



Executive Summary
**Monitoring Water Quality of Large Rivers at
Mississippi National River and Recreation Area**
Summer 2008



Italicized words are defined in a glossary at the end of this summary.

Background – With two park units based on large, non-wadeable rivers, the Great Lakes Inventory and Monitoring Network (GLKN or Network) recognized early-on the importance of large rivers among ecosystems found within Network parks. Key water quality concerns for the Mississippi National River and Recreation Area (MISS) include: (1) excess nutrients (particularly nitrogen and phosphorous) from urban and agricultural runoff and wastewater treatment facilities; (2) fluctuations in flow regime caused by climate change, farming drainage, urban growth and the associated increase of impervious-surfaces, or *channel engineering*; (3) sediment loading from streambank and agricultural field erosion; (4) invasion of exotic species such as common carp (*Cyprinus carpio*) and zebra mussels (*Dreissena polymorpha*); and (5) the presence of environmental contaminants of emerging concern, including polybrominated diphenyl ether flame retardants (PBDE), mercury, and endocrine disrupters.

MISS does not have a water quality monitoring program of its own, but other federal, state, and regional agencies have collected data from within or near the park's boundaries since the 1920s. The GLKN protocol is designed to guide monitoring the physical and chemical water quality of large non-wadeable rivers at MISS. We will look for potential links between data collected under this monitoring protocol and information gathered from Bald Eagles (*Haliaeetus leucocephalus*) and fish under our bioaccumulative contaminants protocols. This combined effort will provide a more holistic view of interactions between water quality and contaminant loads and how the two affect higher levels of the aquatic community food web.

Methods – The large rivers monitoring program involves collecting information from both a *core suite* and an *advanced suite* of water quality variables. Core suite water quality variables are collected monthly, and advanced suite variables collected quarterly, which is three times in a given field season. The core suite variables are river flow, temperature, *specific conductance*, *pH*, *dissolved oxygen* (DO), and *water clarity*. River flow data are collected from eight pre-existing U.S. Geological Survey (USGS) stream gages that currently operate within or near MISS park boundaries; temperature, specific conductance, pH, and DO are measured at each site using a multi-probe instrument and data logger; and water clarity is determined by using a *Secchi disk* or *transparency tube*.

The advanced suite consists of measuring levels of *nutrients* (total phosphorous and total nitrogen, nitrate+nitrite-nitrogen [$\text{NO}_3+\text{NO}_2\text{-N}$], ammonium-nitrogen [$\text{NH}_4\text{-N}$]), *ions* (sulfate [SO_4^{-2}], chloride [Cl^-], magnesium [Mg^{+2}], calcium [Ca^{+2}], sodium [Na^+], potassium [K^+]), *dissolved silica*, *dissolved organic carbon*, *alkalinity*, *total suspended solids*, and *chlorophyll-a*. We collect water at each site for laboratory analysis of these parameters. Water appearance (such as color or oily surface film, biological activity (such as algae blooms), unusual odors, and watershed or in-stream activities at each site are documented, and photos facing each of the four cardinal directions are taken from a fixed point. Sediment cores are also collected periodically

for analysis of diatom communities, which are a good integrator of water quality conditions over time.

Water sampling at MISS was conducted once a month from April through November 2006. Five sample sites were established along the Mississippi River, extending from just above the Crow River confluence near Dayton, MN, south and east to Spring Lake at river mile 822 (Figure 1). Site descriptions and specific location information are provided in the 2007 annual report.

Results (2006)

Core Suite - Temperature and DO profiles show that all sites were well mixed throughout the open-water season of 2006. Low dissolved oxygen concentrations were recorded above the confluence of the Mississippi and Crow rivers (Site UM880) in July (6.02 mg/L), and Spring Lake (Site UM822) experienced relatively low dissolved oxygen concentrations in August and September, (4.8 and 6.7 mg/L, respectively). These low readings were probably due to a combination of low river flows and high temperatures, both of which were observed at all five sites during that time. Daily minimum DO levels <5 mg/L may be detrimental to aquatic life.

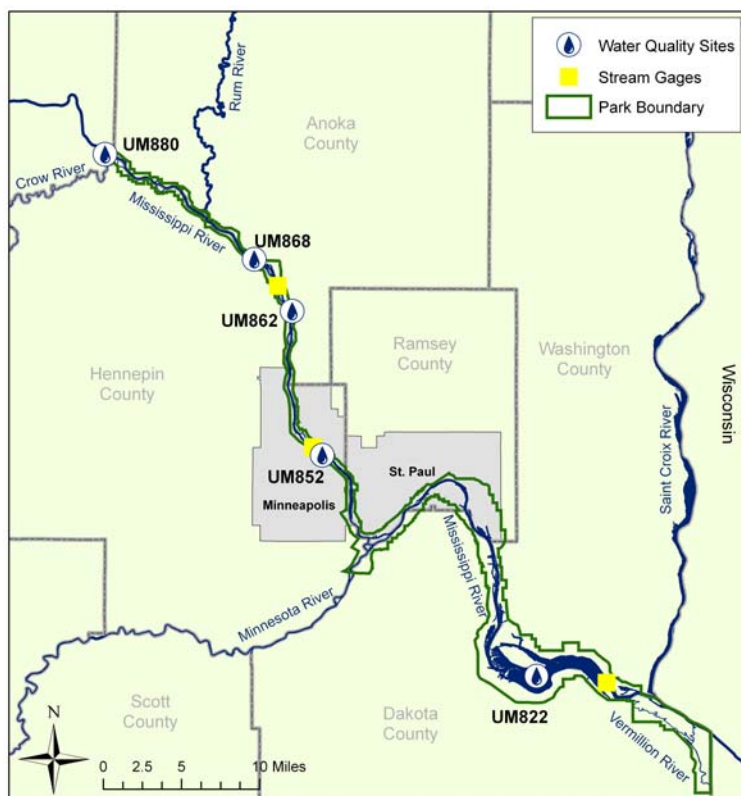


Figure 1. Location of GLKN water quality monitoring sites and USGS streamflow gaging stations in the Mississippi

Specific conductance, ionic strength, and alkalinity values were high at all sites, with Spring Lake (UM822) typically exhibiting the highest values compared to the four upstream sites. Inputs from the Minnesota River and multiple point sources likely caused higher values of specific conductance at UM822. Average pH values for the five sites were relatively high, ranging from 8.29 at Spring Lake (UM822) to 8.52 at UM868.

There was very low flow in the sampled stretch of the river from July until the end of the monitoring season. Average monthly flows were among the lowest on record for the past 30 years.

Advanced Suite – The water at the five sampling sites are well-buffered, with mean alkalinities ranging from a low of 142 mg/L at UM880 to 183 mg/L at UM822.

Ion concentrations were relatively high, with a dramatic increase in these parameters between UM852 and UM822. Road de-icers may contribute large amounts of sodium (Na^{+2}) and chloride (Cl^{-}) to urban streams in winter and spring. However, concentrations of both ions increased throughout the sampling season, suggesting that something in addition to de-icing compounds may be the cause of the high ionic strength. Although Cl^{-} concentrations were high, state water quality standards were not exceeded. Much of the calcium (Ca^{+2}) most likely comes from the underlying clay-rich, calcareous glacial deposits, while concentrations of the remaining ions are derived from weathering of the surrounding rocks and soils, from inputs of fertilizers, and from industrial and urban runoff.

Dissolved organic carbon (DOC) ranged from a low of 6.6 mg/L at UM880 to a high of 12.0 mg/L at UM862. The DOC values measured at MISS are high enough to reduce light penetration and thus reduce photosynthesis, though the similar effect of suspended particles usually dwarfs that of DOC in the MISS sampling area.

Water clarity at most sites was lowest in April and May and highest in October and November, with an inexplicably high measurement at UM880 in July. Total suspended solids (TSS) were remarkably high at UM822 in April and again, to a lesser degree, in September. Total suspended solids measurements at the other four sites were relatively constant throughout the season. Low water clarity and high TSS are related to inputs from tributaries and run-off. TSS measurements >66 mg/L violate the standard set by the Minnesota Pollution Control Agency for EPA Ecoregion 47. Site UM822 had TSS measurements >66 mg/L during April, May, and September, which corresponded with low transparency tube readings there.

Nutrient concentrations showed a parallel pattern to TSS concentrations throughout the season, with the highest values occurring in spring. Nutrient levels were typically much higher at UM822 than at the other sites throughout the field season. Ammonium-nitrogen increased dramatically at UM822 between July and August and declined gradually throughout the remainder of the season. There was no such increase at the other sites, suggesting inputs to the river somewhere between UM852 and UM822. UM822 is the only sample site below the Minnesota River, a tributary with high nutrient concentrations that contributes an additional 50% to the discharge level of the Mississippi River where the two meet.

MISS will be sampled again in 2009 and 2011, with quarterly monitoring in the interim years dependent on additional funding. After completing three full years of monitoring, we will analyze the data for potential trends and will produce a report that synthesizes our data with those from other monitoring efforts.

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Glossary

Advanced suite: Elements of water chemistry that are measured by collecting water samples that are later analyzed in the laboratory using standardized techniques. Advanced suite elements are important because they contribute to a thorough understanding of changes in water quality over time. The elements measured are levels of nutrients, ions, dissolved silica, total organic carbon, alkalinity, total suspended solids, and total chlorophyll-*a*. In addition to these chemical features, water appearance, biological activity, unusual odors, and watershed or in-stream activities at each site are documented, and photos are taken from a fixed point, facing each of the four cardinal directions.

Alkalinity: A closely related parameter to acidity, alkalinity, or acid-neutralizing capacity (ANC) is a measure of the buffering capacity of the water. It is measured in mg/L of CaCO₃ or µeq/L.

Channel engineering: Human-induced modification of the river channel that affects the natural flow regime. Examples of such include impoundment of the river, armoring river banks, channeling water with wing dams, removal of naturally-occurring large woody debris, and shoreline erosion by boat wakes.

Chlorophyll-a: The primary photosynthetic pigment in all green plants including phytoplankton. The concentration of chlorophyll-*a* is a nearly universally accepted measure of algal biomass in the open waters of lakes. Consistent and directional trends in chlorophyll-*a* concentrations are good indicators of change in a lake's trophic status.

Core suite: Seven features, both chemical and physical, of rivers that are measured to provide a baseline of information about water quality. The seven features are river flow, temperature, specific conductance, pH, dissolved oxygen (DO), and water clarity.

Dissolved organic carbon: DOC is usually the largest fraction of organic material in the open waters of lakes. It 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. Lesser amounts are contributed by algae, both from extracellular leakage and through decomposition. The DOC level 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 the lake by absorbing sunlight.

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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 that are in contact with the solution. A DO level of 5 mg/L is the minimum level necessary for

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.

Dissolved silica: Silica (SiO_2) is considered an essential micronutrient for micro-organisms 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.

Ions: There are three major anions (those with a negative charge) – sulfate (SO_4^{2-}), chloride (Cl^-), and bicarbonate (HCO_3^-); and four major cations (those with a positive charge) – calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), and potassium (K^+) being monitored. The ionic concentrations influence water's ability to assimilate pollutants and maintain nutrients in solution.

Nutrients: Nitrogen and phosphorus are the two most influential nutrients for regulating the growth of aquatic plants. Excessive inputs of nutrients can lead to excessive algal growth and eutrophication. The nutrient species of greatest interest for the advanced suite are total phosphorus (TP), total nitrogen (TN), nitrate+nitrite-nitrogen ($\text{NO}_3+\text{NO}_2\text{-N}$), and ammonium-nitrogen ($\text{NH}_4\text{-N}$).

pH: The concentration of hydrogen ions in a body of water. Values range from 1-14. Low pH values (<7) reflect increasingly greater concentrations of hydrogen ions and cause water to be "acidic." Higher values (7-14) reflect lower hydrogen ion concentrations and cause water to be "basic" or "alkaline." A change of one pH unit (e.g., pH 7 to pH 8) reflects a ten-fold change in hydrogen ion concentration. Because organisms can only tolerate a pre-defined range of pH values, the mean and range of pH values at a given site often determine what organisms could exist there. pH also determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (mercury, lead, copper, and cadmium). 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.

Secchi depth: A measurement of water clarity obtained by using a round, flat, black and white disk (called a Secchi disk). Secchi depth is influenced by suspended sediment, such as sediment from agricultural and urban runoff and from shoreline erosion; algae in the water column; and naturally occurring compounds, such as tannic acid and dissolved organic carbon. A change in Secchi depth over time may indicate a change in trophic status.

Specific conductance: Electrical conductivity is a measure of the capacity of water to conduct an electrical current. Specific conductivity (called EC25 or SC25) is a measure that eliminates the temperature dependent variability of electrical conductivity and thus provides a good estimation of the concentration of total dissolved ions in the water. Specific conductance is influenced by the underlying geology (rock types) and soils in the watershed, size of the watershed relative to area of the lake, and pollutant levels. Conductivity is an important indicator of polluted runoff that may contain road salts, excess nutrients, organic matter, heavy metals, and organic contaminants.

Total suspended solids: TSS is the dry weight of particles that are trapped by a pre-weighed filter. TSS of a water sample is determined by pouring a carefully measured volume of water (typically one liter; but less if the particulate density is high, or as much as two or three liters for very clean water) through a pre-weighed filter of a specified pore size, then weighing the filter again after drying to remove all water. The gain in weight is a dry weight measure of the particulates present in the water sample expressed in units derived or calculated from the volume of water filtered (typically milligrams per liter or mg/l). High TSS values often correspond to low water clarity.

Transparency tube: Used to measure water clarity, the “t-tube” is 60 or 125 cm tall with a miniature Secchi disk attached to the bottom. Water is slowly released through a valve at the bottom of the tube until an observer, looking down through the tube, can see the black and white Secchi disk on the bottom.

Water clarity: An indirect measure of how far light can reach below the water’s surface. Light penetration is an important regulator of the rate of primary production and plant abundance. Water clarity provides a visual measurement that relates directly to the aesthetic perceptions of the general public. *See also* Secchi depth *and* Transparency tube.