**National Park Service**
**U.S. Department of the Interior**

**Natural Resource Stewardship and Science**

# Water Quality Conditions and Trends in the Mississippi National River and Recreational Area

*1976-2005*

Natural Resource Technical Report NPS/GLKN/NRTR—2013/691

**ON THE COVER**
A view upstream from a diatom sampling site on the Mississippi River, just above Lock & Dam #1 (River Mile 848).
Photograph by: NPS photo/D. VanderMeulen.

# Water Quality Conditions and Trends in the Mississippi National River and Recreational Area

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# Errata

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**Minor Changes made to** Lafrancois et al., *Water Quality Conditions and Trends in the Mississippi National River and Recreational Area, 1976-2005.* Natural Resource Technical Report NPS/GLKN/NRTR—2013/691.

In converting the final, approved Word document of our report to a PDF, nearly all of the report's many graphs became unreadable. This problem was unexpected, as it had not occurred in previous conversions of this document from Word to PDF. In any case, since we expect widespread electronic access to this report, it was necessary to modify the graph formatting and ensure a clean digital copy. No changes to data, graphic results, or interpretations were made.

Changes:

- Modified the graphs in the original graphing software, removing all dotted line formatting, which seemed to be the root of the problem.
- Replaced each graph in the Word document.
- For figures 17-18, reversed the color gradient so that red denoted periods of low flow and blue denoted periods of high flow, to ease interpretation. Modified the captions for Figures 17 and 18 and the text on p. 44 to reflect this change.

The National Park Service, Natural Resource Stewardship and Science office in Fort Collins, Colorado, publishes a range of reports that address natural resource topics. These reports are of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

The Natural Resource Technical Report Series is used to disseminate results of scientific studies in the physical, biological, and social sciences for both the advancement of science and the achievement of the National Park Service mission. The series provides contributors with a forum for displaying comprehensive data that are often deleted from journals because of page limitations.

All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner.

This report received formal peer review by subject-matter experts who were not directly involved in the collection, analysis, or reporting of the data, and whose background and expertise put them on par technically and scientifically with the authors of the information.

Views, statements, findings, conclusions, recommendations, and data in this report do not necessarily reflect views and policies of the National Park Service, U.S. Department of the Interior. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Government.

This report is available from the Great Lakes Inventory and Monitoring Network website (http://science.nature.nps.gov/im/units/GLKN/monitorreportpubs.cfm#WaterQuality) and the Natural Resource Publications Management website (http://www.nature.nps.gov/publications/nrpm/).

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# Executive Summary

The Mississippi National River and Recreational Area (MNRRA) spans a highly visible and highly developed stretch of the Mississippi River within the Twin Cities Metropolitan Area. Water quality has been a long-standing concern for managers and the public, and many monitoring programs and research studies addressing water quality have developed. Although various agencies monitor water quality in the region, there have been few efforts to analyze water quality data over the long term or for the entire MNRRA corridor. We compiled thirty years of monitoring data for six Mississippi River sites within MNRRA, a nearby Minnesota River site, and the Metropolitan Wastewater Treatment Plant outflow in order to 1) characterize longitudinal patterns within the corridor, 2) evaluate long-term seasonal patterns, and 3) assess interannual trends over the period of record.

Year-round water quality data for these eight sites were compiled from Metropolitan Council Environmental Services (MCES) for the period of January 1976 through December 2005, and included core water quality variables (water temperature, dissolved oxygen, pH, and specific conductance), a suite of other nutrient and sediment-related variables, and chlorophyll-*a*. Ratios of several key variables were calculated to help with data interpretation. Streamflow data were compiled from the U.S. Geological Survey, U.S. Army Corps of Engineers, and Metropolitan Council (from the Metropolitan Wastewater Treatment Plant, hereafter “Metro Plant”). Water quality concentration data were screened for outliers and censored values and flow-adjusted as necessary. Loads were calculated using FLUX32 Software for Load Estimation. Longitudinal and seasonal trends were evaluated graphically, and interannual trends were analyzed statistically using the seasonal Kendall test for trend.

We found clear longitudinal trends in the data, with concentrations of nutrients and sediments increasing from upstream to downstream within MNRRA. The Minnesota River and Metro Plant sites had much higher concentrations of nitrogen and phosphorus variables than did upstream Mississippi River sites, and notable increases occurred downstream of these tributary and point source inputs. Loads of nitrogen and total phosphorus increased most markedly below the Minnesota River confluence, whereas loads of orthophosphate (the more bioavailable form of phosphorus) increased most below the Metro Plant. Turbidity levels and total suspended solids concentrations nearly doubled below the confluence of the Minnesota River, and loads of total suspended solids nearly quadrupled. Similarly, large increases in volatile suspended solids and chlorophyll-*a* levels occurred below the Minnesota River confluence. Constituent ratios suggested elevated proportions of nitrogen (versus phosphorus) in the Minnesota River, phosphorus (versus nitrogen) in Metro Plant effluent, orthophosphate (versus total phosphorus) in Metro Plant effluent, and inorganic sediment (versus total suspended sediment) in the Minnesota River. In general, these results underscore the important influence of Minnesota River and Metro Plant inputs on spatial patterns in water quality in the MNRRA corridor.

Strong seasonal patterns were also apparent in the dataset. Streamflow tended to peak during spring snowmelt, with smaller peaks occurring during early summer and late autumn. Many constituents showed corresponding seasonal patterns, with high nutrient and sediment loads common during spring snowmelt and early summer. Turbidity levels and concentrations of total nitrogen (mostly nitrate) and total suspended solids were consistently high in early summer,

particularly in and downstream of the Minnesota River. Similarly, the proportion of nitrogen (versus phosphorus) in the water peaked in early summer, particularly in and downstream of the Minnesota River. Higher proportions of inorganic solids (versus volatile solids) were present in seston during spring snowmelt compared with other times of year. In general, our results suggest that factors such as spring snowmelt, early summer rainfall on sparsely vegetated agricultural landscapes, and fertilizer applications affected seasonal patterns in MNRRA water quality.

We identified significant long-term trends for many variables from 1976 through 2005. Streamflow varied over the period of record (with notable low flow and high flow years in 1988 and 1993, respectively) but showed a significant long-term increase at all river sites, particularly in and downstream of the Minnesota River. Core water quality variables showed few consistent changes among sites, but dissolved oxygen concentrations increased in and downstream of the Minnesota River and downstream of the Metro Plant over the period of record. Significant trends in many nutrient and sediment variables were detected, and most changes were consistent among sites. Total Kjeldahl nitrogen and total ammonia nitrogen generally decreased (particularly concentrations), whereas nitrate-nitrogen concentrations and loads generally increased. Total and orthophosphate concentrations decreased significantly at all river sites (most notably the Minnesota River site) but total phosphorus loads showed no significant change at any of the river sites and showed a significant increase at the Metro Plant. Similarly, turbidity and suspended solids concentrations decreased at most sites, while suspended solids loads showed few significant changes. Concentrations and loads of chlorophyll-*a* generally increased at riverine sites, and the ratio of total phosphorus to chlorophyll-*a* consistently decreased, suggesting more algal growth per unit of phosphorus in recent years. In general, although we observed substantial interannual variation there were many consistent, compelling changes over the period of record.

We examined the relative effects of key drivers (e.g., climate and hydrology, point sources, agricultural runoff, and urban stormwater) on water quality in the MNRRA corridor over the period of record. Climate and hydrology played an important role, with low-flow years corresponding to reduced loads and elevated concentrations of many variables. Further, the increase in streamflow over the period of record likely affected interannual trend results for concentrations versus loads. Variables typically linked to point source inputs improved significantly at most sites; dissolved oxygen concentrations generally increased and concentrations of total ammonia nitrogen, total phosphorus, and orthophosphate decreased. However, the Metro Plant was still a dominant factor shaping longitudinal trends within MNRRA for many variables (particularly during low-flow periods) and increases in nitrate-nitrogen concentrations were attributed in part to implementation of nitrification at area wastewater treatment facilities. We noted improvements in several variables commonly linked to agriculture; the Minnesota River site (affected by its highly agricultural watershed) and several Mississippi River sites showed decreasing concentrations of total phosphorus and total suspended solids. However, loads of these variables did not decrease significantly, and the Minnesota River remains a dominant factor shaping longitudinal water quality trends within MNRRA. Finally, despite the highly developed character of the MNRRA corridor and the pronounced impacts of urban stormwater on many MNRRA tributaries, we found little evidence from the MCES dataset that urban stormwater exerted a strong influence on overall water quality patterns or trends in the Mississippi River proper.

To provide context for our results, we related MNRRA water quality conditions over the period of record to current water quality standards and criteria and to ongoing Total Maximum Daily Load (TMDL) projects. We found that core water quality variables such as water temperature and dissolved oxygen were generally within acceptable ranges for protecting aquatic health at Mississippi River sites. Nitrate-nitrogen concentrations were well below the federal drinking water standard at all river sites. Total phosphorus concentrations often exceeded current and proposed phosphorus standards at Mississippi River sites, but Metro Plant concentrations have been below the current permit limit since implementation of biological phosphorus removal in 2003. Chlorophyll-*a* concentrations were typically at or below proposed standards, but exceeded standards during certain months and during low-flow years. Concentrations of total suspended solids generally exceeded the draft suspended solids criterion on the Minnesota River and at Mississippi River sites downstream of it.

This trend analysis effort provided a unique opportunity to evaluate the relative roles and contributions of the long-standing MCES monitoring program and the newer National Park Service (NPS) large river monitoring program. To do this, we compared MCES data to NPS data collected within the same year for sites located near one another. We found only minor differences, suggesting that data from the NPS sites do not add substantively to the body of data already available via MCES. As long as the MCES monitoring effort continues at the current sites and sampling frequency, NPS water quality monitoring objectives for MNRRA will be addressed without additional sampling. We concluded that NPS resources could be used most effectively for issue-specific monitoring, or for data synthesis, interpretation, and integration with biological monitoring programs within MNRRA.

Lastly, we identified a variety of monitoring, management, and research recommendations stemming from our analysis of trends. First, we recommend incorporating the most recent (i.e., post-2005) MCES data into the data record in order to 1) better characterize *current* water quality conditions and longitudinal trends, 2) provide insights into how the Metro Plant's biological phosphorus removal program has affected MNRRA's water quality, and 3) better understand links between hydrology and water quality (based on the several unusual water-years that have occurred since 2005). We note the importance of both concentration and loading data for understanding trends, and emphasize the importance of MCES' growing efforts to calculate loads for MNRRA sites. We suggest that future studies address not only water quality, but also links between water quality monitoring trends and key biological endpoints, such as fecal indicator bacteria and biological communities. Additionally, we note that new trend analysis tools have recently been developed and we recommend exploring these methods to better describe the nature and cause of water quality changes in the corridor. Finally, our analysis suggests that several water quality issues would benefit from additional investigation, including 1) the relationship between climate change and MNRRA hydrology and water quality, 2) the causes for increasing nitrate-nitrogen concentrations and loads within MNRRA, and 3) the influence of urban stormwater on MNRRA water quality.

Collectively, this analysis of longitudinal, seasonal, and long-trends clarifies the extent to which drivers such as climate and hydrology, point sources, and agricultural runoff influenced water quality in the MNRRA corridor over the period of record. These water quality drivers remain important considerations for future water quality management efforts. Additionally, our analysis highlights the responsiveness of MNRRA water quality to large-scale changes in point source management and land use practices, and underscores the importance of long-term monitoring data for tracking water quality changes into the future.

## Acknowledgments

We wish to thank the Metropolitan Council for its long-standing support of water quality monitoring within and beyond the Mississippi National River and Recreation Area (MNRRA), and the field and laboratory staff of the Metropolitan Council Environmental Services for their dedication to rigorous data collection and analysis. We thank the National Park Service Great Lakes Inventory and Monitoring Network for providing funding for this work. Joan Elias provided technical, editorial, and moral support throughout this project, Rebecca Key created a map of the study area for inclusion in this report, and Ted Gostomski transformed the raw report into a masterpiece of the NPS Technical Report Series. Lark Weller, Trevor Russell, Joan Elias, and Bill Route worked to ensure these results were communicated to key audiences and integrated into ongoing State of the River/State of the Park projects. We thank colleagues from throughout the region for their interest in this project and park unit; their encouragement helped expedite completion of the report. We thank Robert Hirsch for his helpful insights into future trend analysis work. This report was improved by the reviews and comments of Joan Elias, Steve Heiskary, and Jeff Houser.


## List of Abbreviations

| | |
|---|---|
| Chl-*a* | Chlorophyll-*a* |
| DO | Dissolved oxygen, mg/L |
| DP | Dissolved phosphorous, mg/L |
| GLKN | Great Lakes Inventory and Monitoring Network (of the NPS) |
| MCES | Metropolitan Council Environmental Services |
| MNRRA | Mississippi National River and Recreation Area |
| MPCA | Minnesota Pollution Control Agency |
| $NH_3$-N | Ammonia-nitrogen, mg/L |
| $NH_4$-N | Ammonium-nitrogen, mg/L |
| $NH_x$-N | $NH_3$-N + $NH_4$-N, mg/L |
| $NO_2$-N | Nitrite-nitrogen, mg/L |
| $NO_3$-N | Nitrate-nitrogen, mg/L |
| $NO_x$-N | $NO_2$-N + $NO_3$-N, mg/L |
| NPS | National Park Service |
| OP | Ortho-phosphorus, mg/L |
| pH | hydrogen ion activity, standard units |
| RM | River mile (or location upstream from a given reference point: the reference point for the Minnesota River is the mouth of its confluence with the Mississippi River, and the reference point for the [Upper] Mississippi River is its confluence with the Ohio River.) |
| SC | Specific conductance |
| T | Temperature, $^{o}$ C |
| TAN | Total Ammonia Nitrogen |

## List of Abbreviations (continued)

| | |
|---|---|
| TCMA | Twin Cities Metropolitan Area (seven counties) |
| TN | Total nitrogen, mg/L |
| TP | Total phosphorus, mg/L |
| TSS | Total suspended solids, mg/L |
| USGS | United States Geological Survey |
| VSS | Volatile suspended solids, mg/L |

# Introduction

The Mississippi National River and Recreational Area (MNRRA) protects a prominent and highly developed stretch of the Mississippi River within the Twin Cities Metropolitan Area (TCMA). This riverine park encompasses portions of 25 communities and integrates water from three large rivers (the Upper Mississippi, Minnesota, and St. Croix), as well as many smaller tributaries (Figure 1). Water quality in the 72-mile corridor has been the subject of public attention and management concern for over a century. Rapid urbanization and construction of the locks and dams in the TCMA early in the 20th century led to severely polluted waters, as evidenced by oxygen depletion, extremely high levels of bacteria, formation of floating mats of sewage, and the near extirpation of fish in the river (USEPA 2000). Since then, water quality has improved dramatically, aquatic life has been reestablished, and public use of the corridor has greatly increased. However, urban and industrial development continues, and the Minnesota River Basin continues to contribute heavy loads of sediment, nutrients, and other contaminants.

Over time, a variety of point and nonpoint source pollutants have influenced water quality in the MNRRA corridor. In the 21st century, the dominant point sources include wastewater treatment facilities, most notably the Metropolitan Wastewater Treatment Plant (hereafter “Metro Plant”), which discharges to the Mississippi River downstream of St. Paul. One of the largest wastewater treatment facilities in the U.S., the Metro Plant has undergone many improvements since its establishment as a primary treatment facility in 1938 (Metropolitan Council 2010). Secondary treatment was implemented in 1966 to enhance dissolved oxygen concentrations in the Mississippi River, and in 1984 advanced secondary treatment was implemented to nitrify toxic ammonia. Following those improvements, the Metro Plant continued to be a major source of total phosphorus to the Mississippi River within the TCMA (Barr Engineering Company 2004). However, biological phosphorus removal was fully implemented in 2003, achieving a 90% reduction in phosphorus loading to the river. According to a review by the U.S. Environmental Protection Agency (USEPA 2000), these progressively more intensive wastewater treatment practices, coupled with the 1985-1995 separation of sanitary and storm sewers, have contributed to MNRRA water quality improvements in recent decades. Dominant nonpoint pollution sources to the MNRRA corridor include urban runoff and inputs from local tributaries. The highly agricultural Minnesota River basin contributes up to 90% of the sediment load (Wilcock 2009) and 50-85% of the nonpoint total phosphorus load to Lake Pepin, a natural riverine impoundment located just downstream of MNRRA (Larson et al. 2002, Meyer and Schellhaass 2002, Engstrom et al. 2009).

Water quality trends in MNRRA have been analyzed on several occasions (Lafrancois et al. 2007). Water quality data collected from the 1930s to the 1970s at five long-term monitoring stations showed that dissolved oxygen concentrations changed little but that biochemical oxygen demand and coliform bacteria had increased at most sites due to increasing population in the TCMA (Larson et al. 1976). In a review of historical water quality in the Upper Mississippi River, USEPA (2000) found increases in dissolved oxygen concentrations at Mississippi River sites since the 1970s and documented 90 percent reductions in ammonia-nitrogen (1982-1998) and 95 percent reductions in biological oxygen demand and suspended solids in Metro Plant effluent (1968-1998). As part of a U.S. Geological Survey National Water Quality Assessment Program study, Kroening and Andrews (1997) and Kroening and Stark (1997) analyzed trends

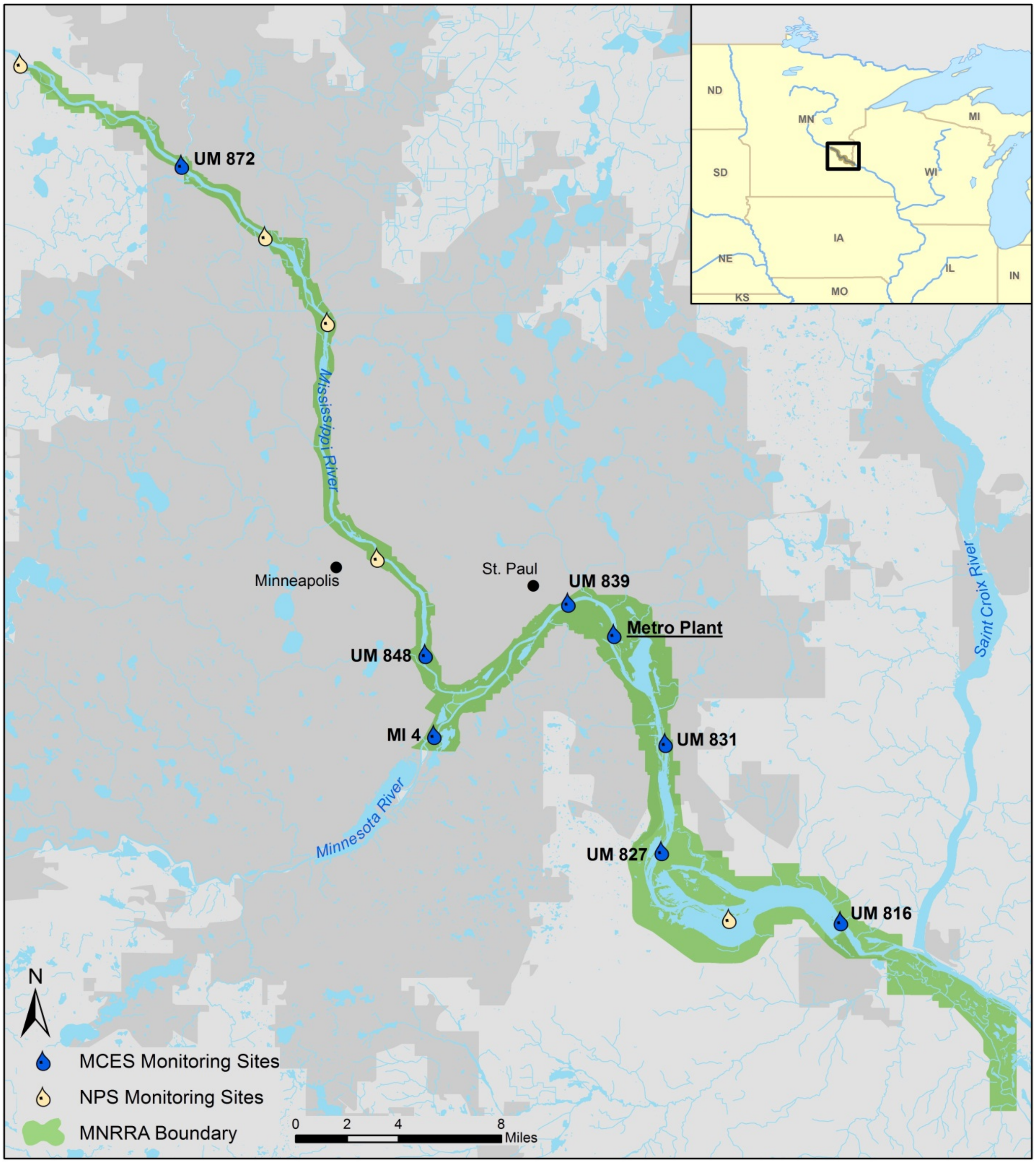


**Figure 1**. Water quality monitoring sites sampled by the Metropolitan Council Environmental Services (MCES) and the National Park Service (NPS) within the Mississippi National River and Recreation Area. Note the location of the Metropolitan Wastewater Treatment Plant (Metro Plant).

within the TCMA from 1984 to 1993, documenting changes in nitrogen species that were likely due to changes in wastewater treatment practices.

More recently, Kloiber (2004) analyzed water quality trends for three major rivers in the TCMA, including one site within MNRRA boundaries (Mississippi River at Anoka, MN), for the period of 1976 to 2000. Trends at this site included reductions in ammonium and total phosphorus concentrations and increases in nitrate-nitrogen concentrations. In a comparative analysis of water quality trends in Lakes St. Croix and Pepin, Lafrancois et al. (2009) analyzed data from Lock and Dam 3, a site just downstream of the MNRRA corridor, similarly finding significant decreases in ammonia and total phosphorus concentrations and significant increases in nitrate-nitrogen and total chlorophyll-*a* concentrations from 1976-2004. As part of a monitoring protocol development project, Magdalene et al. (2008) reviewed water quality information collected by three agencies and found a longitudinal trend of decreasing pH and DO, and increasing TP and $NO_3$+$NO_2$-N (Magdalene et al. 2008). Lastly, the State of Minnesota is in the process of developing statewide river nutrient criteria (Heiskary et al. 2010) and Mississippi River pool-specific eutrophication criteria (Heiskary and Wasley 2010), with resulting criteria based in part on long-term analysis of water quality data collected at sites within MNRRA boundaries from 1993 to 2009.

Despite the fact that many agencies monitor water quality within the corridor, past trend analysis efforts have been sporadic, covered narrow periods of record, or been limited in spatial scope due to individual agency objectives; a comprehensive analysis of available long-term water quality data specific to the MNRRA corridor has not been conducted. We compiled and analyzed water quality data collected by a single entity, the Metropolitan Council Environmental Services (MCES), at several sites in the MNRRA corridor between 1976 and 2005 in order to 1) characterize longitudinal patterns, 2) evaluate seasonal patterns, and 3) assess interannual trends over the 30 year period of record. This analysis aims to fulfill National Park Service objectives related to synthesis of water quality efforts for parks (Lafrancois et al. 2007, Magdalene et al. 2008), and will help document and understand long-term changes in water quality at several of the MCES' prominent Mississippi River monitoring sites.

# Methods

## Study Sites

Eight MCES monitoring sites within MNRRA have 30-year water quality records and were selected for analysis (Figure 1). In the Mississippi River, their locations are denoted by number of river miles above the confluence with the Ohio River, and in the Minnesota River, by the number of river miles above the confluence with the Mississippi River (Table 1). Six sites are located on the Mississippi River: at Anoka (UM872), at Lock and Dam 1 (L&D#1, UM848), at St. Paul (UM839), at Newport (UM831), at Grey Cloud Island (UM827), and at Lock and Dam 2 (L&D#2, UM816). One site is located on the Minnesota River at Ft. Snelling State Park (MI4); the Minnesota discharges to the Mississippi at river mile 844, between the L&D#1 and St. Paul sites. The final site is located at the MCES Metropolitan Wastewater Treatment Plant (Metro Plant), measuring the Metro Plant outfall flow and water quality before it discharges to the Mississippi River at river mile 835, between the St. Paul and Newport sites. The Minnesota River and Metro Plant sites, previously described, were added to assess two major inputs to the Mississippi River in this region.

**Table 1**. Water quality sites and corresponding streamflow gauging sites used in analysis of water quality trends for the MNRRA reach of the Mississippi River. Site codes are used to describe monitoring locations.

| Monitoring Location | Site Code | Flow Data Source(s) |
|---|---|---|
| Upper Miss. R. 871.6 | UM872 | Anoka (USGS 05288500) |
| Upper Miss. R. 847.7 | UM848 | Anoka (USGS 05288500) |
| Upper Miss. R. 839.1 | UM839 | St. Paul (USGS 05331000) |
| Upper Miss. R. 831.0 | UM831 | St. Paul (USGS 05331000) plus MetPlant outflow |
| Upper Miss. R. 826.7 | UM827 | St. Paul (USGS 05331000) plus MetPlant outflow |
| Upper Miss. R. 815.6 | UM816 | St. Paul (USGS 05331000) plus MetPlant outflow |
| Minnesota R. 3.5 | MI4 | Jordan (USGS 05330000) |
| Metropolitan Plant | MetPlant | MetPlant outflow |

## Data Sources and Composition

### *Water quality*

For consistent and high quality data, this project analyzed data from a single agency, MCES. For over 30 years, MCES has been monitoring Mississippi River water quality throughout the TCMA, sampling at high frequencies (weekly to twice monthly) for an extensive list of parameters (Table 2). Data were compiled for all eight sites over a 30-year period of record (1 January 1976 through 31 December 2005). Because electronic data for the Metro Plant site only became available in 1981, we calculated monthly means from hardcopy data sheets (daily records) for this site to populate the 1976-1980 portion of the dataset.

Data for each site consisted of year-round weekly to twice monthly samples from each of the river sites and daily samples from the Metro Plant. Water quality variables for the river sites

**Table 2**. Water quality variables in the compiled 1976-2005 dataset for six Mississippi River sites, one Minnesota River site, and the Metro Plant. "Conc" = concentration, "Load" = load, "X" = variable measured, "*" indicates that concentration was substantially (ρ > 0.3) correlated with flow at all river sites, using monthly median statistics for concentration and flow, and "**" indicates that concentration was substantially correlated with flow at river sites including and downstream of MI4.

| Variable | Abbrev. | Unit (conc) | Unit (load) | River Sites | Metro Plant | Flow-Correl. |
|---|---|---|---|---|---|---|
| Streamflow | Flow | cfs | -- | X | -- | |
| Water Temperature | Temp | °C | -- | X | X^ | * |
| Dissolved Oxygen | DO | mg/L | -- | X | X | |
| Specific Conductance | SC | µmhos | -- | X | -- | |
| pH | pH | SU | -- | X | X | |
| Total Nitrogen | TN | mg/L | kg | X | X | * |
| Total Kjeldahl Nitrogen | TKN | mg/L | kg | X | X | |
| Dissolved Inorganic Nitrogen | DIN | mg/L | kg | X | X | * |
| Total Ammonia Nitrogen | TAN | mg/L | kg | X | X | ** |
| Nitrate- + Nitrite-Nitrogen | $NO_3$+$NO_2$-N | mg/L | kg | X | X | * |
| Total Phosphorus | TP | mg/L | kg | X | X | |
| Orthophosphate-Phosphorus | OP | mg/L | kg | X | -- | |
| Dissolved Phosphorus | DP | Mg/l | Kg | -- | X^ | |
| Turbidity | Turb | JTU/NTU | -- | X | X | * |
| Total Suspended Solids | TSS | mg/L | kg | X | X | * |
| Volatile Suspended Solids | VSS | mg/L | kg | X | -- | * |
| Total Chlorophyll-*a* | TChl-a | µg/L | kg | X | -- | |
| Total Nitrogen: Total Phoshorus | TN:TP | -- | -- | X | X | ** |
| Dissolved Inorganic Nitrogen: Total Phosphorus | DIN:TP | -- | -- | X | X | ** |
| Orthophosphate-Phosphorus: Total Phosphorus | OP:TP | -- | -- | X | -- | |
| Dissolved Phosphorus: Total Phosphorus | DP:TP | -- | -- | -- | X^ | |
| Volatile Suspended Solids: Total Suspended Solids | VSS:TSS | -- | -- | X | -- | * |
| Total Phosphorus: Total Chlorophyll-*a* | TP:Chl-a | -- | -- | X | -- | |

^Water temperature and DP measurements began in late 1990 and do not span entire 1976-2005 data record.

consisted of water temperature, dissolved oxygen (DO), pH, specific conductance (SC), total Kjeldahl nitrogen (TKN), nitrite-nitrogen ($NO_2$-N), nitrate-nitrogen ($NO_3$-N), total ammonia nitrogen (TAN), total phosphorus (TP), orthophosphate-phosphorus (OP), viable chlorophyll-*a* (Chl-*a*), total suspended solids (TSS), volatile suspended solids (VSS), and turbidity. From these raw data, we calculated total nitrogen (TN, as the sum of TKN and $NO_2$+$NO_3$-N), dissolved inorganic nitrogen (DIN, as the sum of $NO_3$+$NO_2$-N and TAN), and several constituent ratios (TN:TP, DIN:TP, OP:TP, VSS:TSS, and TP:Chl-*a*). We used TN:TP and DIN:TP ratios to understand the relative proportions of key nutrients and to provide an indication of algal nutrient limitation status, recognizing the strong role of light availability in turbid waters. We used the ratio of OP:TP (along with concentrations of OP) to examine patterns in phosphorus bioavailability, and the ratio of VSS:TSS to examine patterns in the proportion of organic versus inorganic suspended solids. Finally, we used TP:Chl-*a* to explore variability in the relationship between a potentially limiting nutrient and algal biomass. Water quality variables for the Metro Plant were similar to those of the river sites, but excluded SC, Chl-*a,* and VSS, and included dissolved phosphorus (DP) instead of OP; temperature and DP were not measured consistently at the Metro Plant prior to 1990 and are included in our analysis for context only. Variables generally sampled weekly at river sites included temperature, pH, DO, TAN, and turbidity; other variables were typically sampled twice monthly.

### *Streamflow*

U.S. Geological Survey (USGS) streamflow gauges are located near two of the water quality monitoring sites on the Mississippi River (UM 872 and UM 839), and MCES measures the discharge from the Metro Plant. To estimate streamflow data for the remaining sites, we reviewed available streamflow data from nearby USGS discharge gauging sites at Anoka (USGS 05288500), St. Paul (USGS 05331000), Jordan (USGS 05330000), and Fort Snelling (USGS 05330920), and from U.S. Army Corps of Engineers (USACE) streamflow gauging sites at Lock and Dams 1 and 2, in Minneapolis and Hastings respectively. In developing appropriate streamflow data for each site (Table 2), we considered proximity to existing gauging stations, intervening tributary or Metro Plant inputs, and streamflow relationships between upstream and downstream gauges. Site UM 848 is located just upstream of Lock and Dam 1, between the USGS Anoka gauge and the USACE Lock and Dam 1 gauge. Since long-term streamflow data at these two gauges approximated a 1:1 relationship ($r^2$=0.99), we used Anoka streamflow for the UM 848 site. Sites UM 831, UM 827, and UM 816 are all located downstream of the St. Paul gauging site and the Metro Plant outflow. We added Metro Plant outflow to the St. Paul streamflow data to develop a more accurate streamflow estimate for these sites. The Minnesota River site, MI4, is located at the Fort Snelling gauging station; however, this station has a much more limited streamflow record than the upstream gauging station at Jordan. Since streamflow at Jordan averaged 97 percent of the streamflow at Fort Snelling over their shared period of record, we determined that Jordan streamflow adequately represented streamflow at MI4 and used Jordan streamflow in our analyses.

## Data Preparation

As is typical of long-term water quality monitoring records, values below detection limits occurred for some variables. For most variables, values below detection limits represented less than five percent of the total number of observations for that variable, and were deemed unlikely to influence the accuracy of trend tests or slope estimates (Helsel and Hirsch 1992). For TAN and VSS, however, more than five percent of the values across all sites were below the detection limits, and detection limits varied over time. We determined the most frequently occurring detection limit for these variables (0.02 mg/L and 2 mg/L for TAN and VSS, respectively) and set all “less than” data to that limit.

Since all water quality data were acquired from a single source with known quality assurance procedures, outliers related to lab procedures or data processing errors were not expected. However, to address this possibility we constructed stem and leaf plots for each variable at each monitoring site. We individually evaluated all values exceeding upper or lower hinge limits (i.e., beyond approximately 2.7 standard deviations of the mean. Because our statistical methods were robust to outliers, and because high or low values may represent real system variability, in the end no data points were omitted. To ensure that our final dataset was based on consistent sampling frequencies over time and to reduce the number of data points and the potential influence of serial correlation, we calculated monthly median values (Harcum et al. 1992). We used these monthly median values in subsequent flow-correction procedures and long-term trend analyses.

Exogenous variables such as flow can confound the analysis of water quality concentration trends over time. To determine which variables were related to flow and to reduce this potential source of interference, for each site we constructed scatter plots and a Spearman rank correlation matrix with pair-wise deletion for monthly median water quality variables versus flow. We did not transform variables prior to analysis, since Spearman rank correlations do not assume a linear relationship. We identified important flow-concentration relationships by examining correlation coefficients; variables with correlation coefficients $\geq 0.30$ were considered substantially flow-correlated. We used a locally weighted polynomial regression (LOESS) procedure to remove the effects of flow (Helsel and Hirsch 1992). In order to compute flow-adjusted concentrations for trend analysis and display purposes, median concentration values for each variable at each site were added to residuals from the LOESS fit of concentration to flow (Lettenmaier et al. 1991, Smith et al. 1996).

We calculated loads by analyzing water quality concentration data in conjunction with mean daily flows, using FLUX32 for Windows. Model Method 6, which uses a concentration-versus-flow regression equation applied to the mean daily flow, was selected, since Walker (1999) reported it as the best method for generating load time series. Using the most upstream site (UM 872), various combinations of models and methods of stratifying the data (by flow, date, or season) were evaluated against all concentration variables to minimize the average of the coefficients of variation (CVs) of the six different models embedded within FLUX. The stratification method with the lowest average CVs was the following seasonal stratification: early spring (March 1 – April 15), late spring and summer (April 15 – September 1), autumn (September 1 – December 1), and winter (December 1 – March 1). For consistency in analysis, the same seasonal stratification was used for modeling all combinations of sites and water quality variables. The subsequent models generated estimates of daily, monthly, and annual loads of the modeled variables for the 30-year period at all sites.

### Longitudinal Trend Analysis

To evaluate longitudinal differences in overall water quality conditions across sites, we compared long-term (1976-2005) median concentrations of water quality variables across sites, based on all measured values, and compared long-term median loads of water quality variables across sites using modeled annual loads. We prepared bar graphs showing median concentrations and loads (plus or minus the 25$^{th}$ and 75$^{th}$ percentiles) for each variable across sites, and characterized longitudinal patterns qualitatively.

### Temporal Trend Analysis

#### *Seasonal patterns*

To explore seasonal patterns across sites, we calculated long-term median concentrations of each variable, by month, over the 1976-2005 period of record, and constructed smoothed line plots of these and modeled monthly load values. Seasonal patterns were then characterized qualitatively and compared among sites, based on data summary tables and line plots.

### *Long-term trends*

We explored longer-term temporal trends using both visual representations and statistical trend analyses. For graphical analysis of concentration data, we plotted the annual median for each site (i.e., the median of all measured values at each site for each year). For graphical analysis of loading data, we plotted the annual median of the monthly modeled loads for each site. We analyzed long-term trends statistically using the seasonal Kendall trend test and Sen's Slope Estimator in WQ Stat Plus v. 1.5. This test is suitable for large water quality monitoring data sets because it is nonparametric, can effectively account for seasonal variation, and is robust to outliers, missing values, and values less than detection limits (Hirsch et al. 1991). Since water quality in rivers of the region is strongly linked to time of year (Kloiber 2004), and because no coarser seasonal designation could be applied to all variables, we calculated monthly median concentrations and defined twelve separate seasons for use in the seasonal Kendall tests.

We conducted trend tests for each variable at each site using both the flow-adjusted and unadjusted datasets. This resulted in a large number of statistical tests; as a result we interpreted statistical trend results cautiously, focusing on trends that were most marked and most consistent among all or a meaningful subset of sites. We determined whether to report flow-adjusted vs. unadjusted trends by reviewing the flow-concentration relationships for each variable. Some have cautioned against using flow-adjusted data in situations with strong human influences on streamflow (Helsel and Hirsch 1992), and streamflow has in fact been altered by human activities in the study reach over the period of record. Increasing agricultural tile drainage in the Minnesota River Basin (Magner et al. 2004, Blann et al. 2009) and increasing impervious surfaces in the TCMA (Bauer et al. 2004, Manson and Bauer 2006) have likely contributed to increased streamflows in the Mississippi River, and inputs from the Metro Plant have varied as a result of population growth, sewer separation, and infiltration and inflow reduction efforts. For these reasons, we were cautious in our use of flow-adjusted data, using flow-adjusted trends only if a substantial and consistent flow-concentration relationship could be identified across all or most sites for each variable (Table 1). We presented interannual trend results in terms of trend direction (expressed as up or down) and trend magnitude (expressed as 1) total change over the period of record, in original units, and 2) percent change, calculated by dividing the total change over the period of record by the median value for each variable at each site, times 100).

### *Spatiotemporal loading trends*

To incorporate the effects of climate and flow conditions into our analysis of longitudinal loading trends, we prepared additional graphs for review and interpretation. We broke the dataset into five-year increments (i.e., 1976-1980, 1981-1985, 1986-1990, 1991-1995, 1996-2000, and 2001-2005), calculated median annual flows for each five-year increment, and characterized each increment as low-flow (0-33 percentile rank), moderate-flow (34-66 percentile rank), or high-flow (67-99 percentile rank). For selected variables, we then calculated median annual loads for each five-year increment and plotted them from the uppermost site at UM872 to the lowermost site at UM816. We used the resulting graphs to better characterize the relationship of longitudinal trends to flow conditions and time.

# Results

## Longitudinal Patterns

This section addresses overall longitudinal patterns in the 30-year medians and interquartile ranges of the selected variables, irrespective of temporal trends in the data.

### *Core water quality variables*

Longitudinal trends in the NPS core suite of variables (i.e., flow, temperature, dissolved oxygen (DO), specific conductance (SC), and pH) are presented in Figure 2. Streamflow increased from upstream to downstream, primarily due to inputs from the Minnesota River, the Metro Plant, and smaller tributaries and stormwater outflows (these sources accounted, respectively, for approximately 26, three, and six percent of the stream flow at UM816 over the period of record). The long-term median temperature of the Metro Plant outfall was about 5 °C warmer than the mainstem of the Mississippi River, but due to its low flow volume, it had very little influence on the long-term median temperatures in the Mississippi River below the Metro Plant. At all river sites, the long-term median DO concentrations were well above the State of Minnesota water quality standard of 5 mg/L (as a daily minimum) (Table 3). Although the long-term median DO concentration at the Metro Plant outfall was very close to that standard, it did not cause a major decrease in DO levels in the Mississippi River. There was a slight decrease in SC between UM872 and UM848, then a large increase at UM 839 below the Minnesota River (which had median SC values over twice as high as upstream Mississippi River values), and another smaller increase below the Metro Plant. The long-term median pH was fairly constant across the entire study area, with relatively small interquartile ranges at each site.

**Table 3**. State and federal water quality standards for sections of the Mississippi River, the Lower Minnesota River (RM 22 to mouth), and Metro Plant effluent. pH, dissolved oxygen, and nitrate + nitrite nitrogen standards were based on designated use classifications. Total suspended solids, total phosphorus, and total chlorophyll-*a* for Mississippi River sites are proposed criteria based on site-specific or regional plans in development.

| Variable | Above St. Anthony Falls | Above Lock and Dam 1 | Below Lock and Dam 1 | Lower Minnesota River | Met Plant |
|---|---|---|---|---|---|
| DO (mg/L) | >5 | >5 | >5 | >5 | 7 – 9 |
| pH (SU) | 6.5 – 8.5 | 6.5 – 9.0 | 6.5 – 9.0 | 6.5 – 9.0 | 6.0 – 9.0 |
| $NO_3$+$NO_2$-N (mg/L) | 10 | 10 | 10 | 10 | None |
| TP (mg/L) | 0.10 | 0.10 | * | 0.13 – 0.15** | 1.00 |
| TSS (mg/L) | 31 | 31 | 32 | ca. 65*** | 30 |
| TChl-*a* (µg/L) | 20 | 35 | 35 | 40 | None |

*Not available since a strong relationship between TP and Chl-*a* could not be established in Pool 2 (Heiskary and Wasley 2010).

**The proposed TP standard for the southern river region is 0.15 mg/l (Heiskary and Wasley 2010), but the Minnesota River low oxygen TMDL states TP must be less than 0.131 mg/l in order to meet oxygen goals (Gunderson and Klang 2004).

*** Based on a turbidity standard of 25 NTUs.

***Nutrients***

Longitudinal trends in the concentrations and annual loads of nitrogen species (TN, TKN, DIN, TAN, $NO_3$+$NO_2$-N) are presented in Figures 3a and 3b. For all nitrogen variables, the Minnesota River and Metro Plant sites had much higher concentrations than upstream Mississippi River sites (UM 872 and UM 848). Additionally, the long-term median nitrogen concentrations at the Metro Plant were about two to three times higher than those of the Minnesota River. However, because of differences in relative flow volumes, the increases in median loads downstream of the Metro Plant were relatively minor compared to increases in median loads below the Minnesota River for all nitrogen species except TAN. The total Kjeldahl nitrogen:total nitrogen (TKN:TN) ratios (not shown) were higher at UM 872 and UM 848, reflecting a greater proportion of organic nitrogen at these upstream sites. In contrast, nitrogen below the confluence of the Minnesota River was dominated by inorganic nitrogen, mostly $NO_3$+$NO_2$-N.

Long-term longitudinal trends in the concentrations and annual loads of phosphorus (TP and OP or DP) are shown in Figure 4. Both Minnesota River and Metro Plant inputs resulted in higher mainstem Mississippi River phosphorus concentrations and loads. The long-term median phosphorus concentrations in the Minnesota River were much higher than those in the Mississippi River sites upstream of its confluence, such that concentrations and annual loads approximately doubled below the confluence. Total phosphorus loads increased more substantially below the Minnesota River than below the Metro Plant. Conversely, OP loads, representing the more bioavailable phosphorus, increased more substantially below the Metro Plant than below the Minnesota River. Longitudinally, Mississippi River TP and OP concentrations and loads peaked below the Metro Plant and decreased slightly through the remainder of the study area.

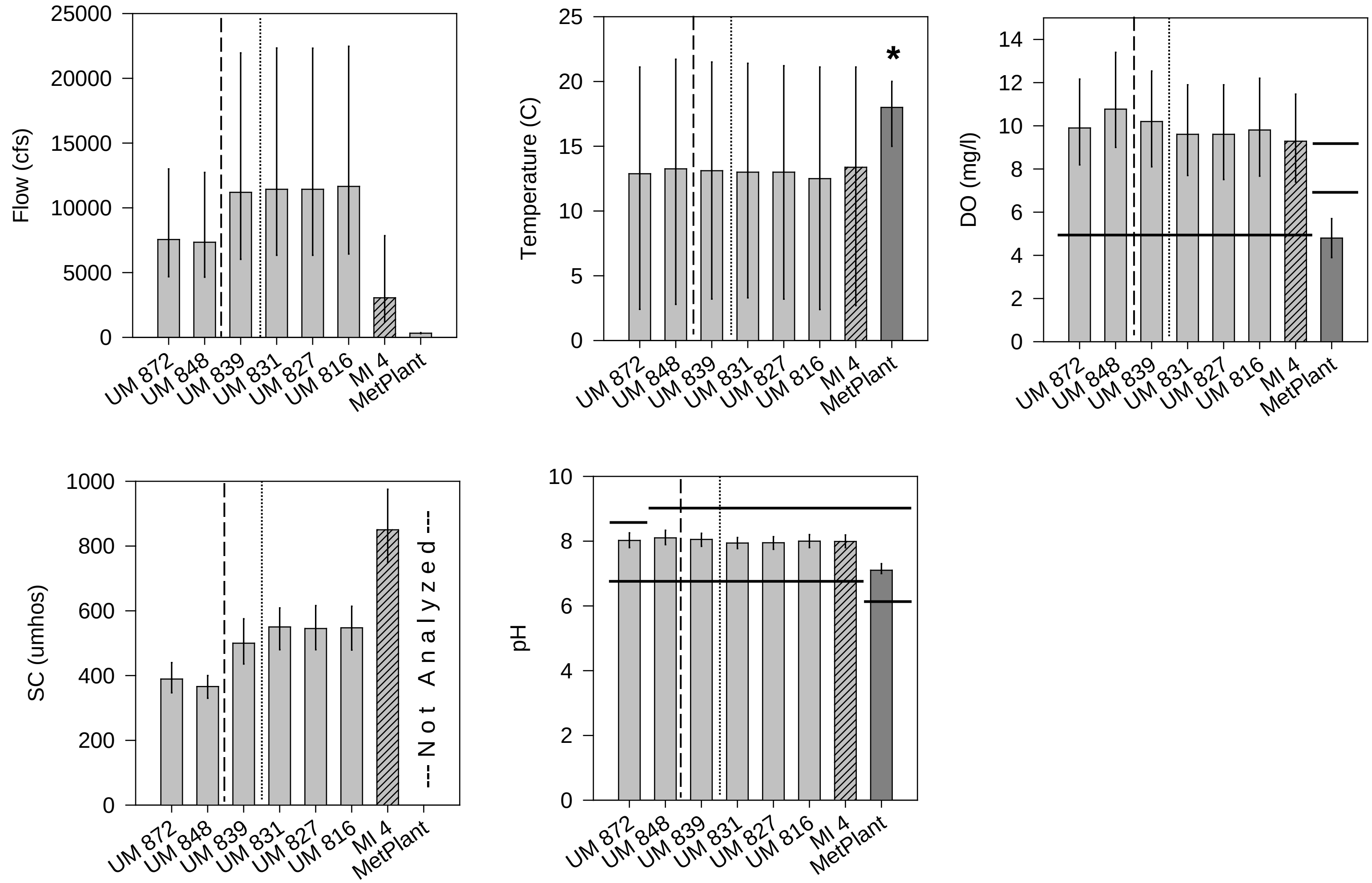


**Figure 2.** Spatial trends in long-term median values for streamflow and core water quality variables at six Mississippi River sites (UM872, UM848, UM839, UM831, UM827, and UM816), one Minnesota River site (MI 4), and the Metro Plant (Met Plant), 1976-2005. Error bars denote 25th and 75th percentiles. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively. State water quality standards (see Table 3) are shown as solid black lines for pH (lower and upper limit) and DO concentrations (lower limit for river sites, lower and upper limit for MetPlant effluent). *Note: At the Metro Plant, water temperature data are not available for the full period of record; 1994-1999 data are included for comparative purposes.

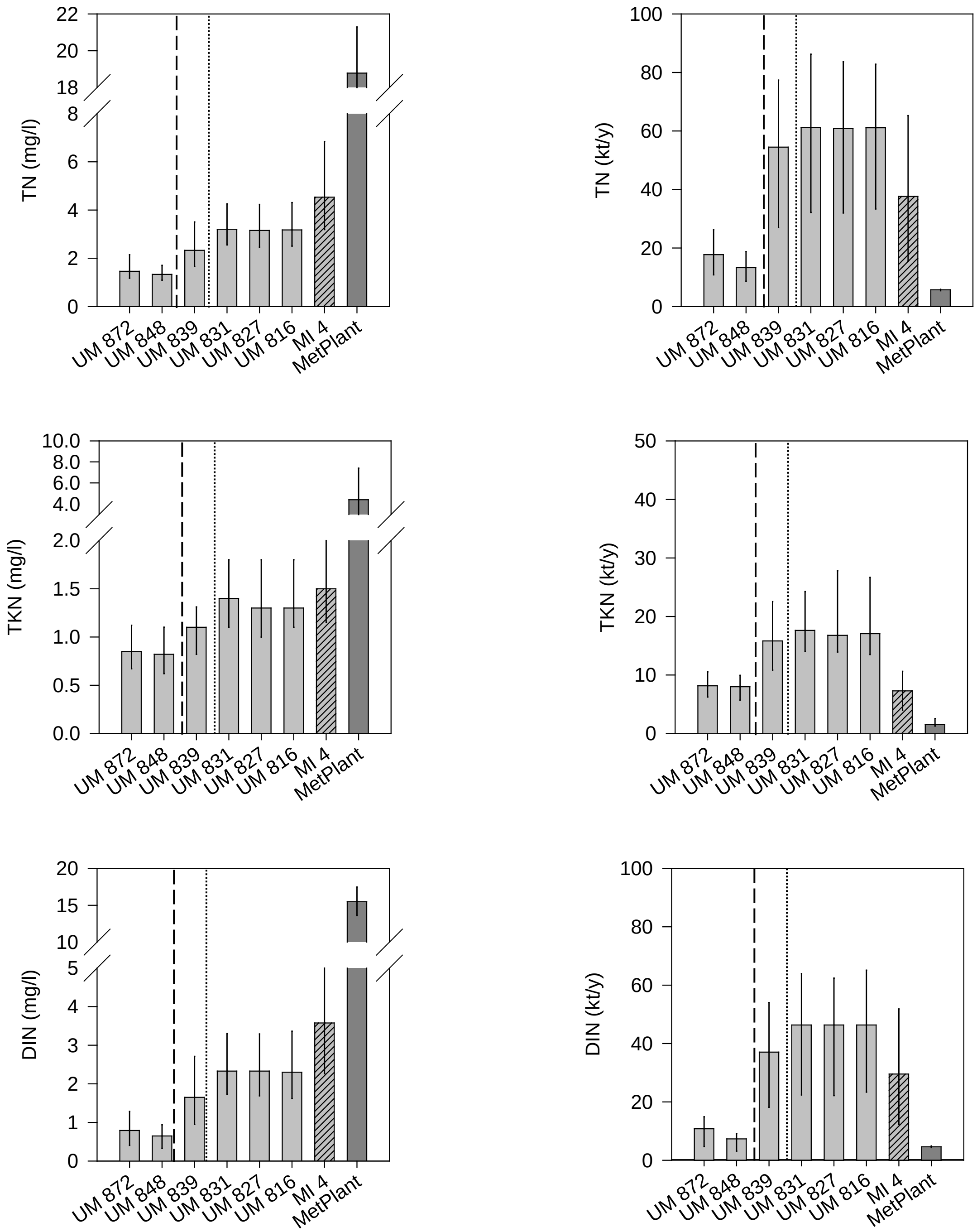


**Figure 3.** Spatial trends in long-term median concentrations (left) and loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, from 1976-2005. Error bars denote 25th and 75th percentiles. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively. The federal water quality standard for nitrogen oxide concentration (see Table 3) is depicted by a solid black line.

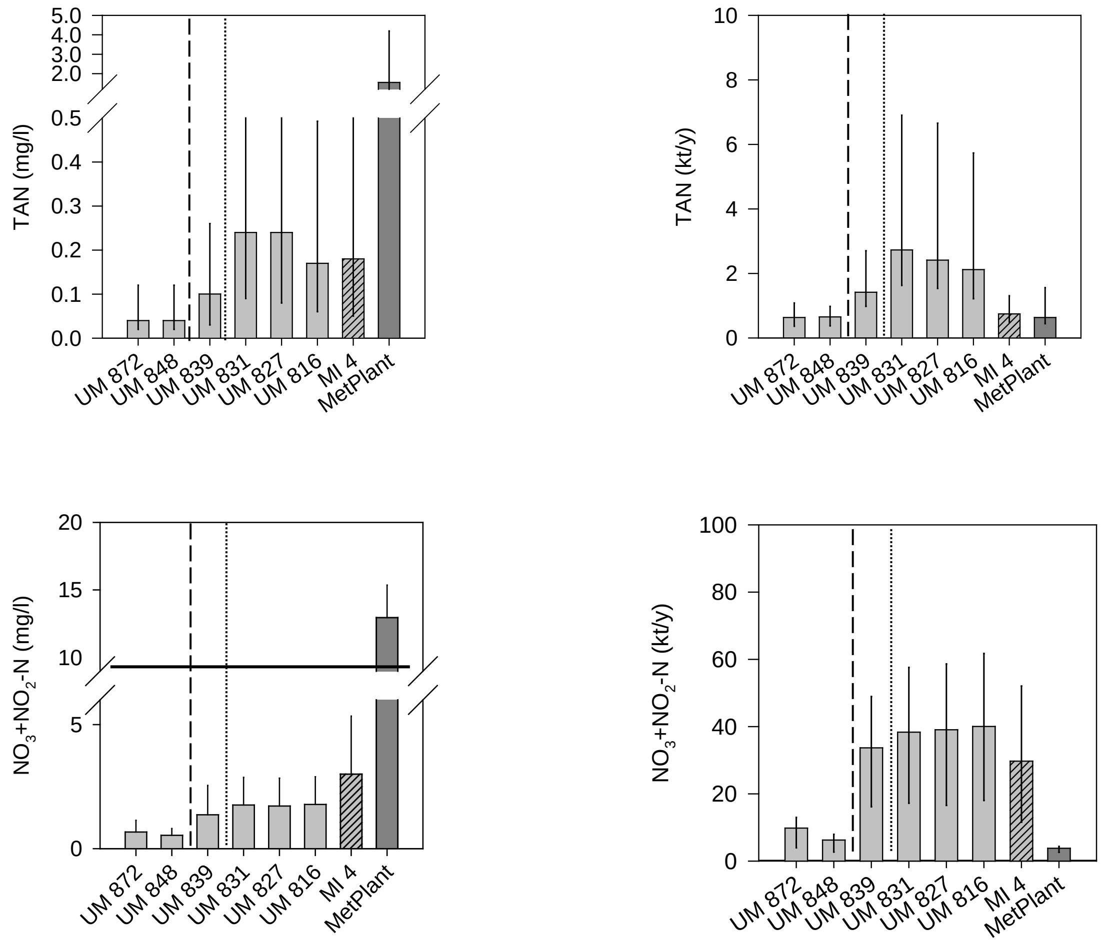


**Figure 3**. Spatial trends in long-term median concentrations (left) and loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, from 1976-2005. Error bars denote 25th and 75th percentiles. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively. The federal water quality standard for nitrogen oxide concentration (see Table 3) is depicted by a solid black line (continued).

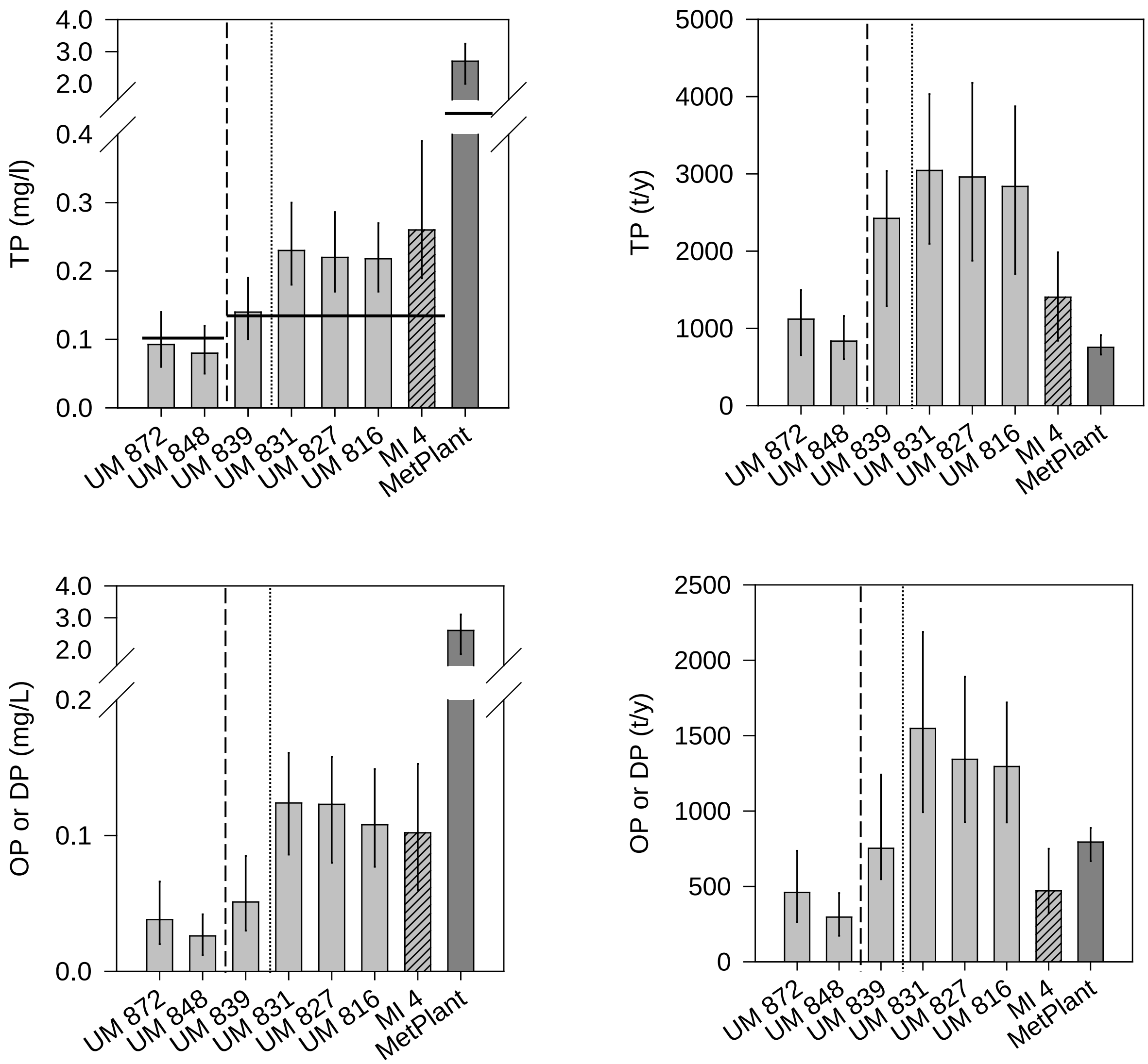


**Figure 4.** Spatial trends in long-term median concentrations (left) and loads (right) for phosphorus variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. Error bars denote 25th and 75th percentiles. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively. The proposed reach-specific state water quality criterion for TP (see Table 3) is depicted with a solid black line. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, is included for general comparison.

### *Seston*

Longitudinal trends in concentrations and annual loads of seston (turbidity, TSS, VSS, Chl-*a*) are shown in Figures 5a and 5b. Seston was highly variable, with large long-term interquartile ranges, especially at the Minnesota River site which had the highest concentrations for all of these parameters. Turbidity levels and TSS concentrations at Mississippi River sites nearly doubled below the confluence of the Minnesota River, and TSS loads nearly quadrupled, with no discernible increases occurring downstream of the Metro Plant. Likewise, VSS and Chl-*a* concentrations and loads increased greatly below the confluence of the Minnesota River.

### *Water quality ratios*

Longitudinal trends in concentration ratios between selected water quality variables (TN:TP, DIN:TP, OP:TP, VSS:TSS, and TP:Chl-*a*) are shown in Figure 6. Variability in these ratios was generally high. Long-term median TN:TP and DIN:TP ratios were relatively high at all riverine sites, suggesting phosphorus limitation of algal growth. The ratio of DIN:TP increased downstream of the nitrogen-dominated Minnesota River confluence and decreased downstream of the phosphorus-dominated Metro Plant outflow. The bioavailability of phosphorus, assessed here by long-term median OP concentrations and the ratio of OP:TP, decreased slightly between UM 872 and UM 848, but increased slightly below the Minnesota River and increased even more due to wastewater inputs below the Metro Plant. The lower long-term median VSS:TSS at MI4, and within the Mississippi River below its confluence with the Minnesota River, indicates the relatively greater proportion of inorganic solids in this agricultural tributary. Although TP:Chl-*a* ratios were highly variable at all sites, TP:Chl-*a* increased downstream of the Metro Plant as a result of the Plant's high phosphorus concentrations.

## Seasonal Patterns

This section discusses seasonal patterns over the 30-year period of record by assessing the long-term medians for each month at each site. To avoid repetition, we have left out most observations related to longitudinal trends, though many of those are apparent in the seasonal trend figures.

### *Core water quality*

Seasonal patterns in the core water quality variables (flow, temperature, DO, SC, and pH) are depicted in Figure 7. Streamflow at Mississippi River sites reached annual lows in late winter and reached annual peaks during snowmelt runoff in April. The hydrograph receded rapidly until leveling off in May-June and receding to a seasonal low point in August. A smaller rise in river flows typically occurred in late autumn, after which streams and rivers began to freeze up for the winter. The Minnesota River followed a similar seasonal pattern, except that the early summer runoff peak was larger than the spring snowmelt peak. The monthly median water temperature for all river sites followed a simple annual curve, with a low of 0 °C in January and a high of 25 °C in July; Metro Plant monthly median temperatures peaked in September. Seasonal DO concentrations followed a pattern opposite that of water temperature, with summertime low concentrations of 7-9 mg/L and wintertime high concentrations of 12-14 mg/L (except in the Minnesota River, which had winter DO concentrations of 10-12 mg/L). At Mississippi River sites, SC showed elevated winter levels, a marked depression during spring snowmelt, and relatively stable levels during summer and early fall. In contrast, the Minnesota River site had SC values twice those of the Mississippi River sites and showed a slightly different seasonal pattern, with marked increases occurring in the fall. Although pH showed little among-site variability (Figure 2), it varied seasonally, showing elevated values during the growing season (Figure 7). Summertime pH values (and DO concentrations) at UM 848 were higher than those of other river sites, including the upstream UM872 site.

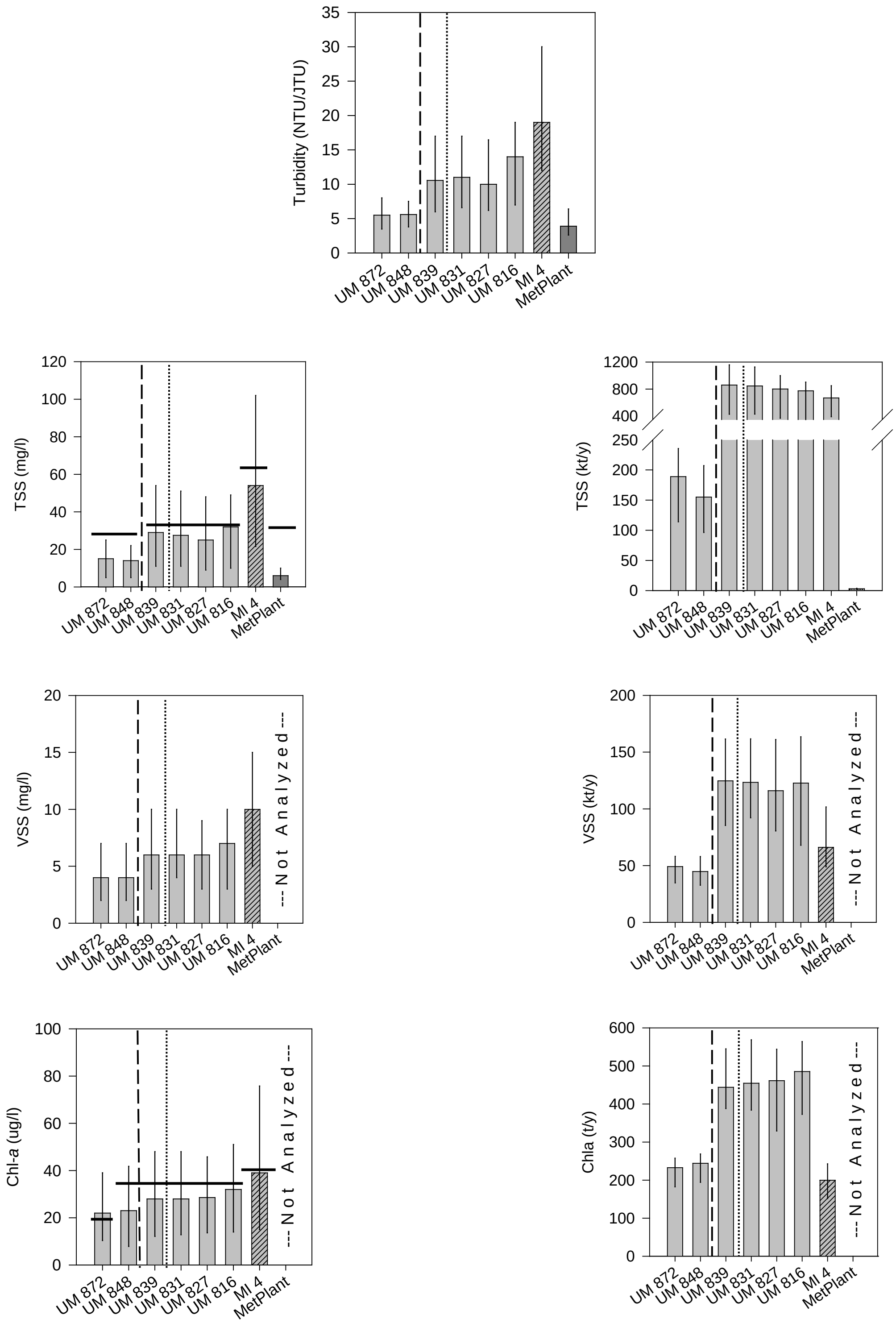


**Figure 5.** Spatial trends in long-term median concentrations (left) and loads (right) for seston variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, from 1976-2005. Error bars denote 25th and 75th percentiles. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively. Reach-specific state water quality standards for TSS and chlorophyll-a (see Table 3) are shown as solid black lines.

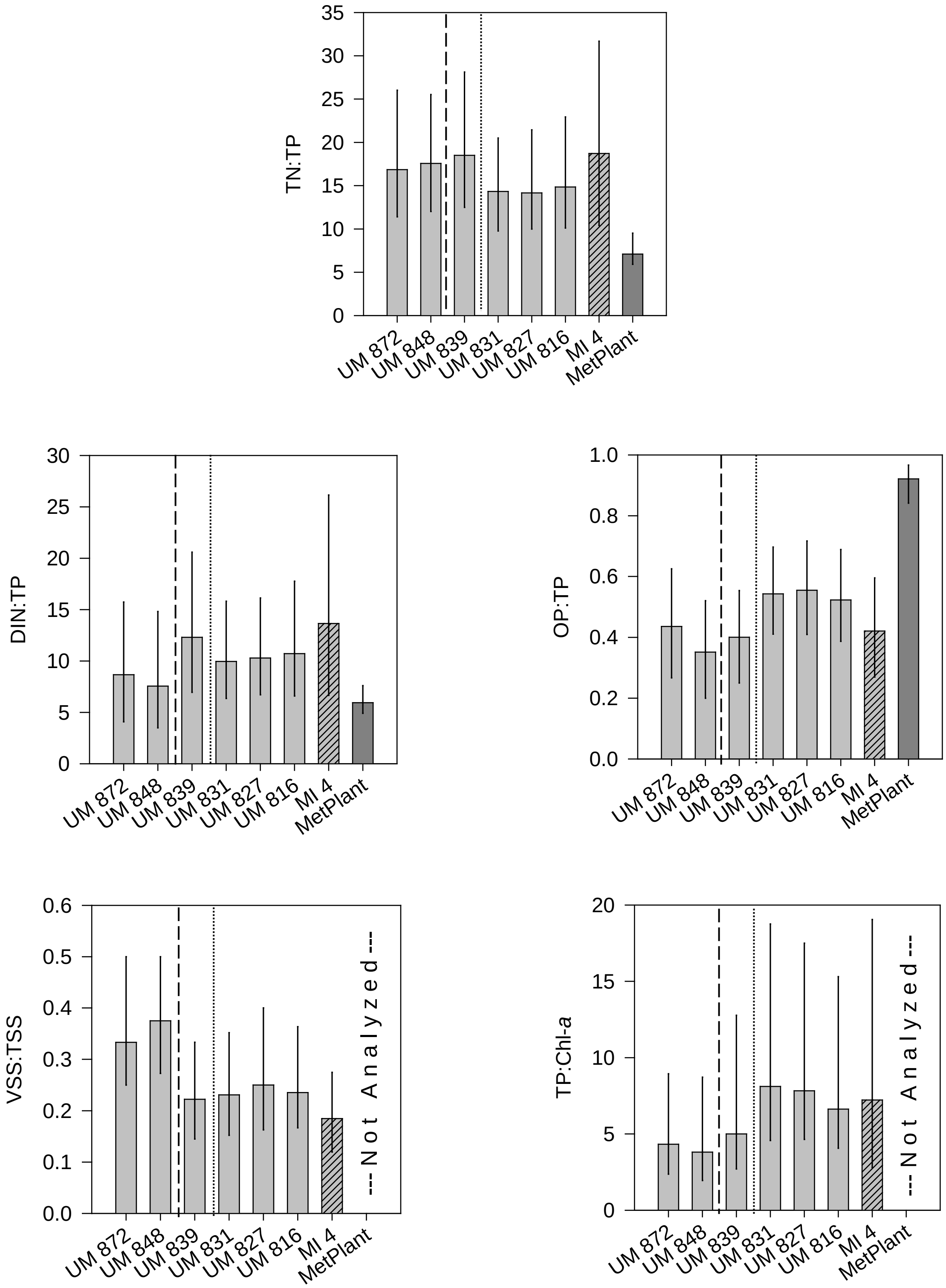


**Figure 6.** Spatial trends in long-term median values for nutrient and sediment ratios at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. Error bars denote 25th and 75th percentiles. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, was used to calculate DP:TP for general comparison.

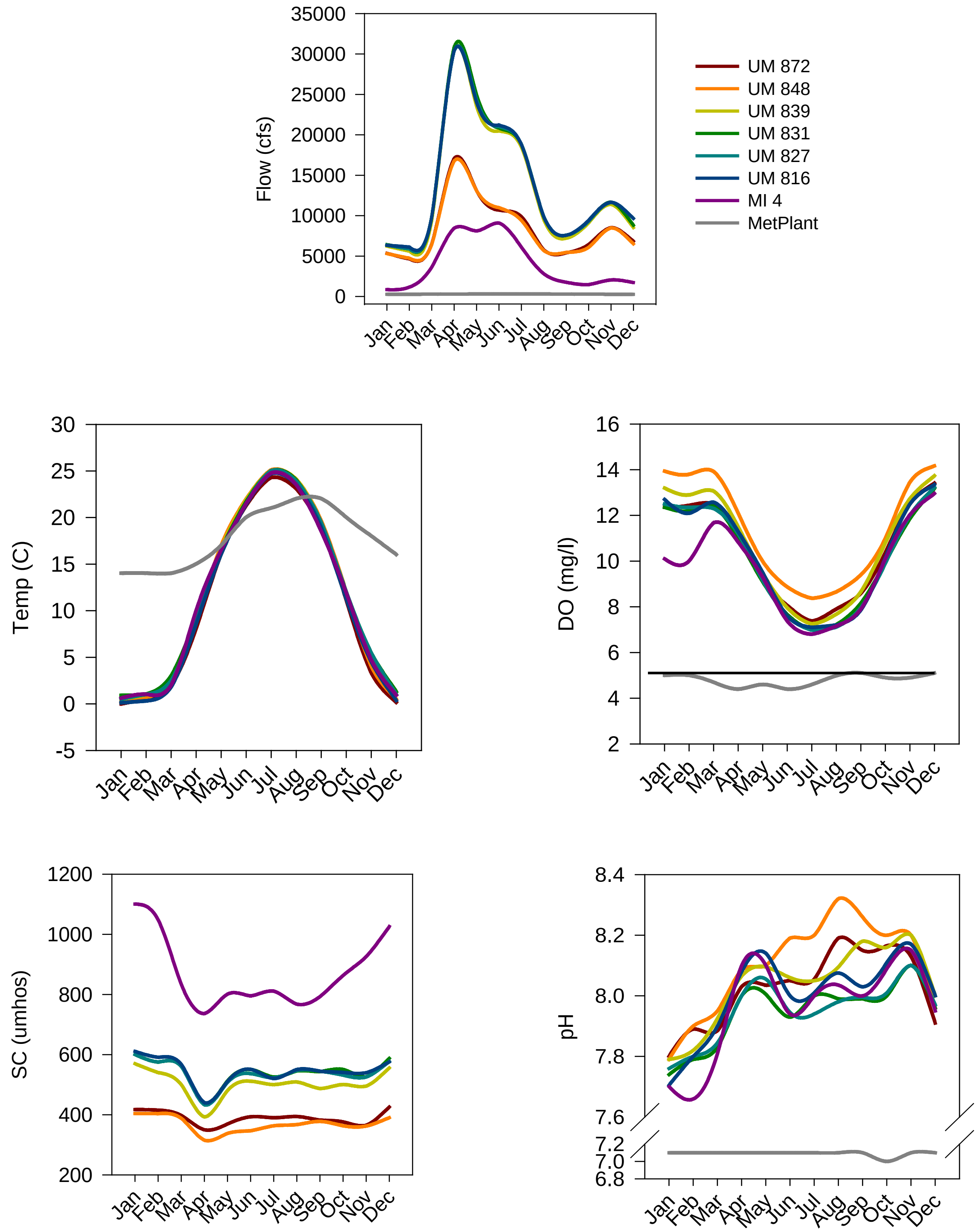


**Figure 7.** Seasonal trends for streamflow and core water quality variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values recorded for each month. Specific conductance was not analyzed at the Metro Plant. State water quality standard for DO (see Table 3) is depicted with a solid black line. *Note: At the Metro Plant, water temperature data are not available for the full period of record; 1994-1999 data are included for comparative purposes.

### *Nutrients*

Seasonal patterns in the concentrations and loads of nitrogen variables (TN, TKN, DIN, TAN, $NO_3$+$NO_2$-N) are displayed in Figure 8. At river sites, TN concentrations showed a marked peak in June, with the Minnesota River showing a secondary peak in November-December. Total nitrogen loads showed a different seasonal pattern, with a marked peak occurring during spring snowmelt and secondary peaks occurring in June and November-December. Seasonal patterns in both TN concentrations and loads at riverine sites were driven largely by changes in $NO_3$+$NO_2$-N, although TAN concentrations and loads also varied seasonally (peaking in February and March, respectively, and reaching seasonal lows during the summer months). Seasonal patterns in Metro Plant TN concentrations differed substantially from those of river sites, and were driven by changes in TKN and TAN rather than $NO_3$+$NO_2$-N. Loads of TAN and $NO_3$+$NO_2$-N showed seasonal patterns distinct from one another, with the majority of TAN loading occurring during late winter, and the majority of $NO_3$+$NO_2$-N loading occurring from March through July.

Seasonal patterns in the concentrations and loads of phosphorus variables (TP, OP at river sites or DP at the Metro Plant) are shown in Figure 9. At the Metro Plant, total and dissolved phosphorus concentrations were highest in winter and lowest in summer. In contrast, at river sites, TP and OP concentrations and loads showed strong peaks during spring snowmelt and in early summer. The springtime peaks in TP concentrations occurred later at the upper three Mississippi River sites (April) than in the Minnesota River and the lower three Mississippi River sites (March), likely reflecting geographical differences in the timing of snowmelt. All river sites experienced seasonal low concentrations of TP and OP in May, followed by secondary peaks in June and July (upper three MNRRA sites) or September (lower three MNRRA sites). Differences in the timing of these secondary peaks in phosphorus concentration at upstream sites (UM 872, UM 848, UM 839) versus downstream sites (UM 831, UM 827, UM 816) were likely driven by elevated Metro Plant phosphorus concentrations during the lower flow periods of late summer and autumn.

### *Seston*

Seasonal patterns in the concentrations and loads of seston variables (turbidity, TSS, VSS, Chl-*a*) are shown in Figures 10a and 10b. The lowest annual value for all seston variables occurred in winter (December through February), but turbidity, TSS, and VSS showed a distinctly different pattern than Chl-*a* during the growing season. Turbidity and the concentrations of TSS and VSS showed an initial peak in April, followed by a second larger peak in June. These two peaks are likely tied to runoff events from spring snowmelt and large, early summer rain events. The lowermost Mississippi River site (UM816, below Spring Lake) differed from the other river sites, showing a third peak in September for turbidity and concentrations of TSS and VSS. Chlorophyll-*a* concentrations at all sites remained low through March, peaked in May (when turbidity and suspended solids concentrations had declined), and reached a seasonal low in June-July (while turbidity and suspended solids concentrations were high), not climbing again until turbidity and suspended solid concentrations subsided in late summer. These observations suggest that light conditions (along with nutrients, water temperature, and hydrology) are important in determining algal growth within MNRRA.

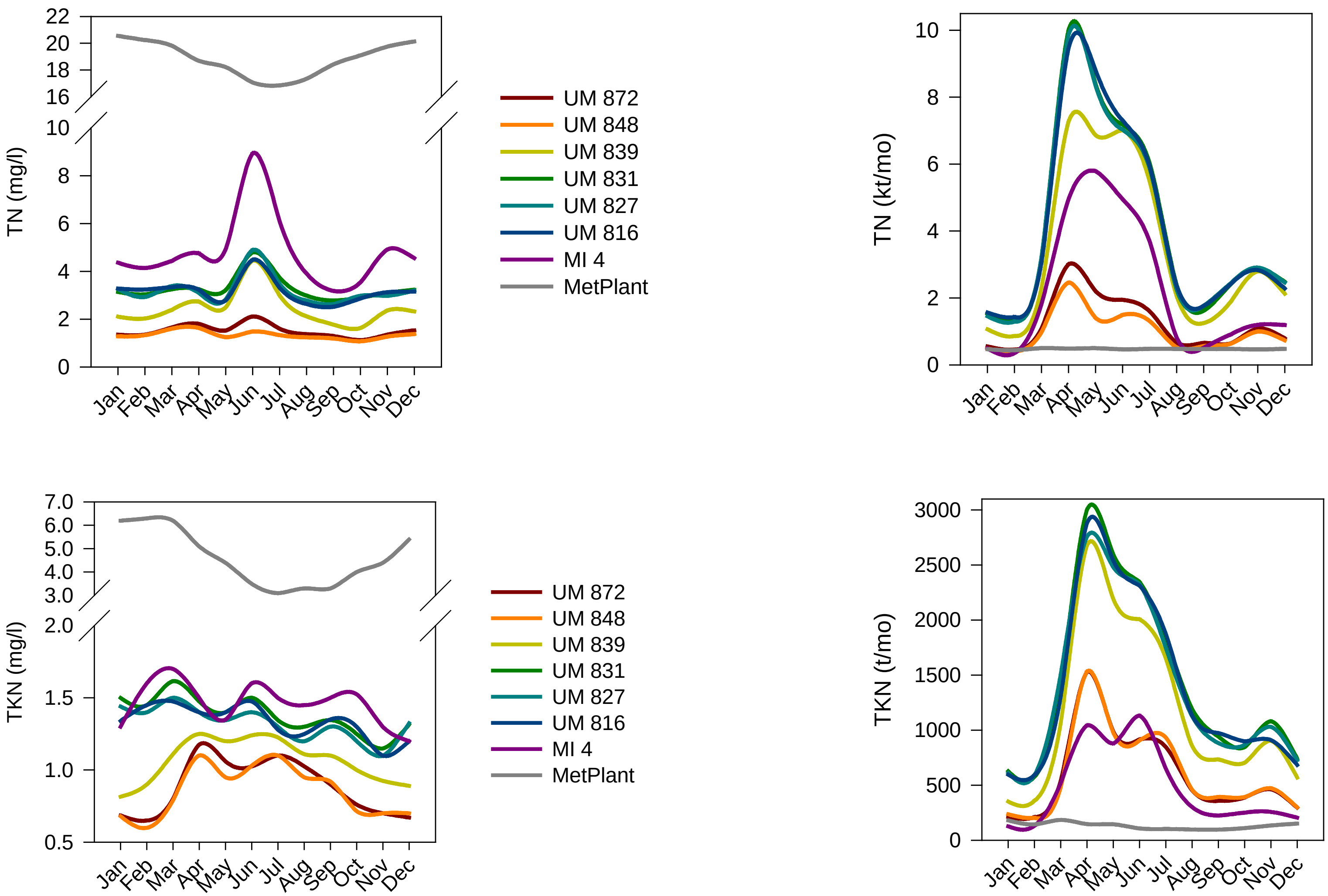


**Figure 8.** Seasonal trends in concentrations (left) and loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values recorded for each month. Nitrogen oxide concentrations are compared to the federal water quality standard (see Table 3).

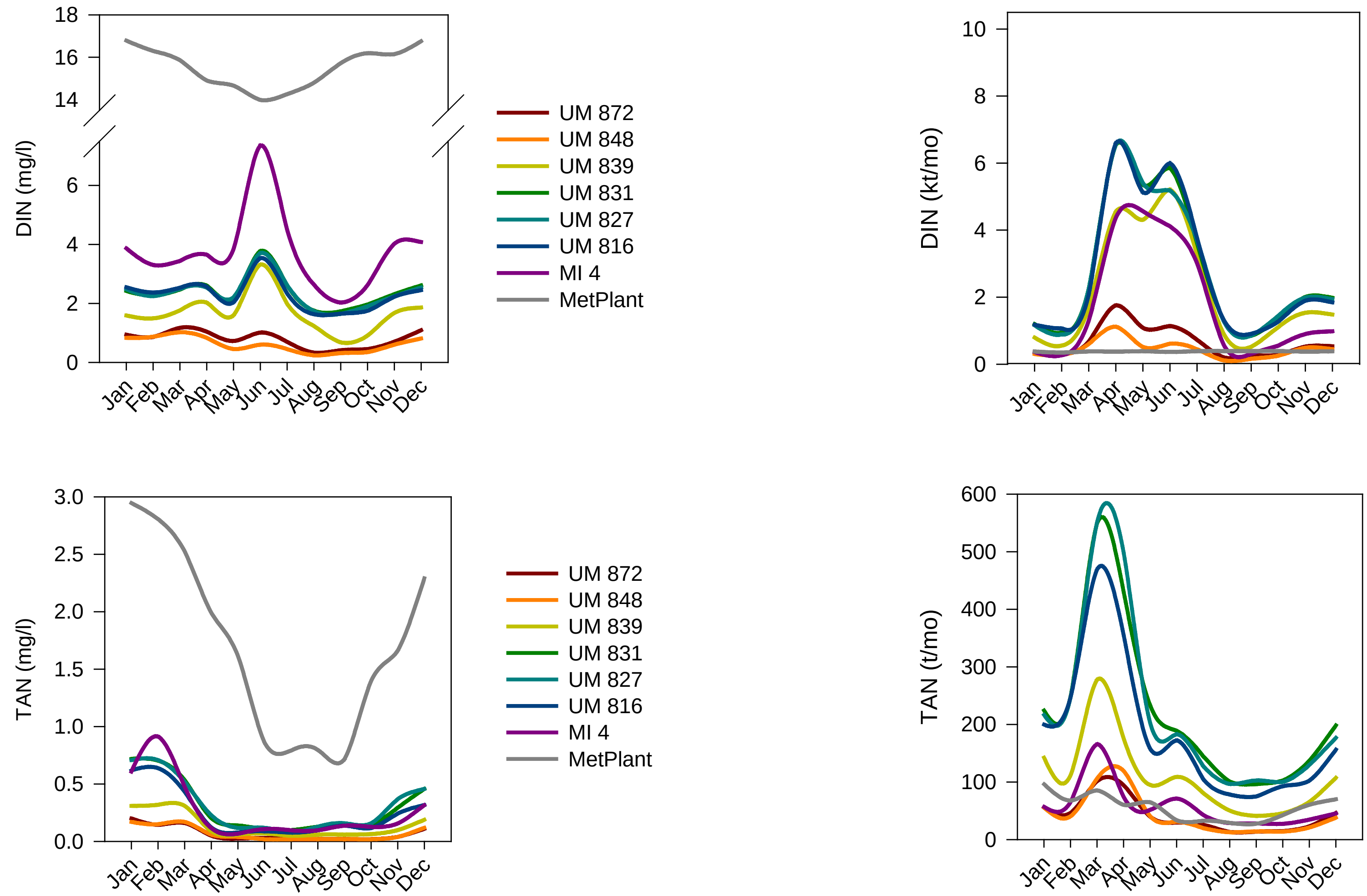


**Figure 8.** Seasonal trends in concentrations (left) and loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values recorded for each month. Nitrogen oxide concentrations are compared to the federal water quality standard (see Table 3) (continued).

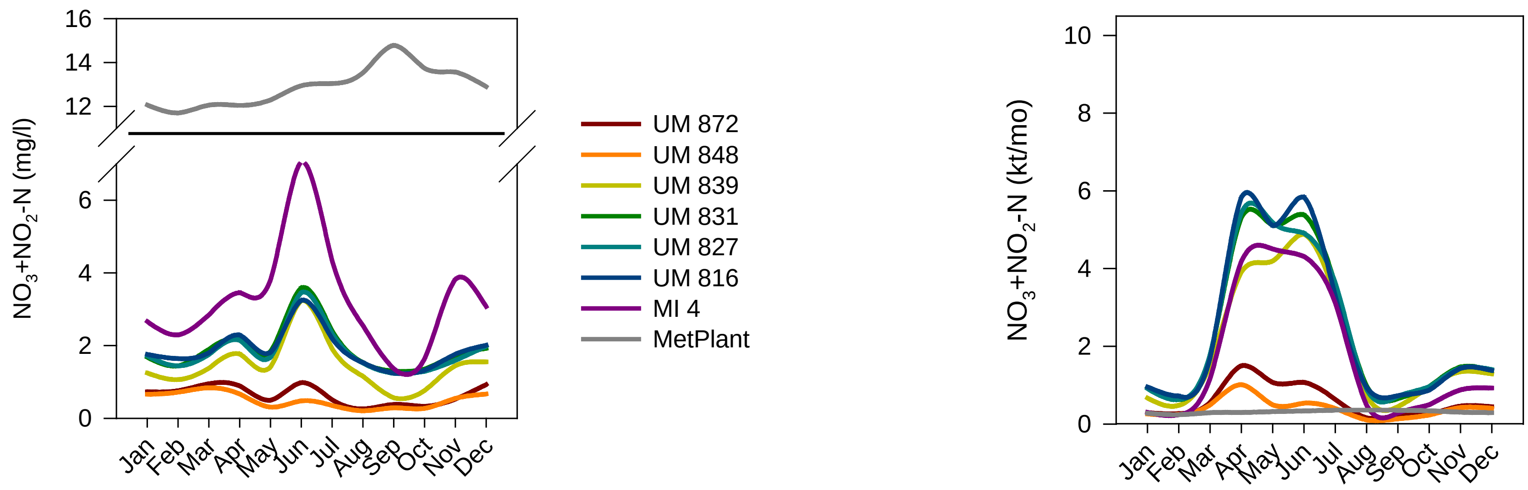


**Figure 8.** Seasonal trends in concentrations (left) and loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values recorded for each month. Nitrogen oxide concentrations are compared to the federal water quality standard (see Table 3) (continued).

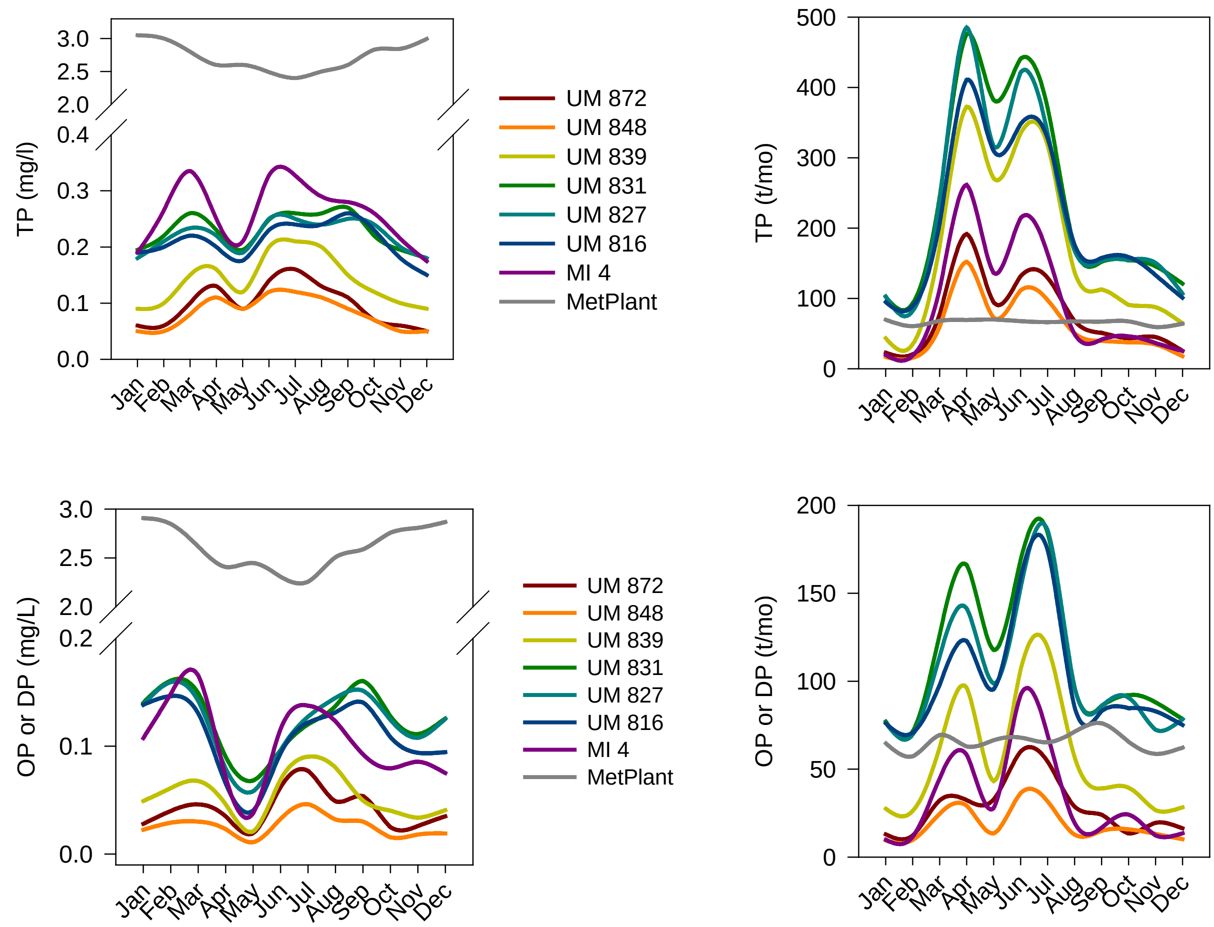


**Figure 9.** Seasonal trends in concentrations (left) and loads (right) for phosphorus variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values recorded for each month. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, is included for general comparison.

Seasonal loads of TSS and VSS showed strong peaks in April and June. Total suspended solids loads were lower at UM 816, the lowermost Mississippi River site, than at other sites downstream of the Minnesota River, suggesting sediment settling and deposition may be occurring in Spring Lake. Chlorophyll-*a* loads in the Minnesota River were similar to loads at upstream Mississippi River sites, such that Chl-*a* loads at sites below the Minnesota River were consistently almost double those of sites UM 872 and UM 848.

### *Water quality ratios*

Seasonal patterns in water quality ratios are shown in Figure 11 (TN:TP, DIN:TP, OP:TP, VSS:TSS, and TP:Chl-*a*). The ratios of TN:TP and DIN:TP tended to be elevated in winter and experienced an additional peak in June, particularly at sites in and downstream of the nitrogen-rich Minnesota River. The ratio of OP:TP, which describes the bioavailability of phosphorus, reached seasonal lows at all river sites in late spring, likely reflecting the coinciding decline in

OP loading (Figure 9) and the uptake of OP by phytoplankton during the Chl-*a* peak in May (Figure 10a, b). The proportion of organic solids to total solids (VSS:TSS) was greatest at all sites during winter months and declined rapidly during spring snowmelt, likely reflecting large snowmelt inputs of inorganic solids. The ratio of TP:Chl-*a* was also high in the winter months,

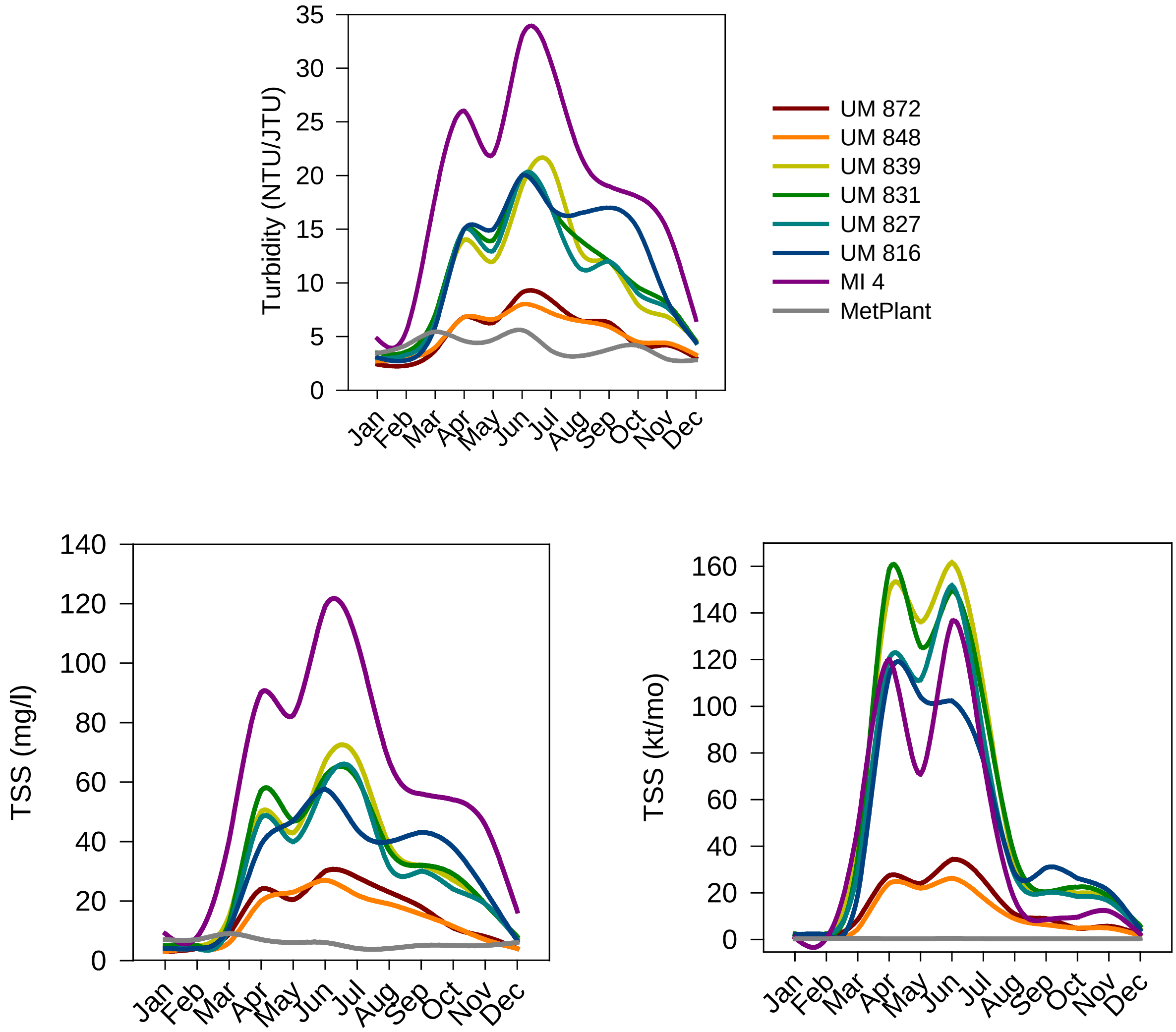


**Figure 10.** Seasonal trends in concentrations (left) and loads (right) for seston variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values for each month. VSS and Chl-a were not analyzed at the Metro Plant.

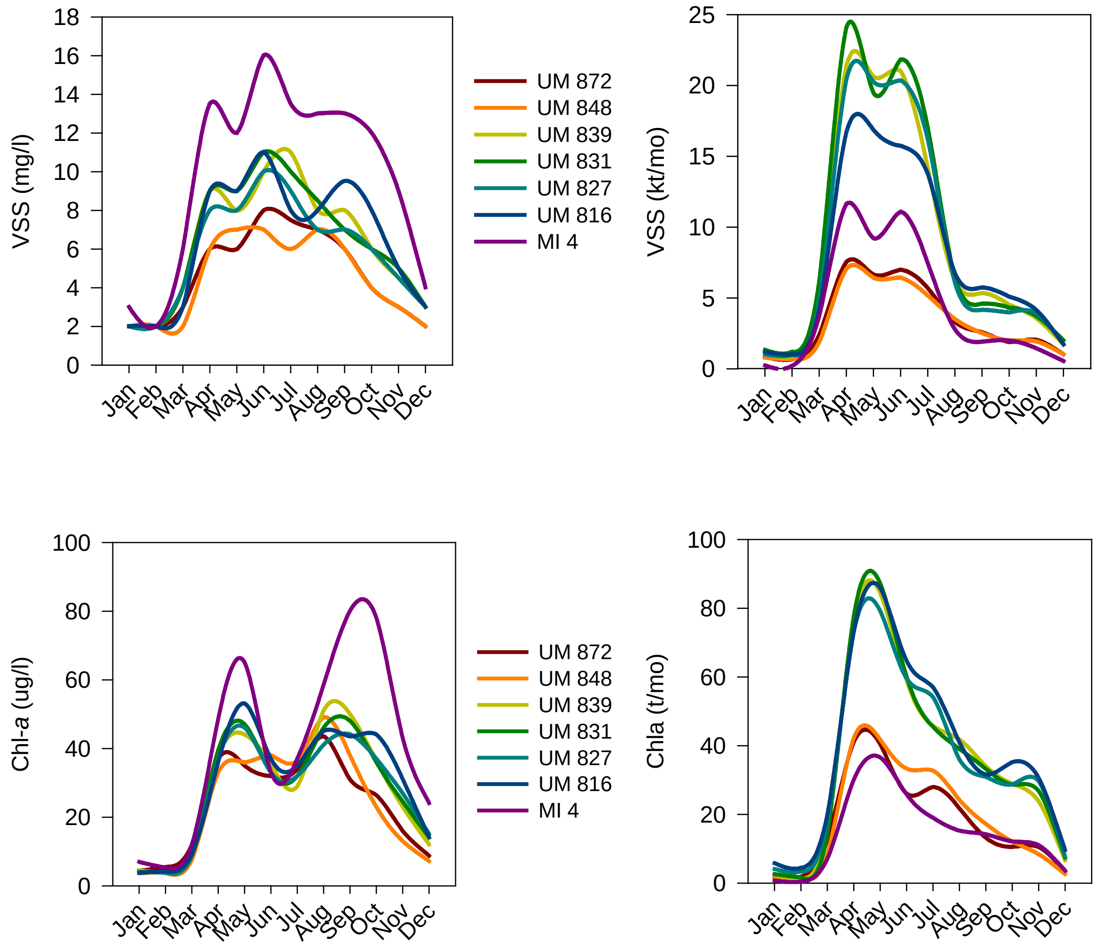


**Figure 10.** Seasonal trends in concentrations (left) and loads (right) for seston variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values for each month. VSS and Chl-a were not analyzed at the Metro Plant (continued).

likely due to the limited amount of algal growth occurring at this time (Figure 10a, b). A secondary peak in TP:Chl-*a* occurred in June, perhaps due to suppression of algal growth by high turbidity at that time (Figure 10a, b).

## Interannual Trends

This section discusses temporal trends in the concentrations and loads of water quality variables from 1976 through 2005, and addresses longitudinal differences for a few of the temporal trends. In addition to temporal plots, interannual trends in concentrations and loads are compiled into three tables detailing direction of change, magnitude of change, and percent change over the 30-year period.

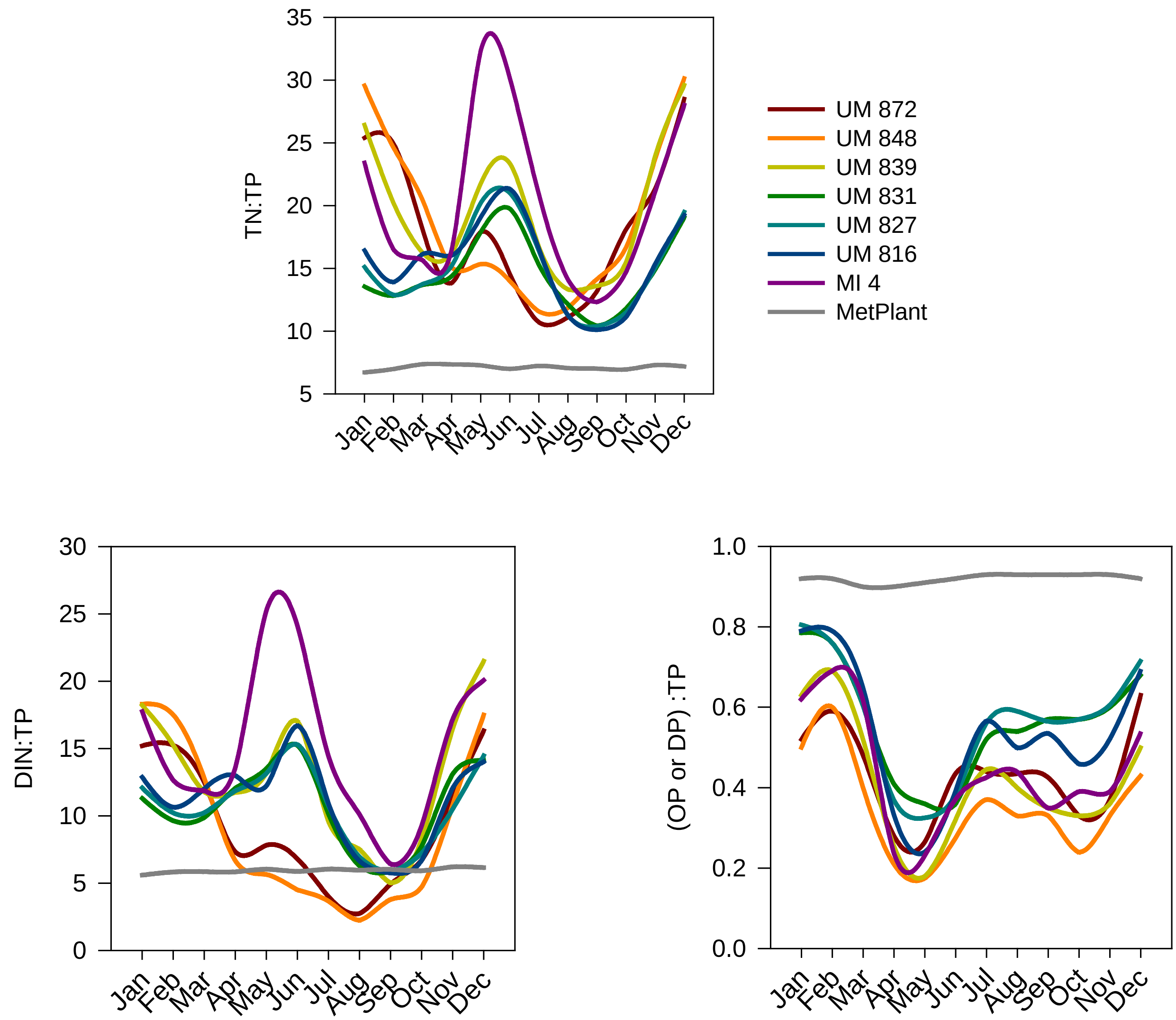


**Figure 11.** Seasonal trends in nutrient and sediment ratios at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values for each month. VSS:TSS and TP:Chl-a were not analyzed at the Metro Plant. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, was used to calculate DP:TP for general comparison.

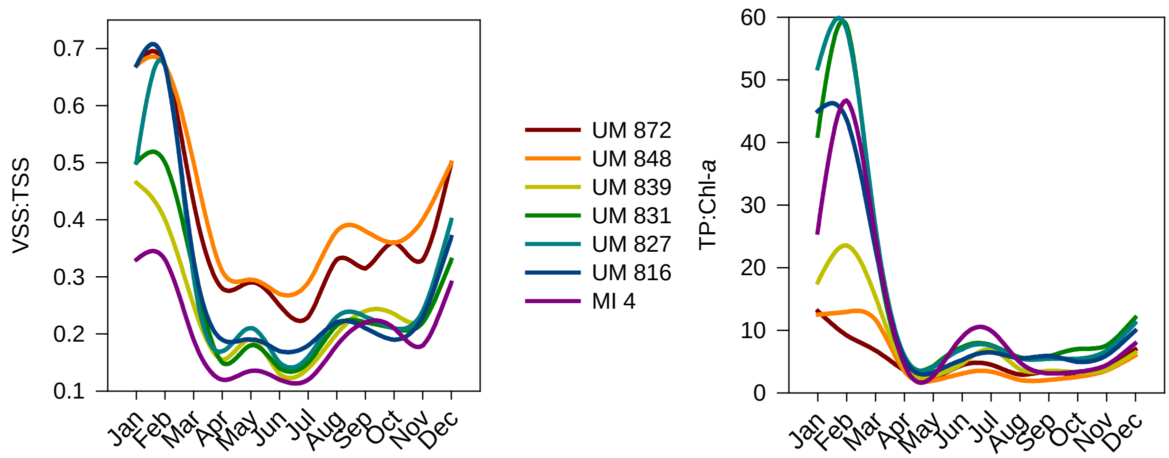


**Figure 11.** Seasonal trends in nutrient and sediment ratios at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005, based on long-term median values for each month. VSS:TSS and TP:Chl-a were not analyzed at the Metro Plant. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, was used to calculate DP:TP for general comparison (continued).

***Core water quality***

Flow increased significantly at all river sites over the period of record (Table 4), with the greatest increases occurring downstream of the Minnesota River confluence (Table 5), due to a sizable 44 percent increase in Minnesota River flows over the 30-year period (Table 6). Annual median flows were highly variable over the period of record, with a marked low flow years during the late 1980s drought (Figure 12), pointing to the important influence of climate variability on MNRRA hydrology. For the core water quality variables (i.e., temperature, DO, SC, and pH), trends varied among sites; most either increased or exhibited no significant change, with two exceptions. Temperature increased significantly at many Mississippi River sites, but decreased in the Minnesota River. Significant increases in pH were noted at two Mississippi River sites, (UM831 and UM827), but significant decreases were noted at the Metro Plant, especially after 1985, perhaps the result of sewer separation efforts (which removed higher pH surface waters from Metro Plant) over this time period. Specific conductance increased significantly at most Mississippi River sites, but showed no change in the Minnesota River (MI4) or immediately downstream of its confluence (UM839). Dissolved oxygen showed no change at the most upstream Mississippi River sites (UM872 and UM848), but increased significantly at all other river sites and the Metro Plant, with the greatest increases occurring in the Minnesota River and the Metro Plant (Table 6).

**Table 4**. Direction of concentration trends for water quality variables at six Mississippi River sites ("UM" plus river mile), one Minnesota River site ("MI" plus river mile), and the Metro Plant ("MetPlant"), 1976-2005, as evaluated using seasonal Kendall test for trend. "↑" and "↓" denote significant positive and negative trends at the 95% confidence level, respectively, "n.s." denotes variables for which no significant trend was detected.

| Variable | UM872 | UM848 | UM839 | UM831 | UM827 | UM816 | MI4 | MetPlant |
|---|---|---|---|---|---|---|---|---|
| **Flow** | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | n.s. |
| **Temp**** | ↑ | ↑ | ↑ | ↑ | n.s. | n.s. | ↓ | no data |
| **pH** | n.s. | n.s. | n.s. | ↑ | ↑ | n.s. | n.s. | ↓ |
| **SC** | ↑ | ↑ | n.s. | ↑ | ↑ | ↑ | n.s. | no data |
| **DO** | n.s. | n.s. | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| **TN*** | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | ↓ |
| **TKN** | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| **DIN*** | n.s. | ↑ | n.s. | n.s. | n.s. | n.s. | n.s. | ↑ |
| **TAN**** | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| **$NO_3$+$NO_2$-N*** | ↑ | ↑ | n.s. | ↑ | ↑ | ↑ | n.s. | ↑ |
| **TP** | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | n.s. |
| **OP** | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | no data |
| **TSS*** | ↓ | ↓ | ↓ | ↓ | ↓ | n.s. | ↓ | ↓ |
| **VSS*** | ↓ | ↓ | ↓ | ↓ | ↓ | n.s. | ↓ | no data |
| **TChl-*a*** | n.s. | n.s. | ↑ | ↑ | ↑ | n.s. | ↑ | no data |
| **Turb*** | ↓ | ↓ | ↓ | ↓ | ↓ | n.s. | ↓ | ↓ |
| **TN:TP**** | ↑ | ↑ | ↑ | n.s. | n.s. | ↑ | ↑ | n.s. |
| **DIN:TP**** | ↑ | ↑ | ↑ | n.s. | n.s. | n.s. | ↑ | ↑ |
| **OP:TP** | n.s. | n.s. | ↓ | n.s. | n.s. | n.s. | ↓ | no data |
| **VSS:TSS*** | n.s. | ↑ | ↑ | n.s. | n.s. | n.s. | ↑ | no data |
| **TP:Chl-*a*** | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | no data |

* Variable was consistently correlated with flow across all sites.

** Variable was consistently correlated with flow across most sites (i.e., downstream of MI 3.5). For these, we used flow-adjusted magnitudes for MI 3.5 and below.

**Table 5.** Magnitude of concentration trends expressed as total change over period of record in original units (see Table 1) for water quality variables at six Mississippi River sites ("UM" plus river mile), one Minnesota River site ("MI" plus river mile), and the Metro Plant ("MetPlant"), 1976-2005, as evaluated using seasonal Kendall test for trend. "n.s." denotes variables for which no significant trend was detected.

| Variable | UM872 | UM848 | UM839 | UM831 | UM827 | UM816 | MI4 | MetPlant |
|---|---|---|---|---|---|---|---|---|
| **Flow** | 1,278 | 1,454 | 3,054 | 3,006 | 3,123 | 2,873 | 1,341 | n.s. |
| **Temp**** | 1.6 | 1.7 | 1.0 | 1.1 | n.s. | n.s. | -1.2 | no data |
| **pH** | n.s. | n.s. | n.s. | 0.09 | 0.16 | n.s. | n.s. | -0.46 |
| **SC** | 49 | 28 | n.s. | 50 | 42 | 46 | n.s. | no data |
| **DO** | n.s. | n.s. | 0.52 | 0.73 | 0.93 | 0.69 | 1.20 | 2.81 |
| **TN*** | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | -1.31 |
| **TKN** | -0.27 | -0.27 | -0.45 | -1.12 | -1.15 | -0.96 | -0.89 | -12.57 |
| **DIN*** | n.s. | 0.13 | n.s. | n.s. | n.s. | n.s. | n.s. | 1.07 |
| **TAN**** | -0.09 | -0.09 | -0.23 | -0.72 | -0.68 | -0.60 | -0.40 | -10.52 |
| **$NO_3$+$NO_2$-N*** | 0.33 | 0.31 | n.s. | 1.03 | 0.91 | 0.84 | n.s. | 14.79 |
| **TP** | -0.014 | -0.021 | -0.041 | -0.069 | -0.081 | -0.061 | -0.184 | n.s. |
| **OP** | -0.010 | -0.012 | -0.036 | -0.026 | -0.022 | -0.027 | -0.090 | no data |
| **TSS*** | -3 | -6 | -9 | -5 | -7 | n.s. | -33 | -13 |
| **VSS*** | -1 | -1 | -2 | -1 | -2 | n.s. | -2 | no data |
| **TChl-*a*** | n.s. | n.s. | 3.9 | 8.2 | 6.5 | n.s. | 8.4 | no data |
| **Turb*** | -0.8 | -1.6 | -1.5 | -1.5 | -1.4 | n.s. | -4.1 | -43.5 |
| **TN:TP**** | 7.30 | 8.11 | 5.84 | n.s. | n.s. | 3.24 | 8.09 | n.s. |
| **DIN:TP**** | 5.51 | 6.26 | 4.45 | n.s. | n.s. | n.s. | 5.53 | 0.90 |
| **OP:TP** | n.s. | n.s. | -0.15 | n.s. | n.s. | n.s. | -0.08 | no data |
| **VSS:TSS*** | n.s. | 0.05 | 0.06 | n.s. | n.s. | n.s. | 0.03 | no data |
| **TP:Chl-*a*** | -1.82 | -1.99 | -2.93 | -6.47 | -5.84 | -1.96 | -8.44 | no data |

* Variable was consistently correlated with flow across all sites.

** Variable was consistently correlated with flow across most sites (i.e., downstream of MI 3.5). For these, we used flow-adjusted magnitudes for MI 3.5 and below.

**Table 6.** Magnitude of concentration trends expressed as percent change over period of record, for water quality variables at six Mississippi River sites ("UM" plus river mile), one Minnesota River site ("MI" plus river mile), and the Metro Plant ("MetPlant"), 1976-2005, as evaluated using seasonal Kendall test for trend. "n.s." denotes variables for which no significant trend was detected.

| Variable | UM872 | UM848 | UM839 | UM831 | UM827 | UM816 | MI4 | MetPlant |
|---|---|---|---|---|---|---|---|---|
| **Flow** | 17 | 20 | 27 | 26 | 27 | 25 | 44 | n.s. |
| **Temp**** | 12 | 13 | 8 | 8 | n.s. | n.s. | -9 | no data |
| **pH** | n.s. | n.s. | n.s. | 1 | 2 | n.s. | n.s. | -6 |
| **SC** | 13 | 8 | n.s. | 9 | 8 | 8 | n.s. | no data |
| **DO** | n.s. | n.s. | 5 | 8 | 10 | 7 | 13 | 59 |
| **TN*** | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | -7 |
| **TKN** | -31 | -34 | -41 | -80 | -89 | -74 | -59 | -286 |
| **DIN*** | n.s. | 20 | n.s. | n.s. | n.s. | n.s. | n.s. | 7 |
| **TAN**** | -214 | -234 | -230 | -300 | -284 | -353 | -221 | -679 |
| **$NO_3$+$NO_2$-N*** | 49 | 58 | n.s. | 59 | 53 | 47 | n.s. | 114 |
| **TP** | -15 | -27 | -29 | -30 | -37 | -28 | -71 | n.s. |
| **OP** | -28 | -46 | -70 | -21 | -18 | -25 | -88 | no data |
| **TSS*** | -20 | -40 | -32 | -20 | -26 | n.s. | -62 | -222 |
| **VSS*** | -27 | -30 | -28 | -19 | -25 | n.s. | -25 | no data |
| **TChl-*a*** | n.s. | n.s. | 14 | 29 | 23 | n.s. | 22 | no data |
| **Turb*** | -14 | -28 | -14 | -13 | -14 | n.s. | -22 | -1115 |
| **TN:TP**** | 43 | 46 | 32 | n.s. | n.s. | 22 | 43 | n.s. |
| **DIN:TP**** | 64 | 83 | 36 | n.s. | n.s. | n.s. | 41 | 15 |
| **OP:TP** | n.s. | n.s. | -37 | n.s. | n.s. | n.s. | -20 | no data |
| **VSS:TSS*** | n.s. | 14 | 26 | n.s. | n.s. | n.s. | 19 | no data |
| **TP:Chl-*a*** | -42 | -52 | -59 | -80 | -75 | -30 | -117 | no data |

* Variable was consistently correlated with flow across all sites.

** Variables was consistently correlated with flow across most sites (i.e., downstream of MI 3.5). For these, we used flow-adjusted magnitudes for MI 3.5 and below.

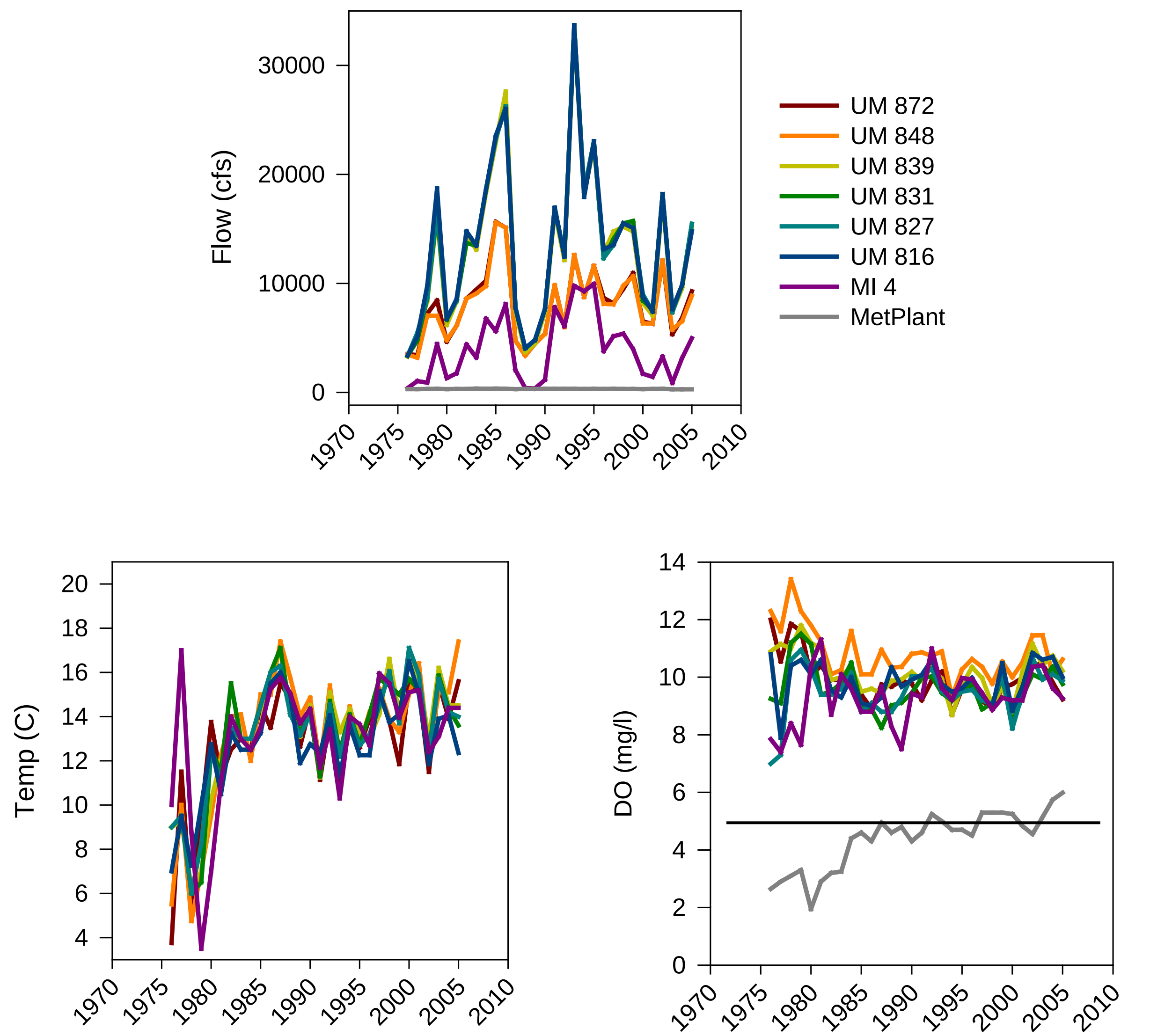


**Figure 12.** Trends in annual median values for streamflow and core water quality variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. Specific conductance was not analyzed at the Metro Plant. The state water quality standard for DO (see Table 3) is depicted as a solid black line. *Note: At the Metro Plant, water temperature data are not available for the full period of record; 1994-1999 data are included for comparative purposes.

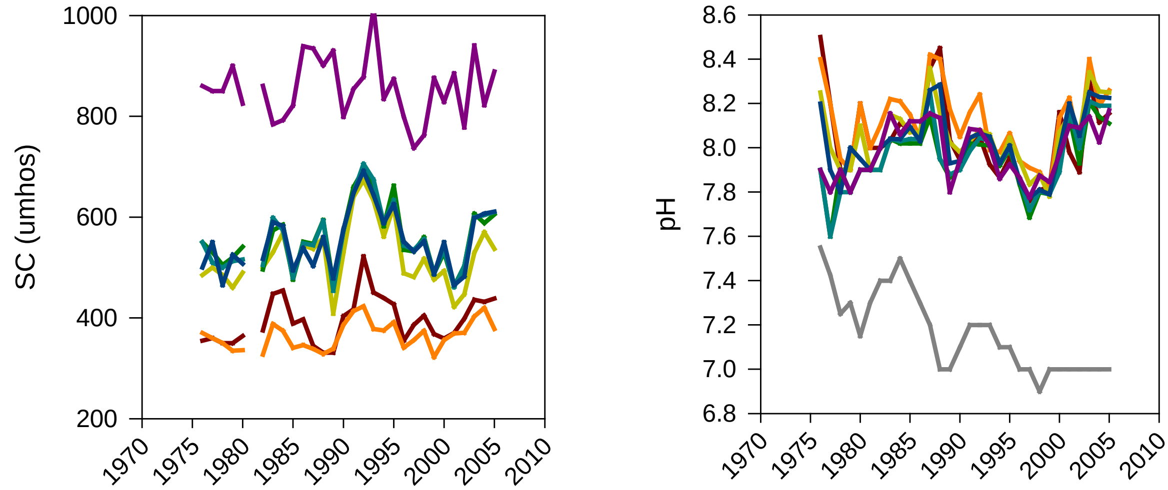


**Figure 12.** Trends in annual median values for streamflow and core water quality variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. Specific conductance was not analyzed at the Metro Plant. The state water quality standard for DO (see Table 3) is depicted as a solid black line. *Note: At the Metro Plant, water temperature data are not available for the full period of record; 1994-1999 data are included for comparative purposes (continued).

***Nutrients***

Significant trends in the concentration of many nutrients were detected (see Table 4), and although they differed in magnitude (see Table 5), most changes were consistent in direction among sites (see Table 4; Figures 13 and 14). Few significant changes in TN or DIN concentrations were detected at any river site, but at the Metro Plant TN decreased and DIN increased significantly. Total Kjeldahl nitrogen and TAN concentrations both decreased significantly at all sites. The greatest reductions occurred at the Metro Plant and MNRRA sites downstream of it (see Table 5), though large reductions in TAN occurred at all sites (see Table 6). Most of these reductions occurred after changes in wastewater treatment practices in 1985 (Figure 13). During the late 1980s drought, TKN and TAN concentrations in the Minnesota River were two to three times higher than median annual concentrations for these variables. In contrast to TKN and TAN, the concentration of $NO_3$+$NO_2$-N increased significantly at nearly all Mississippi River sites, though no significant changes in $NO_3$+$NO_2$-N were detected within the Minnesota River (MI4) or immediately downstream of its confluence (UM839). The greatest increases in $NO_3$+$NO_2$-N concentration occurred at and downstream of the Metro Plant, where the increase in concentration over the period of record approached 15 mg/L (see Table 5), exceeding a 100% increase at the Metro Plant (see Table 6). Most of the mainstem sites exhibited a 50-60 percent increase in $NO_3$+$NO_2$-N concentrations (see Table 6).

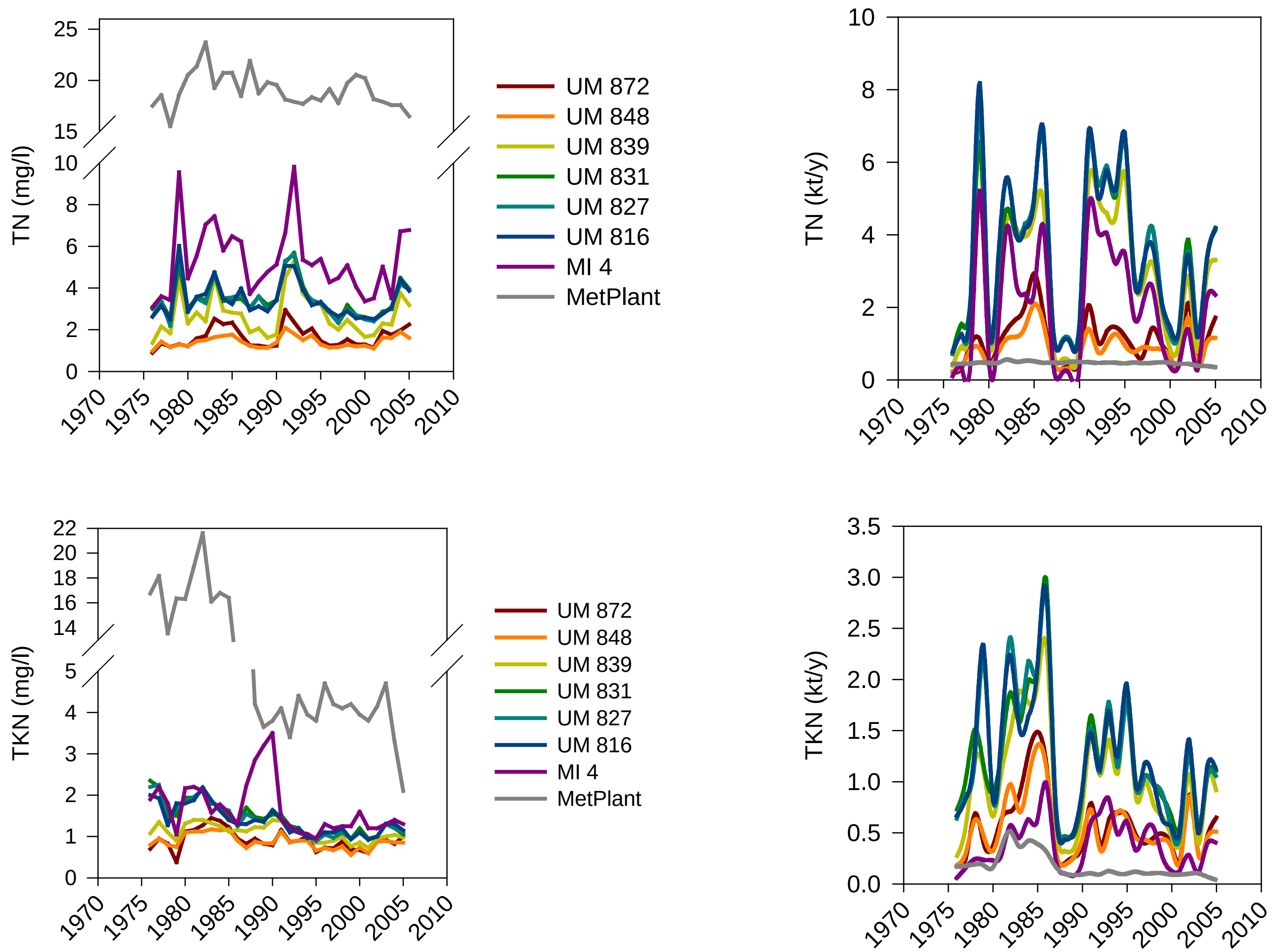


**Figure 13**. Trends in annual median concentrations (left) and annual loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. The state water quality criterion for nitrogen oxide concentration (Table 3) is depicted as a solid black line.

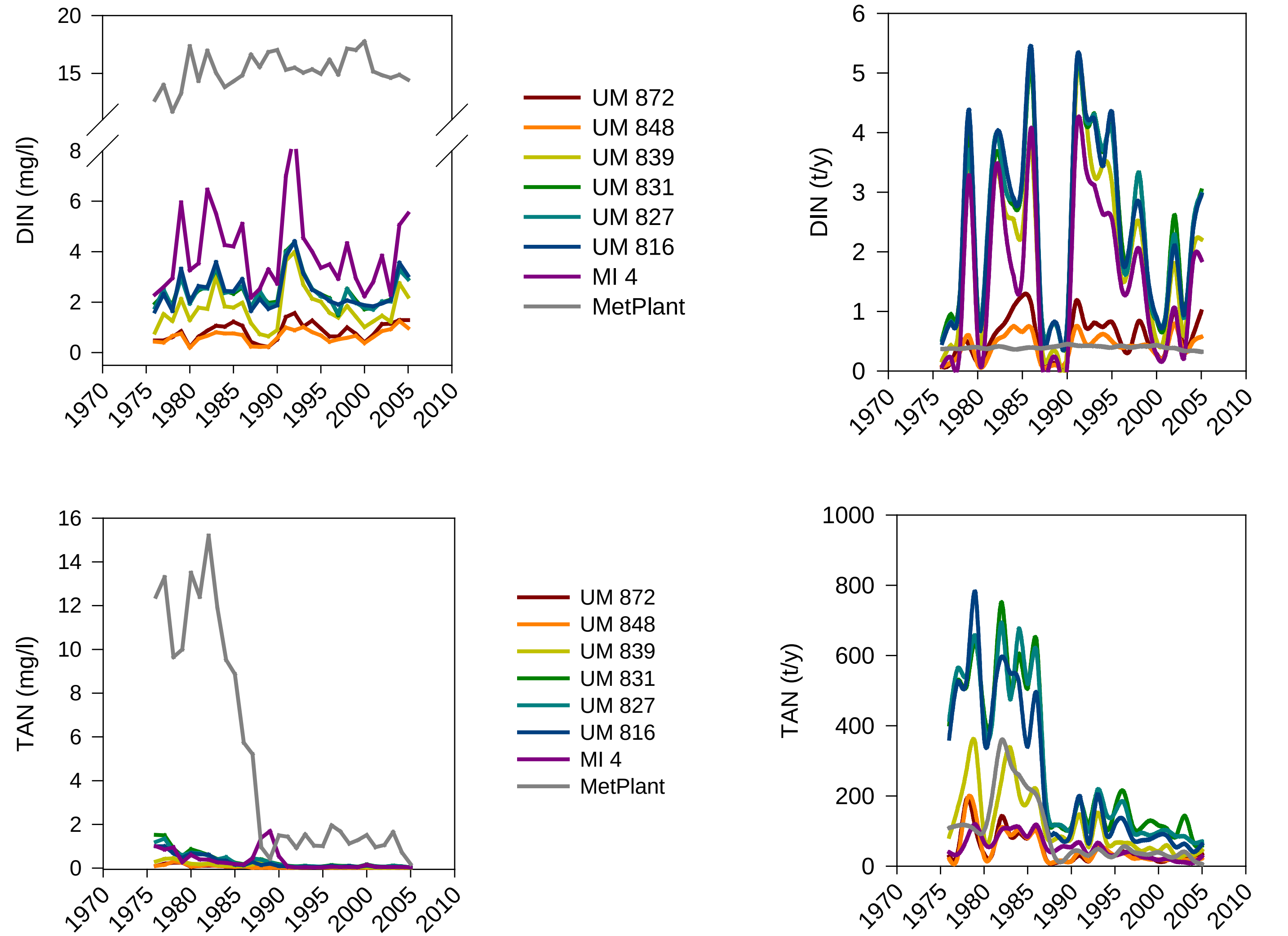


**Figure 13**. Trends in annual median concentrations (left) and annual loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. The state water quality criterion for nitrogen oxide concentration (Table 3) is depicted as a solid black line (continued).

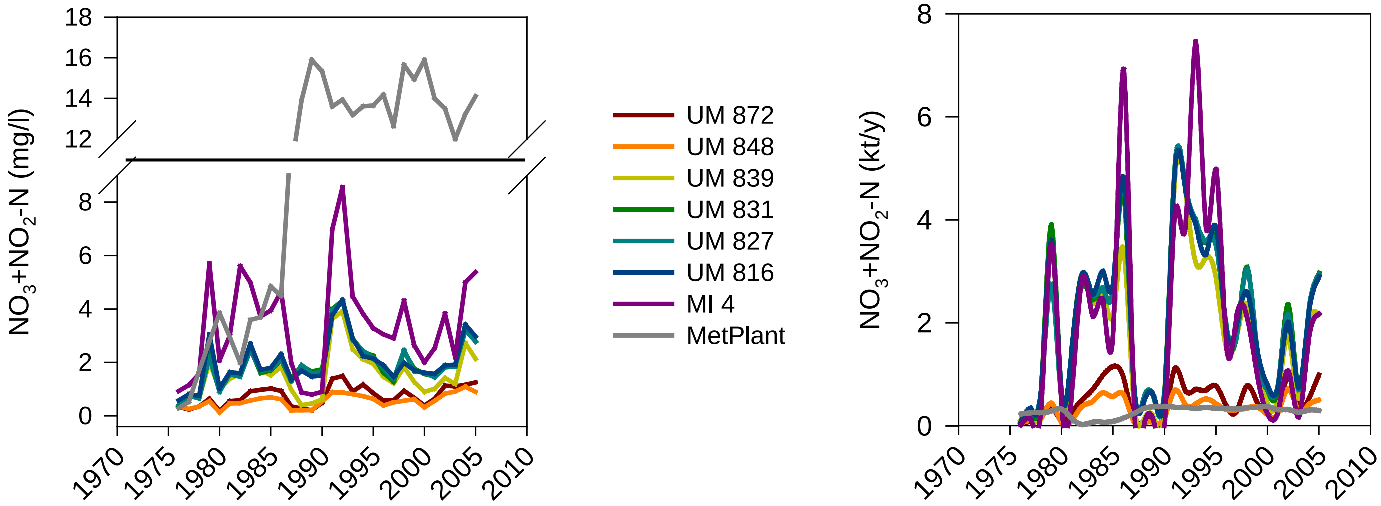


**Figure 13**. Trends in annual median concentrations (left) and annual loads (right) for nitrogen variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. The state water quality criterion for nitrogen oxide concentration (Table 3) is depicted as a solid black line (continued).

The influence of climate variability is evident in the comparison of median annual concentrations and loads of nitrogen (Figure 13). Decreases in loads of TKN and TAN at the Metro Plant resulted in decreases in loads at downstream sites within the Mississippi River (Tables 8, 9). Commensurate increases in $NO_3$+$NO_2$-N loads (Tables 7-9) are not as readily obvious graphically (Figure 13), but increases of more than 50 percent over the study period were typical for many river sites (Table 9). In contrast to concentration trends, the highest percent-difference increases in $NO_3$+$NO_2$-N loads occurred at the two upstream Mississippi River sites, likely due to the dilution influence of the Minnesota River, with its less substantial increase in $NO_3$+$NO_2$-N loads.

**Table 7**. Direction of load trends for water quality variables at six Mississippi River sites ("UM" plus river mile), one Minnesota River site ("MI" plus river mile), and the Metro Plant ("MetPlant"), from 1976-2005, as evaluated using seasonal Kendall test for trend. "↑" and "↓" denote significant positive and negative trends at the 95% confidence level, respectively, "n.s." denotes variables for which no significant trend was detected.

| Variable | UM872 | UM848 | UM839 | UM831 | UM 827 | UM816 | MI4 | MetPlant |
|---|---|---|---|---|---|---|---|---|
| **TN** | ↑ | ↑ | n.s. | n.s. | n.s. | n.s. | ↑ | ↓ |
| **TKN** | n.s. | n.s. | n.s. | ↓ | ↓ | ↓ | n.s. | ↓ |
| **DIN** | ↑ | ↑ | ↑ | n.s. | ↑ | n.s. | ↑ | n.s. |
| **TAN** | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| **$NO_3$+$NO_2$-N** | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| **TP** | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | ↑ |
| **OP** | n.s. | ↓ | n.s. | n.s. | ↑ | n.s. | n.s. | no data |
| **TSS** | n.s. | ↓ | n.s. | n.s. | n.s. | n.s. | n.s. | ↓ |
| **VSS** | n.s. | ↓ | n.s. | n.s. | n.s. | n.s. | ↑ | no data |
| **TChl-*a*** | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | no data |

**Table 8.** Magnitude of load trends, expressed as total change over period of record (in kg) for water quality variables at six Mississippi River sites ("UM" plus river mile), one Minnesota River site ("MI" plus river mile), and the Metro Plant ("MetPlant"), 1976-2005, as evaluated using seasonal Kendall test for trend. "n.s." denotes variables for which no significant trend was detected.

| Variable | UM872 | UM848 | UM 839 | UM831 | UM 827 | UM816 | MI4 | MetPlant |
|---|---|---|---|---|---|---|---|---|
| **TN** | 234,540 | 179,130 | n.s. | n.s. | n.s. | n.s. | 266,580 | -57,810 |
| **TKN** | n.s. | n.s. | n.s. | -389,760 | -450,660 | -478,740 | n.s. | -128,070 |
| **DIN** | 203,880 | 147,270 | 376,080 | n.s. | 374,970 | n.s. | 230,160 | n.s. |
| **TAN** | -43,050 | -41,640 | -166,710 | -468,390 | -467,520 | -458,190 | -72,150 | -113,430 |
| **$NO_3$+$NO_2$-N** | 263,130 | 221,310 | 578,430 | 950,730 | 962,010 | 861,810 | 282,240 | 144,210 |
| **TP** | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | 12,648 |
| **OP** | n.s. | -4,113 | n.s. | n.s. | 20,691 | n.s. | n.s. | no data |
| **TSS** | n.s. | -888,870 | n.s. | n.s. | n.s. | n.s. | n.s. | -174,120 |
| **VSS** | n.s. | -338,850 | n.s. | n.s. | n.s. | n.s. | 241,620 | no data |
| **TChl-a** | 3,792 | 2,302 | 5,866 | 8,023 | 4,869 | 4,881 | 3,381 | no data |

**Table 9.** Magnitude of load trends, expressed as percent change over period of record, for water quality variables at six Mississippi River sites ("UM" plus river mile), one Minnesota River site ("MI" plus river mile), and the Metro Plant ("MetPlant"), 1976-2005, as evaluated using seasonal Kendall test for trend. "n.s." denotes variables for which no significant trend was detected.

| Variable | UM872 | UM848 | UM839 | UM831 | UM827 | UM816 | MI4 | MetPlant |
|---|---|---|---|---|---|---|---|---|
| **TN** | 24 | 22 | n.s. | n.s. | n.s. | n.s. | 18 | -12 |
| **TKN** | n.s. | n.s. | n.s. | -33 | -39 | -40 | n.s. | -100 |
| **DIN** | 41 | 37 | 22 | n.s. | 18 | n.s. | 21 | n.s. |
| **TAN** | -129 | -133 | -182 | -238 | -251 | -271 | -142 | -226 |
| **$NO_3$+$NO_2$-N** | 62 | 68 | 37 | 53 | 55 | 51 | 27 | 46 |
| **TP** | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | n.s. | 19 |
| **OP** | n.s. | -27 | n.s. | n.s. | 22 | n.s. | n.s. | no data |
| **TSS** | n.s. | -14 | n.s. | n.s. | n.s. | n.s. | n.s. | -77 |
| **VSS** | n.s. | -13 | n.s. | n.s. | n.s. | n.s. | 10 | no data |
| **TChl-a** | 28 | 16 | 22 | 30 | 16 | 15 | 31 | no data |

Total phosphorus and OP concentrations decreased significantly at all river sites over the period of record, with the smallest percent change occurring upstream at UM872 and the largest percent change occurring at MI4 (see Tables 4 and 6). In contrast, there was no significant change in TP at the Metro Plant (see Table 4) despite clear step-wise downward trends in median annual concentrations in the late 1970s and early 2000s, following, respectively, the state-wide TCMA regional ban on phosphate in laundry detergents (1977) and the onset of phosphorus reduction technology at the Metro Plant (2000) (Figure 14). Unlike TP and OP concentrations, TP loads showed no significant change at any of the river sites, and OP loads showed mixed results, with no change at most river sites and modest reductions and increases at UM848 and UM827, respectively. At the Metro Plant, TP loads increased significantly over the period of record. TP and OP concentrations were highest during the low flow years of the late 1980s, particularly at sites downstream of the Metro Plant, but TP and OP *loads* were generally reduced during those years and highest during high flow years (Figure 14).

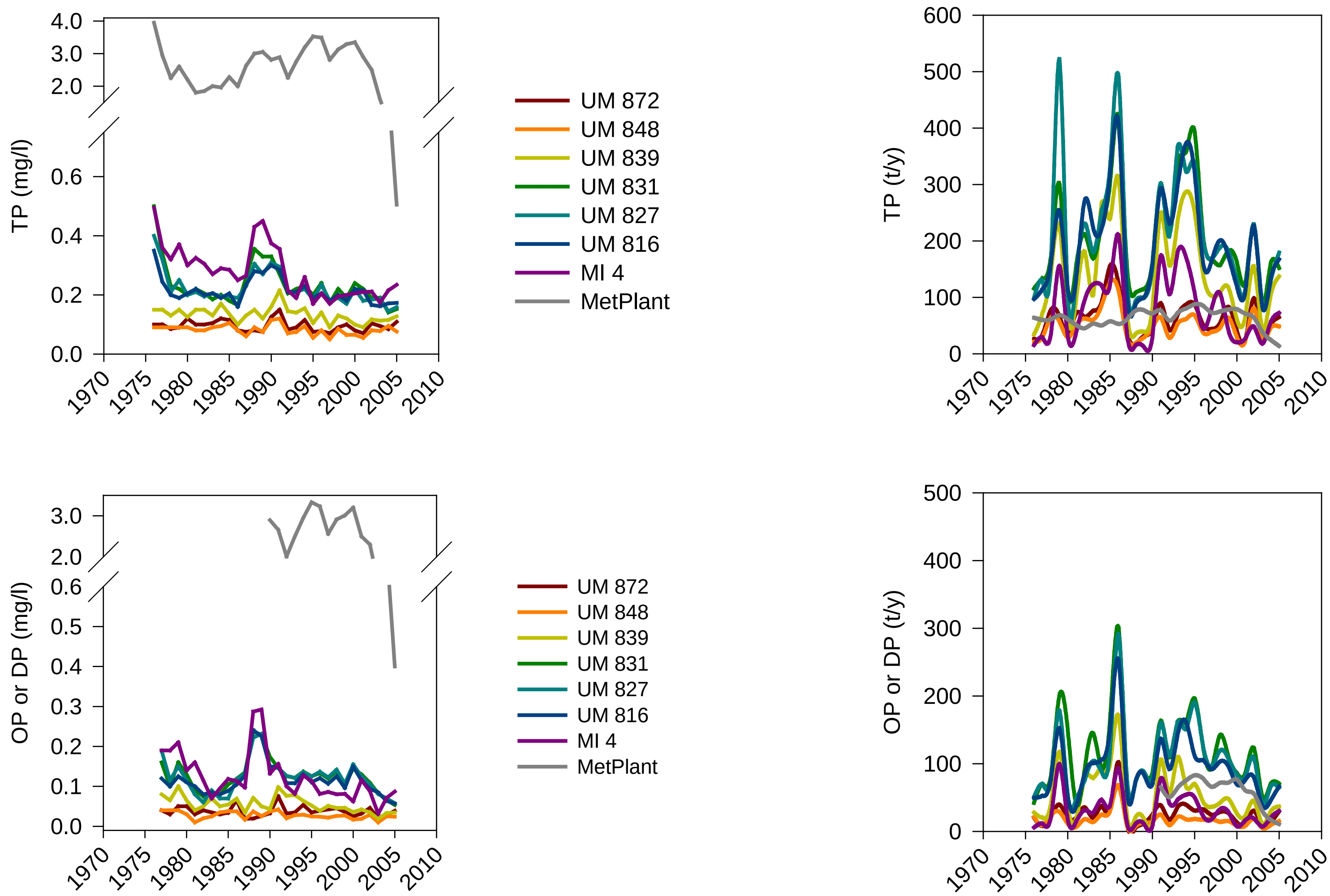


**Figure 14**. Trends in annual median concentrations (left) and annual loads (right) for phosphorus variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. The proposed state water quality criterion for TP concentration (see Table 3) is depicted as a solid black line. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, is included for general comparison.

***Seston***

Over the period of record, turbidity and concentrations of suspended solids decreased significantly at the Metro Plant and all river sites except UM 816 (Table 4), with the greatest percent changes found at MI 4 and UM848 (Table 6). In contrast, TSS and VSS loads showed no significant change at most sites, decreasing only at U848 and the Metro Plant (Table 7); and VSS loads actually increased over the period of record at MI4 (Tables 7, 9). The drought of the late 1980s was associated with reduced turbidity and TSS and VSS loads (Figure 15a, b).

Chlorophyll-*a* concentrations increased significantly at MI4 and at most downstream Mississippi River sites. Though Chl-*a* was not measured at the Metro Plant, the magnitude of the increase in Chl-*a* concentration was 15 percent greater downstream of the Metro Plant at UM831 than upstream of the Metro Plant at UM839 (Table 6). The drought of the late 1980s was associated with reduced turbidity and TSS loads (Figure 15a, b). Chlorophyll-*a* loads increased at all riverine sites, with the largest percent increases occurring at UM872, at MI4, and at sites immediately below the Minnesota River (UM839) and Metro Plant (UM831) (Table 9).

***Water quality ratios***

All ratios considered in this analysis showed substantial interannual variability, and only some showed consistent long-term trends over the period of record. Ratios of TN:TP and DIN:TP increased significantly over time at the uppermost three Mississippi River sites and at MI4 (Table 4), with historic lows occurring during the drought of the late 1980s and historic peaks occurring during the higher flow periods of the early 1990s (Figure 16). The ratio of OP:TP decreased significantly at MI4 and immediately downstream of this site (Tables 4-6), suggesting that phosphorus within the Minnesota River has become less bioavailable over the period of record. The ratio of VSS:TSS increased significantly at MI4 and two Mississippi River sites, and the ratio of TP:Chl-*a* decreased significantly at all river sites, suggesting more algal growth per unit of phosphorus in recent years.

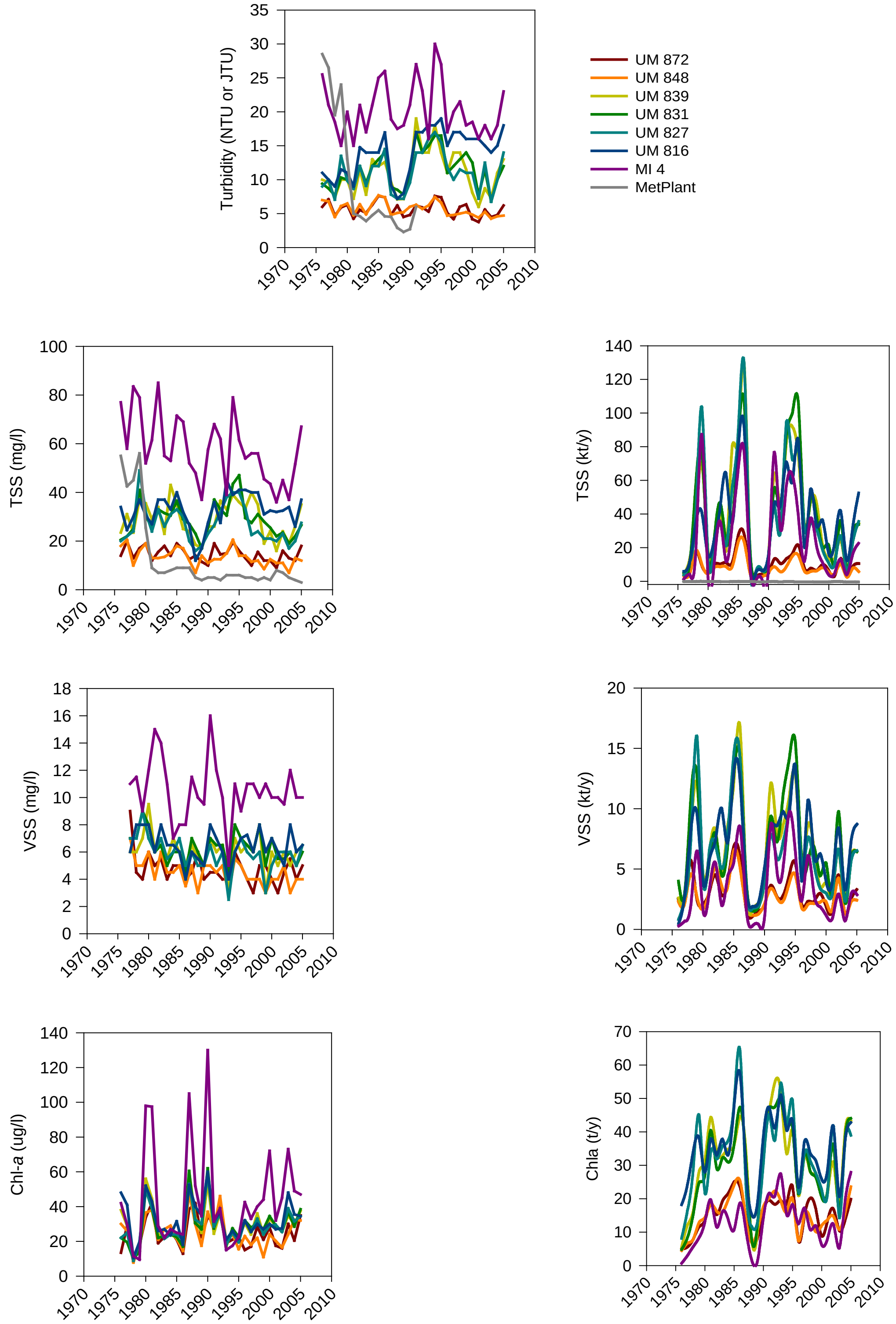


**Figure 15.** Trends in annual median concentrations (left) and annual loads (right) for seston variables at six Mississippi River sites, one Minnesota River site, and the Metro Plant, from 1976-2005. VSS and Chl-a were not analyzed at the Metro Plant. The state water quality criteria for TSS and Chl-a concentrations (see Table 3) are depicted as solid black lines.

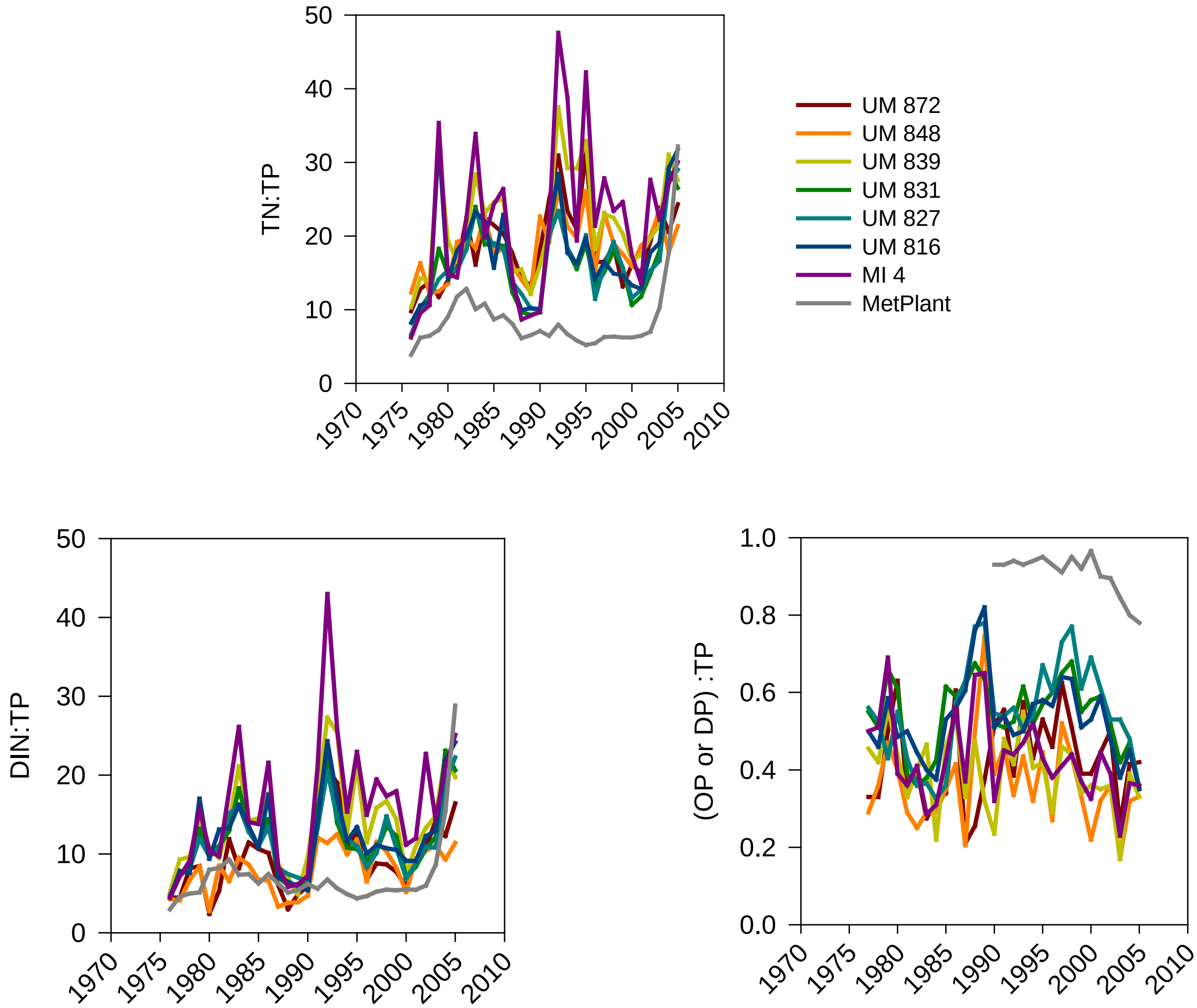


**Figure 16**. Trends in annual median values for nutrient and sediment ratios at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. VSS:TSS and TP:Chl-a were not analyzed at the Metro Plant. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, was used to calculate DP:TP for general comparison.

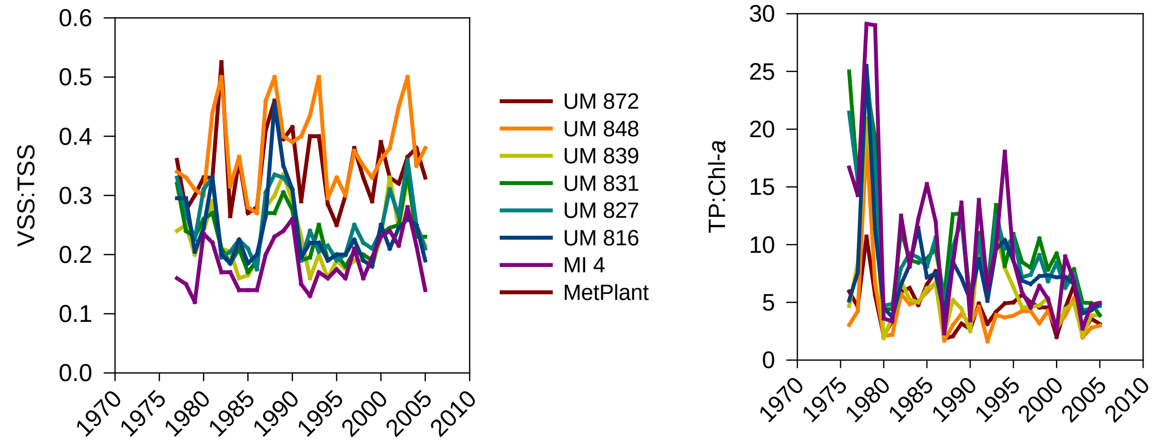


**Figure 16**. Trends in annual median values for nutrient and sediment ratios at six Mississippi River sites, one Minnesota River site, and the Metro Plant, 1976-2005. VSS:TSS and TP:Chl-a were not analyzed at the Metro Plant. *Note: No OP data are available for the Metro Plant. Instead DP, which has been measured there since the 1990s, was used to calculate DP:TP for general comparison (continued).

## Spatiotemporal Loading Trends

This section discusses spatiotemporal trends in the loads of select water quality variables at mainstem Mississippi River sites (Figures 17 and 18). These graphs provide an additional visual representation of the longitudinal and interannual trends described above, and help characterize interactions among longitudinal, temporal, and flow-related patterns in the dataset. This analysis underscores the substantial roles of the Minnesota River and the Metro Plant in shaping longitudinal water quality patterns in MNRRA, and further characterizes their relative importance under varying flow regimes.

### *Flow*

The late 1970s and late 1980s were characterized as low-flow periods (shown in red), the early 1980s and early 1990s as high-flow periods (shown in blue), and late 1990s and early 2000s as moderate-flow periods (shown in green). Streamflow in wet, high flow periods was more than double that of dry, low flow periods, and the effect of the Minnesota River on Mississippi River streamflows was readily apparent (Figure 17).

### *Nutrients*

Because of the strong relationship between streamflow and constituent loading, spatiotemporal graphs for many variables were similar to those described for flow (Figures 17, 18). Total nitrogen and phosphorus loads were low during dry periods, high during wet periods, and showed marked longitudinal increases downstream of site UM839 due to inputs from the Minnesota River and Metro Plant (Figures 17, 18). In contrast, loads of other nutrient variables showed the effects of factors other than flow, such as wastewater inputs. For example, the increase in TAN between sites above and below the Metro Plant (i.e., between UM839 and UM831) was greatest early in the data record (i.e., 1976-1980 and 1981-1985), prior to implementation of advanced secondary treatment and nitrification of TAN at the Metro Plant in 1984. Further, during low-flow periods in the late 1970s and the late 1980s, OP loads increased minimally downstream of the Minnesota River but sharply below the Metro Plant, showing the relatively greater importance of point source inputs during low flow conditions.

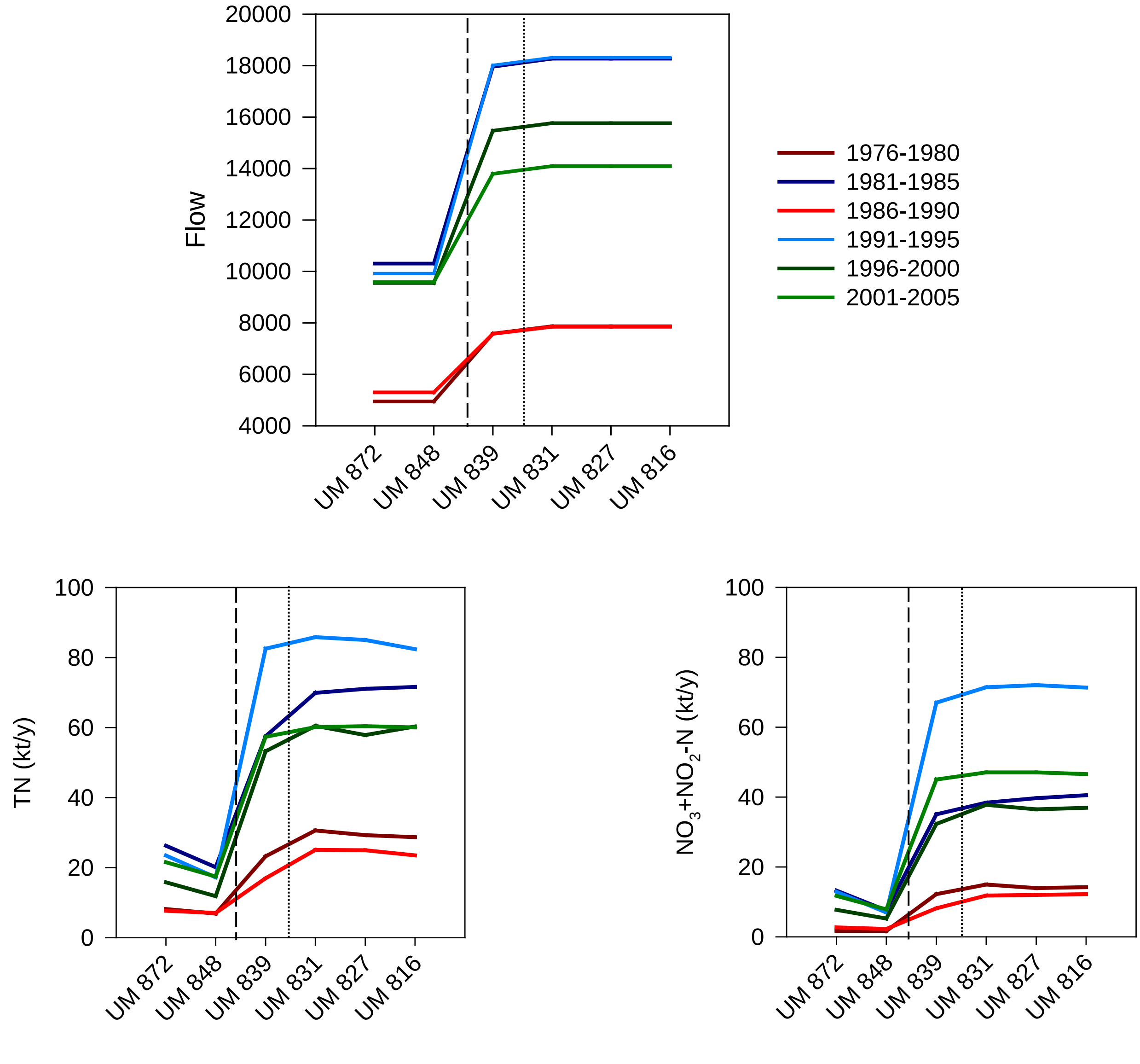


**Figure 17.** Spatial trends in flow and loads of nitrogen variables, by half-decades, across six Mississippi River sites, 1976-2005. Low-flow half-decades are coded in red, high-flow half-decades are coded in blue, and intermediate-flow half-decades are coded in green. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively.

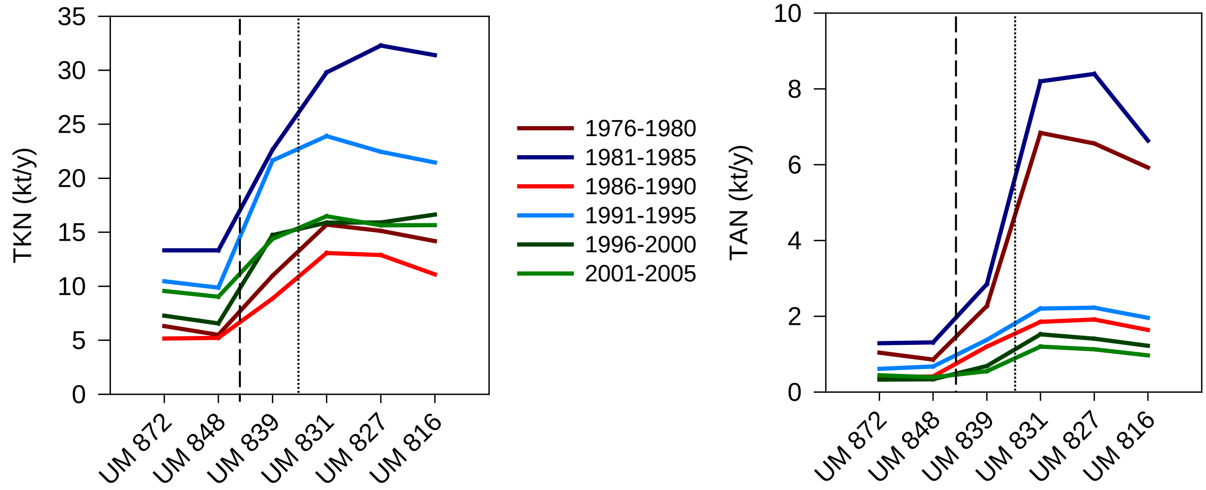


**Figure 17.** Spatial trends in flow and loads of nitrogen variables, by half-decades, across six Mississippi River sites, 1976-2005. Low-flow half-decades are coded in red, high-flow half-decades are coded in blue, and intermediate-flow half-decades are coded in green. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively (continued).

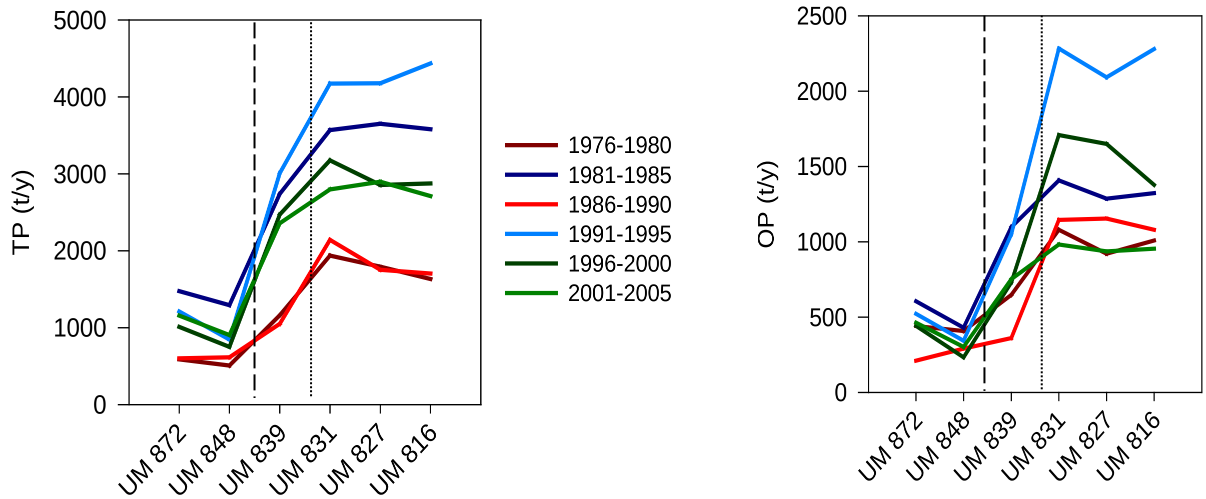


**Figure 18**. Spatial trends in loads of phosphorus and seston variables, by half-decades, across six Mississippi River sites, 1976-2005. Low-flow half-decades are coded in red, high-flow half-decades are coded in blue, and intermediate-flow half-decades are coded in green. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively.

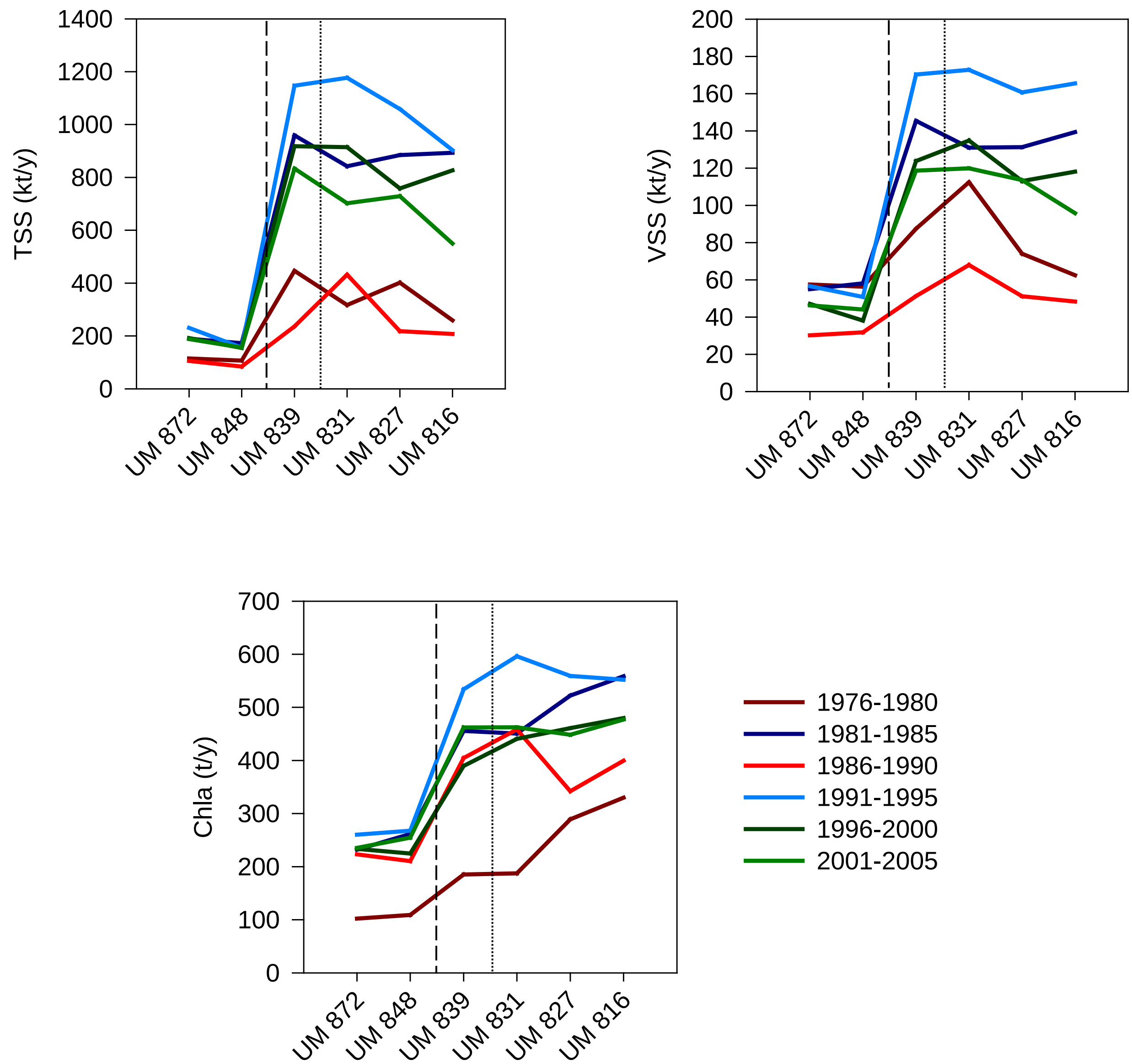


**Figure 18**. Spatial trends in loads of phosphorus and seston variables, by half-decades, across six Mississippi River sites, 1976-2005. Low-flow half-decades are coded in red, high-flow half-decades are coded in blue, and intermediate-flow half-decades are coded in green. Dashed and dotted lines indicate where the Minnesota River and Metro Plant enter the Mississippi, respectively (continued).

### *Seston*

Total suspended solid loads were strongly influenced by drought, with very low loads during the low-flow periods of the late 1970s and late 1980s (Figure 18). During low-flow conditions, VSS peaked at UM831 below the Metro Plant and declined through the remaining study reach. In contrast, during high-flow conditions, VSS peaked at UM839 below the confluence with the Minnesota River. Chlorophyll-*a* loads rose most steeply between UM848 and UM839, below the confluence of the Minnesota River, especially during high-flow periods. A smaller increase in chlorophyll-*a* loads occurred between UM839 and UM831, below the confluence of the Met Plant, especially in the middle of the study period 1986-2000.

# Discussion

## Drivers of Water Quality Trends

### *Climate and hydrology*

Climate and hydrology exert a strong influence on water quality in streams and rivers. In reviewing the hydrologic impacts of climate change, Arnell and Liu (2001) noted strong links between climate, streamflow, and stream water quality, and identified potential effects of climate change scenarios on both concentrations and loads of key variables. Further, in their reviews of water quality trend analysis tools, Helsel and Hirsch (1992) and Hirsch et al. (2010) identified streamflow as a key consideration, noting potential for either dilution or increased delivery of dissolved constituents as streamflow increases.

Within MNRRA we found clear effects of climatic and hydrologic variation on long-term and seasonal trends over the period of record. Dry periods such as the major drought of 1988 corresponded with reduced loads of many nutrient and sediment variables, but elevated concentrations of several variables of management interest. Concentrations of TAN, OP, and TP were markedly elevated in and downstream of the Minnesota River during in 1988, reflecting the relatively greater importance of point source inputs during low-flow conditions. Wet years, on the other hand, corresponded with high concentrations and loads of some variables. For example, concentrations and loads of $NO_3$+$NO_2$-N were elevated in MNRRA during the flood year of 1993. On a much larger scale, Goolsby et al. (2001) noted that large interannual changes in nitrogen flux to the Gulf of Mexico were linked to variation in precipitation.

Streamflow increased over the period of record at all sites, with the most notable increases occurring in the Minnesota River. Similarly, Novotny and Stefan (2007) found trends of increasing streamflow in many Minnesota rivers over the 1973-2002 period. They documented a strong correlation between precipitation and streamflow, but also noted the potential roles of urbanization and agricultural drainage to increased streamflow. Schottler et al. (in review) suggested that climate and crop conversions account for less than half of the observed increases in streamflow in Minnesota's agricultural watersheds, and concluded that artificial drainage is a significant contributor to this trend; this interpretation is consistent with the trend toward decreasing water temperatures at MI4 (but not at MNRRA sites) over the period of record. Whatever the cause of increased streamflow within MNRRA, it likely affected interannual trend results for nutrient and sediment loads, and may account for some of the differences in trend detection for concentrations versus loads. Improvements in point source phosphorus management, for example, likely contributed to the long-term decrease in TP concentrations, but increases in streamflow and inputs of diffuse phosphorus appear to have offset these improvements, resulting in no significant change in TP loads.

Seasonal hydrologic patterns also affected water quality patterns within MNRRA. Spring snowmelt and early summer storm events resulted in seasonal peak loads and concentrations of many nutrient and sediment variables. The role of snowmelt in nutrient and sediment delivery to streams is well documented regionally. In their study of the St. Croix River, a major tributary to MNRRA, Fallon and McNellis (2000) noted that a large proportion of annual nutrient and sediment loads were delivered during the snowmelt period, and the National Research Council

(2009) noted that in northern areas snowmelt runoff can be a significant pollutant contributor to rivers, due to gradual accumulation in the snowpack and rapid transport through the storm drainage system. Additionally, intense early season rainstorms appear to play a role in seasonal water quality dynamics. Such storms are common in the Upper Midwest (Nangia et al. 2010) and likely contribute to the strong June peaks in turbidity and concentrations of suspended solids and $NO_3$+$NO_2$-N (and, consequently, DIN and TN) within MNRRA. Effects of these early season storms on streamflow and constituent transport are exacerbated by artificial tile drainage, particularly in the heavily drained Minnesota River basin (Randall and Mulla 2001; Schottler et al. in review). Indeed, the June peaks in $NO_3$+$NO_2$-N and suspended solid concentrations were most pronounced in the Minnesota River and at MNRRA sites downstream of the Minnesota River confluence.

#### *Point sources*

Because MNRRA is situated in an urban setting and receives direct wastewater discharge from Minnesota's largest wastewater treatment facility (the Metro Plant), point source inputs and point source management have played an important role in shaping water quality patterns within the corridor (Larson et al. 2002). In fact, Meyer and Schellhaass (2002) found that from 1976-1996 (i.e., prior to implementation of biological phosphorus removal in 2003) the Metro Plant contributed an average of at least 20% of the TP load and 40% of the reactive phosphorus load to Lake Pepin, just downstream of MNRRA. In low flow years like 1988, the Metro Plant previously contributed nearly 90% of the TP load to Lake Pepin.

Effects of wastewater inputs and wastewater management on MNRRA water quality were even more dramatic historically (Metropolitan Council 2010). In the early 1900s, sewers in Minneapolis and St. Paul discharged untreated storm water and sewage directly to the Mississippi River. In 1917, construction of Lock and Dam Number 1 (at UM848) caused sewage and sludge to accumulate within MNRRA, polluting the river for 30 miles, decimating aquatic biota, and leading to a serious typhoid epidemic in 1935. After the Metro Plant began operating with primary wastewater treatment, the Mississippi River experienced significant improvements for several decades. In response to a growing population and deteriorating water quality, the Metro Plant upgraded to secondary treatment in 1966, implemented advanced secondary treatment with nitrification in 1984 (which converted toxic TAN into $NO_3$+$NO_2$-N), and most recently implemented biological phosphorus removal in 2003. Improvements in wastewater management at the Metro Plant were also made at other treatment facilities affecting the Mississippi River upstream of MNRRA. In addition to these improvements, a phosphate detergent ban was in place by 1977, an industrial pretreatment program was initiated in 1982 (reducing toxic metal inputs to the river), and a comprehensive sewer separation project was completed in 1995 (reducing biological oxygen demand and improving compliance with fecal coliform bacterial standards).

These improvements in municipal wastewater treatment contributed to major water quality changes in the MNRRA corridor during the period of record addressed by this study. Several variables typically linked to wastewater inputs and aquatic health changed significantly at all or most sites. DO concentrations increased and TAN, TP, and OP concentrations decreased. The magnitude of change for DO and TAN over the period of record, in particular, was greatest for MNRRA sites downstream of the Metro Plant, and the seasonal patterns in TAN concentrations at sites downstream of the Metro Plant closely tracked those of the Metro Plant effluent. Such patterns demonstrate the important role of point source controls in determining seasonal and long-term trends in these variables. In their evaluation of water quality changes since the Clean Water Act, the U.S. Environmental Protection Agency called these water quality improvements in the MNRRA corridor a "national environmental success story" (US EPA 2000). Further, the Metro Plant's most recent improvements (which reduced Metro Plant TP loads by 80% between 2000 and 2005) will likely result in marked improvements to water quality in downstream MNRRA waters.

Improvements in river water quality have been noted by others, both regionally and on larger scales, and attributed at least in part to improved point source management. Kloiber (2004) and Lafrancois et al. (2009) noted similar reductions in TP and TAN concentrations in recent decades at several monitoring sites on the Minnesota, St. Croix, and Mississippi Rivers, despite major differences in watershed land use among monitoring stations, and noted that TAN trends in particular appeared to be driven by point source controls. On a broader scale, Alexander and Smith (2006) analyzed nutrient trends nationwide, noting statistically significant decreases in TP and TN concentrations at a high percentage of sites from 1975-1994 and suggesting a likely link to improved wastewater treatment following the passage of the Clean Water Act in 1972. Similarly, Räike et al. (2003) documented decreasing nutrient concentrations from 1975-2000 in Finnish rivers and lakes previously affected by wastewater inputs, and noted the importance of wastewater treatment in improving water quality at these sites.

Despite these long-term and largely positive changes, the influence of point sources on MNRRA water quality was apparent for certain variables over the 1976-2005 period of record. The Metro Plant was the most important factor shaping longitudinal patterns within MNRRA for three of the study variables; TAN, TP, and OP concentrations (as well as TAN and OP loads) all increased most substantially below the discharge from the Metro Plant. This longitudinal pattern was particularly apparent during low-flow periods, and, in the case of TAN, particularly apparent early in the data record. Ratios of OP:TP ratios and TAN, TP, and OP concentrations reached their seasonal and long-term peaks during the periods of lowest flows, when point source inputs would be expected to predominate. This pattern was especially evident at MNRRA sites downstream of the Metro Plant – and, somewhat surprisingly, at the Minnesota River site, which during higher flow conditions was heavily influenced by nonpoint source inputs.

Because low flow periods and peak concentrations in these nutrients often coincide with the peak growing season, and because point source nutrient inputs are often highly bioavailable (Boström et al. 1988), point sources may have a disproportionately strong effect on biological endpoints such as algal growth in the MNRRA corridor and downstream receiving waters (Larson et al. 2002). Further, changes in wastewater treatment practices have contributed to increased concentrations of $NO_3$+$NO_2$-N in MNRRA and other regional waters, as noted in Lafrancois et al. (2009). Many regional wastewater facilities implemented advanced secondary treatment with nitrification in the 1980s, and $NO_3$+$NO_2$-N concentrations and loads in Metro Plant discharge increased 114% and 46%, respectively, from 1976-2005. The magnitudes of the increasing $NO_3$+$NO_2$-N trends, expressed as total change over the period of record, were greatest at MNRRA sites downstream of the Metro Plant discharge, where point sources were relatively more important. Conversely the Minnesota River, where relative point source contributions are smaller, showed fewer changes in $NO_3$+$NO_2$-N, with no significant trend in concentrations and a more modest increase in loads than downstream MNRRA sites.

### *Agriculture and nonpoint sources*

Although the MNRRA corridor is highly developed and home to some large point source inputs, nonpoint sources of nutrients and sediments exerted a strong influence on MNRRA water quality over this study's period of record. On broad scales, agricultural landscapes contribute high levels of nonpoint source nutrients and sediments to surface waters. Alexander et al. (2008) found that agricultural sources in the Mississippi River Basin contribute more than 70% of the N and P delivered to the Gulf of Mexico. Closer to home, the highly agricultural Minnesota River basin has been identified as the main contributor of sediment (Wilcock et al. 2009), phosphorus (Larson et al. 2002), and $NO_3$+$NO_2$-N (this study) to the Mississippi River near Lake Pepin, and an important contributor of excess nitrate to the Mississippi River and the Gulf of Mexico (Musser et al. 2009).

In our study, the Minnesota River was the single most important factor shaping longitudinal patterns within MNRRA for many variables. Flow, SC, TN, TKN, $NO_3$+$NO_2$-N, TP (loads), turbidity, TSS, VSS, and chlorophyll-*a* all increased most substantially immediately below the confluence of the Minnesota River. Heiskary and Wasley (2010) noted that chlorophyll-*a* concentrations in the Minnesota River were among the highest recorded for rivers worldwide. Other indications of agricultural influences on water quality within MNRRA include the marked seasonal peaks in $NO_3$+$NO_2$-N that occured in the Minnesota River during June and November. In a study of heavily drained parts of the Minnesota River Basin, Magner et al. (2004) also noted that the highest $NO_3$+$NO_2$-N concentrations occurred during June. These seasonal nitrogen patterns are likely linked to seasonal applications of nitrogen-based fertilizer or mineralization of soil organic matter in heavily drained landscapes (Kroening et al. 2002, Randall and Mulla 2001), and visibly affected seasonal patterns in nitrogen concentrations in downstream MNRRA sites.

We observed improvements in some variables commonly linked to agriculture over the period of record. Total phosphorus and TSS concentrations decreased significantly at all but one of the study sites. In fact, the magnitude of TP and TSS reductions was greater in the highly agricultural Minnesota River than in mainstem Mississippi sites. Additionally, in contrast to the marked increases in $NO_3$+$NO_2$-N concentrations and loads observed at mainstem MNRRA sites, no significant increase in nitrate concentrations occurred in the Minnesota River over the period of record (although Johnson et al. (2009) noted a significant increase in flow-adjusted nitrate concentrations in the latter part of this period, from 1995-2003). It is possible that changes in agricultural practices influenced concentrations of these key nutrient and sediment variables. On the Minnesota River, Johnson et al. (2009) attributed reductions in TP and OP concentrations from 1976-2003 to conservation measures such as conservation tillage. Horowitz (2010) documented widespread declines in suspended sediment flux and flow-weighted concentrations from 1981-2007 in the Mississippi River Basin, and attributed these declines in part to improvements in land management practices (e.g., contour plowing, conservation tillage, bank stabilization, and reforestation). Similarly, Meade and Moody (2010) asserted that large scale soil conservation efforts in the 1930s played an important role in suspended sediment declines in the Mississippi River system, particularly since the 1960s. Alexander and Smith (2006) noted that two U.S. conservation efforts (increases in conservation tillage and retirement of farmed lands via the Conservation Reserve Program) likely affected soil erosion and related water quality variables since the 1980s.

Although better land management since the 1970s very likely benefitted water quality in the Minnesota River and within the MNRRA corridor, this interpretation is complicated by several factors. First, the area of land under row cropping actually increased from 1970s to the 1990s in Upper Mississippi, Minnesota, and St. Croix River basins (Mulla and Sekely 2009). Second, the dominant source of the sediment in Minnesota River is non-field sediment eroded from steam banks, bluffs, and ravines (Wilcock et al. 2009) so the extent to which field-based land use improvements could have produced the observed trends is not clear. Additionally, the largest decrease in Minnesota River TSS concentrations occurred early in the data record, before widespread implementation of conservation tillage or conservation reserve programs (Johnson et al. 2009), and the largest decrease in Minnesota River TP and OP concentrations took place after 1990, following improvements at two major wastewater treatment facilities (Johnson et al. 2009). Further, *loads* of TP and TSS did not decrease, likely due to the substantial increase in flow over the period of record. Increased streamflow in the Minnesota River Basin has itself been linked to agriculture, via increases in artificial tile drainage and row cropping (Mulla and Sekely 2009; Schottler et al. in review), suggesting that improvements in water quality due to improved land use practices may be partially offset by the effects of expanding agricultural drainage networks and shifts in crop types. Such trade-offs were noted in a recent summary of national water quality trends in U.S. rivers (Dubrovsky et al. 2010), in which the authors noted that factors contributing to decreases in concentration (such as implementation of best management practices) may be offset by additional factors. Continued attention to nonpoint sources of nutrients and sediments (and to factors that mediate their delivery to surface water, including climate and artificial drainage) is clearly warranted.

#### ***Urban stormwater***

Urban runoff results in a variety of hydrologic, chemical, physical changes to waterways and is a prominent cause of water quality impairments (Maestre and Pitt 2005) and biological degradation (Coles et al. 2012) nationally. In a recent synthesis of urban stormwater effects and management options, the National Research Council (2009) identified urban stormwater as the primary source of impairment for 13 percent of the nation's rivers, 18 percent of lakes, and 32 percent of estuaries, and noted that these numbers are particularly striking given that urban areas cover just three percent of the land mass of the United States.

Some portions of the MNRRA contributing watershed feature high populations and increasing proportions of developed land. From 1974 to 2000 urban land area in the TCMA increased by 59% (Yuan et al. 2005). High proportions of impervious surfaces occur in some areas draining to the MNRRA corridor, including in St. Paul's Capitol Region Watershed District, which features 42% impervious surfaces (Capitol Region Watershed District 2012). An extensive network of stormwater outfalls and channels drain these urbanized lands in the TCMA, and many discharge directly to the Mississippi River within the MNRRA corridor, including some 55 storm sewer outlets within Capitol Region Watershed District alone. Despite improvements in urban stormwater quality following an intensive sewer separation effort in the 1980s and a ban on phosphorus in lawn fertilizers in the 2000s, rapid increases in impervious surfaces have overwhelmed many of the newer storm water systems (USACE 2004), and nearly all the older storm drains in the TCMA discharge to rivers with no treatment. Consequently urban stormwater remains a primary water quality concern for the MNRRA (Lafrancois et al. 2007) and various Watershed Management Organizations and Districts in the area.

In order to explore the effects of urban stormwater on MNRRA water quality patterns and trends, we focused on particular pollutants and particular reaches of the river. Common stormwater pollutants include sediment, nutrients, metals, bacteria, pesticides, trash, and polycyclic aromatic hydrocarbons (Maestre and Pitt 2005). Of these pollutants, we focused on the sediment and nutrient variables included in the MCES dataset. Although urban stormwater inputs are present throughout the MNRRA corridor, their relative importance in shaping water quality is arguably strongest between the uppermost two monitoring sites (UM872 and UM848). This reach of river passes through a predominantly urbanized landscape and contains no major wastewater inputs or agricultural tributaries. As such it provides a unique opportunity to identify independent effects of urban stormwater inputs on MNRRA water quality.

Data from tributaries in this reach show that the concentrations of nutrients and sediments in urban streams can be high (particularly during storm events), can far exceed concentrations in similarly sized forested streams or nearby Mississippi River sites (e.g., Kroening et al. 2003), and can result in a variety of chemical and biological impairments. Consider for example Shingle Creek, which enters the Mississippi between UM872 and UM848 after passing through an almost entirely developed urban and suburban watershed. With its network of storm sewers and 30-35% impervious surface land cover, water quality in Shingle Creek is typical of urban streams in the TCMA (Wenck Associates, Inc. 2012). Based on synoptic surveys and historical datasets, Wenck Associates, Inc. (2010) showed that nutrient and sediment concentrations occasionally exceeded proposed state criteria in parts of the Shingle Creek watershed. Likewise, monitoring from 2011 showed that nutrient and sediment concentrations from Shingle Creek near the Mississippi River ranged widely, with several samples exceeding the State's proposed TP and TSS criteria during storm events (Wenck Associates, Inc. 2012).

Despite these occasionally high levels of nutrients and sediments in Shingle Creek (and presumably other urban tributaries and stormwater outfalls in this reach), we found no indication of substantial increases in the concentrations or loads of nutrients and sediments between UM872 and UM848. In fact, long-term median concentrations and loads of TP, OP, nitrate-N, and TSS appeared to decrease between the two sites. In contrast, large increases in nutrients and sediments occurred between UM848 and UM839, the reach in which the Minnesota River joins the Mississippi, suggesting that impacts from urban runoff may be dwarfed by agricultural and nonpoint source inputs. Similarly, in a large scale regional study Kroening et al. (2003) found the highest nutrient and sediment concentrations and yields in agricultural tributaries of the Minnesota River basin, followed by urban tributaries in the TCMA, and forested tributaries in the St. Croix River basin.

This interpretation of urban runoff's importance to MNRRA water quality is likely influenced by several factors. First, urban streams and stormwater inputs to MNRRA accounted for only about six percent of the streamflow at UM816 over the period of record (in comparison to 26 percent from Minnesota River). As such, we might expect the urban influence on nutrient and sediment loads to be proportionately smaller. Secondly, the MCES monitoring program does not routinely sample during storm events, and as a result their dataset may underestimate the importance of urban runoff. Additionally, our comparison of UM872 and UM848 does not account for the potential effects of sedimentation and nutrient processing in the slightly pooled waters above the Coon Rapids Dam (river mile 866) and Lock and Dam 1. Finally, it is clear that urban runoff has a pronounced impact on the tributaries themselves, contributes pollutants not addressed by the MCES monitoring program, profoundly affects biological communities (Coles et al. 2012), and may become a more important source of nutrients and sediments to the Mississippi River if storm frequency and intensity increase with climate change (Yetka and Mamayek 2012).

### Relationship to Water Quality Standards and Criteria

Within MNRRA, sections of the Mississippi River are on the 303(d) List of Impaired Waters for Minnesota due to water quality standard exceedences for turbidity, fecal coliform bacteria, polychlorinated biphenyl (PCB), perflourooctane sulfonate (PFOS), and mercury (MPCA 2007, MPCA 2012, NPS 1995). The Minnesota River at MCES monitoring site MI4 is listed as impaired for turbidity, PCB's, and mercury (MPCA 2007, 2012). A number of site-specific (e.g., total maximum daily load) and state-wide water clarity (total suspended solids) and eutrophication (total phosphorus, total chlorophyll-*a*) criteria are under development. Assessment for impairment is variable-specific, and often based on factors such as seasonality, flow condition, and frequency and duration of exceedence. Here we explore how our longitudinal, seasonal, and inter-annual trend results relate to current and proposed water quality standards for a few select variables (Table 3). This comparison is simply to provide context and does not suffice as an actual impairment determination.

Long-term values for pH were well within the standard range across all river sites, and DO median values were also well above the 5 mg/L minimum threshold (Figures 2, 7, and 12). Although not evident in this analysis, the Lower Minnesota River has experienced low oxygen conditions during low flow periods and has been the subject of a dissolved oxygen TMDL study (Gunderson and Klang 2004). Over the 30-year period of record, annual median DO concentrations in Metro Plant effluent have steadily increased, with values near or above 5 mg/L from 1985 to 2005 (Figure 12). Calendar week average DO concentrations have generally complied with Metro Plant permit standards (D. Kent Johnson, MCES, personal communication); since 2005 annual median DO concentrations at the Metro Plant have been > 6 mg/L and within state water quality standards as well (MPCA 2010).

The $NO_2$+$NO_3$-N standard is based on the federal drinking water standard, and median values were well below 10 mg/L across all sites, seasons, and years, except for Metro Plant effluent, which is not subject to the drinking water standard (Figures 3, 8, and 13). As discussed earlier, $NO_2$+$NO_3$-N concentrations at the Metro Plant increased significantly in 1984 when advanced secondary treatment to nitrify toxic TAN to $NO_2$+$NO_3$-N was implemented, with annual median values typically between 12 to 16 mg/L since then.

The State of Minnesota is in the process of developing statewide river nutrient criteria (Heiskary et al. 2010) and Mississippi River pool-specific eutrophication criteria (Heiskary and Wasley 2010). These plans, along with the dissolved oxygen TMDL for the Lower Minnesota River (Gunderson and Klang 2004) and current Metro Plant permits, form the basis of the TP and Chl-*a* standards. Median TP values over the period of record were at or above the current and proposed TP standards for all sites (Figures 4, 9, and 14). Although not shown in this analysis, annual median TP concentrations for the Metro Plant have been well below the current permit limit of 1 mg/L as a 12-month moving average since 2005 (MPCA 2010). Median total Chl-*a* concentrations were typically at or below proposed standards at each site across all years (Figure 5) but monthly medians (see Figure 10a, b) and annual medians (see Figure 15a, b) were above proposed standards during the summer months and low flow years, respectively.

As with statewide nutrient and pool-specific eutrophication criteria, the State of Minnesota is in the process of developing regional river criteria for TSS (Markus 2010). Additionally, TMDLs are in development for the South Metro (Senjem et al. 2010) and Minnesota River (in progress), which coincide with sites below Lock and Dam 1 and near the mouth of the Minnesota River (MI4), respectively. Over the period of record, Mississippi River sites upstream of the confluence with the Minnesota River fell below the TSS criterion, while the Minnesota River site (MI4) and downstream Mississippi River sites exceeded it (Figures 5, 10, 15). This is especially evident when examining monthly median TSS values from spring and summer months (May – September). Median TSS values for the Metro Plant Site were well below its associated criterion across all years and seasons.

### National Park Service Monitoring Considerations

Water quality monitoring within the MNRRA corridor is conducted by many different agencies for many different purposes. The MCES monitoring dataset used for this analysis comes from the longest running and most comprehensive monitoring program in the region, but was not specifically designed to address NPS information needs. To fill minor gaps in existing monitoring programs and establish a more substantial scientific presence in the corridor, the NPS recently began conducting monitoring at five sites within MNRRA. Because of our familiarity with the MCES dataset and involvement with the NPS sampling program, we were well positioned to review the relative roles and contributions of NPS and MCES monitoring in understanding water quality patterns and trends within MNRRA.

As is clearly evidenced in this report, MCES has an extensive long-running water quality monitoring program in place, and is responsible for monitoring many water quality parameters at several sites within MNRRA boundaries. This monitoring has occurred on a weekly to semimonthly basis, year-round, from 1976 to present. The NPS initiated a monitoring program at MNRRA in 2006, which includes an abbreviated (as compared with MCES) number of water quality parameters on a monthly basis, every other year, April through November, sampled in alternate years at five sites. The NPS sites were primarily selected to fill in spatial gaps in the larger MCES effort (Magdalene et al. 2008). All NPS sites are located on the Mississippi River, with one site just upstream of the park’s northern boundary near river mile 880. The next three sites (river miles 868, 862, and 852) are above Lock and Dam #1 (river mile 848) and the confluence of the Mississippi and Minnesota Rivers (river mile 845). The last site is 23 river miles below the confluence of the Minnesota and Mississippi River, located in Spring Lake (river mile 822).

Based on our analysis, differences in water quality among MCES sites above the confluence of the Minnesota River are almost negligible as compared to differences between sites above and below the confluence of the Minnesota River over the 30-year period of record. Three of the sites monitored by NPS above the confluence of the Minnesota River at river miles 868, 862, and 852 do not provide meaningful long-term information beyond that shown through analysis of water quality data collected at the two MCES sites at river miles 872 and 848. Water quality conditions at the northernmost NPS site (river mile 880) could be reasonably estimated by assessing water quality at the MCES monitoring at UM872 and sites on the Crow and Rum Rivers, which are the two main tributaries to the Mississippi River between river miles 880 and 872. The single site monitored by NPS below the confluence of the Minnesota River at Spring Lake (river mile 822) is bracketed by two long-term MCES sites at Grey Cloud Island (UM 827) and Lock and Dam 2 (UM 816). Therefore, conditions at the NPS Spring Lake site can be assessed through examination of water quality data from the two MCES sites.

Comparisons of NPS and MCES data collected within the same year for sites located near each other revealed only minor differences that are likely attributable to differences in sampling frequency or very site-specific factors (e.g., urban runoff, reservoir catchment of nutrients and sediment, and within-lake nutrient dynamics). With respect to long-term trends and current status of water quality pollutants that are negatively impacting the park (e.g., excess nutrients and sediment), biennial monthly data collected from the NPS sites do not add substantively to insights already available via the MCES dataset. Though the NPS sites serve to fill in spatial gaps, the sampling frequency of the NPS monitoring program is much less intensive than that of the MCES monitoring program. Further, the current MCES water quality dataset fully addresses the measurable objectives and monitoring questions identified in the NPS Large Rivers Water Quality Monitoring Protocol (Magdalene et al. 2008). As long as MCES continues monitoring their existing sites at the ongoing frequency and continues to provide timely access to their data, our review indicates that NPS monitoring efforts at MNRRA are largely redundant. The NPS might more efficiently direct resources toward issue-specific monitoring (e.g., urban stormwater inputs), or toward data synthesis, interpretation, and integration with biological monitoring activities in the corridor.

### Overall Monitoring, Management and Research Recommendations

The MCES dataset used here is exceptional in terms of data quality, sampling frequency, spatial breadth, and duration; we recommend continued monitoring by MCES as well as additional data analysis and synthesis. First, we recommend incorporating the most recent MCES data (2006-2012) into the data record in order to 1) better characterize current water quality conditions and modern longitudinal trends within the MNRRA corridor, 2) provide further insights into how the Metro Plant's biological phosphorus removal program has affected MNRRA water quality, and 3) better understand links between hydrology and water quality (based on the several unusual water-years that have occurred since 2005). Secondly, our analysis showed the importance of both concentration and loading data for understanding the nature and implications of water quality trends. We emphasize the importance of MCES' increasing efforts to calculate loads for large river monitoring sites within and beyond MNRRA. Finally, although our work addresses water quality trends in detail, it does not address trends in the aquatic health and biological endpoints of greatest interest to the public. Additional aspects of the MCES dataset should be analyzed to address other issues of management concern. For example, long-term data on fecal indicator bacteria should be analyzed to understand how current bacterial impairments developed. Trends in fish and plankton communities, mussel populations, or other aquatic health indicators should be assessed and their links to water quality improvements should be quantified and more fully interpreted for the public.

In addition to the considerations above, new trend analysis tools have emerged since our analysis and we recommend using them to further explore and interpret the MCES dataset. Our analysis relied on effective and well tested trend analysis techniques developed over the last two or more decades. However, these methods are limited by their focus on hypothesis testing rather than description of change and by several inherent assumptions (i.e., linear patterns of change, constant flow versus concentration relationships, constant seasonal patterns, etc.). To overcome these and other limitations, Hirsch et al. (2010) recently proposed a new trend analysis method (Weighted Regressions on Time, Discharge, and Season (WRTDS). This approach has the potential to better describe the nature of long-term changes and identify the cause of those changes (e.g., point source, surface water, groundwater, etc.), and we recommend using it to re-analyze trends in key variables of management interest.

Results of our analysis highlight several water quality issues that would benefit from additional investigation. Firstly, we documented a strong influence of climatic and hydrologic factors in shaping long-term water quality trends within MNRRA. Efforts to model and quantify the effects of climate change and agricultural practices on the hydrology and water quality of MNRRA and its contributing watersheds should be supported by NPS and other management agencies in the region. Secondly, we found widespread increases in $NO_3$+$NO_2$-N concentrations and loads in the MNRRA corridor from 1976 to 2005. Such increases have been documented previously, and have been attributed to increased N export from drained agricultural watersheds or the implementation of nitrification at wastewater treatment facilities. Given that $NO_3$+$NO_2$-N loads from the Upper Mississippi River Basin are relevant to the Gulf of Mexico hypoxia issue, research addressing the relative importance of agricultural versus wastewater $NO_3$+$NO_2$-N sources would be useful. Finally, although our results suggested that urban stormwater was not the most important factor shaping MNRRA water quality from 1976 to 2005 we noted that the MCES large river monitoring program was not designed to address stormwater inputs and that the importance of these inputs may have increased recently due to urban and suburban development. Urban stormwater data specific to the MNRRA corridor should be compiled (as MCES has begun to do for two key MNRRA tributaries) and fully synthesized to characterize the spatial and temporal influence of stormwater runoff on Mississippi River water quality.

# Conclusions

We undertook this analysis in order to 1) characterize longitudinal patterns within the MNRRA corridor, 2) evaluate seasonal patterns, and 3) assess interannual trends over the period of record. We found clear longitudinal trends in the data, with concentrations of nutrients and sediments increasing from upstream to downstream within MNRRA. These results emphasized the particular influence of Minnesota River and Metro Plant inputs on MNRRA water quality. Strong seasonal patterns were also apparent in the dataset. Streamflow tended to peak during spring snowmelt, with smaller peaks occurring during early summer and late autumn; correspondingly high nutrient and sediment loads were common during spring and early summer. Factors such as snowmelt, rainfall summer events on sparsely vegetated agricultural landscapes, and fertilizer applications appeared to influence seasonal patterns in MNRRA water quality. Despite substantial interannual variation in streamflow and water quality, we identified compelling long-term trends for many variables from 1976 through 2005, particularly in terms of nutrient and sediment reductions. Load reductions were less apparent, likely due to increased streamflow over the period of record. Variables typically linked to point source inputs improved at most sites; DO concentrations generally increased and concentrations of TAN, TP, and OP decreased. Several variables commonly linked to agriculture also improved consistently; the highly agricultural Minnesota River and many Mississippi River sites showed decreasing concentrations of TP and TSS. Collectively these results suggest that drivers such as climate and hydrology, point sources, and agricultural practices strongly influenced water quality in the MNRRA corridor over the period of record and remain important considerations for future water quality management efforts. Additionally, our analysis highlights the responsiveness of MNRRA water quality to large-scale changes in point source management and land use practices, and underscores the importance of long-term monitoring data for tracking water quality changes into the future.

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