$15,000
Salary and benefits	$160,000–$180,000
Travel	$7,500
Laboratory analyses	$12,500
Total	**$190,000–$215,000**

6.4 Procedures for Revising and Archiving Previous Versions of the Protocol

As our water quality monitoring program matures, revisions to both the protocol narrative and specific standard operating procedures (SOPs) are likely. Documenting changes and archiving copies of previous versions of the protocol and SOPs are essential for maintaining consistency in the collection of data and for appropriate interpretation of the data summaries and analyses. The NPSTORET database contains a field for each monitoring component that identifies which version of the protocol was being used when the data were collected.

The rationale for dividing a sampling protocol into a protocol narrative with supporting SOPs is based on the following:

- The protocol narrative is a general overview of the protocol that gives the history and justification for doing the work and an overview of the sampling methods, but does not provide all methodological details. The protocol narrative will only be revised if major changes are made to the protocol.
- The SOPs are specific step-by-step instructions for performing a given task. They are expected to be revised more frequently than the protocol narrative.
- Usually, when a SOP is revised, it is not necessary to revise the protocol narrative to reflect the specific changes made to the SOP.

All versions of the protocol narrative and SOPs will be archived.

The steps for changing the protocol (either the protocol narrative or the SOPs) are outlined in Procedures for Revising the Protocol, SOP #13. Each SOP contains a Revision History Log that must be updated each time a SOP is revised, to explain why the change was made and to assign a new version number to the revised SOP. The new version of the SOP or protocol narrative should then be archived in the appropriate folder of the GLKN database structure.

Literature Cited

Ayers, M., R. Brown, and G. Oberts. 1985. Runoff and chemical loading in small watersheds in the Twin Cities Metropolitan Area, Minnesota. U.S. Geological Survey Water-Resources Investigations Report 85-4122. U.S. Geological Survey, St. Paul, Minnesota.

Burkart, M. R., and D. E. James. 1999. Agricultural-nitrogen contributions to hypoxia in the Gulf of Mexico. Journal of Environmental Quality 28:850–859.

Clesceri, L. S., A. E. Greenberg, and A. D. Eaton (editors). 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition. American Public Health Association, Washington, D.C.

Driscoll, C. T., C. Yan, C. L. Schofield, R. Munson, and J. Holsapple. 1994. The chemistry and bioavailability of mercury in remote Adirondack lakes. Environmental Science and Technology 28:136–143.

Driscoll, C. T., V. Blette, C. Yan, C. L. Schofield, R. Munson, and J. Holsapple. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. Water, Air, and Soil Pollution 80:499–508.

Elias, J. E., R. Axler, E. Ruzycki, and D. VanderMeulen. 2015. Water quality monitoring protocol for inland lakes: Great Lakes Inventory and Monitoring Network, version 1.1. Natural Resource Report NPS/GLKN/NRR—2015/1027. National Park Service, Fort Collins, Colorado.

Elias, J. E., and J. L. Sieracki. 2007. Report on 2006 water quality sampling at Mississippi National River and Recreation Area. Great Lakes Inventory and Monitoring Network Annual Monitoring Report GLKN/2007/07. National Park Service, Ashland, Wisconsin.

Fallon, J., and R. McNellis. 2000. Nutrients and suspended sediment in snowmelt runoff from part of the Upper Mississippi River Basin, Minnesota and Wisconsin, 1997. Water-Resources Investigations Report 00-4165, U.S. Geological Survey, Mounds View, Minnesota.

Fenelon, J. M. 1998. Water quality in the White River Basin, Indiana, 1992–1996. U.S. Geological Survey Circular 1150. Available at http://pubs.usgs.gov/circ/circ1150/.

Gerrodette, T. 1987. A power analysis for detecting trends. Ecology 68:1364–1372. Available at http://swfsc.nmfs.noaa.gov/PRD/software/Trends.html.

Gilliom, R. J., W. M. Alley, and M. E. Gurtz. 1995. Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions. United States Geological Survey Circular 1112. Available at http://water.usgs.gov/pubs/circ/circ1112.

Gergel, S. E., M. G. Turner, and T. K. Kratz. 1999. Dissolved organic carbon as an indicator of the scale of watershed influence on lakes and rivers. Ecological Applications 9:1377–1390.

Goldman, C., A. Jassby, and T. Powell. 1989. Interannual fluctuations in primary production: Meteorological forcing at two subalpine lakes. Limnology and Oceanography 34:310–323.

Guthery, F. S., J. J. Lusk, and M. J. Peterson. 2001. The fall of the null hypothesis: Liabilities and opportunities. Journal of Wildlife Management 65:379–384.

Hart, M., and U. Gafvert (editors). 2006. Data management plan: Great Lakes Inventory and Monitoring Network. National Park Service Great Lakes Inventory and Monitoring Network Report GLKN/2006/20. National Park Service, Ashland, Wisconsin. Available at https://irma.nps.gov/DataStore/Reference/Profile/660509.

Heiskary, S. A., and R. W. Bouchard, Jr. 2015. Development of eutrophication criteria for Minnesota streams and rivers using multiple lines of evidence. Freshwater Science 34:574–592.

Heiskary, S., R. W. Bouchard, Jr., and H. Markus. 2013. Minnesota nutrient criteria for rivers (draft). Minnesota Pollution Control Agency, St. Paul, Minnesota. Available at www.pca.state.mn.us/index.php/view-document.html?gid=14947 (accessed 11 March 2016).

Heiskary, S., and D. Wasley. 2012. Mississippi River Pools 1 through 8: Developing river, pool and Lake Pepin eutrophication criteria. Minnesota Pollution Control Agency, St. Paul, Minnesota. Available at www.pca.state.mn.us/index.php/view-document.html?gid=14927 (accessed 11 March 2016).

Hirsch, J., R. Alexander, and R. Smith. 1991. Selection of methods for the detection and estimation of trends in water quality. Water Resources Research 27:803–813.

Holdren, C., W. Jones, and J. Taggart. 2001. Managing Lakes and Reservoirs. EPA 841-B-01-006. North American Lake Management Society (NALMS) and Terrene Institute, in cooperation with the Office of Watershed Assessment and Watershed Protection Division, U.S. Environmental Protection Agency, Madison, Wisconsin.

Horne, A., and C. Goldman. 1994. Limnology, 2nd edition. McGraw-Hill Inc., New York.

Irwin, R. 2004. Vital signs long-term aquatic monitoring projects, part B: Planning process steps. Issues to consider and then to document in a detailed study plan that includes a quality assurance project plan (QAPP) and monitoring protocols (standard operating procedures). National Park Service, Ft. Collins, Colorado.

Irwin, R. 2006. Part B lite (Just the Basics). QA/QC review checklist for aquatic vital sign monitoring protocols and SOPs. National Park Service, Ft. Collins, Colorado.

Kloiber, S. 2004. Regional progress in water quality: Analysis of water quality data from 1976–2002 for the major rivers in the Twin Cities. Regional Report Number 32-04-045, Metropolitan Council Environmental Services, St. Paul, Minnesota.

Kraft, G. J., C. Mechenich, D. J. Mechenich, J. E. Cook, and J. L. McNelly. 2015a. Natural resource condition assessment: Mississippi National River and Recreation Area. Natural Resource Report NPS/MISS/NRR—2015/990. National Park Service, Fort Collins, Colorado.

Kraft, G. J., C. Mechenich, D. J. Mechenich, J. E. Cook, and J. L. McNelly. 2015b. Natural resource condition assessment: Saint Croix National Scenic Riverway. Natural Resource Report NPS/SACN/NRR—2015/1003. National Park Service, Fort Collins, Colorado.

Kroening, S. 1998. Nutrient sources within the Upper Mississippi River Basin, Minnesota and Wisconsin, 1991–93. U.S. Geological Survey Fact Sheet 121-98, U.S. Geological Survey, Mounds View, Minnesota.

Kroening, S., and W. Andrews. 1997. Water quality assessment of part of the Upper Mississippi River Basin, Minnesota and Wisconsin—nitrogen and phosphorus in streams, streambed sediment and ground water, 1971–94. Water-Resources Investigations Report 97-4107, U.S. Geological Survey, Mounds View, Minnesota.

Kroening, S., K. Lee, and R. Goldstein. 2002. Water quality assessment of part of the Upper Mississippi River Basin study unit, Minnesota and Wisconsin—nutrients, chlorophyll-*a*, phytoplankton and suspended sediment in streams, 1995–98. Water-Resources Investigations Report 02-4287, U.S. Geological Survey, Mounds View, Minnesota.

Lafrancois, B. M., and J. Glase. 2005. Aquatic studies in national parks of the upper Great Lakes states: Past efforts and future directions. Water Resources Division Technical Report. NPS/NRWRD/NRTR—2005/334. National Park Service, Denver, Colorado. Available at http://www1.nature.nps.gov/im/units/glkn/reports.htm.

Lafrancois, B. M., K. Johnson, and M. Tomasek. 2004. Insights from 25 years of water-quality monitoring: Trends and patterns on the lower St. Croix. Appendix 5 *in* St. Croix Basin phosphorus-based water-quality goals—Report on the recommended water-quality goals of the St. Croix Basin Water Resources Planning Team and the proceedings of the 5th annual conference Protecting the St. Croix: Reducing and managing nutrients and sediments. Available at http://www.pca.state.mn.us/publications/reports/stcroixbasin-phosreport04.pdf.

Lafrancois, B. M., S. Magdalene, D. K. Johnson, D. VanderMeulen, and D. Engstrom. 2013. Water quality conditions and trends in the Mississippi National River and Recreational Area: 1976–2005. Natural Resource Technical Report NPS/GLKN/NRTR—2013/691. National Park Service, Fort Collins, Colorado.

Lafrancois, B. M., S. Magdalene, and D. K. Johnson. 2009. Recent water quality trends and a comparison to sediment-core records for two riverine lakes of the Upper Mississippi River Basin: Lake St. Croix and Lake Pepin. Journal of Paleolimnology 41:603–622.

Ledder, T. 2003. Water resource information and assessment report for the Great Lakes Inventory and Monitoring Network. Great Lakes Network Technical Report GLKN/2003/05. National Park

Service, Ashland, Wisconsin. Available at http://www1.nature.nps.gov/im/units/glkn/Water resource information and assessment.pdf.

Lenz, B. N. 2004. Analysis of streamflow and water-quality data at two long-term monitoring sites on the St. Croix River, Wisconsin and Minnesota. Water-Resources Investigations Report 03-4334, U.S. Geological Survey, Madison, Wisconsin.

Lenz, B. N., D. M. Robertson, J. D. Fallon, and R. Ferrin. 2003. Nutrient and suspended-sediment concentrations and loads, and benthic invertebrate data for tributaries to the St. Croix River, Wisconsin and Minnesota. Water-Resources Investigations Report 01-4162, U.S. Geological Survey, Middleton, Wisconsin.

Lorenz, D. L., D. M. Robertson, D. W. Hall, and D. A. Saad. 2009. Trends in streamflow and nutrient and suspended sediment concentrations and loads in the Upper Mississippi, Ohio, Red, and Great Lakes river basins, 1975–2004. U.S. Geological Survey Scientific Investigations Report 2008–5213 USGS, Reston, Virginia. Available at http://pubs.usgs.gov/sir/2008/5213/ (accessed 11 March 2016).

Lubinski, K. S. 2004. Large river conceptual model. *In* S. Gucciardo, B. Route, and J. Elias, editors. Conceptual ecosystem models for the Great Lakes Network. Great Lakes Network Report GLKN/2004/04. National Park Service, Ashland, Wisconsin. Available at https://irma.nps.gov/DataStore/Reference/Profile/660501 (accessed 25 April 2016).

Magdalene S., D. R. Engstrom, and J. Elias. 2008. Large rivers water quality monitoring protocol, Version 1.0. National Park Service, Great Lakes Network, Ashland, Wisconsin. NPS/GLKN/NRR—2008/060. National Park Service, Fort Collins, Colorado. Available at https://irma.nps.gov/DataStore/Reference/Profile/660483 (accessed 25 April 2016).

McCune, B., and J. B. Grace. 2002. Analysis of ecological communities. MjM Software Design, Gleneden Beach, Oregon.

McDonald, T. L., and P. H. Geissler. 2004. Systematic and stratified sampling designs in long-term ecological monitoring studies. West Inc., Cheyenne, Wyoming. Available at http://science.nature.nps.gov/im/monitor/docs/SampleDesigns.doc.

McDonald, M. E., S. Paulsen, R. Blair, J. Dlugosz, S. Hale, S. Hedtke, D. Heggem, L. Jackson, K. B. Jones, B. Levinson, A. Olsen, J. Stoddard, K. Summers, and G. Veith. 2002. Research strategy of the Environmental Monitoring and Assessment Program. EPA 620/R-02/002. Available at http://www.epa.gov/emap/html/pubs/docs/resdocs/EMAP_Research_Strategy.pdf.

Meybeck, M., and R. Helmer. 1989. The quality of rivers: From pristine stage to global pollution. Palaeogeography, Palaeoclimatology, and Palaeoecology 75: 283–309.

MDEQ (Michigan Department of Environmental Quality). 2004. Lake water quality assessment monitoring program for Michigan's inland lakes. Baseline water quality and trophic status

monitoring protocol. Michigan Department of Environmental Quality, East Lansing, Michigan. Available at www.michigan.gov/deq/0,1607,7-135-3313_3686_3731---,00.html.

MDEQ (Michigan Department of Environmental Quality). 2001. The Michigan Department of Environmental Quality's lake water quality assessment monitoring program for Michigan's inland lakes. Michigan Department of Environmental Quality, Land and Water Management Division, and U.S. Geological Survey, WRD–Michigan District.

MDEQ. 2005. Michigan Department of Environmental Quality environmental and drinking water testing labs directory. Available at http://www.michigan.gov/deq/0,1607,7-135-6132_6828-18205--,00.html.

MDH. 2005. Minnesota Department of Environmental Health Laboratory Certification Program. Available at http://www.health.state.mn.us/divs/phl/cert/index.html.

MPCA (Minnesota Pollution Control Agency). 2005a. Secchi transparency—Just the facts. Available at www.pca.state.mn.us/water/clmp-publications.html (accessed 27 January 2006).

MPCA (Minnesota Pollution Control Agency). 2012. Draft South Metro Mississippi River total suspended solids TMDL. Document number wq-iw9-12b. Available at http://www.pca.state.mn.us/index.php/view-document.html?gid=15794 (accessed 11 March 2016).

MPCA (Minnesota Pollution Control Agency) and WDNR (Wisconsin Department of Natural Resources). 2012. Lake St. Croix nutrient total maximum daily load. Available at https://www.pca.state.mn.us/sites/default/files/wq-iw6-04b.pdf (accessed 11 March 2016).

Monson, P. 2010. Aquatic life water quality standards technical support document for nitrate. Triennial water quality standard amendments to Minn. R. chs. 7050 and 7052. Draft for external review, November 12, 2010. Minnesota Pollution Control Agency, St. Paul, Minnesota. Available at http://www.pca.state.mn.us/index.php/view-document.html?gid=14949 (accessed 11 March 2016).

NEMI (National Environmental Methods Index). 2006. National Environmental Methods Index website. Available at www.nemi.gov (accessed July 2006).

NPS (National Park Service). 2002. Recommendations for core water quality monitoring parameters and other key elements of the NPS vital signs program. National Park Service Freshwater Workgroup Subcommittee, Fort Collins, Colorado. Available at http://science.nature.nps.gov/im/monitor/protocols/COREparam.doc.

NPS (National Park Service). 1995a. Baseline water quality data inventory and analysis: Mississippi National River and Recreation Area. Natural Resource Technical Report NPS/NRWRD/NRTR—95/61. National Park Service, Water Resources Division, Fort Collins, Colorado.

NPS (National Park Service). 1995b. Baseline water quality data inventory and analysis: St. Croix National Scenic Riverway. Natural Resource Technical Report NPS/NRWRD/NRTR—95/69. National Park Service, Water Resources Division, Fort Collins, Colorado.

Olsen, A. R. 2002. Probability survey design: An overview. Presented at National Forest Health Monitoring meeting, February 2002. Available at http://www.fs.fed.us/institute/fhm_riparian/feb2002/survey_design_overview.ppt.

O'Ney, S. E. 2005. Regulatory water quality monitoring protocol. Version 1.0. National Park Service, Greater Yellowstone Network, Bozeman, Montana. Available at http://science.nature.nps.gov/im/monitor/protocoldb.cfm.

Patton, C. J., and J. R. Kryskalla. 2003. Evaluation of alkaline persulfate digestion as an alternative to Kjeldahl digestion for determination of total and dissolved nitrogen and phosphorus in water. U.S. Geological Survey Water-Resources Investigations Report 03-4174. http://nwql.usgs.gov/Public/pubs/WRIR03-4174/WRIR03-4174.html.

Penoyer, P. 2003. Vital signs long-term aquatic monitoring projects, part C: Draft guidance on WRD required and other field parameter measurements, general monitoring methods and some design considerations in preparation of a detailed study plan. National Park Service, Ft. Collins, Colorado.

Preisendorfer, R. W. 1986. Secchi disk science: Visual optics of natural waters. Limnology and Oceanography 31: 909–926.

Route, B. 2004. Process and results of selecting and prioritizing vital signs for the Great Lakes Network. U. S. National Park Service. Great Lakes Inventory and Monitoring Network. Technical Report GLKN/2004/05. National Park Service, Ashland, Wisconsin.

Route, B., W. Bowerman, and K. Kozie. 2009. Protocol for monitoring environmental contaminants in bald eagles, Version 1.2: Great Lakes Inventory and Monitoring Network. Natural Resource Report NPS/GLKN/NRR—2009/092. National Park Service, Fort Collins, Colorado. Available at https://irma.nps.gov/DataStore/Reference/Profile/661149.

Route, B. and J. Elias (editors). 2006. Phase III report: Long-term ecological monitoring plan for the Great Lakes Network. U.S. National Park Service, Great Lakes Inventory and Monitoring Network. Technical Report GLKN/2006/02. National Park Service, Ashland, Wisconsin.

Russell, T. A., and L. Weller. 2013. State of the river report: Water quality and river health in the metro Mississippi River. Friends of the Mississippi River and Mississippi National River and Recreation Area, St. Paul, Minnesota. Available at http://stateoftheriver.com/ (accessed 11 March 2016).

Schindler, D. W. 1988. Effects of acid rain on freshwater ecosystems. Science 239: 149–157.

Schindler, D. W., and P. J. Curtis. 1997. The role of DOC in protecting freshwaters subjected to climatic warming and acidification from UV exposure. Biogeochemistry 36: 1–8.

Schindler, D. W., K. H. Mills, D. F. Malley, D. L Findlay, J. A. Shearer, and D. R. Cruikshank. 1985. Long-term ecosystem stress: The effects of years of experimental acidification on a small lake. Science 228: 1395–1407.

Stednick, J. D., and D. M. Gilbert. 1998. Water quality inventory protocol: Riverine environments. Natural Resource Technical Report NPS/NRWRD/NRTR—98/177. National Park Service, Fort Collins, Colorado.

Stevens, D. L., and A. R. Olsen. 2004. Spatially balanced sampling of natural resources. Journal of the American Statistical Association 99: 262-278.

Stevens, D. L., and A. R. Olsen. 1991. Statistical issues in environmental monitoring and assessment. Proceedings of the American Statistical Association Annual Section on Environmental Statistics. American Statistical Association, Alexandria, Virginia.

Swift, T. J., J. Perez-Losada, S. G. Schladow, J. E. Reuter, A. D. Jassby, and C. R. Goldman. 2006. Water clarity modeling in Lake Tahoe: Linking suspended matter characteristics to secchi depth. Aquatic Sciences—Research Across Boundaries 68: 1–15.

Thomas, L., and C. J. Krebs. 1997. A review of statistical power analysis software. Bulletin of the Ecological Society of America 78: 126–139.

Triplett, L., M. Edlund, and D. Engstrom. 2003. A whole-basin reconstruction of sediment and phosphorus loading to Lake St. Croix. Final Project Report to the Metropolitan Council Environmental Services, St. Croix Watershed Research Station, Marine on St. Croix, Minnesota.

USEPA (United States Environmental Protection Agency). 2000. Ambient water quality criteria recommendations: Information supporting the development of state and tribal nutrient criteria for rivers and streams in nutrient ecoregion VII. EPA-822-B-00-018. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division, Washington, D.C. Available at http://water.epa.gov/scitech/swguidance/standards/upload/2007_09_27_criteria_nutrient_ecoregions_rivers_rivers_7.pdf (accessed 11 March 2016).

USEPA (United States Environmental Protection Agency). 2001. Ambient water quality criteria recommendations: Information supporting the development of state and tribal nutrient criteria, rivers and streams in nutrient ecoregion VIII. EPA 822-B-01-015, United States Environmental Protection Agency, Office of Water 4304, Washington, D.C. Available at http://water.epa.gov/scitech/swguidance/standards/upload/2007_09_27_criteria_nutrient_ecoregions_rivers_rivers_8.pdf (accessed 11 March 2016).

VanderMeulen, D. 2011. Large rivers water quality monitoring: 2009 and 2010 summary report. Natural Resource Data Series NPS/GLKN/NRDS—2011/164. National Park Service, Fort Collins, Colorado. Available at https://irma.nps.gov/DataStore/Reference/Profile/2170875.

VanderMeulen, D. 2009. Monitoring water quality of large rivers, 2008. Annual summary report. National Park Service, Great Lakes Inventory and Monitoring Network Report GLKN/2009/03. National Park Service, Ashland, Wisconsin.

VanderMeulen, D. 2012. St. Croix National Scenic Riverway water quality monitoring: 2011 summary report. Natural Resource Data Series NPS/GLKN/NRDS—2012/366. National Park Service, Fort Collins, Colorado. Available at https://irma.nps.gov/DataStore/Reference/Profile/2190298.

VanderMeulen, D. 2013. Water quality monitoring at Mississippi National River and Recreation Area: 2012 summary report. Natural Resource Data Series NPS/GLKN/NRDS—2013/577. National Park Service, Fort Collins, Colorado.

VanderMeulen, D., and J. E. Elias. 2008. Water quality sampling at St. Croix National Scenic Riverway, 2007. Great Lakes Inventory and Monitoring Network Annual Monitoring Report GLKN/2008/03. National Park Service, Ashland, Wisconsin.

VanderMeulen, D., K. Johnson, D. Hansen, R. Ferrin, S. Magdalene, and B. Moraska-LaFrancois. 2010. Monitoring plan for the St. Croix River: 2010. St. Croix Basin Water Resources Planning Team. Available at https://www.pca.state.mn.us/sites/default/files/wq-b6-13.pdf (accessed 22 March 2016).

Walker, W. W., Jr. 1988. Lake/reservoir sampling design worksheet, LRSD-1.0. Software Package No. 3, North American Lake Management Society, Alachua, Florida.

Ward, R. C., J. C. Loftis, and G. B. McBride. 1990. Design of Water Quality Monitoring Systems. Nostrand Reinhold Publishing, New York, New York.

WOW (Water on the Web). 2005. Water on the Web: Monitoring Minnesota lakes on the internet and training water science technicians for the future—A national online curriculum using advanced technologies and real-time data. Module 8A. University of Minnesota–Duluth, Duluth, Minnesota. Available at http://waterontheweb.org.

West, N. E., and T. P. Yorks. 2002. Vegetation responses following wildfire on grazed and ungrazed sagebrush semi-desert. Journal of Range Management 55: 171–181.

WDNR (Wisconsin Department of Natural Resources). 2005. Water resources monitoring strategy for Wisconsin, version 1:2-4-2005. Wisconsin Department of Natural Resources, Madison, Wisconsin.

WDNR (Wisconsin Department of Natural Resources). 2010. Chapter NR 102, water quality standards for Wisconsin surface waters. Available at http://legis.wisconsin.gov/rsb/code/nr/nr102.pdf (accessed 11 March 2016).

WSLH (Wisconsin State Laboratory of Hygiene). 2003. Wisconsin State Laboratory of Hygiene, Environmental Health Division analytical services and methods. University of Wisconsin, Madison, Wisconsin. Available at http://www.slh.wisc.edu/services/index.php.

Wiener, J., R. Haro, K. Rolfhus, M. Sandheinrich, and B. Route. 2009. Protocol for monitoring and assessing methylmercury and organic contaminants in aquatic food webs (DRAFT). Unpublished protocol. National Park Service, Great Lakes Inventory and Monitoring Network, Ashland, Wisconsin.

Wetzel, R. G. 2001. Limnology: Lake and River Ecosystems, 3rd edition. Academic Press, San Diego, California.

Wetzel, R. G, and G. E. Likens. 2000. Limnological Analyses, 3rd edition. Springer-Verlag, New York, New York.

Zar, J. H. 1999. Biostatistical Analysis, 4th edition. Prentice Hall, New Jersey.

Zhang, J., H. T. Chen, Z. F. Zhang, S. M. Liu, and Y. Wu. 1999. Human impacts on the large world rivers: Would the Changjiang (Yangtze) River be an illustration? Global Biogeochemical Cycles 13: 1099–1105.

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