How's the River Doing?

Mississippi River Clean Water Act Pilot Water Quality Summary for Minnesota-Wisconsin

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About this Report

This Clean Water Act (CWA) Pilot is the first effort to implement the Upper Mississippi River Clean Water Act Monitoring Strategy 2013-2022 (UMRBA, 2014). This CWA Pilot was implemented by Metropolitan Council Environmental Services, Minnesota Department of Natural Resources, Minnesota Pollution Control Agency, Wisconsin Department of Natural Resources and Upper Mississippi River Basin Association between April 2016 and March 2017.

The pilot utilized Clean Water Act Provisional Methodology procedures, based on the original monitoring strategy, that was developed in 2015 by UMRBA to better understand spatial and temporal patterns among water quality and biota of the Upper Mississippi River (UMR). The CWA Pilot produced a robust dataset that was examined in the Project Pilot Evaluation Report as well as the Water Quality Condition Assessment report released in January 2019.

In Wisconsin, this Water Quality Report was created under the State's Office of Great Waters Mississippi River Work Unit. The plan reflects water quality program priorities and Water Resources Monitoring and, in part, fulfills Wisconsin's Areawide Water Quality Management Plan requirements under Section 208 of the Clean Water Act. Condition information and resource management recommendations support and guide program priorities for the planning area.

This summary report is a formal amendment to Wisconsin's Statewide Areawide Water Quality Management Plan and will be forwarded to USEPA for formal certification.

Acknowledgments

From the author, Shawn Giblin. Special thanks to Kent Johnson, Jack Barland, Eric Lund and Megan Moore, Pam Anderson, Joel Chirhart, Jordan Donatell, Mike Feist, Lee Ganske, Dan Helwig, Ron Arneson, Andy Bartels, Deanne Drake, Kraig Hoff, John Kalas, Alicia Carhart, Wes Bouska, Lisa Kosmond Helmuth, Jeremy King, Brian Weigel, Mike Shupryt, Jim Fischer, Ashley Beranek, Marcia Willhite, John Sullivan, John Olson, Dave Hokanson, Matt Jacobson, Kirsten Wallace, Josh Ney, Lauren Salvato, Andrew Stephenson, Madeline Magee and Matt Short for all the hard work and dedication that it took to execute the Clean Water Act Pilot.

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Introduction

Clean water is the lifeblood of communities situated along and near the Mississippi River. There is wide agreement that investment in the preservation and improvement of water quality results in wide ranging societal and economic benefits. Diminished water quality can have far-reaching effects on the economy and quality of life, impacting tourism, property values, commercial fishing, recreational businesses and reducing regional ability to attract new businesses and a skilled workforce. A recent economic profile of the Upper Mississippi River corridor provides critical context related to the need to maintain and improve water quality of this globally significant ecosystem (UMRBA 2017). The profile, for counties adjoining the Mississippi River and one county inland, within the states of Minnesota, Wisconsin, Iowa, Illinois and Missouri, revealed the following findings:

- Economic sectors in the Mississippi corridor generate more than $345 billion annually, supporting over 1 million jobs;
- Tourism draws millions of people annually- with annual expenditures over $20.6 billion that support 358,000 jobs;
- Outdoor recreation in the river corridor generates revenue of $4 billion annually; and
- Commercial harvest, including fish and furbearers, generates $21.7 million annually.

This work seeks to address the frequent question asked of biologists at Mississippi River boat ramps: How's the river doing? The report explores the water quality data collected as part of the Clean Water Act Monitoring Pilot (CWA Pilot) to characterize the status of water quality in the Mississippi River. These data help to establish baseline differences among sites as well as longitudinal trends along a 160-mile study reach. Water quality samples were collected from four stations on the Mississippi River as well as one site each on the St. Croix and Minnesota Rivers to characterize water chemistry in those rivers as part of the CWA Pilot. The findings of this report will assist the state of Wisconsin to more effectively target water quality improvement actions on the landscape to improve river health. This is a unique effort in that two states came together to reach consensus on conclusions regarding the health of the Mississippi River. This joint monitoring effort is a first step toward a joint assessment of the river.

The CWA Pilot was a first effort to implement the Upper Mississippi River Clean Water Act Monitoring Strategy 2013-2022 (UMRBA, 2014). The CWA Pilot was implemented by Metropolitan Council Environmental Services, Minnesota Department of Natural Resources, Minnesota Pollution Control Agency, Wisconsin Department of Natural Resources and Upper Mississippi River Basin Association between April 2016 and March 2017. The CWA Pilot utilized Clean Water Act Provisional Methodology procedures, based on the original monitoring strategy, that was developed in 2015 by UMRBA to better understand spatial and temporal patterns among water quality and biota of the Upper Mississippi River (UMR). The CWA Pilot produced a robust dataset that was examined in the Project Pilot Evaluation Report as well as the Water Quality Condition Assessment report released in January 2019.

The purpose of this report is to explore the water quality data collected as part of the CWA Pilot study in greater detail, including parameters that were not part of the Water Quality Condition Assessment Report.

Methods

Water quality sampling was divided into fixed and probabilistic sites. One fixed site was located in each of the four Mississippi River sampling reaches (0-3; Figure 1). In addition, fixed sites were sampled on the Minnesota and St. Croix Rivers. These six fixed sites were sampled monthly from May 2016 to April 2017 (n=12). The sites on the St. Croix River (SC-0.3), Minnesota River (MN-3.5) and two Mississippi River sites (UMR-815.6 and UMR-796.9) were sampled by the Metropolitan Council (Figure 1). The site names are abbreviated (e.g. SC = St. Croix River) and the number following the abbreviation represents the mileage upstream from the river mouth or miles upstream of the of the confluence with the Ohio R. for the Mississippi River sites. One UMR site was sampled by Minnesota Pollution Control Agency (UMR-728.5) and one site was sampled by Wisconsin DNR (UMR-702.5). Three sampling entities resulted in samples analyzed at three separate labs: The Metropolitan Council Laboratory, the Minnesota Department of Health Laboratory, and Wisconsin State Laboratory of Hygiene. A comparison table of water quality and quality control processes and methods was incorporated into the Field Operations Manual (UMRBA 2016). Split sampling between the three labs was conducted on three occasions. The differences between the laboratories were within a margin of acceptable difference based on the study design. Further details regarding collection methods, laboratory analysis, and procedures of the CWA Pilot are outlined in the Clean Water Act Provisional Methodology procedures report and the Field Methods Manual.

Probabilistic sites were sampled at fifteen sites per reach in each of the four reaches (Reaches 0-3; Table 1). Each reach was sampled monthly on three occasions from July to September 2016 (n=3 x 15 sites per reach). For probabilistic sampling, Minnesota Pollution Control Agency sampled reaches 0 and 1 while Wisconsin DNR sampled reaches 2 and 3 (Figure 1). Discharge data for each site were obtained from the nearest gauging location on the day that water quality sampling occurred. Discharge data presented from Prescott, WI and Winona, MN were obtained from United States Geologic Survey (USGS) gauges. Several of the parameter descriptions were adopted from prior reporting of long-term trends for rivers within Wisconsin (WI DNR, 2006).

Statistical evaluations were performed with the statistical language R 3.02 (R Development Core Team, 2013). Probability distributions of variables were examined and in most cases were highly skewed. Non-parametric Kruskal-Wallis rank sum tests (R function; kruskal.test) and non-parametric multiple test procedures (Package; pgirmess, function; kruskalmc) were used to examine differences between sites and reaches (Giradoux, 2012). Significance levels were set at $p<0.05$. Analytical values below the laboratory limit of detection were set at one-half the limit of detection regardless of the laboratory. The three different labs had different detection limits for parameters in several instances.

Figure 1. Fixed site water quality sampling locations for the CWA Pilot. The location of fixed site water quality sampling locations for the CWA Pilot are denoted in red. Geographic extent of each of the four reaches for the probabilistic sampling portion of the CWA Pilot are indicated by sampling reach. Reach 0 = river mile (RM) 854-811.5; Reach 1 = RM 811.5-763.4; Reach 2 = RM 763.4-714.2; Reach 3 = RM 714.2-693.7. Fifteen randomly selected sites were sampled within each reach during each of the three probabilistic sampling months (July-September; total study n=180 samples).

Table 1: Reach number, reach description, river miles encompassing each reach and reach segment length (in miles).

Reach Number	Reach Name (Description/8-digit HUC code)	River Miles	Segment Length (miles)
0	Assessment Reach 0 (Upper St. Anthony Falls to St. Croix River)	854-811.5	42.5
1	Assessment Reach 1 (Rush-Vermillion) (St. Croix River to Chippewa River/ HUC 07040001)	811.5-763.4	48.1
2	Assessment Reach 2 (Buffalo-Whitewater) (Chippewa River to Lock and Dam 6/ HUC 07040003)	763.4-714.2	49.2
3	Assessment Reach 3 (La Crosse-Pine) (Lock and Dam 6 to Root River/HUC 07040006)	714.2-693.7	20.5

Results and Discussion

Discharge

River discharge is an important driver of water quality. Extreme variability in discharge related to floods and droughts can result in negative consequences for vegetation, fish and wildlife. Shorter-term effects of discharge variability can drive important water quality and physical variables such as water depth, water clarity, water velocity, water temperature, dissolved oxygen and nutrient input.

Substantial differences were observed in discharge among the six fixed sites over the twelve-month sampling period (Figure 2). Discharge increased substantially over the 160-mile study area as major tributaries entered the UMR. The Kruskall-Wallis multiple comparison test showed statistically different discharge tiers. Examination of median discharge values showed roughly a doubling in discharge between Lock and Dam 2 (River Mile; RM 815.6) and Lock and Dam 7 (RM 702.5). The increase between these two sites was largely related to the large discharge contribution from the Chippewa River. The twelve-month fixed site sampling window was characterized by a majority of sampling events occurring during discharge greater than the long-term median at both the Prescott, WI and Winona, MN USGS gauges (Figures 3 and 4). Most samples collected during the three-month probabilistic sampling window (July-September) also occurred during discharge greater than the long-term median.

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Figure 2. River discharge in cubic feet per second (CFS). River discharge in cubic feet per second (CFS) for each of the six fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

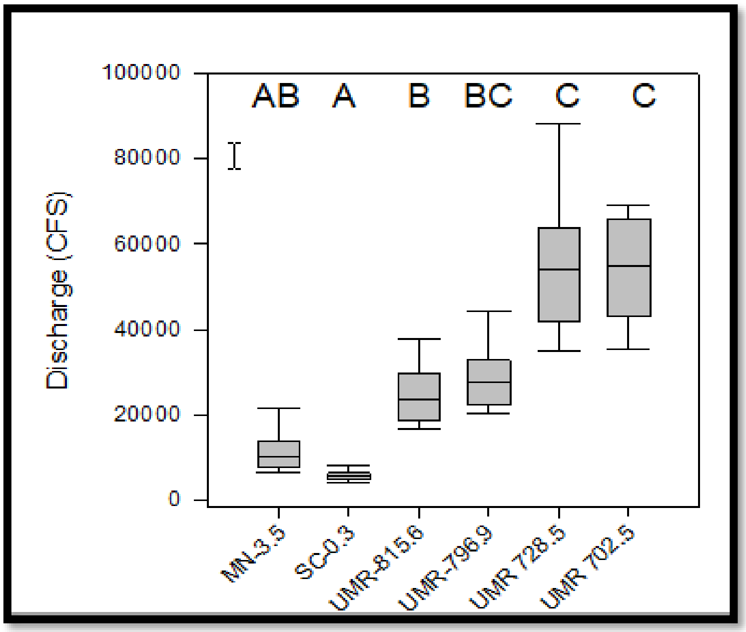


Figure 3. River discharge in cubic feet per second (CFS) over the twelve-month sampling period at the USGS Prescott, WI gauging station. The yellow triangles represent the long-term median discharge on each sampling day over the 89-year period of record.

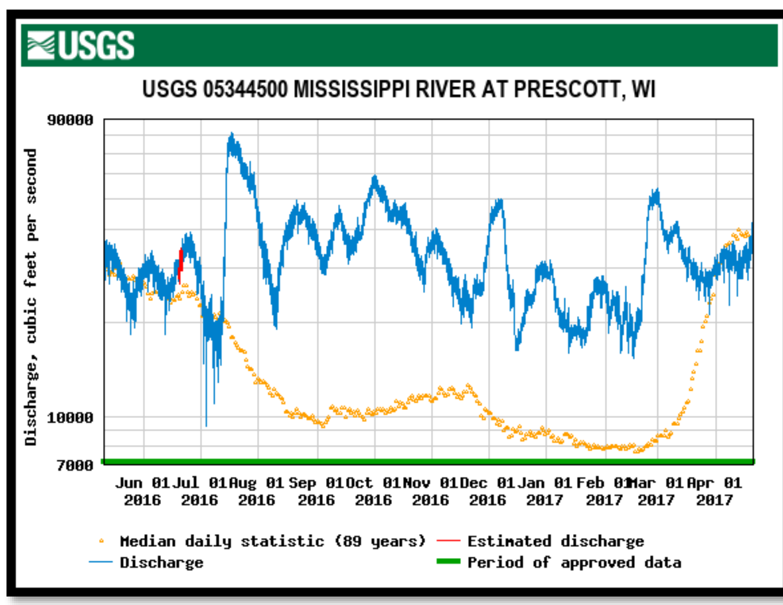
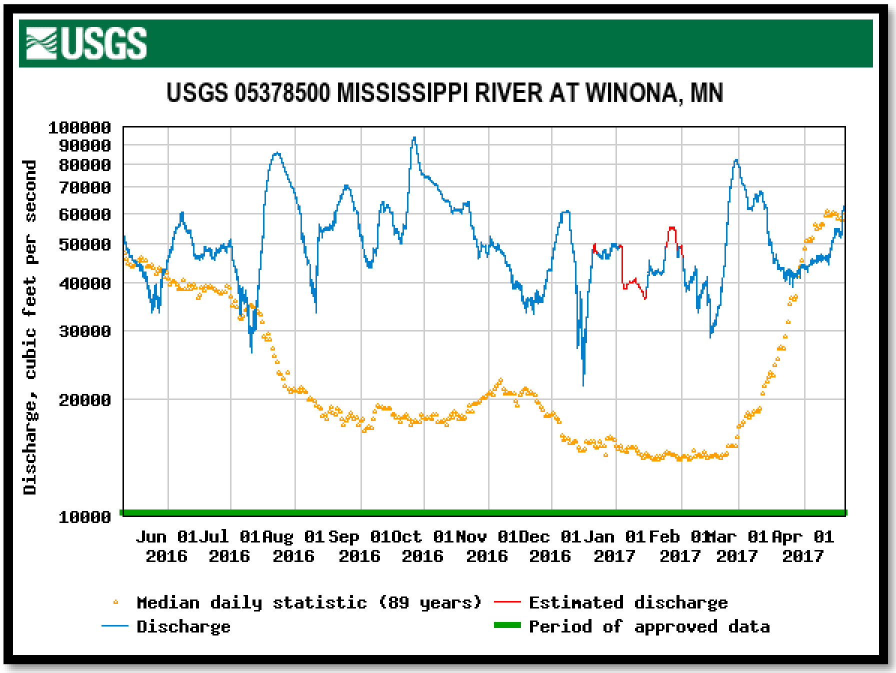


Figure 4. River discharge in cubic feet per second (CFS) over the twelve-month sampling period at the USGS Winona, MN gauging station. The yellow triangles represent the long-term median discharge on each sampling day over the 89-year period of record.



Field Parameters

Water Temperature

Water temperature is an important physical property of water that influences the growth and distribution of aquatic organisms and is an important factor regulating chemical and biochemical reactions. Surface water temperature is strongly influenced by seasonality, local climate and groundwater inflows. Differential heating of water induces thermal stratification, which may affect mixing and other water quality conditions. Wisconsin uses water temperature as an important variable in the designation of fish and aquatic life uses. Water temperature data are useful for interpreting temporal variability. Seasonally adjusted data can be particularly useful in interpreting other water quality data and are used for effluent limits calculations.

The Kruskall-Wallis multiple comparison test failed to show any statistical difference in water temperature among the fixed sites and probabilistic sampling reaches (Figures 5 and 6).

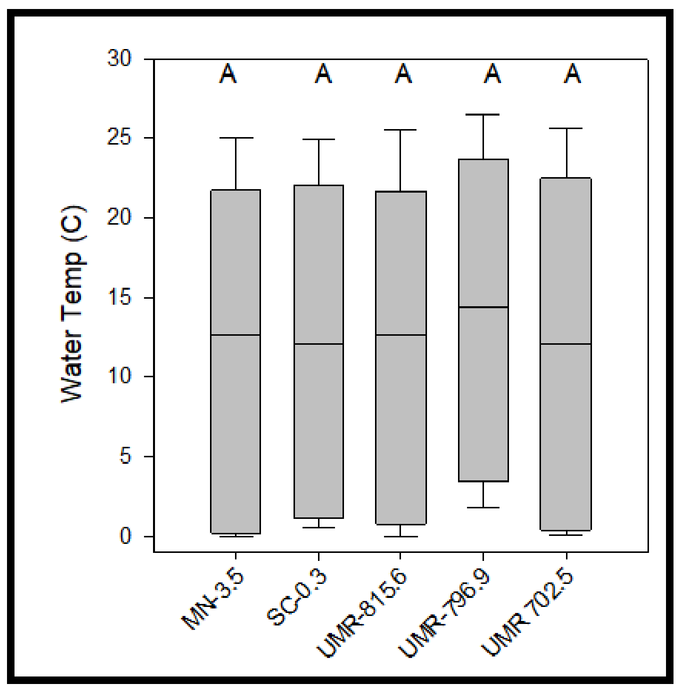


Figure 5. Water temperature (in Celsius) for five of the fixed sites over the twelve-month sampling period (n=12). Data from UMR-728.5 were omitted due to missing data. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Figure 6. Water temperature (in Celsius) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows water temperature by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.

Reach Number	Reach Name (Description/8-digit HUC code)	River Miles	Segment Length (miles)
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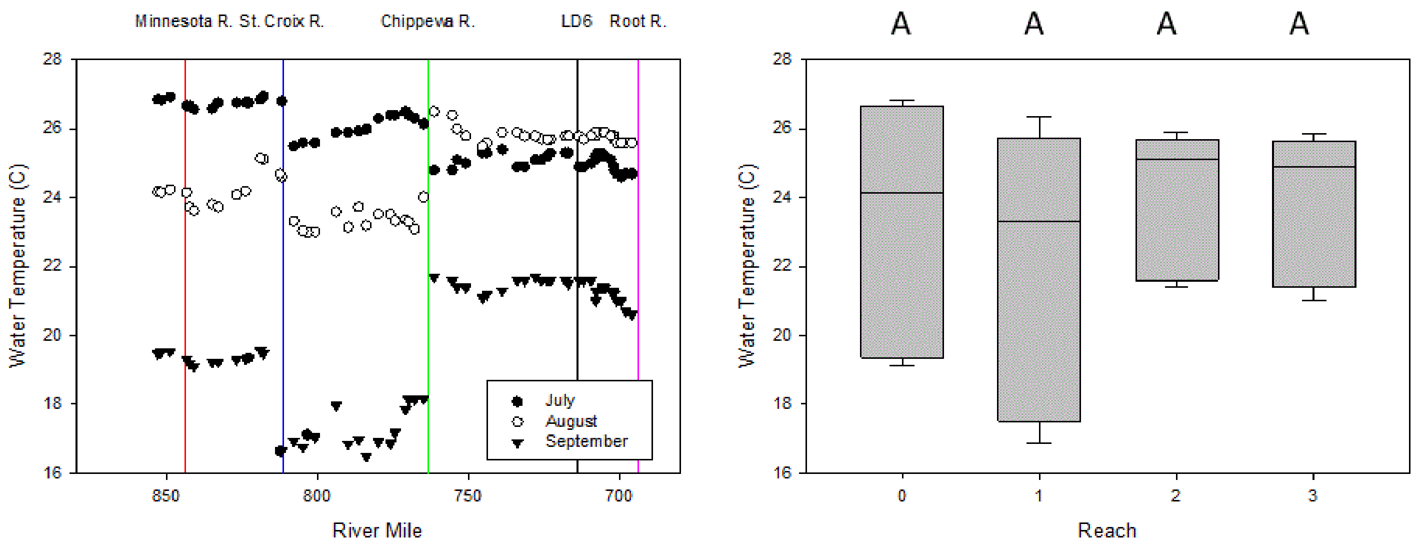


Dissolved Oxygen

Dissolved oxygen (DO) is a gas found in water that is critical for sustaining aquatic life. Dissolved oxygen enters water through mixing with air or through photosynthetic processes via aquatic macrophytes and algae. Decomposition of organic materials, plant respiration and benthic oxygen demand are important factors contributing to DO losses in the aquatic environment. Wisconsin has a minimum criterion of 5 mg/L to protect fish and aquatic life use as prescribed in Chapter NR 102 (Wis. Adm. Code). In addition to DO concentration, DO percent saturation was also examined (sampled at 0.2 m below surface). DO saturation is calculated as the percentage of DO relative to that when completely saturated at a given temperature and pressure. As temperature increases, the concentration at which DO is at 100% saturation decreases.

No significant differences were observed in DO concentrations among the fixed sites sampled (Figure 7). A significant difference in DO concentration and percent of saturation was observed between reach 1 and reaches 0, 2 and 3 during probabilistic sampling (Figures 8 and 9).

Figure 7. Dissolved oxygen (in mg/L) for five of the fixed sites over the twelve-month sampling period (n=12). Data from UMR-728.5 were omitted due to missing data. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

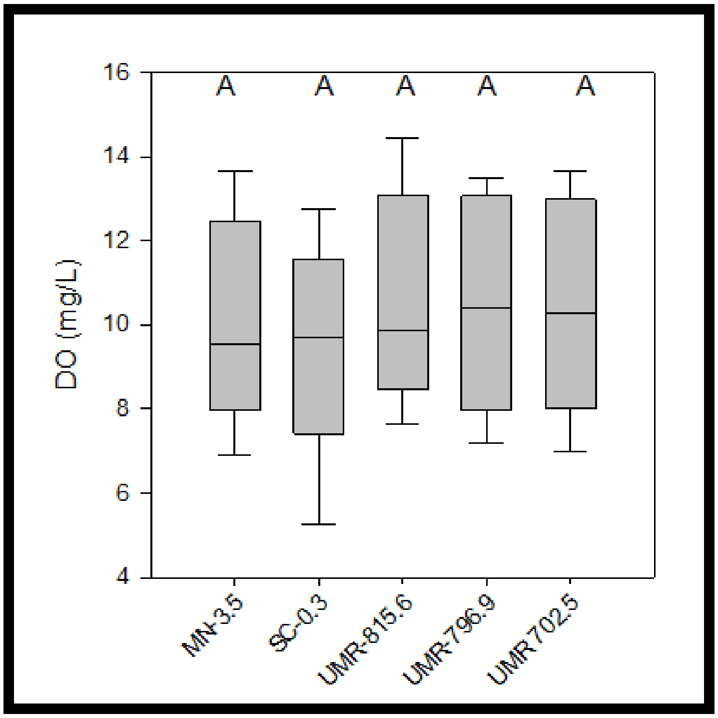


Figure 8. Dissolved oxygen (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows DO by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.

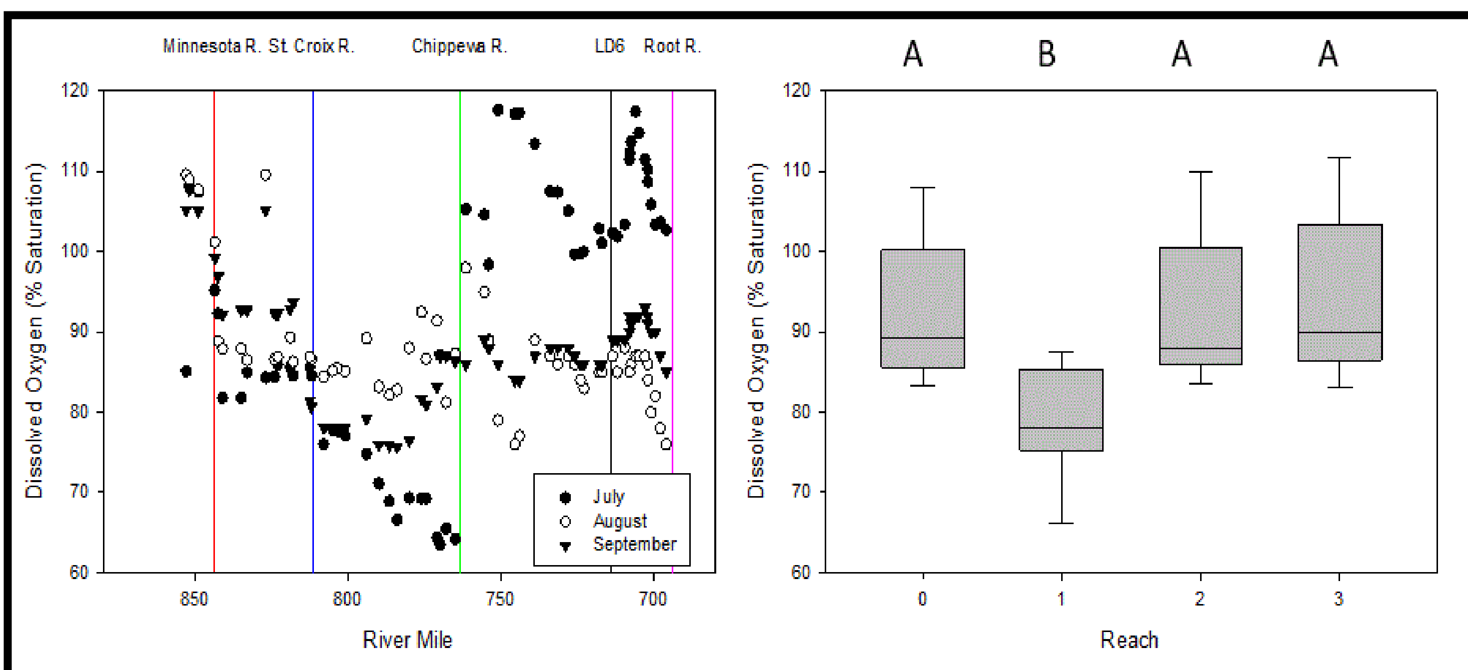
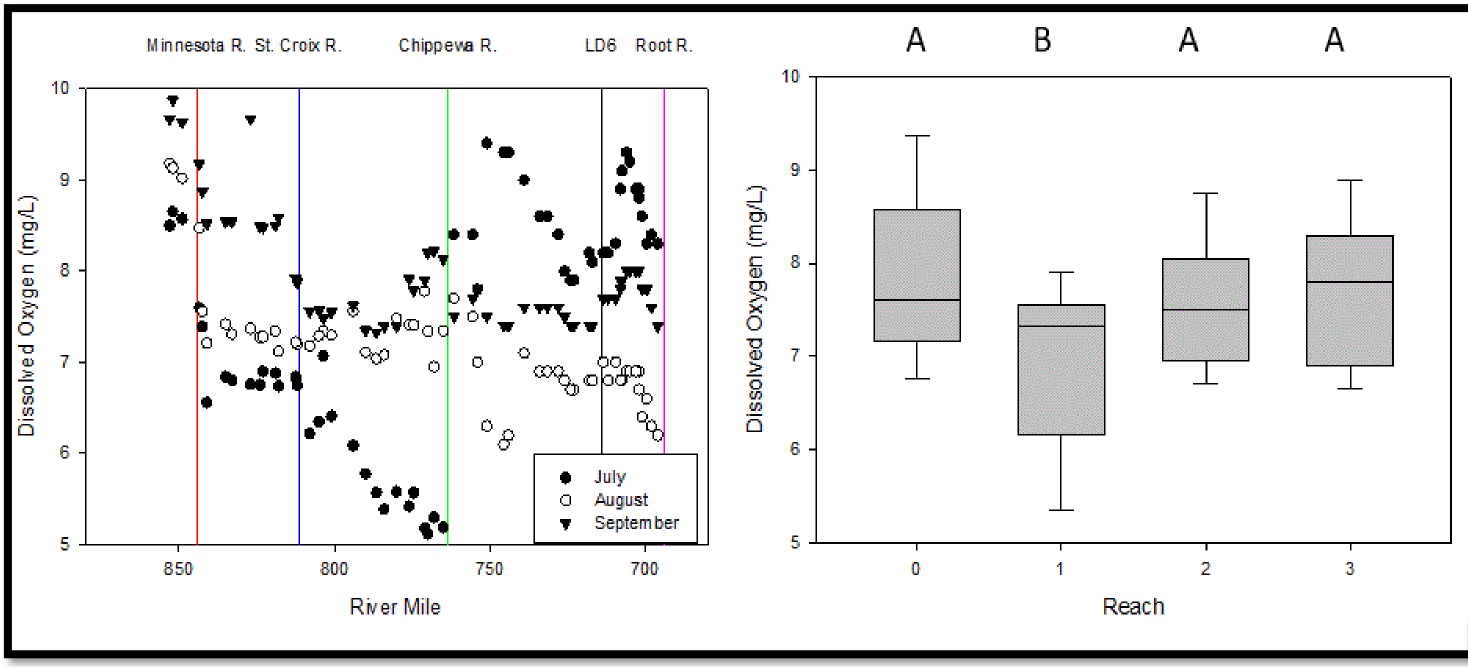


Figure 9. Dissolved oxygen (in % of saturation value) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows percent DO saturation, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.

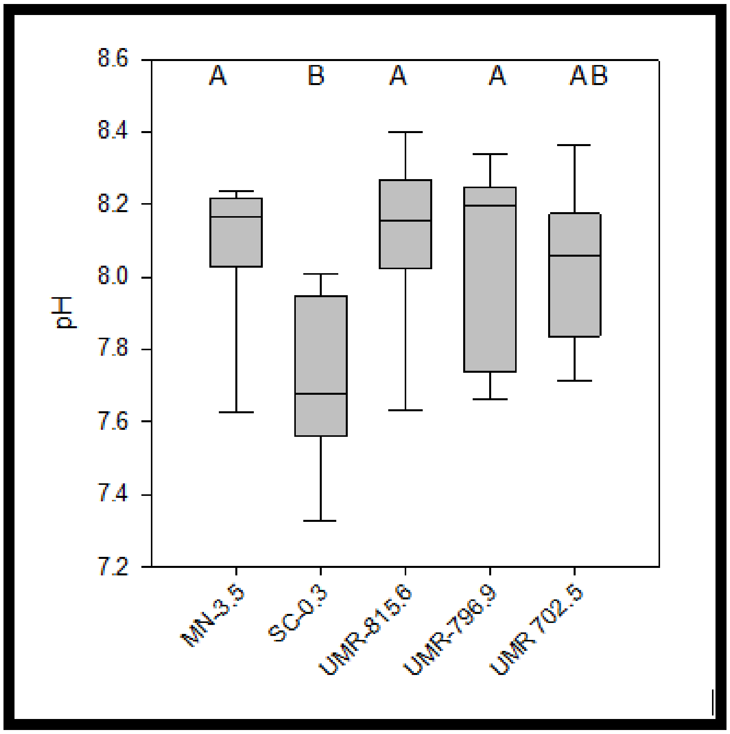


pH

pH is a measure of the hydrogen-ion activity of water and is expressed as a logarithmic unit that ranges from 1 to 14 standard units (su). Waters with high hydrogen-ion activity have low pH and are considered acidic. Dissolved carbon dioxide, carbonic acid, bicarbonate ions and carbonate ions form complex acid-base equilibrium reactions that strongly influence the pH of freshwater systems. pH may exhibit strong diurnal fluctuations associated with carbon dioxide utilization (photosynthesis) or release (respiration) by aquatic plants and algae in poorly buffered (low alkalinity) waters. Dissolved metal ions typically exhibit increasing concentrations with increased acidity and as a result, pH is an important factor influencing toxicity of metals. pH also affects the concentration of un-ionized ammonia nitrogen, a form of reduced nitrogen that is extremely toxic to aquatic life. Wisconsin has adopted a water quality standard that incorporates a range of 6 to 9 units to support aquatic life use.

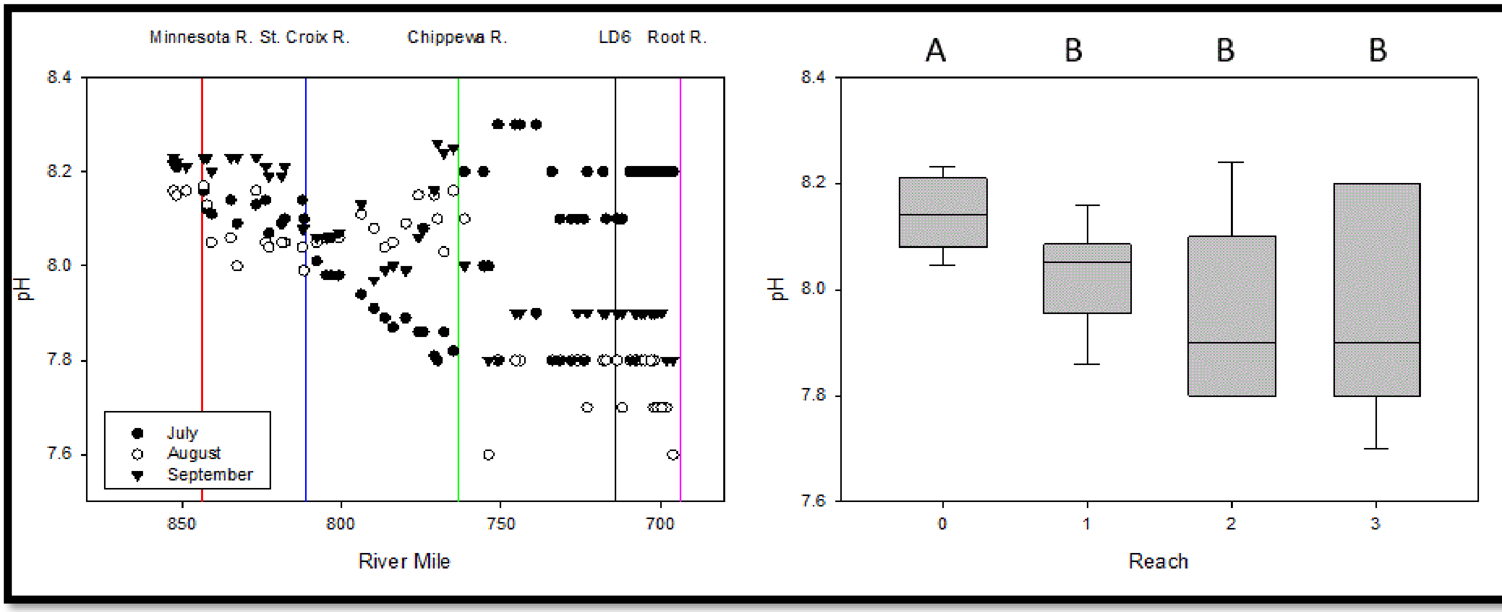
Among the fixed sites, pH at station SC-0.3 on the St. Croix River was significantly different from the Minnesota River and two Mississippi River sites (Figure 10). Significant differences were observed in pH among reaches, with a general decline in pH moving downstream for probabilistic sampling (Figure 11).

Figure 10. pH (in standard units) for five of the fixed sites over the twelve-month sampling period (n=12). Data from UMR-728.5 were omitted due to missing data. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



The beauty of fall colors along the Mississippi River

Figure 11. pH (in standard units) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows pH, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



Conductivity

Conductivity is a measure of water's capacity to conduct an electrical current and varies directly with the dissolved solids content of water. Conductivity increases with increasing temperature; therefore, specific conductance measurements are temperature-adjusted to 25° C to account for the influence of water temperature. Municipal and industrial wastewater or groundwater inflows containing dissolution products of rocks and minerals may contribute to high conductivity values in surface waters. Rainwater or snowmelt runoff contains little dissolved solids and, as a result, usually has low conductance.

Significant differences in conductivity were observed for many of the fixed sites and probabilistic reaches (Figures 12 and 13). A general decline in conductivity was observed as sites progressed downstream.

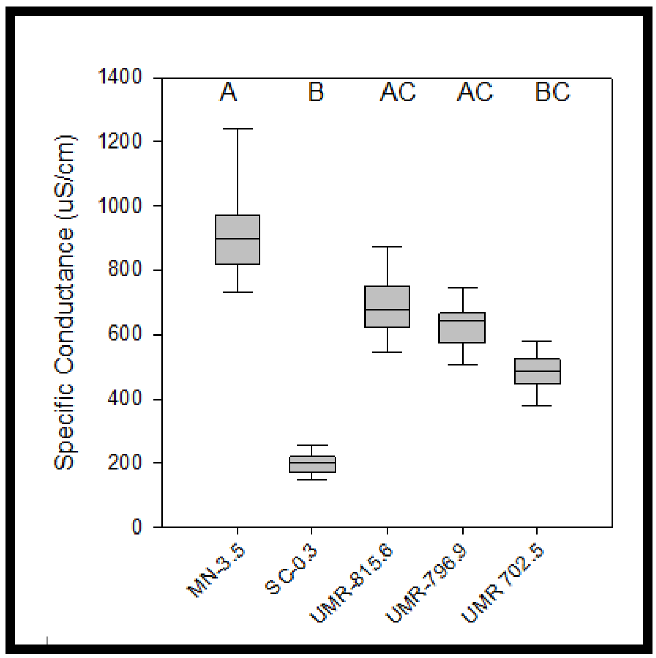
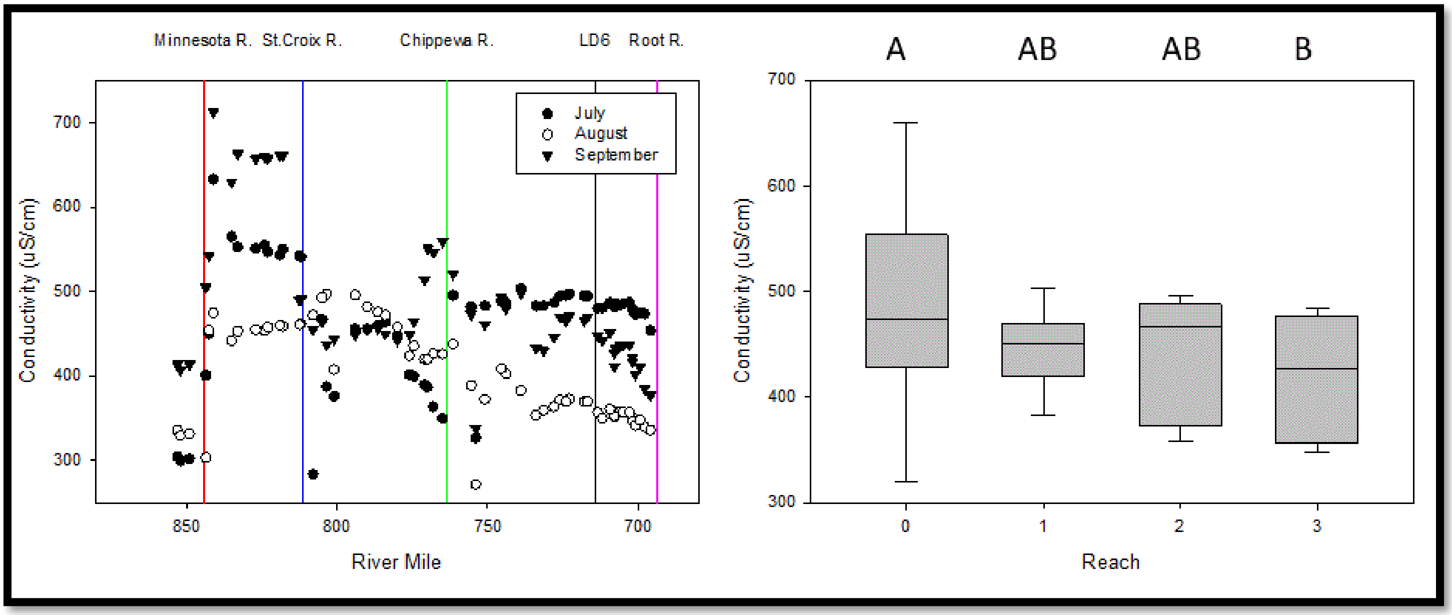


Figure 12. Specific conductance (in uS/cm) for five of the fixed sites over the twelve-month sampling period (n=12). Data from UMR-728.5 were omitted due to missing data. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Figure 13. Specific conductance (in uS/cm) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows conductivity, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



Laboratory Parameters

Total Alkalinity

Total alkalinity is a measure of the buffering capacity of water contributed by bases in solution. Waters that are well buffered resist abrupt changes or fluctuations in pH that may arise from snowmelt runoff and rainfall, which typically have low pH, or by caustic or acidic wastewater inflows. Bicarbonates and carbonates are typically the dominant bases found in surface waters though other anions (hydroxides, borates, silicates, and phosphates) can add additional alkalinity. Total alkalinity is expressed in units of milligrams per liter calcium carbonate though the actual bases contributing to alkalinity are not defined. Waters draining regions of limestone and other sedimentary rocks contain carbonate minerals that contribute to high alkalinity. In contrast, igneous rocks are carbonate-poor and yield low alkalinity values. Low alkaline waters favor methylation of mercury, influence the bioavailability of other metals and may promote greater pH fluctuations due to photosynthetic activity by aquatic macrophytes and algae.

Significant differences in total alkalinity were observed for the majority of fixed sites and probabilistic reaches (Figures 14 and 15). A general decline in alkalinity was observed as sites progressed downriver. All samples for alkalinity were greater than the limit of detection. For laboratory parameters, values below the limit of detection were set at one-half of the detection limit.

Figure 14. Alkalinity (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

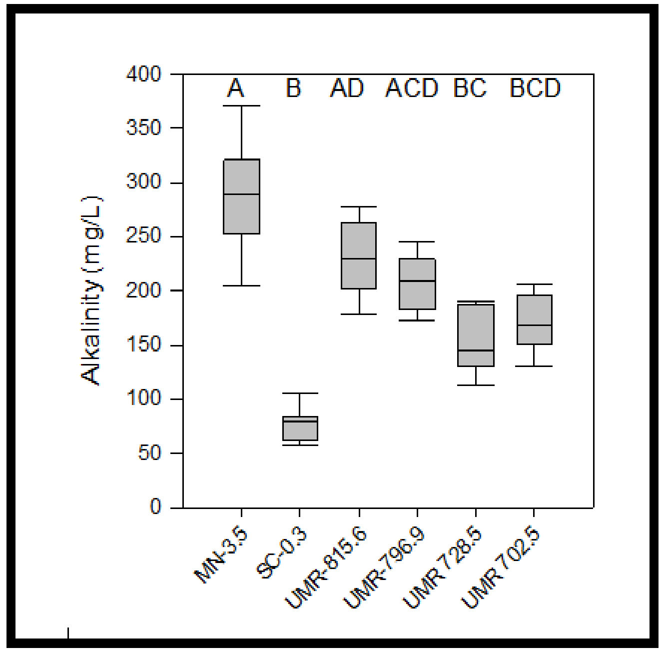
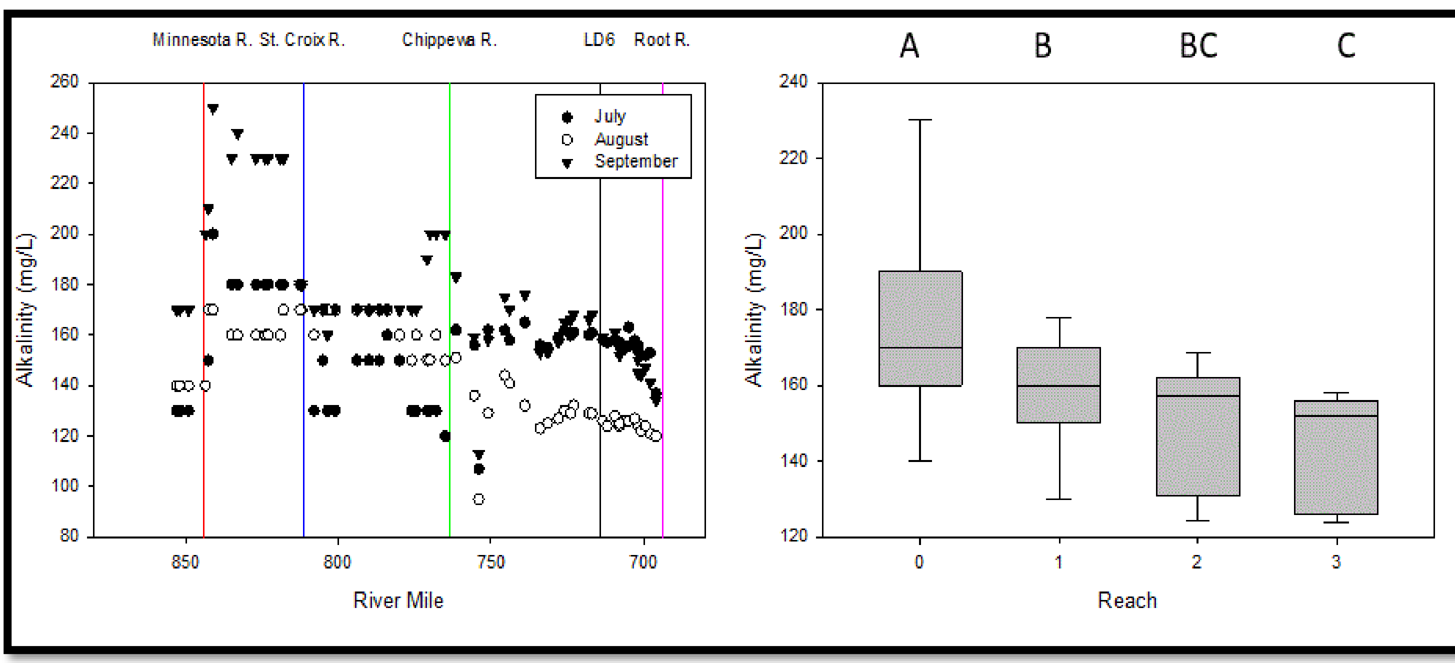


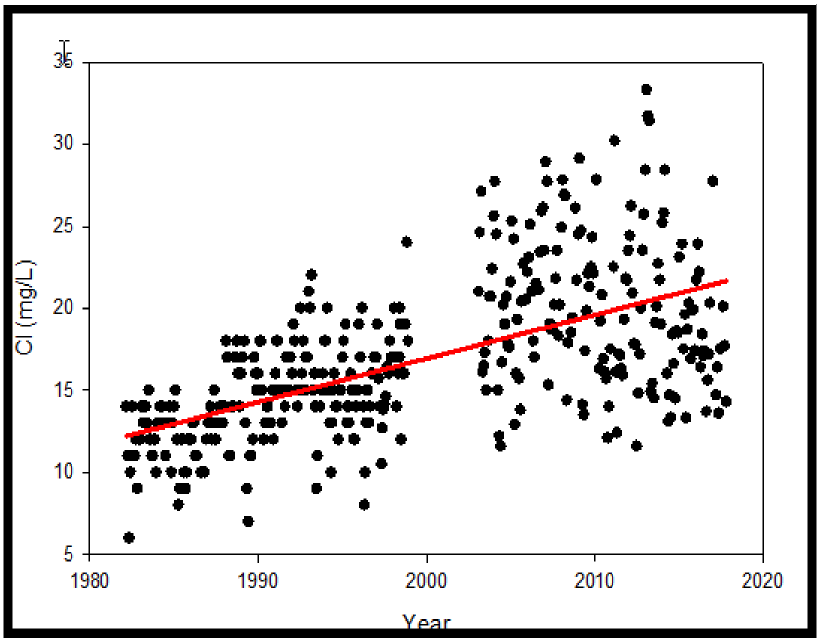
Figure 15. Alkalinity (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows alkalinity, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



Chloride

Chloride is a stable anion of the element chlorine, which is commonly found in surface waters. Natural sources of chloride include sedimentary rocks with formations closely tied to seawater or in enclosed drainage basins. Important anthropogenic inputs to surface waters include road salt runoff and wastewater treatment plant discharges, especially those that are affected by water softening treatments. Wisconsin has established acute and chronic chloride criteria of 757 and 395 mg/L, respectively, to protect fish and aquatic life. Although no exceedances of either the acute or chronic chloride criteria were observed in this study, chloride continues to increase in the UMR on an annual basis. A recent analysis of WDNR long-term trend (LTT) data from Lock and Dam 9 (Lynxville, WI) indicated a 77% increase in chloride concentration between 1982 and 2017 (Figure 16).

Figure 16. Lock and Dam 9 (Lynxville, WI) chloride concentration between 1982 and 2017.



The fixed site data showed significant differences in chloride concentrations among sites, with stark differences between the Minnesota and St. Croix Rivers (Figure 17). The probabilistic data also showed significant differences in chloride concentrations among reaches (Figure 18).

Figure 17. Chloride (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

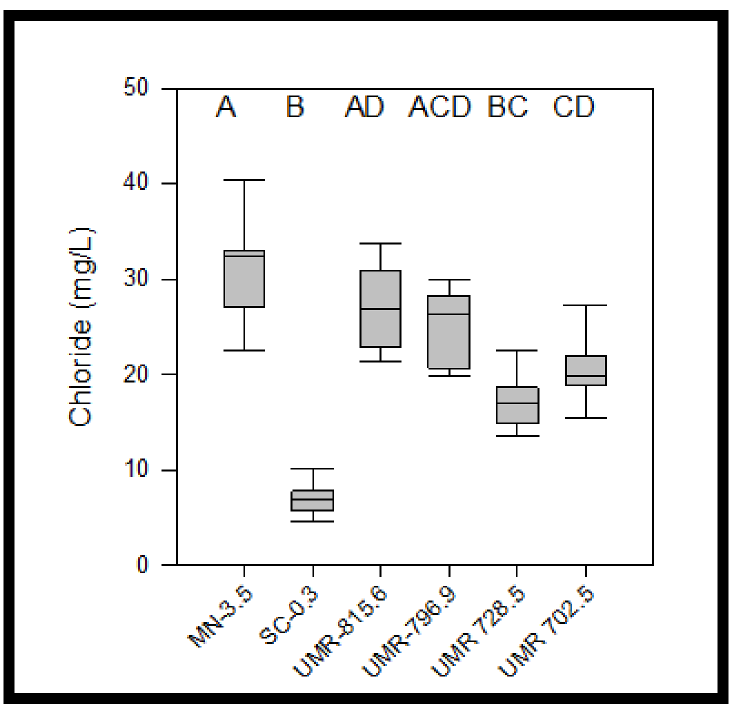
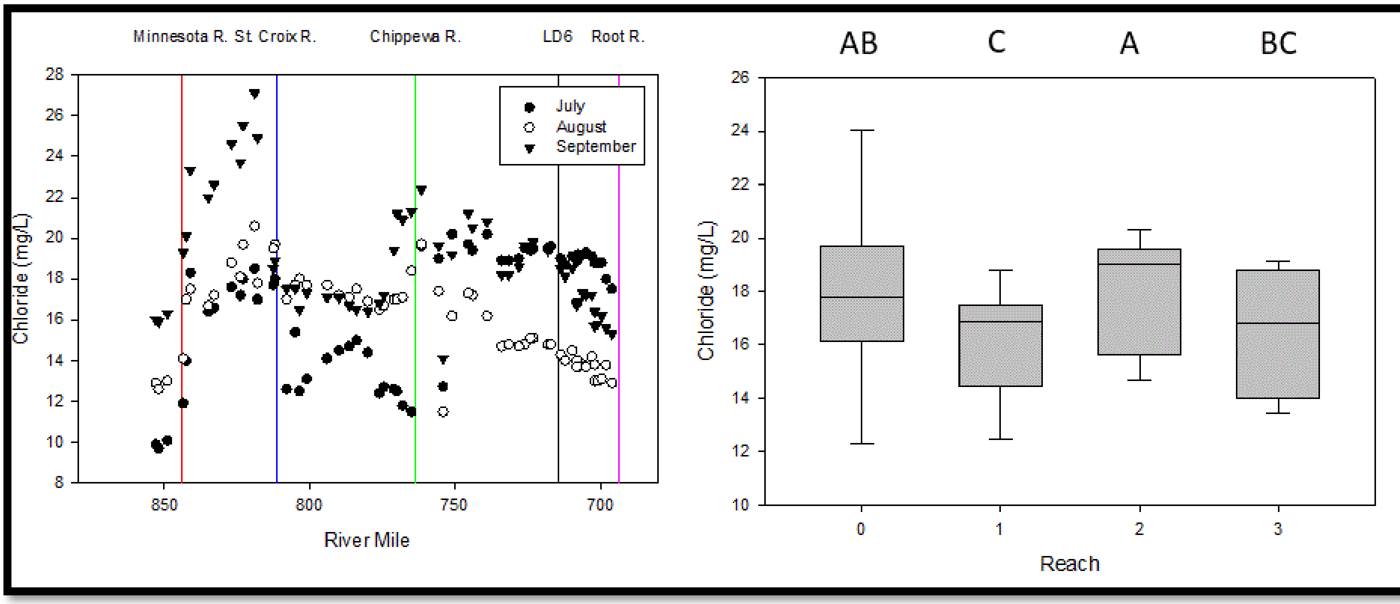


Figure 18. Chloride (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows chloride, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



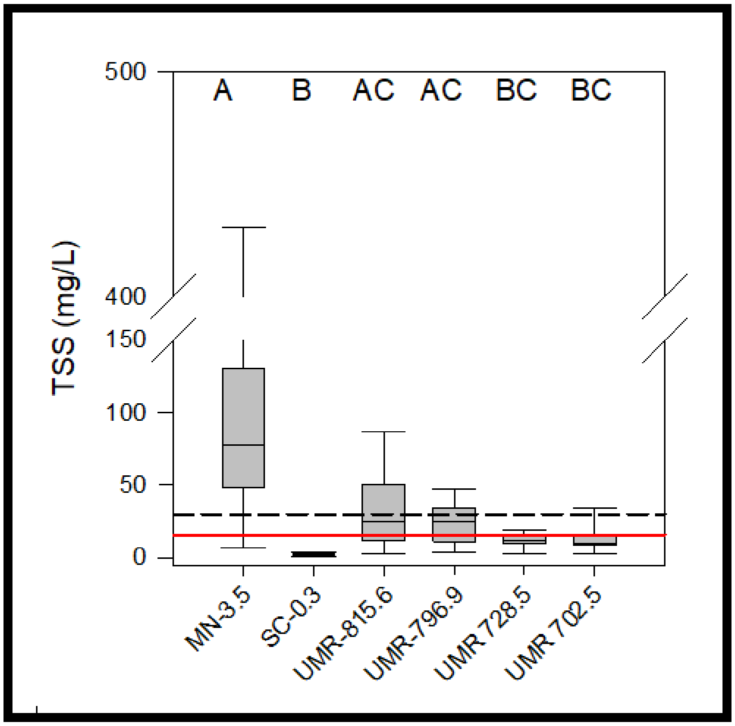
Total Suspended Solids

Total suspended solids (TSS) represent the weight of filtered particulate material in water. Sources of this solid matter may include both inorganic and organic material from soil or stream bank erosion, decaying plant matter, algae, and wastewater discharges. In general, the concentration of TSS increases with increasing river flow due to erosional processes and bed sediment resuspension. TSS in Wisconsin's Rivers tend to increase as the percentage of agricultural land use increases. Particulate material in water strongly limits light penetration, which may have a negative impact on aquatic primary production. Elevated TSS levels may also impair aquatic organisms by blocking gas exchange in membranes used for respiration, interfering with filter feeding mussels or by restricting predation by sight-feeding fish. Prior research for the UMR indicates a threshold of <30 mg/L TSS to sustain submersed vegetation (UMRCC 2003, Giblin et al., 2010). A threshold has also been identified that delineates a shift from native to non-native fisheries assemblage at concentrations exceeding 16 mg/L TSS (Giblin 2017).

For fixed and probabilistic sites, significant differences were observed between most sites and reaches, with TSS concentration decreasing as sites progressed downriver (Figures 19 and 20).

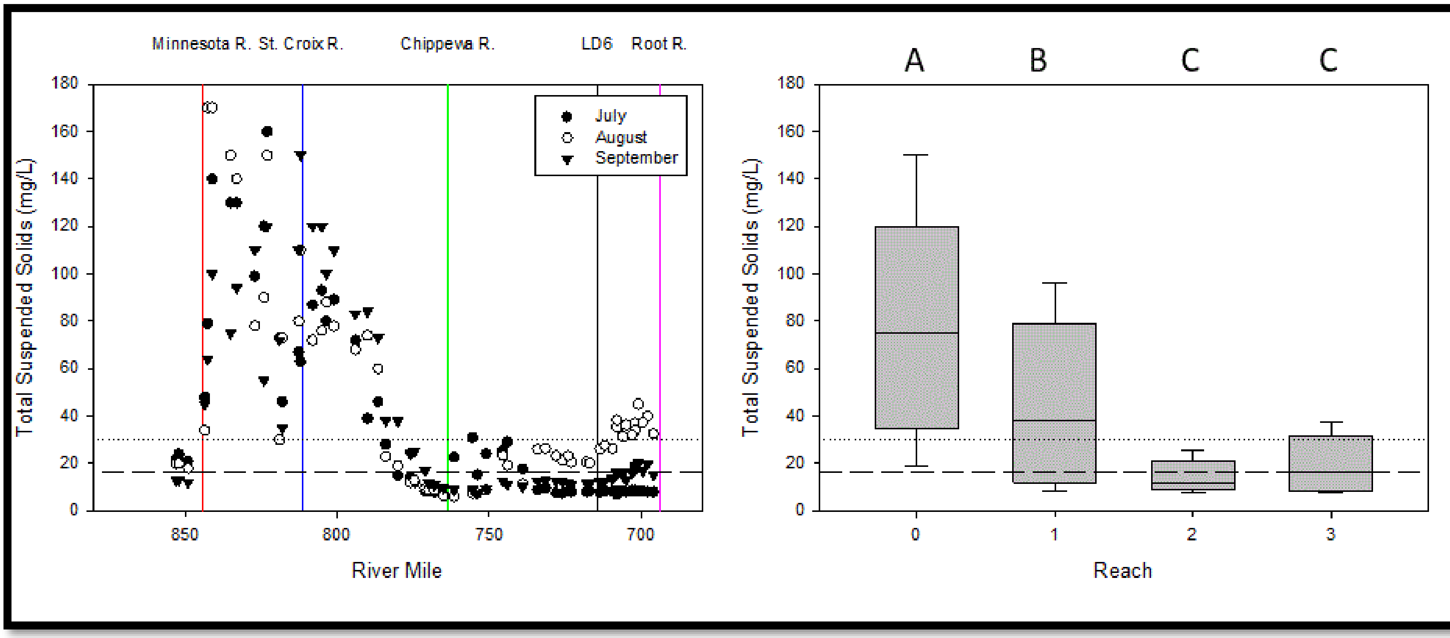
Brady's Bluff View, Mississippi River.

Figure 19. Total suspended solids (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters. The solid red line indicates the TSS threshold delineating a shift from a native to non-native dominated (mean >16 mg/L) fish community (Giblin 2017). The dashed line indicates the threshold (mean <30 mg/L) required to sustain submersed aquatic vegetation in the Mississippi River (UMRCC 2003).



Aquatic life in the Mississippi is truly unique! This flathead catfish, also called the mudcat, flatty, or shovelhead cat, is a large species of North American freshwater catfish. It demonstrates the enormous size this and other aquatic life can reach in the Mississippi.

Figure 20. Total suspended solids (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows TSS, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters. The dashed line indicates the TSS threshold delineating a shift from a native to non-native dominated (mean >16 mg/L) fish community (Giblin 2017). The dotted line indicates the threshold (mean <30 mg/L) required to sustain submersed aquatic vegetation in the Mississippi River (UMRCC 2003).



Nitrogen

Nitrogen (N) in surface water may be present in various organic and inorganic forms and has a complex cycle. Ammonia nitrogen is a reduced form of inorganic N and is usually associated with the decay of organic matter, animal waste runoff or municipal wastewater discharges that lack the nitrification process (conversion of ammonia to nitrate-N). Ammonia nitrogen occurs in water as ammonium and un-ionized ammonia N with both forms represented as total ammonia N (NHx). Un-ionized ammonia N is toxic to aquatic life and its proportion of total ammonia increases at higher pH and temperature. Nitrite and nitrate (NOx-N) are oxidized forms of inorganic N that are present in surface runoff or groundwater discharges from areas dominated with agricultural lands and from municipal wastewater inputs that receive advanced treatment (nitrification). Surface waters generally have little nitrite nitrogen. Organic N includes those forms of nitrogen that are "combined" into various organic molecules such as proteins, amino acids and other cellular materials.

Organic N in surface waters may be present as suspended particulate matter or as dissolved organic molecules. In sediments, bacteria may convert organic and inorganic nitrogen to molecular N though the processes of ammonification and denitrification. Nitrogen is an important plant nutrient and has been used in agricultural fertilizers to stimulate the production of agricultural crops. In oxygenated surface waters, the dominant form of nitrogen is normally nitrate nitrogen. As a result, total nitrogen concentrations closely follow the patterns and trends exhibited by nitrate nitrogen. Excessive nitrogen inputs from the Mississippi River basin to the Gulf of Mexico have been implicated in nutrient enrichment and hypoxia problems in the Gulf of Mexico (Rabalais et al. 2002). Wisconsin has adopted acute and chronic criteria for total ammonia N in Chapter NR 105 (Wis. Adm. Code) that varies as a function of pH, water temperature and aquatic life use. For surface waters serving as a source-water for drinking water, the maximum nitrate-N criterion is 10 mg/L. Nitrate-N is the dominant form of nitrogen in surface water and can be linked to agricultural land use and wastewater inputs.

For fixed site total nitrogen (TN), significant differences were observed between the Minnesota River, St. Croix River and UMR sites (Figure 21). For probabilistic sampling, some significant differences were observed for TN, with generally declining concentration as sampling sites progressed downriver (Figure 22). The majority of TN samples were in the eutrophic range (>1.5 mg/L) described by Dodds et al. 1998. For fixed site NOx, significant differences were observed between the Minnesota River and St. Croix River (Figure 23). For probabilistic sampling, significant differences were observed between reaches 0 and 2 for NOx, with generally declining concentration as sampling sites progressed downriver (Figure 24). For NHx, significant differences were not observed among the fixed sites. For probabilistic sites, significant differences were observed for NHx among some reaches, but these results should be viewed with some caution as the MPCA lab had a higher detection limit (0.05 mg/L) than the WI DNR lab (0.015 mg/L; Figures 24-25).

Figure 21. Total nitrogen (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters. The red line delineates the lower boundary for eutrophic condition (>1.5 mg/L) described by Dodds et al. 1998.

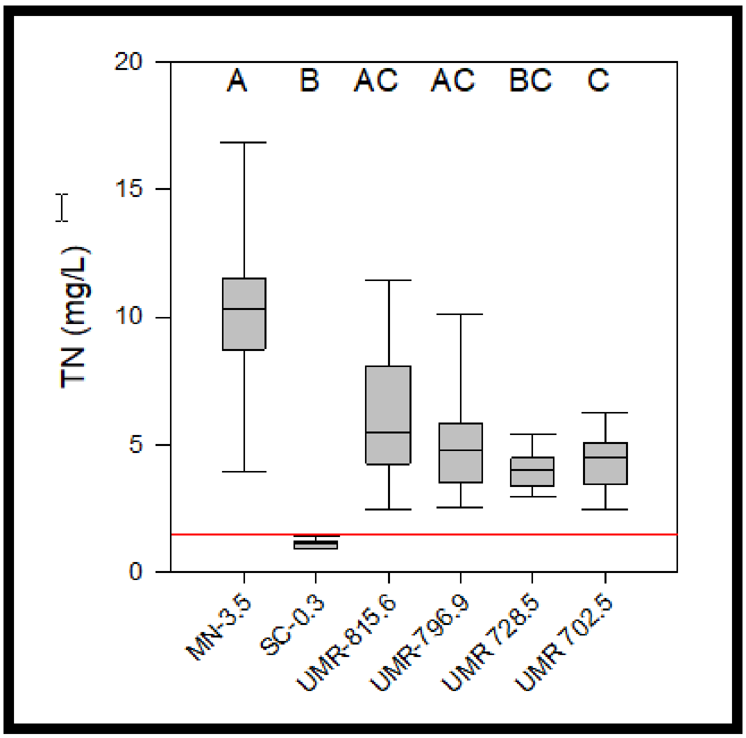


Figure 22. Total nitrogen (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows TN, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters. The dashed line delineates the lower boundary for eutrophic condition (>1.5 mg/L) described by Dodds et al. 1998.

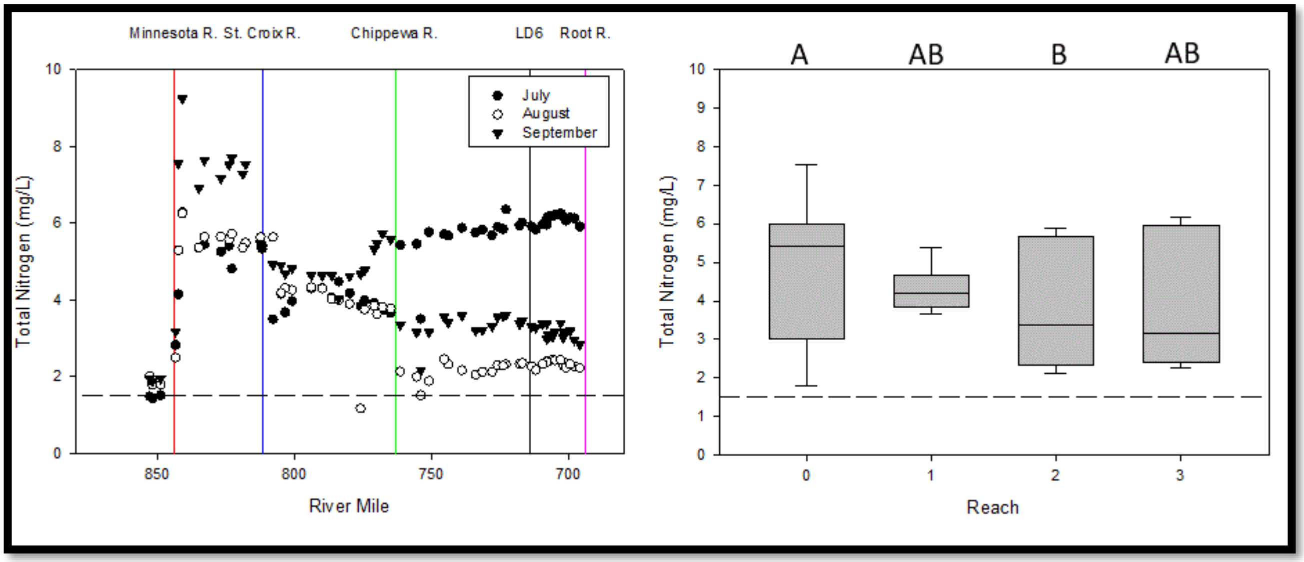


Figure 23. Nitrate+Nitrite-N (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

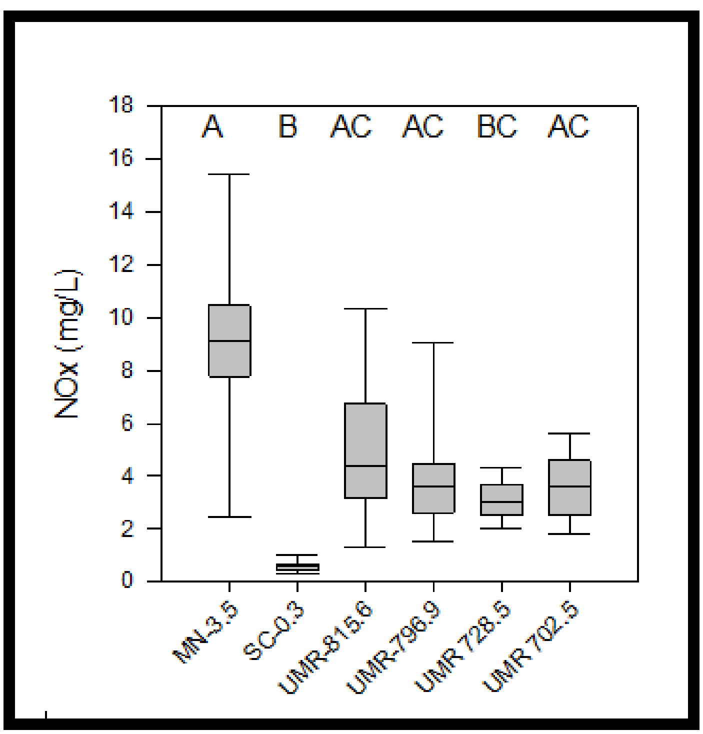


Figure 24. Nitrate+Nitrite-N (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows NOx, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.

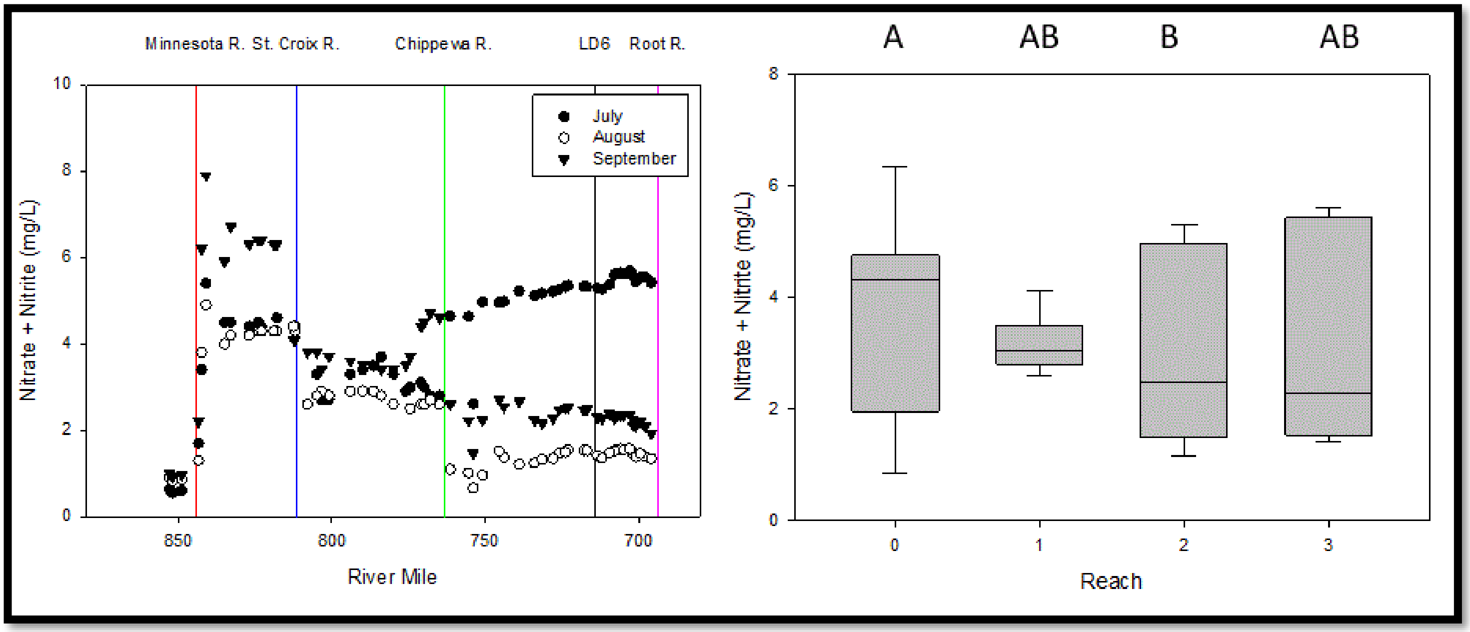


Figure 25. Total ammonia-N (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

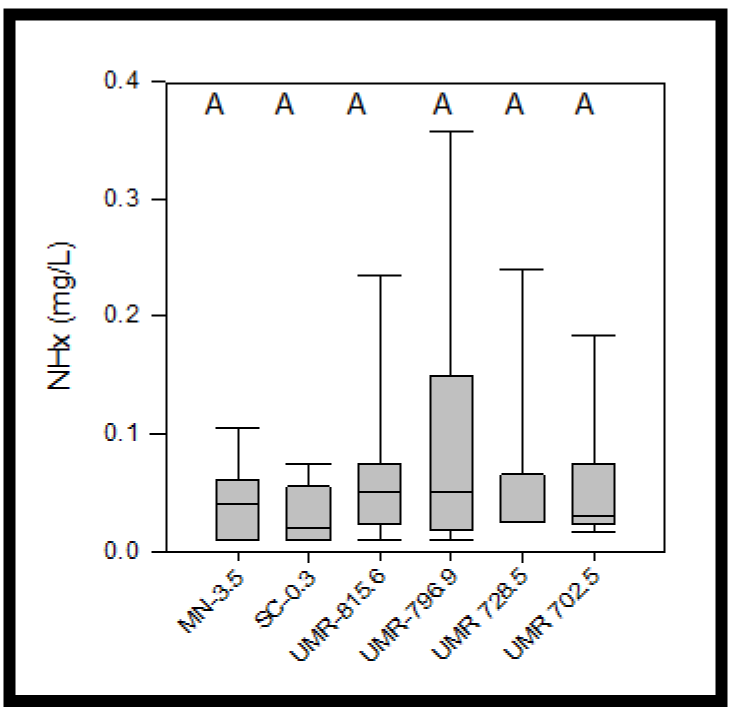
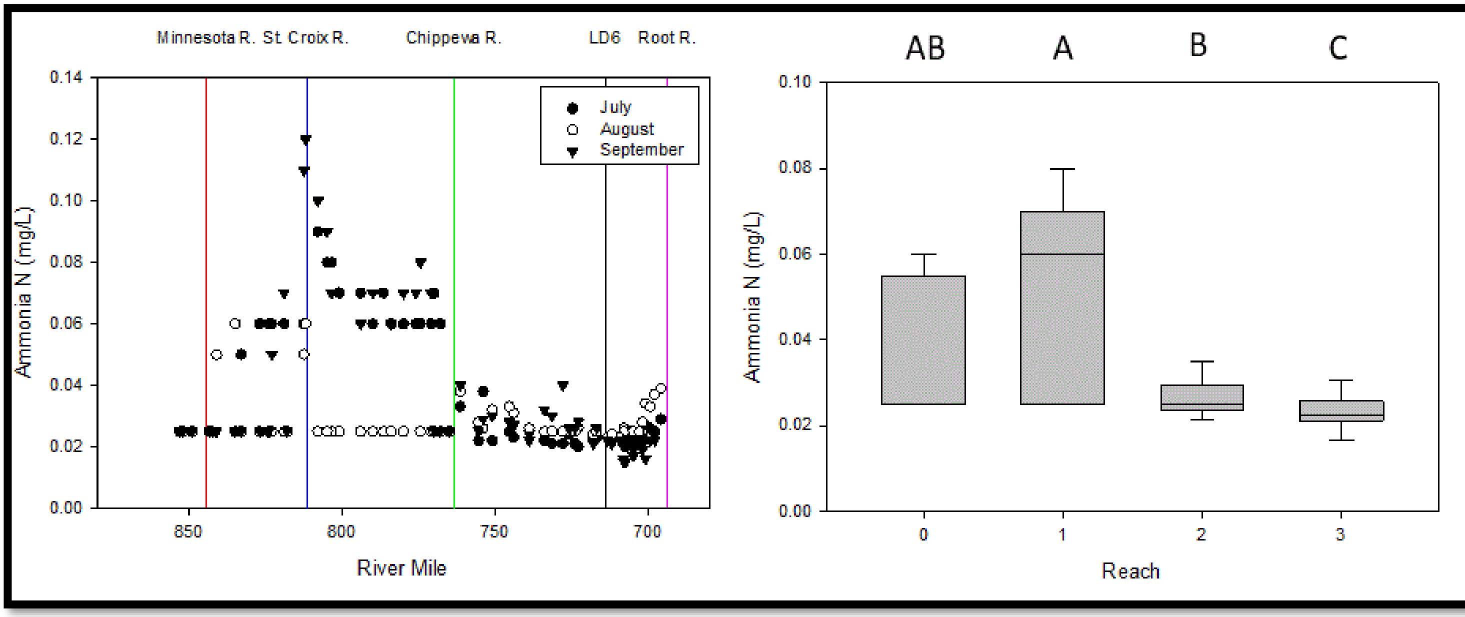


Figure 26. Total ammonia-N (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows NHx, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters. These results should be viewed with caution due to values below the detection limit for reaches 0 and 1.



Phosphorus

Like nitrogen, phosphorus (P) is an essential plant nutrient and is normally the major element affecting eutrophication in freshwater systems. Phosphorus can be measured in several forms, but total P and dissolved inorganic P (reactive or ortho-P) are the forms most commonly measured in water quality monitoring programs. Although dissolved inorganic P is more directly available for plant uptake, this form of phosphorus may cycle quickly in aquatic systems and may often be assimilated by plants in excess of nutritional needs (luxury consumption). Phosphorus sources are similar to those reported for nitrogen. However, phosphorus tends to bind or adsorb to particulate material and is normally not found in high concentrations in groundwater. Wisconsin has a total phosphorus concentration criterion of 0.1 mg/L P for non-wadeable rivers to prevent eutrophication problems such as severe algal blooms and nuisance plant growth (Wis. Adm. Code NR 102.06).

Numerous statistical differences were observed among sites and reaches for TP and dissolved P. The Minnesota River site tended to be notably high for total phosphorus. Nearly all water samples exceeded the non-wadeable river total phosphorus criterion (> 0.1 mg/L TP). A general trend of decreasing TP concentration was observed as sampling sites progressed downriver, with a slight increase in concentration at site UMR-702.5 (Figure 27). The probable cause for the increase in TP upstream of site UMR-702.5 is high phosphorus from Driftless Area rivers, such as the Trempealeau River, emptying to the UMR upstream. For probabilistic sampling, significant differences did exist among the reaches, with a general TP decrease as sampling sites progressed downriver (Figure 28). For dissolved P, a significant difference was observed between the Minnesota River and the St. Croix River for the fixed sites (Figure 29). Among the probabilistic sites, dissolved P tended to show a general decline as sites progressed downriver (Figure 30).

Figure 27. Total phosphorus (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters. The red line denotes the total phosphorus, non-wadeable river criterion (< 0.1 mg/L total phosphorus) for Wisconsin.

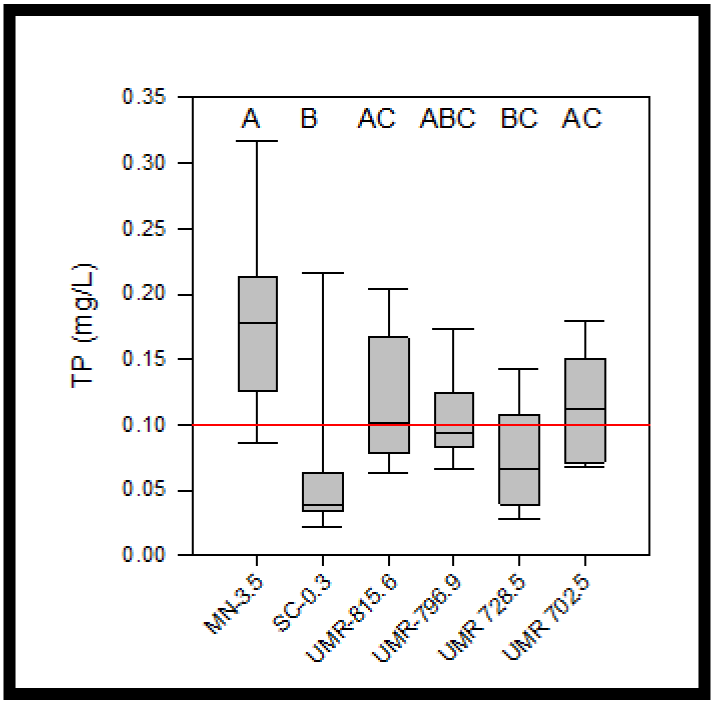


Figure 28. Total phosphorus (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows TP, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters. The dashed line denotes the total phosphorus, non-wadeable river criterion (< 0.1 mg/L total phosphorus) for Wisconsin.

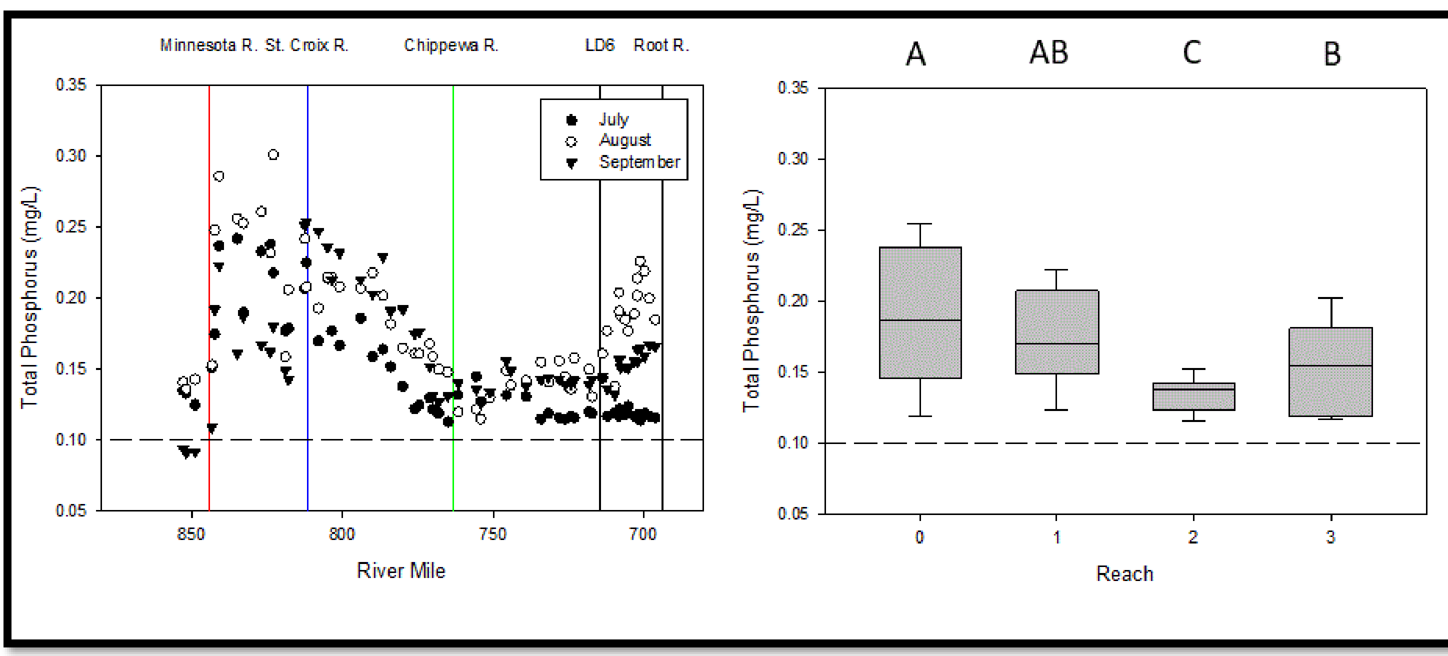


Figure 29. Dissolved phosphorus (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

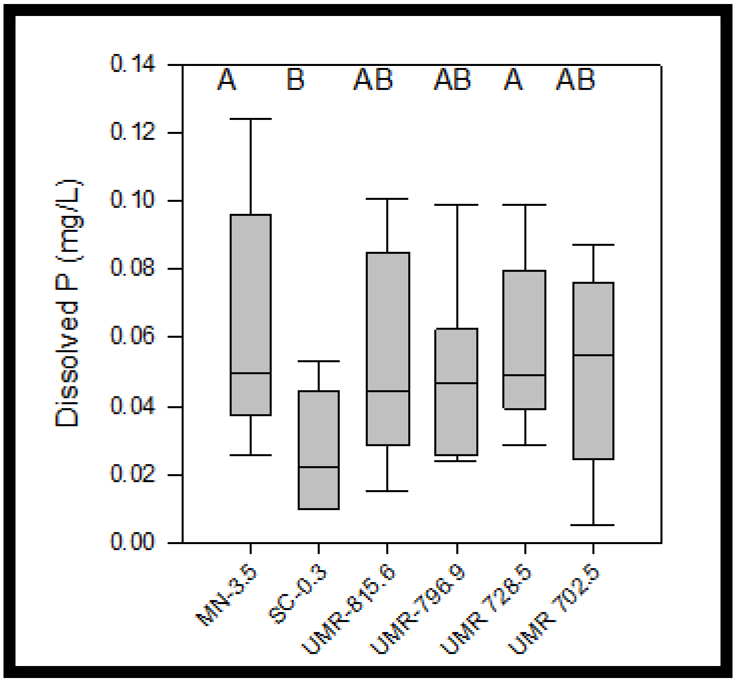
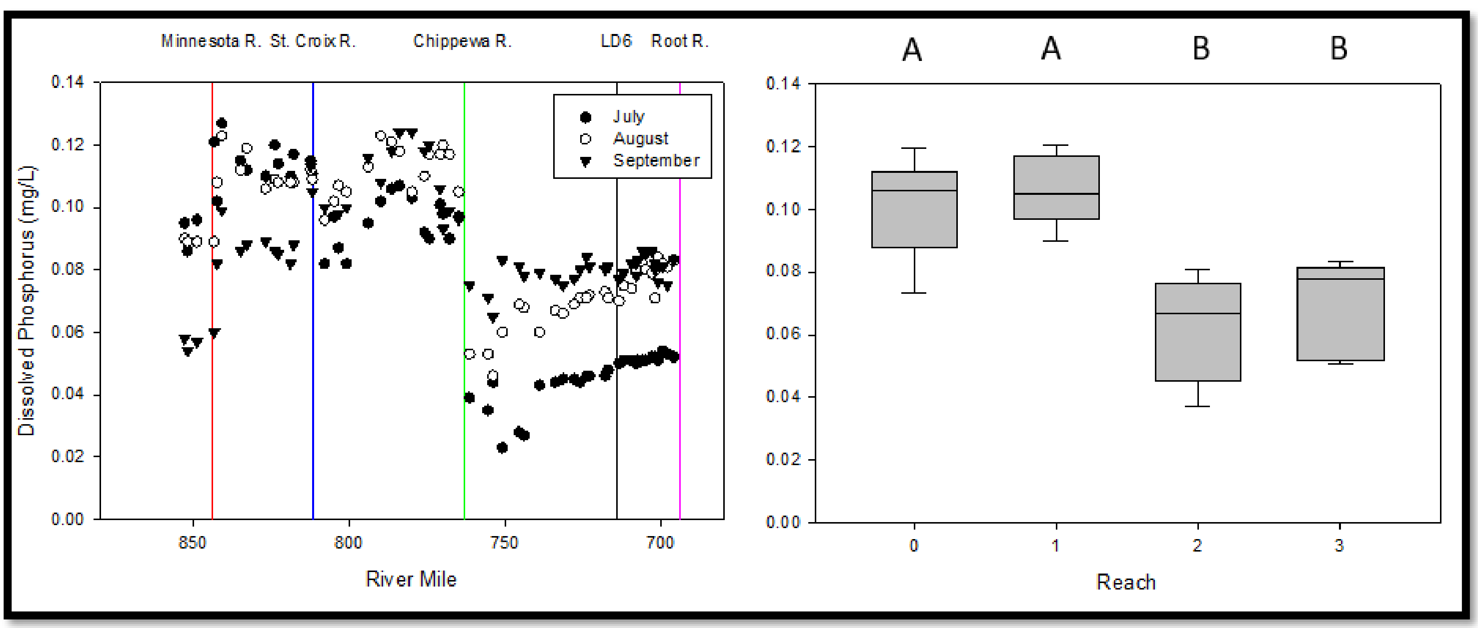


Figure 30. Dissolved phosphorus (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows dissolved P, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



Chlorophyll *a*

Chlorophyll *a* (CHLa) is a major plant pigment and provides an indication of the biomass of algae that is present in water. Excessive algae growth may develop in lakes, impoundments, and slow-moving rivers, like the Mississippi, that are overly enriched with N and P. Chlorophyll analysis provides a way to quantify eutrophication impacts. Chlorophyll pigments are extracted from water samples that may contain a diverse phytoplankton community including diatoms and other chrysophytes, green algae, and cyanobacteria (bluegreen "algae"). However, most serious nuisance algae problems are generally attributed to several members of the bluegreen algae family that may form surface blooms during the warm summer months in eutrophic waters. Wisconsin is proposing 20 ug/L CHLa as a threshold for "moderate algal blooms" not to be exceeded on more than 30% of days during the summer months. Surveys of public perception indicate that algal blooms exceeding 20 ug/L result in reduced enjoyment among one-half of Wisconsin lake users. Algal blooms greater than 60 ug/L CHLa are defined as severe nuisance blooms (Heiskary and Walker 1995).

CHLa was one of the few parameters that showed differing signals for fixed and probabilistic sampling (Figures 31 and 32). The probabilistic data showed an increasing trend in CHLa as sites progressed downriver. This trend, the opposite of the fixed sites, was likely tied to increased summer turbidity due to elevated precipitation and discharge shading out phytoplankton in the upstream reaches during probabilistic sampling. Probabilistic reaches two and three were sampled in early-July prior to major mid-summer flooding, whereas reaches 0 and 1 were sampled after the flooding (Figures 3 and 4). The major differences in the probabilistic July data likely accounted for the statistical differences in the probabilistic data.

Figure 31. Chlorophyll a (in ug/L) for five of the fixed sites over the twelve-month sampling period (n=12). Data from UMR-728.5 were omitted due to missing data. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters. The red line indicates the proposed threshold (> 20 ug/L) to denote a "moderate algal bloom" for rivers in Wisconsin. The dashed line indicates the threshold for a severe nuisance bloom (> 60 ug/L) described by Heiskary and Walker (1995).

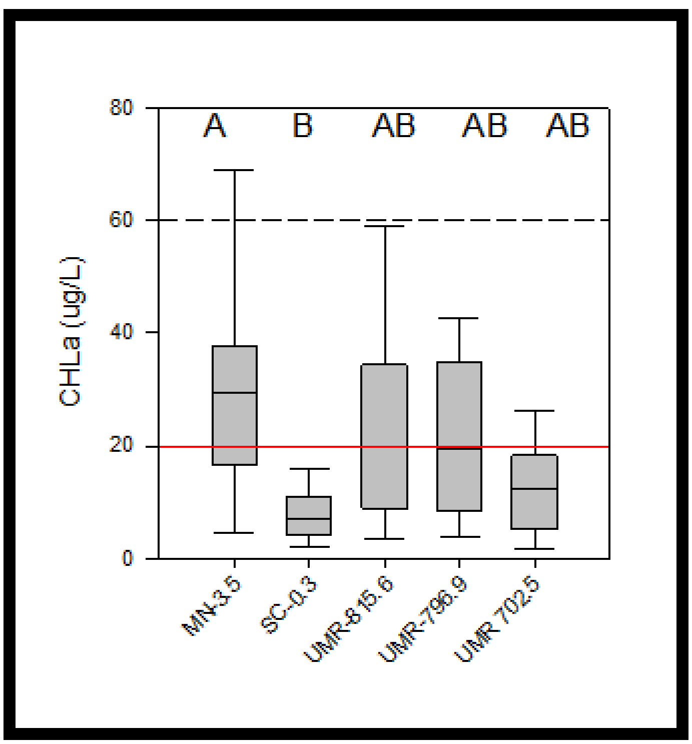
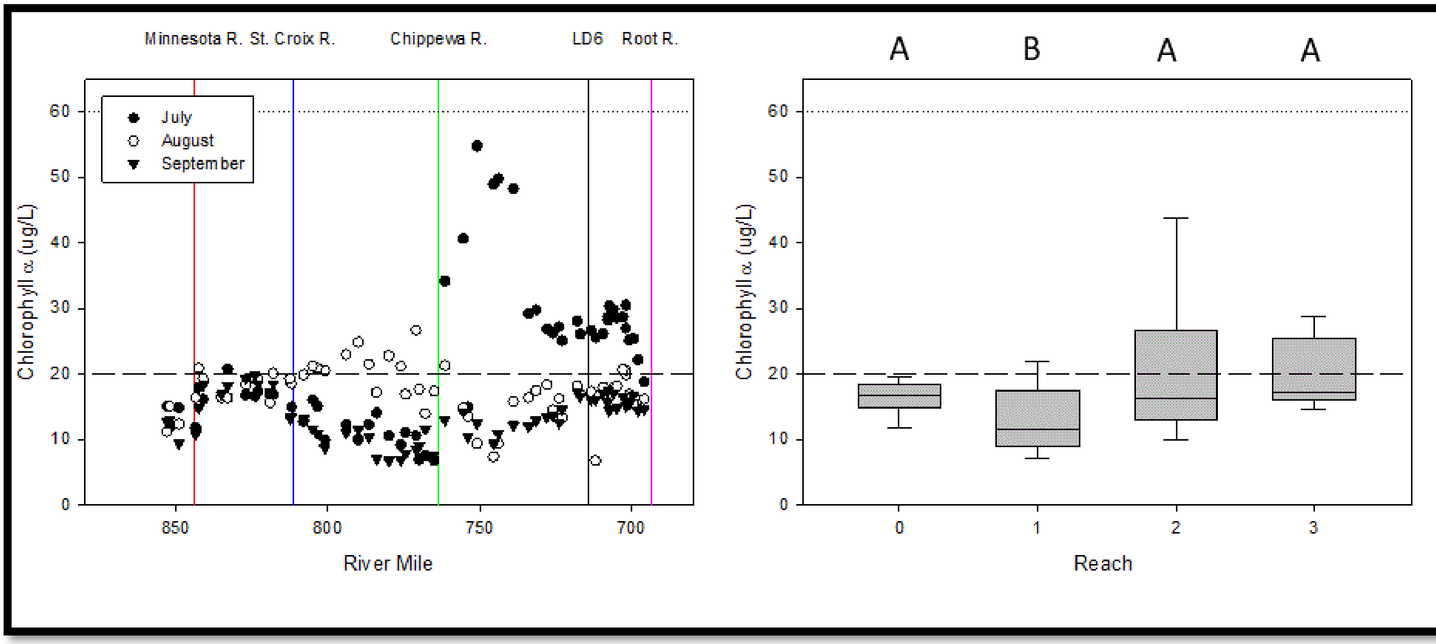


Figure 32. Chlorophyll a (in ug/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows CHLa, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters. The dashed line indicates the proposed threshold (> 20 ug/L) to denote a "moderate algal bloom" for rivers in Wisconsin. The dotted line indicates the threshold for a severe nuisance bloom (> 60 ug/L) described by Heiskary and Walker (1995).

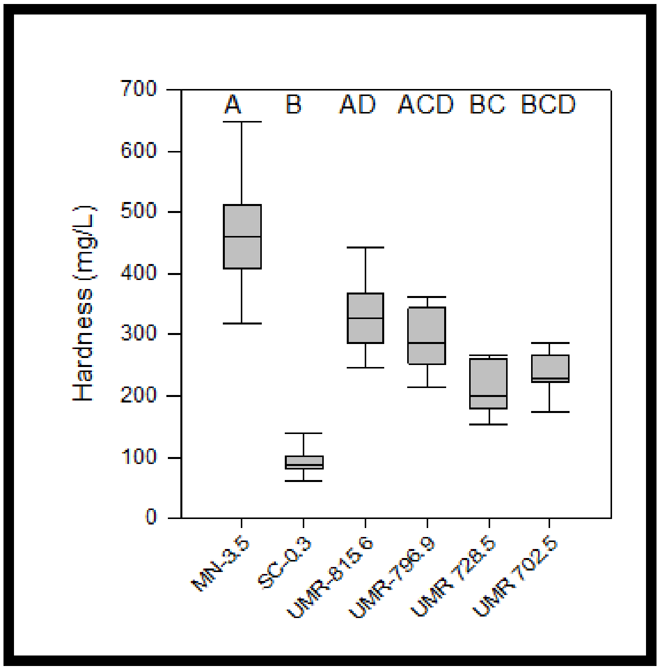


Total Hardness

A high level of hardness in water can interfere with the cleaning effectiveness of detergents and can result in precipitates (hard water stains) when the water is heated. Hardness is an important property of water that influences the toxicity of some metals. Waters with low hardness increase the bioavailability of metals and as a result, water quality criterion concentrations for many metals are lower as compared to waters with high hardness. Receiving water hardness information is necessary for the calculation of water quality based effluent limits for wastewater containing regulated metals. Calcium and magnesium are the primary ions contributing to hardness and their combined concentrations are used to derive a value for total hardness. As with alkalinity, hardness is expressed as equivalent concentrations of calcium carbonate.

Significant differences existed among the fixed sites (Figure 33). Hardness in the Minnesota River was notably high, and the St. Croix River was notably low. For the UMR sites, a general decrease in hardness was observed as sites progressed downriver.

Figure 33. Hardness (in mg/L) for fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



E. coli

Escherichia coli (*E. coli*) is a bacterium often used as water quality indicator. The presence of *E. coli* indicates fecal contamination of the waterbody. The presence of *E. coli* can indicate that other disease-causing organisms, in addition to *E. coli*, are present. Animal (including livestock, pets and wildlife) and human sewage are possible sources of *E. coli* bacteria. The Environmental Protection Agency (EPA) considers the acceptable *E. coli* level to be <126 colony forming units/100 mL measured as a geometric mean over a 30-day period (EPA 2015).

For fixed sites, a statistical difference was observed between the Minnesota and St. Croix Rivers (Figure 34). For probabilistic sites, a statistical difference was observed between reach 0 and reaches 1, 2 and 3. In general, *E. coli* concentration tended to decline as sites progressed downriver.

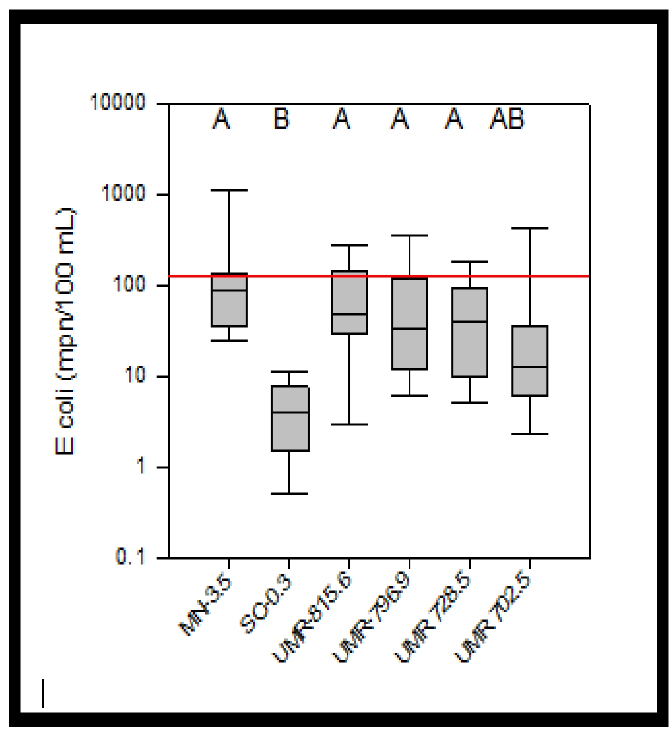
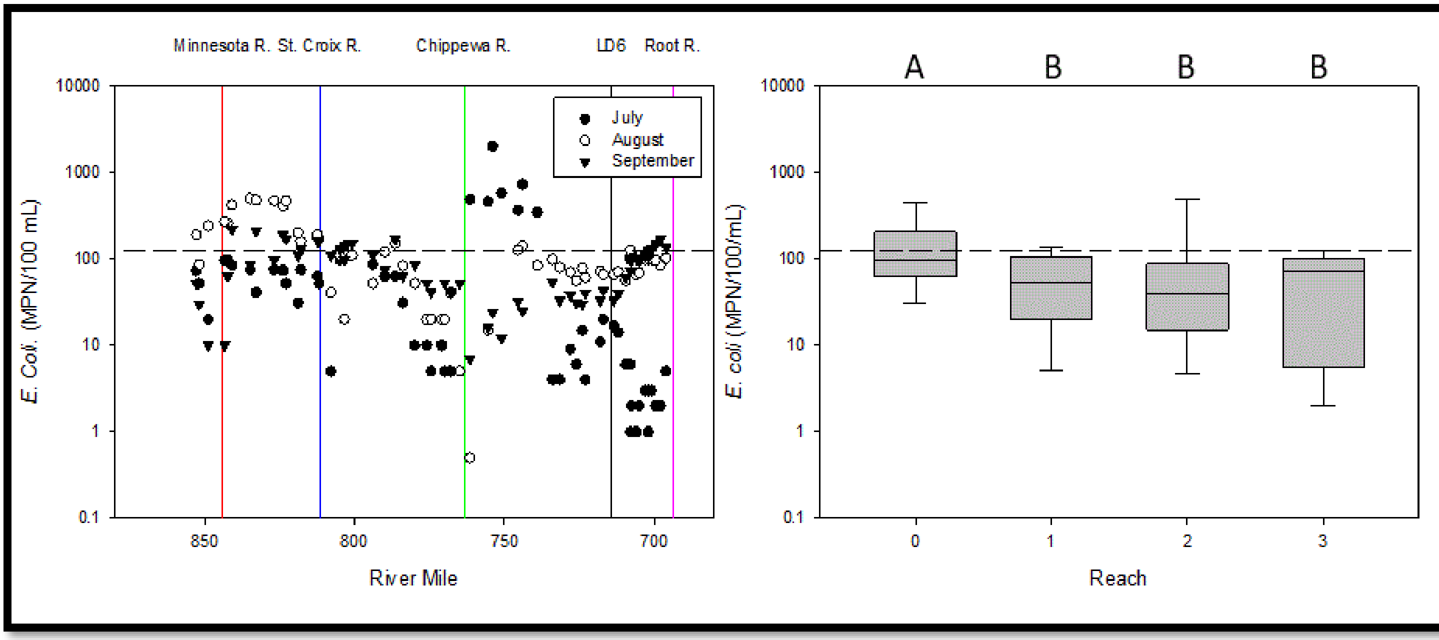


Figure 34. E. coli (most probable number/100 mL) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters. The red line indicates the acceptable level (<126 units/100 mL) for *E. coli*. measured as a geometric mean over a 30-day period (EPA 2015).

Figure 35. E. coli (in mpn/100 mL) for each of the four probabilistic sampling reaches over the three-month sampling period in logarithmic scale. The left panel shows *E. coli*, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters. The dashed line indicates the acceptable level (<126 units/100 mL) for *E. coli*. measured as a geometric mean over a 30-day period (EPA 2015).



BOD

Biochemical oxygen demand (BOD) is a measure of the amount is dissolved oxygen required to break down organic matter in a given water sample. BOD provides a measure of the impact of organic wastes on the oxygen concentration of a waterbody. Wastes are broken down by microbial organisms that require oxygen to facilitate the breakdown of waste products. The discharge of wastes with elevated levels of BOD can result in hypoxia and fish kills.

Substantial statistical differences exist among the sites and reaches for BOD (Figures 36 and 37). These results should be viewed with some caution as different detection limits existed for the Minnesota and Wisconsin labs, resulting in many observations below the detection limit.

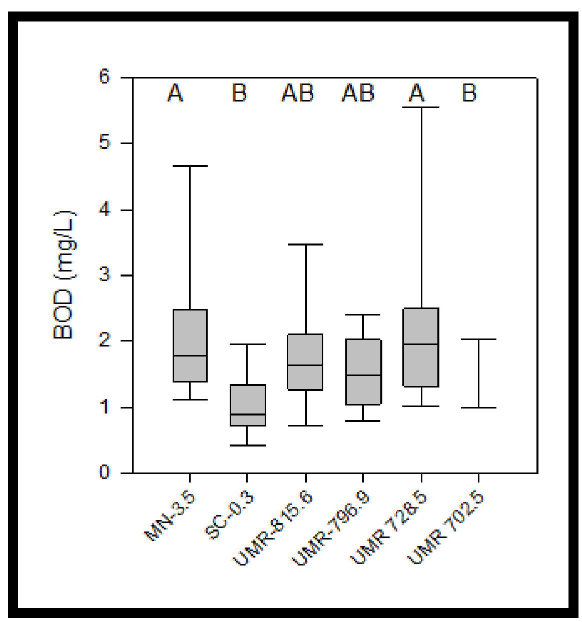
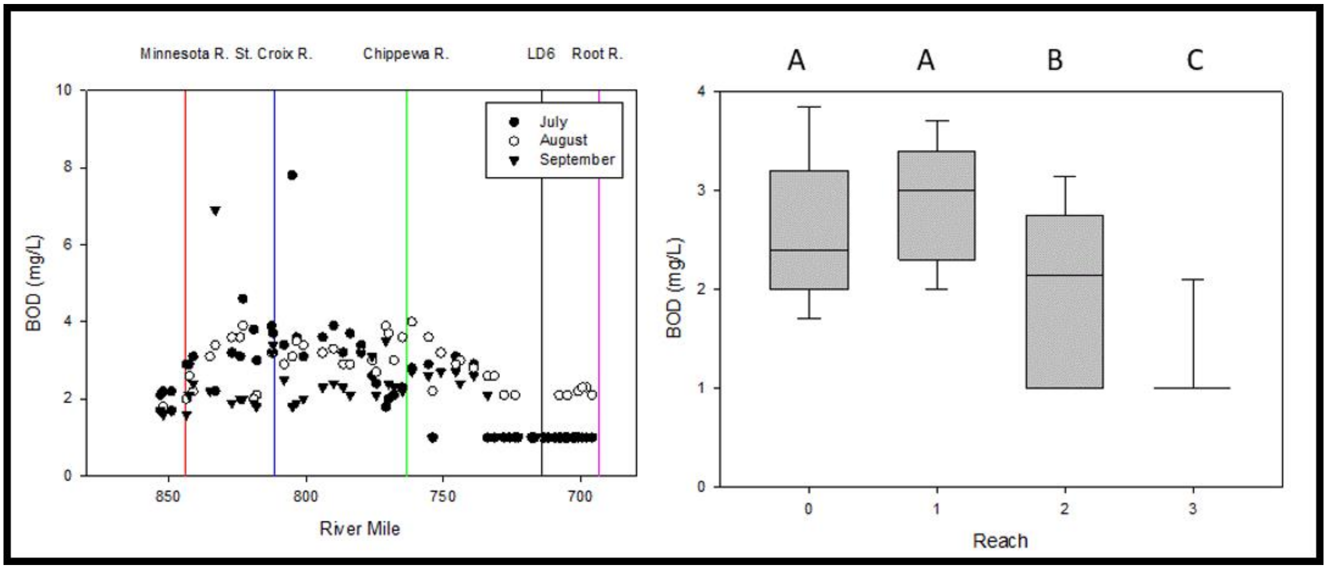


Figure 36. BOD (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Figure 37. BOD (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows BOD, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



Sulfate

Most dissolved sulfur in surface waters occurs as sulfate. Sulfate occurs naturally in mineral salts found in soil. Anthropogenic sources of sulfate include fossil fuel combustion, gas processing, wastewater treatment plants and industrial sources.

Significant differences in sulfate concentrations were observed for the fixed sites, but not the probabilistic sites (Figures 38 and 39). For fixed sites, sulfate in the Minnesota River was notably high and the UMR sites showed declining concentration as sites progressed downriver.

Figure 38. Sulfate (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

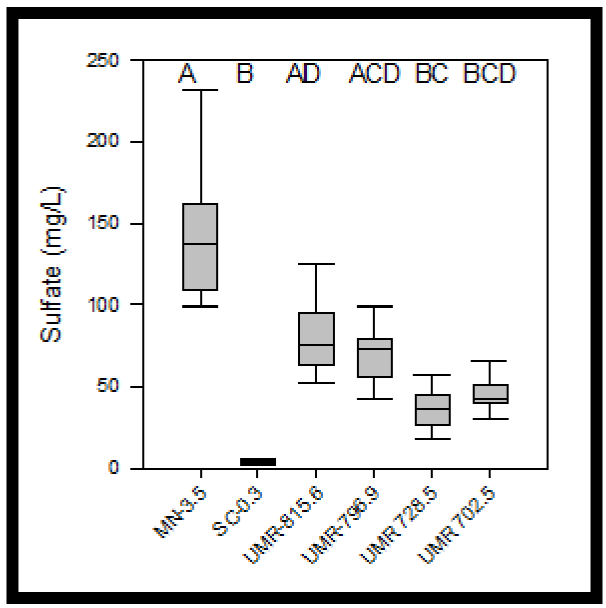
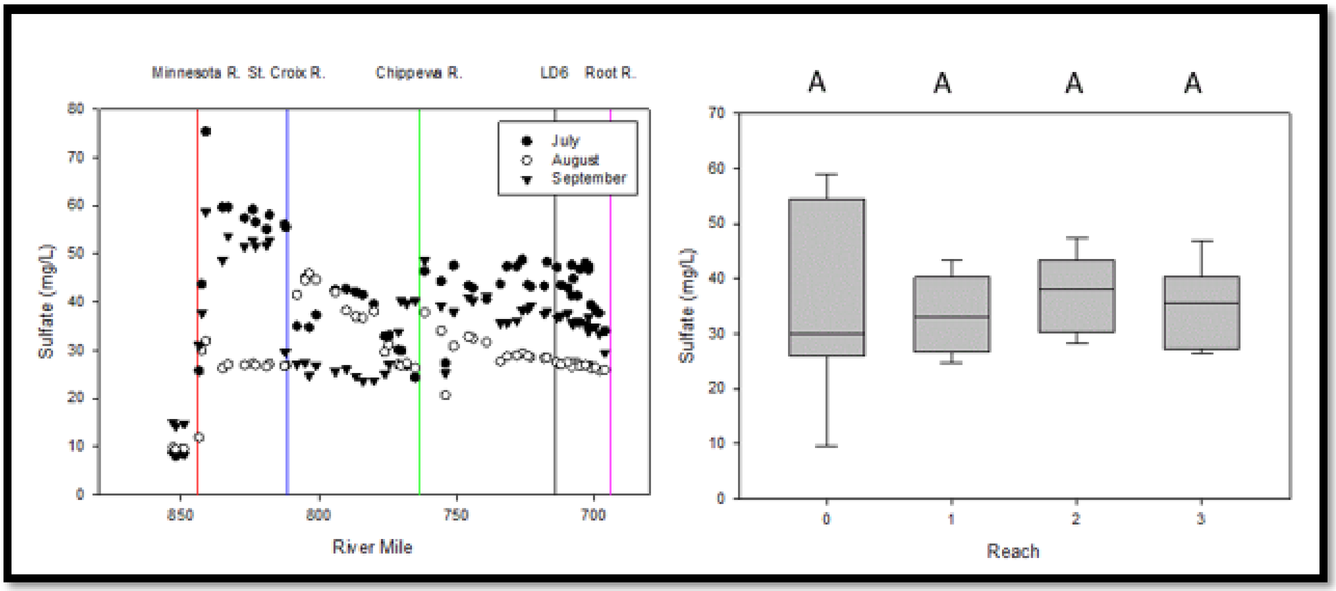


Figure 39. Sulfate (in mg/L) for each of the four probabilistic sampling reaches over the three-month sampling period. The left panel shows sulfate, by river mile, at each site, during each of the three probabilistic sampling episodes (July-September). The vertical lines indicate where a major tributary river enters the UMR. The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles for each reach. The letters above each reach show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between reaches with different letters.



TOC

Total organic carbon (TOC) is a measure of the total amount of carbon in organic compounds of a water sample. TOC is frequently correlated with BOD and is often used as a surrogate for that test. TOC is comprised of particulate organic carbon (POC) and dissolved organic carbon (DOC). DOC is a strong complexing agent for toxic metals such as iron, copper, aluminum, zinc and mercury. Significant differences were observed between the St. Croix River and most other fixed sites (Figure 40).

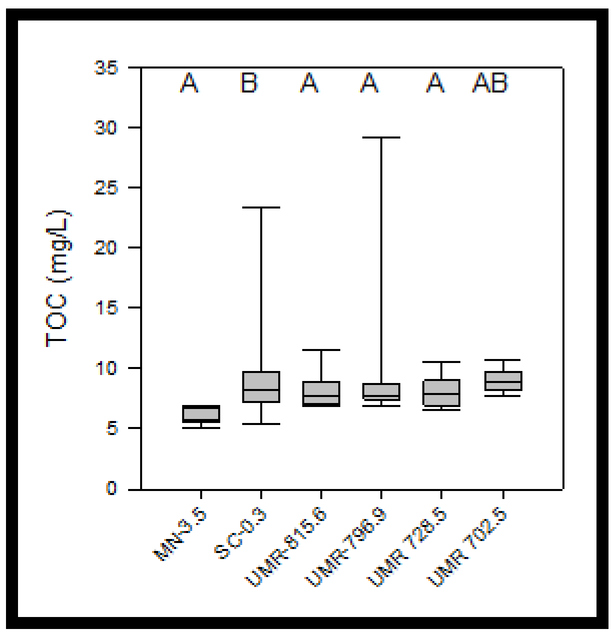


Figure 40. TOC (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Total Metals and Other Constituents

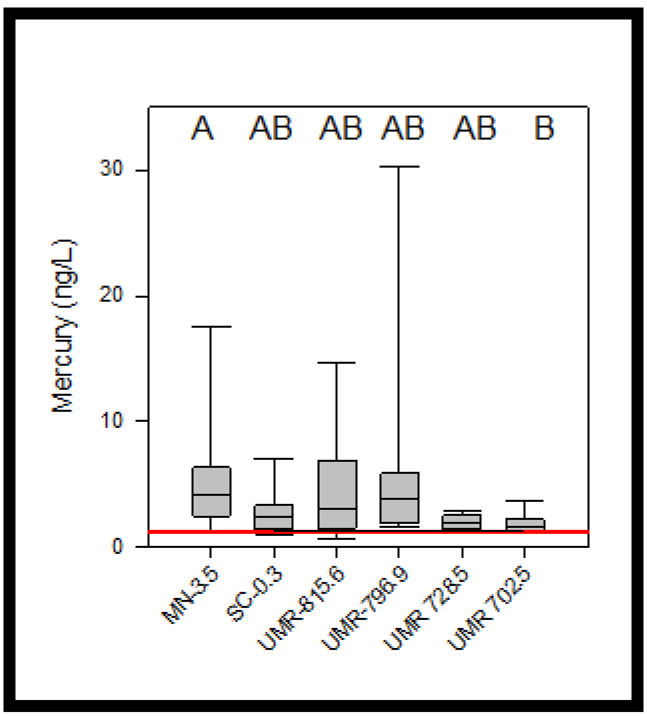
Metals in the aquatic environment are an important factor in determining the ability of surface waters to support aquatic communities. Metals occur naturally in our waters and vary in concentration based on the soil types and bedrock geology. When combined with anthropogenic sources, metals at some locations may approach or exceed concentrations that are considered harmful to human health and aquatic life. The data collected as part of the CWA Pilot provide necessary background data for water quality assessments and effluent limit calculations. Urban areas generally contribute higher concentrations of metals than rural areas. However, mercury concentrations in fish tissue have resulted in fish consumption advisories for many lakes and streams primarily from atmospheric deposition. In general, metal concentrations tended to be below the water quality criteria established in Ch. NR 105 (Wis. Adm. Code).

Mercury

Mercury is a hazardous material that causes serious environmental and human health problems. Although it is found naturally, it is most often released from man-made products like thermometers and fluorescent lights or produced as a by-product of energy production. Mercury is a bio-accumulative pollutant, which means that it does not break down over time and accumulates in animal tissues.

Some significant differences were observed in mercury among the fixed sites (Figure 41). Wisconsin's wildlife criterion for mercury from Ch. NR 105 is 1.3 ng/L. All sample sites that were tested for total mercury had exceedances of the wildlife criteria. Roughly 89% of total study sites exceeded the criterion. A general decline in mercury concentration was observed as sites progressed downriver.

Figure 41. Mercury (in ng/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The red line indicates the wildlife criterion in NR 105. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



Cadmium

Cadmium is typically a minor constituent of surface and groundwater. Cadmium enters rivers via erosion of soils, through atmospheric deposition, through direct discharge from industrial operations, and leakage from landfalls and contaminated sites. Much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment.

Greater than 95% of samples for cadmium were below the limit of detection for the three labs. For this reason, a statistical evaluation among the sampling sites was not performed (Figure 42).

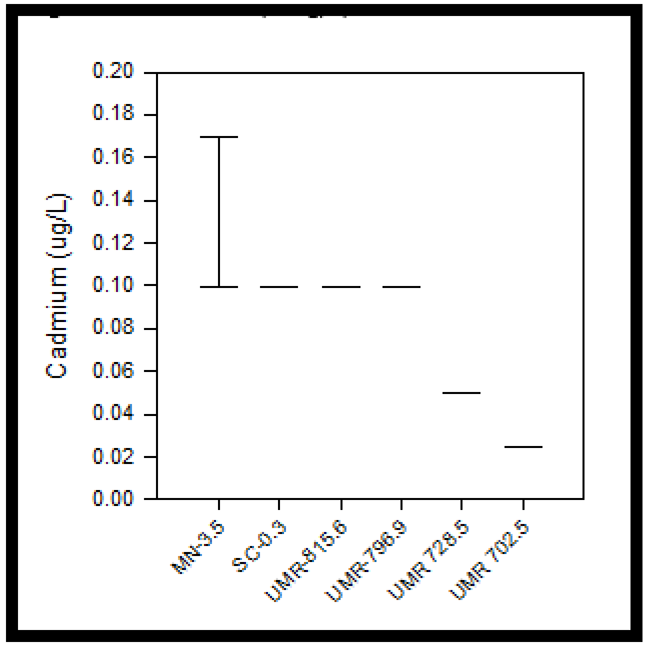
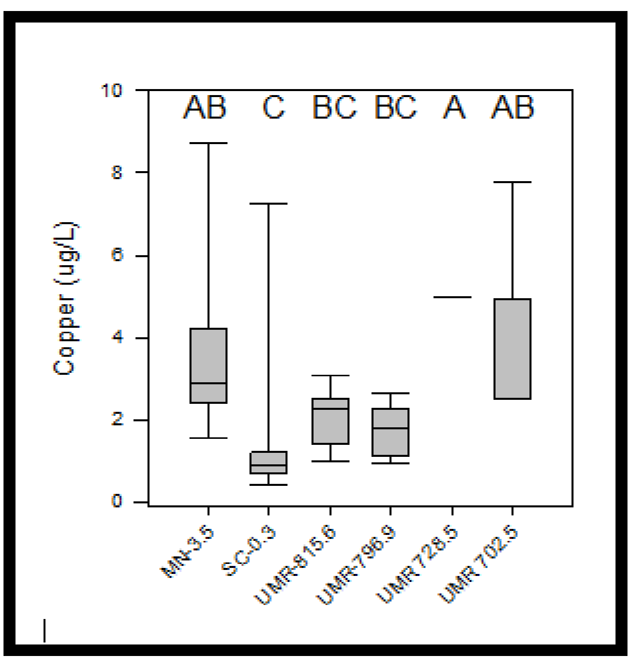


Figure 42. Cadmium (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. Nearly all values were below the limit of detection for all three labs. As a result, a statistical evaluation among the sites was not performed.

Copper

Copper is a common element found in the earth's crust and is generally present in surface waters. Copper is an essential micronutrient for both plants and animals at low concentrations. However, it may become toxic to aquatic life at elevated concentrations. Anthropogenic sources of copper include mining, pesticides, metal and electrical manufacturing and wastewater treatment plant effluent. Some significant differences were observed among the fixed sites (Figure 43). The copper results should be viewed with significant caution due to variable lab detection limits- 10 ug/L for the MPCA laboratory and 5 ug/L for the WDNR laboratory.

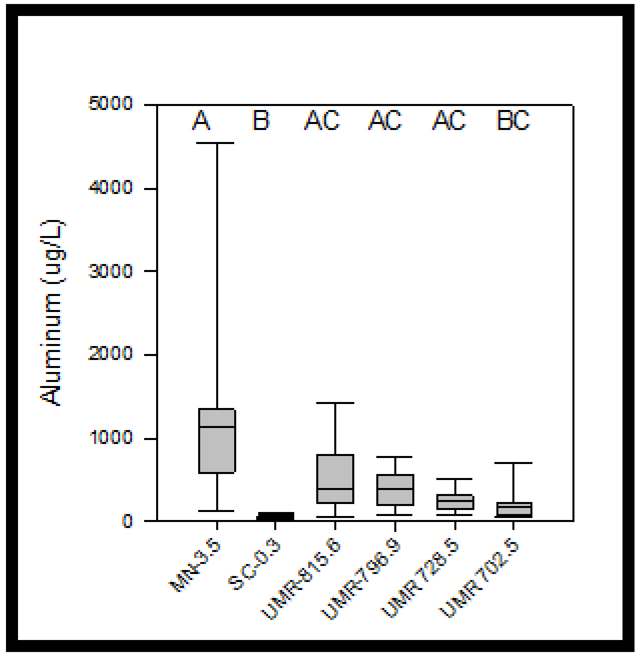
Figure 43. Copper (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



Aluminum

Aluminum is the most common metal in the earth's crust. It is found in varying concentrations in most soil and rocks. Aluminum enters the water via natural processes, like weathering of rocks. Aluminum can also be released to water by mining, industrial processes using aluminum, and wastewater treated with alum, an aluminum compound. Aluminum is a non-essential metal due to fish and other aquatic life not needing it to function. Elevated levels of aluminum can result in impairment to aquatic life. The Minnesota River site was significantly different from the St. Croix and UMR-702.5 sites (Figure 44).

Figure 44. Aluminum (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

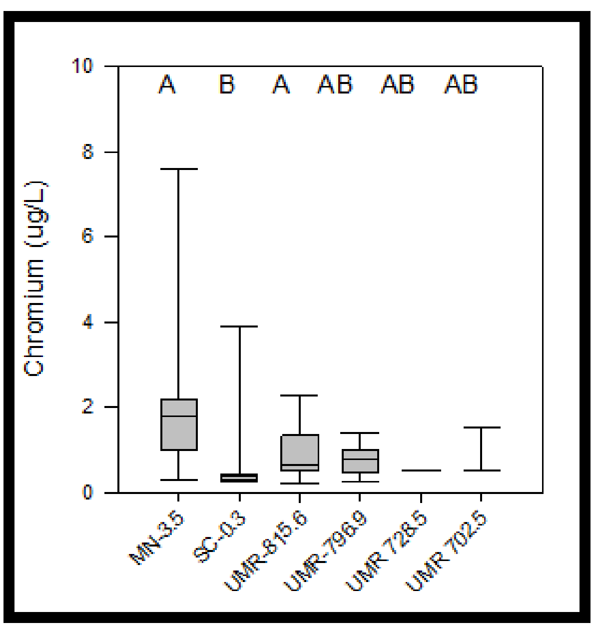


Chromium

Chromium is a naturally occurring element in soil, rocks, animals, and plants. Chromium can be toxic to humans, fish and invertebrates, especially when it exists in the hexavalent form. The most important industrial sources of chromium in the atmosphere are those related to ferrochrome production. Ore refining, chemical and refractory processing, cement-producing plants, automobile brake lining and catalytic converters for automobiles, leather tanneries, and chrome pigments also contribute to the atmospheric burden of chromium.

Some significant differences were observed among the fixed sites in chromium concentration (Figure 45). These results should be viewed with some caution due to a high number of observations below the detection limit for sites UMR-728.5 and UMR-702.5. The labs used for both sites had a detection limit of 1 ug/L, which was higher than the Met Council Laboratory.

Figure 45. Chromium (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



Iron

Iron is the fourth most abundant, by weight, of the elements that make up the earth's crust. Common in many rocks, it is an important component of many soils, especially the clay soils where it usually is a major constituent. Iron in water may be present in varying quantities depending upon the geology of the area and other chemical components of the waterway. Iron is an essential trace element required by both plants and animals. It is a vital oxygen transport mechanism in the blood of all vertebrate and some invertebrate animals.

The Minnesota River site was significantly different from the St. Croix and UMR-702.5 sites (Figure 46).

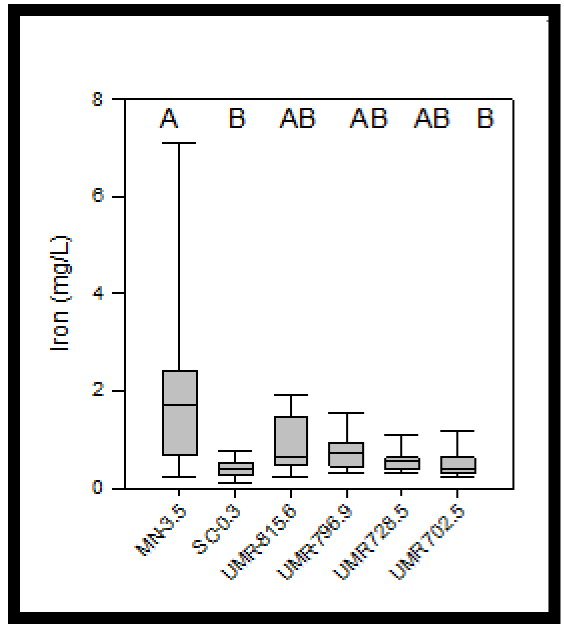


Figure 46. Iron (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Lead

Lead has been introduced into aquatic environments for centuries, and lead toxicity has been well known for decades. Lead toxicity to both plants and animals is well documented. Plants can take up available lead from the sediment or water through roots or leaves. Animals can be exposed to lead through a variety of pathways resulting in lethal effects or sublethal effects such as delayed development and physical deformities. Negative consequences of lead to humans include learning difficulties, developmental delay, anemia, hearing loss, declines in mental functioning and memory loss, cardiovascular and kidney problems, and reproductive problems.

Lead concentration on the St. Croix River was significantly lower than the other five sites (Figure 47). These results should be viewed with some caution due to several samples below the detection limit for the MPCA and WDNR Laboratories. The detection limit at these labs were higher (1 ug/L) than the Met Council Laboratory.

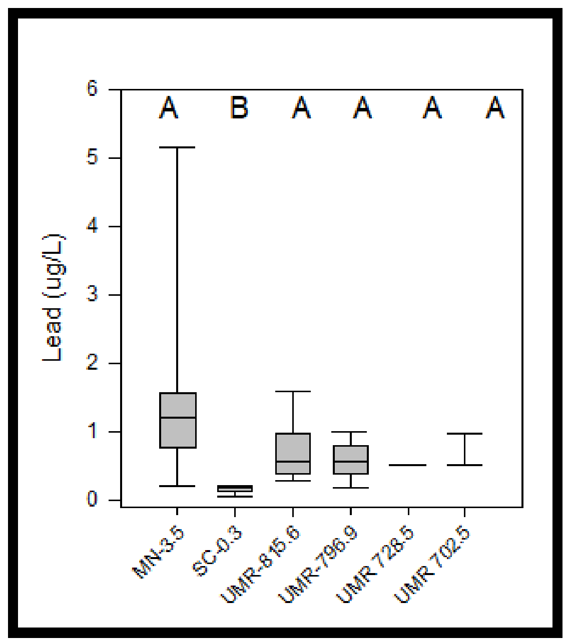


Figure 47. Lead (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Calcium

Calcium is a natural component of surface waters. It is a required nutrient for both higher plants and animals. Many animal species are found to increase or decrease in direct proportion to the concentration of calcium (e.g. snails). Substantial differences were observed between the Minnesota and St. Croix Rivers (Figure 48). The UMR sites showed a general decline in concentration as sites progressed downstream.

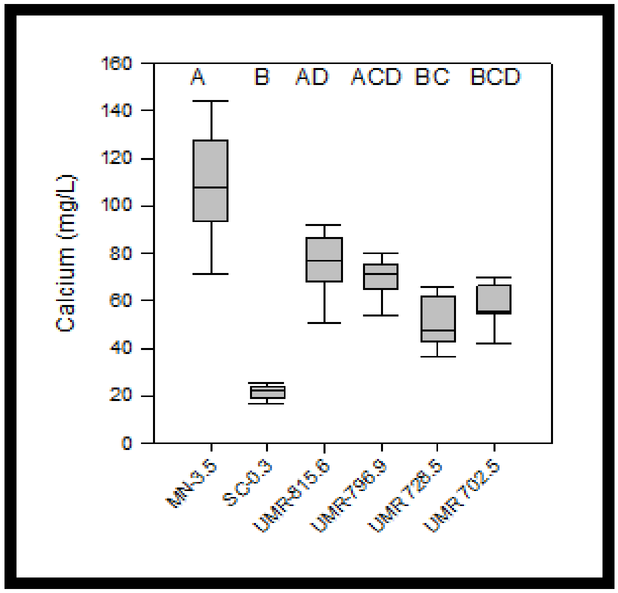


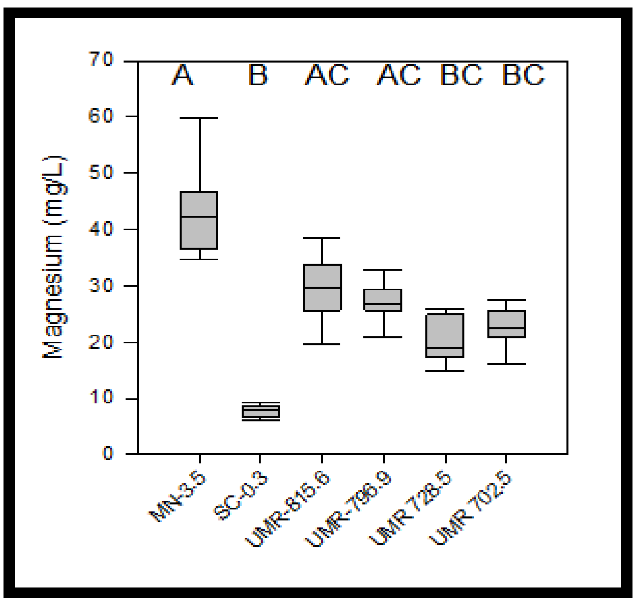
Figure 48. Calcium (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Magnesium

Magnesium is a natural component of surface waters. Magnesium is required by plants as a micronutrient in enzyme transformation. Magnesium usually exists well above biotic demand in aquatic environments and is deemed to be fairly conservative in aquatic systems. For this reason, it is frequently used to calculate inflow/outflow budgets in lakes.

Substantial differences were observed between the Minnesota and St. Croix Rivers (Figure 49). The UMR sites showed a general decline in concentration as sites progressed downstream. The magnesium data showed strong resemblance to the calcium data.

Figure 49. Magnesium (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



Potassium

Potassium is a common component of agricultural fertilizers as it is known to be a limiting nutrient for terrestrial vegetation under certain conditions. In aquatic systems, potassium tends to be an abundant cation and is rarely depleted to limiting concentrations. For this reason, only slight seasonal changes in potassium concentration are generally observed in aquatic ecosystems.

Substantial differences were observed between the Minnesota and St. Croix Rivers (Figure 50). The UMR sites showed a general, but statistically insignificant, decline in concentration as sites progressed downstream.

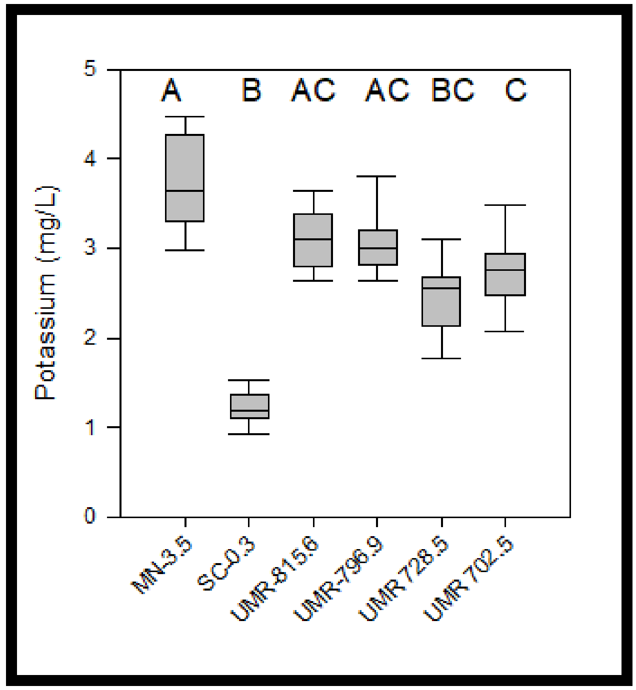
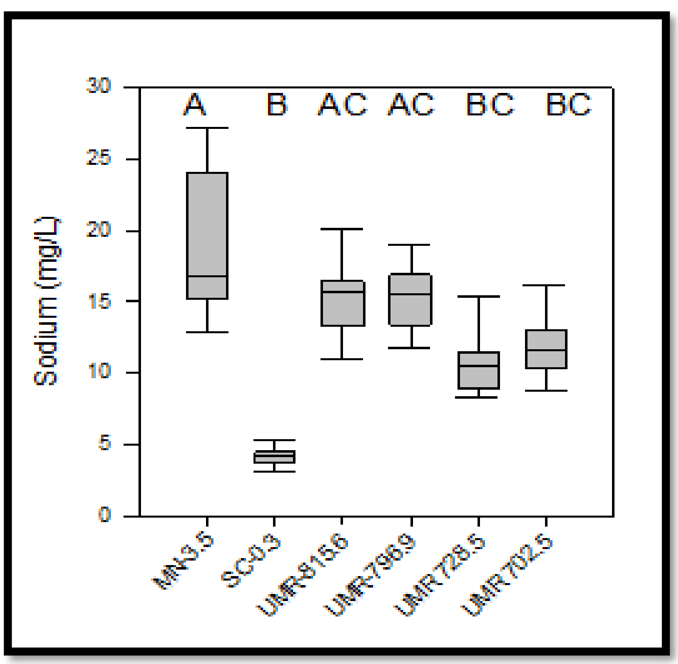


Figure 50. Potassium (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Sodium

Sodium is a common background component of soil and rocks. Road salt application tends to be a major source of sodium, in concert with chloride, in aquatic ecosystems. Sodium plays a major role in ion transport and exchange. Negative consequences can result if concentrations become too elevated. In drinking water, elevated sodium can be problematic for people with hypertension or heart conditions. Substantial differences were observed between the Minnesota and St. Croix Rivers (Figure 51). The UMR sites showed a general decline in concentration as sites progressed downstream.

Figure 51. Sodium (in mg/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

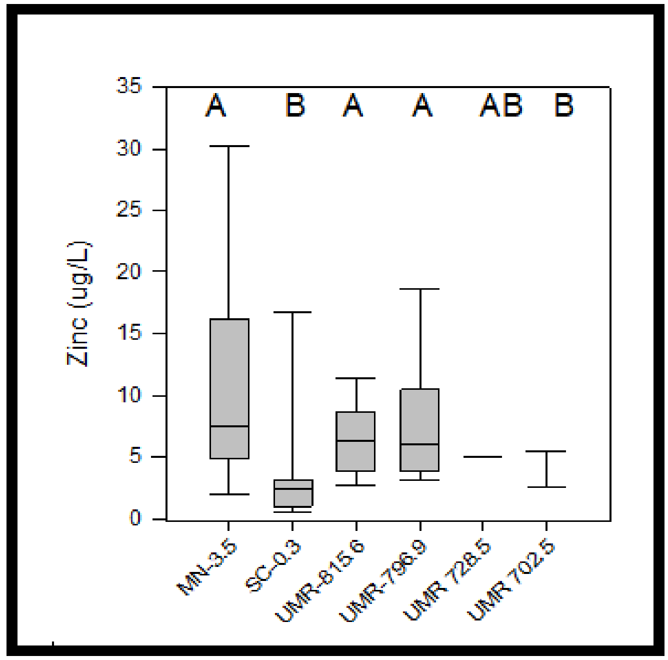


Zinc

Zinc is among the most highly utilized metals in the world for industrial purposes. Zinc is also an essential micronutrient for all living organisms. When found in elevated concentrations, zinc can be toxic to aquatic organisms and humans. The toxicity of zinc is dependent on other water quality characteristics such as hardness and pH.

Substantial differences were observed between the Minnesota and St. Croix Rivers (Figure 52). The UMR sites showed a general decline in concentration as sites progressed downstream. These sites should be viewed with some caution due to higher detection limits at the MPCA (10 ug/L) versus the WDNR (5 ug/L) laboratory.

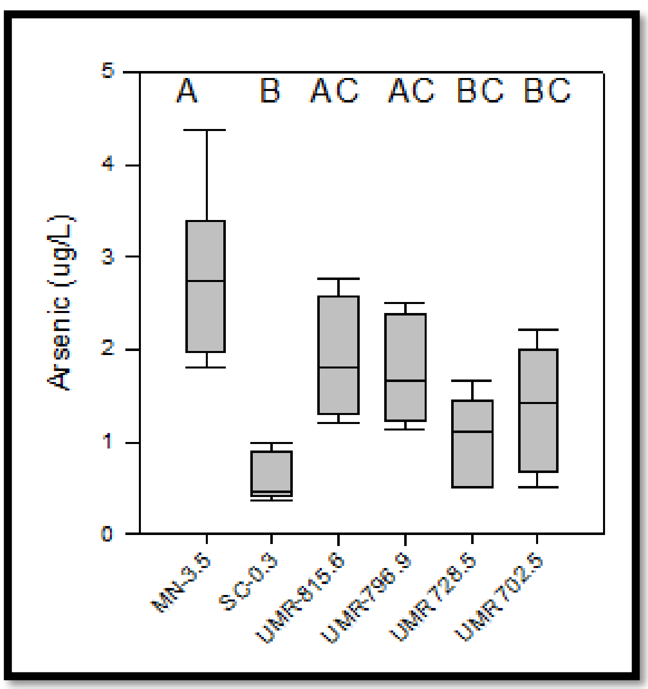
Figure 52. Zinc (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



Arsenic

Arsenic is a common element found naturally in rocks, soil and surface waters. Human activities such as mining, burning fossil fuels and application of herbicides and pesticides can result in elevated arsenic concentration. Arsenic in drinking water poses the largest threat to human health. Arsenic concentrations were highest in the Minnesota River, lowest in the St. Croix, and generally declined on the UMR as sites progressed downriver (Figure 53).

Figure 53. Arsenic (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.



Selenium

Selenium is a naturally occurring element present in rocks, soil and surface waters. Selenium can be released into surface waters by natural sources via weathering and by anthropogenic sources, such as mining, burning fossil fuels, and agriculture. Selenium is an essential nutritional element for animals in small amounts, but toxic at higher concentrations. Selenium bioaccumulates in the aquatic food chain, and chronic exposure in fish and aquatic invertebrates can cause reproductive impairments (e.g., larval deformity or mortality). Selenium can also adversely affect juvenile growth and mortality. Selenium can be toxic to waterfowl and other birds that consume aquatic organisms with high levels of selenium.

Substantial differences were observed between the Minnesota and St. Croix Rivers for selenium concentrations (Figure 54). The UMR sites showed a general decline in concentration as sites progressed downstream. These results should be viewed with some caution, as many sites (~40% of samples) showed concentrations below the limit of detection.

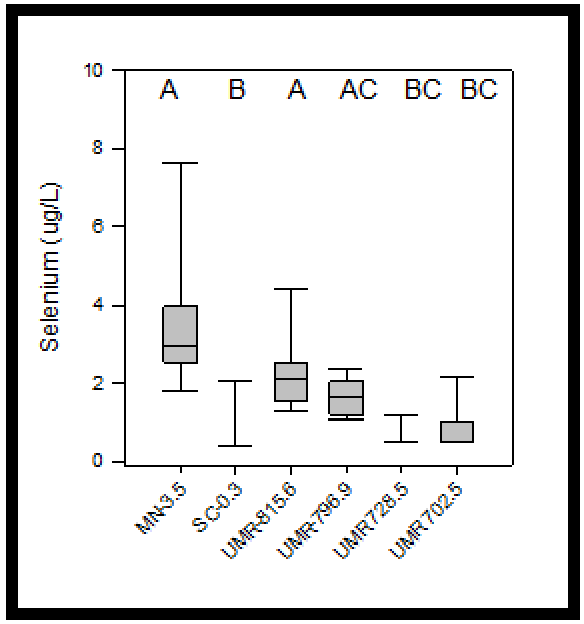


Figure 54. Selenium (in ug/L) for the fixed sites over the twelve-month sampling period (n=12). The boxplots represent the 10th, 25th, 50th 75th and 90th percentiles. The letters above each site show the Kruskall-Wallis comparison grouping. A statistically significant difference exists between sites with different letters.

Comparison to Chronic Water Quality Standards (NR 105)

Data collected were compared to chronic toxicity standards for aquatic life codified in Wisconsin Administrative Code Chapter NR 105. Water evaluation methods prescribed in NR 105 were applied to the CWA Pilot data to determine if any exceedances of the acute or chronic toxicity criteria occurred. No exceedances of the acute toxicity criteria were observed among the CWA Pilot dataset. For chronic toxicity criteria, only one exceedance (for copper on the St. Croix River) was measured. In general, concentration data from the CWA Pilot were only a fraction of the chronic standards prescribed in NR105 (Table 2). All data were tested using NR 105 standards. These criteria were also applied to sites completely within Minnesota (MN-3.5 and UMR-815.6) and are for demonstrative purposes only, with the goal of better testing the CWA methodology for future efforts.

Table 2. Average percent of chronic toxicity criteria value for fish and aquatic life based on Wisconsin NR105 criteria for toxic substances.

Site	Cr	Cu	Pb	Zn	Se	As	Cd	Hg
MN-3.5	0.54	9.77	1.42	2.51	69.67	1.86	1.4	1.33
SC-0.3	0.69	21.93	0.54	3.78	12.67	0.39	4.5	0.64
UMR-815.6	0.30	7.59	0.91	2.00	45.54	1.30	1.6	1.13
UMR-796.9	0.27	7.07	0.80	2.40	32.77	1.18	1.8	1.51
UMR 728.5	0.22	27.52	0.95	2.34	12.52	0.64	1.2	0.47
UMR 702.5	0.27	17.61	0.89	1.23	15.57	0.95	0.5	0.47

*** For each parameter, 100% would be equal to the chronic toxicity criteria value in NR105*

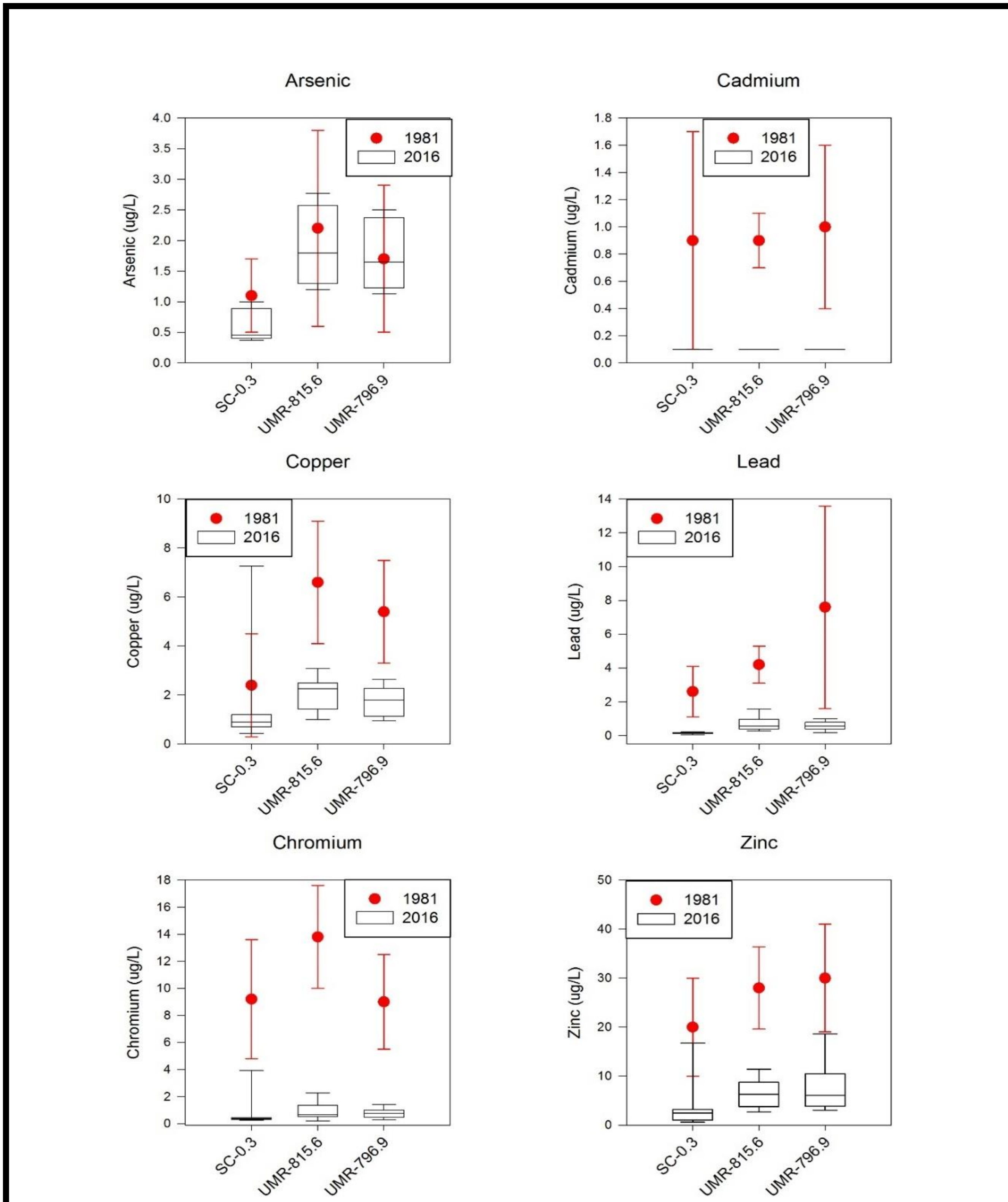
Comparison to Historical Data- 1981

It's important to put the recently collected CWA Pilot data in context with historical data to determine if water quality conditions are improving or declining over time. Very similar water quality data were collected in 1981 near three of the CWA Pilot sites (St. Croix-0.3, UMR-815.6 and UMR-796.9). The historical data were collected bi-monthly in 1981 and included very rigorous quality assurance procedures resulting in very high-quality dataset for comparative purposes (Wiener et al. 1984).

Discharge was different among the years sampled, with nearly double the mean annual discharge in 2016 and 2017 compared with 1981. Although the discharge difference between the two time periods results in some level of caution regarding the decline in metal concentration, the comparison of 1981 data to recent data (2016-2017) suggests substantial water quality improvement for the suite of contaminants examined. Modern arsenic concentration was similar to 1981, but the other five contaminants examined suggest varying degrees of improvement between 1981 and 2016 (Figure 55). Long term studies of metals concentrations in sediment traps collected on the Mississippi River demonstrate similar declines to the water quality results presented here (Giblin 2018). This provides an additional line of evidence to support declining metals concentrations in the Clean Water Act era due to improved water treatment and reduced metal usage over the 35-year period.

Avid recreationalists enjoy various aspects of the Mississippi throughout the year.

Figure 55. Comparison of CWA Pilot and historical data. The boxplots depict the CWA fixed site data from 2016-2017 (n=12 for each site). Box and whiskers illustrate the 10th, 25th, 50th 75th and 90th percentiles. The red dots and error bars represent the data collected in 1981 (bimonthly; n=6). The red error bars represent one standard deviation.



Summary and Conclusions

So…how is the river doing?

The CWA Pilot water quality sampling represented a very successful collaborative effort across multiple agencies and collaborators to characterize UMR water quality. The data collected describe current water quality conditions in the study reach in a comprehensive fashion. The summary of this robust dataset provides a useful roadmap of spatial water quality conditions in this diverse river reach. The statistical analysis produced in this report puts this information into context and provides a useful interpretation of longitudinal water quality changes and stressors over this 160-mile river reach. A clear decline in numerous water quality parameter concentrations was evident as sampling sites progressed downstream on the UMR. Stark differences for most parameters were also observed between the Minnesota and St. Croix Rivers. Additionally, established thresholds and criteria for a variety of water quality parameters were not met in many instances (e. g. nitrogen, phosphorus and TSS). Clear distinctions in water quality criteria attainment were evident for point source parameters currently regulated under the Clean Water Act (e. g. metals) and those nonpoint dominated parameters not currently regulated under the Clean Water Act (e. g. nitrogen and TSS).

Comparison of CWA Pilot water quality data to standards prescribed in Wisconsin Administrative Code NR 105 provides a useful inference regarding proximity of current water quality parameter concentrations to established water quality criteria for Wisconsin. Also, comparison of this modern dataset to historical data from 35 years prior provides valuable insight into UMR water quality trends over time. Although challenges remain, and stressors continue to change over time, many of these results (especially metals data) provide an encouraging account of the quantifiable water quality improvements that have occurred since the establishment of the Clean Water Act. Future challenges will need to focus on contaminants currently not regulated under the Clean Water Act (e.g. non-point sources- sediment, nutrients and chloride). Special attention should be paid to contaminants, of largely nonpoint origin, not regulated under the Clean Water Act that have increased in recent decades (chloride and nitrogen).

Question: So… how is the river doing?

Answer: Improving, especially for point source contaminants regulated by the Clean Water Act (like metals)- but we still have a long way to go for nonpoint source contaminants not regulated by the Clean Water Act (like sediment, nutrients and chloride).

Monitoring work by field biologists is essential to provide the data and analyses presented in this and other similar reports.

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