# Nitrogen in Minnesota Surface Waters

Conditions, trends, sources, and reductions



Prepared by the Minnesota Pollution Control Agency, in collaboration with the University of Minnesota and U.S. Geological Survey

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### **Executive Summary**

#### **Purpose**

This study of nitrogen (N) in surface waters was conducted to better understand the N conditions in Minnesota's surface waters, along with the sources, pathways, trends and potential ways to reduce N in waters. Nitrogen is an essential component of all living things and is one of the most widely distributed elements in nature. Nitrate ( $NO_3$ ), the dominant form of N in waters with high N, is commonly found in ground and surface waters throughout the country. Human activities can greatly increase nitrate, which is typically found at low levels in undisturbed landscapes.

Concern about N in Minnesota's surface waters has grown in recent decades due to: 1) increasing studies showing toxic effects of nitrate on aquatic life, 2) increasing N concentrations and loads in the Mississippi River combined with nitrogen's role in causing a large oxygen-depleted zone in the Gulf of Mexico, and 3) the discovery that some Minnesota streams exceed the 10 milligrams per liter (mg/l) standard established to protect potential drinking water sources.

Minnesota recently initiated two state-level efforts related to N in surface waters. The Minnesota Pollution Control Agency (MPCA) is developing water quality standards to protect aquatic life from the toxic effects of high nitrate concentrations. The standards development effort, which is required under a 2010 Legislative directive, draws upon recent scientific studies that identify the concentrations of nitrate harmful to fish and other aquatic life.

Also in development is a state-level Nutrient Reduction Strategy, as called for in the 2008 Gulf of Mexico Hypoxia Action Plan. Minnesota contributes the sixth highest N load to the Gulf and is one of 12 member states serving on the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. The cumulative N and phosphorus (P) contributions from several states are largely the cause of a hypoxic (low oxygen) zone in the Gulf of Mexico. This hypoxic zone affects commercial and recreational fishing and the overall health of the Gulf, since fish and other aquatic life cannot survive with low oxygen levels. Minnesota is developing a strategy which will identify how further progress can be made to reduce N and P entering both in-state and downstream waters.

The scientific foundation of information documented in this report will be useful as the MPCA and other state and federal organizations further their nitrogen-related work, and also as local government considers how high N levels might be reduced in their watersheds.

The Minnesota Department of Agriculture is completing a separate but concurrent effort to revise the state's Nitrogen Fertilizer Management Plan, as required under Minnesota's Ground Water Protection Act. The plan addresses groundwater protection from nitrate. Yet because groundwater baseflow is an important contributor to surface water nitrate, certain groundwater protection efforts will also benefit surface waters.

#### **Approach**

The general approach for conducting this study was to:

1) Collaborate with other organizations. This study was conducted and written by 15 authors and coauthors. The University of Minnesota led the assessment of agricultural and nonpoint sources of N. The U.S. Geological Survey assisted with nitrate trends evaluations and certain modeling and mapping efforts. Assistance and review was provided by several other organizations including Metropolitan Council, Minnesota Department of Agriculture, Board of Water and Soil Resources, and others.

- 2) Build from existing information, tools, and data. The study incorporated:
  - Recent water N concentration results from more than 50,000 water samples collected at more than 700 stream sites in Minnesota;
  - Water N loads calculated from monitoring results at more than 75 Minnesota watersheds;
  - Monitoring results from approximately 1976 to 2010 at 50 river sampling sites in Minnesota;
  - · Findings from more than 300 published studies;
  - · Findings from six previously developed computer models and two newly developed models; and
  - · More than 40 existing Geographic Information System (GIS) spatial data layers.
- 3) Include both total nitrogen and nitrate. The study assesses total nitrogen (TN) for understanding downstream N loads to the Gulf of Mexico and Lake Winnipeg, and also assesses the nitrate form of N (concentrations, loads, trends) due to its impact on in-state aquatic life and drinking water.
- 4) Develop results for large scales. Results were determined for large-scale areas, such as statewide, major basins, and 8-digit Hydrologic Unit Code (HUC8) watershed outlets. Minnesota has 81 HUC8 watersheds, each averaging over 1000 square miles. Results should not be applied to the small watershed scale.
- 5) **Verify results**. The study results were verified with alternative methods, data, and studies, so that the conclusions are supported by more than one approach.

#### Nitrogen conditions in surface waters

Nitrogen conditions in surface waters are usually characterized in four different ways: 1) concentration, 2) load, 3) yield, and 4) flow weighted mean concentration.

- Concentrations are determined by taking a sample of water and having a laboratory determine
  how much N mass is in a given volume of that water sample, typically reported as mg/l. Load is
  the amount of N passing a point on a river during a period of time, often measured as pounds of
  N per year.
- Loads are calculated by multiplying N concentrations by the amount of water flowing down the river. Nitrogen loads are influenced by watershed size, as well as land use, land management, hydrology, precipitation, and other factors.
- Yield is the amount (mass) of N per unit area coming out of a watershed during a given time period (i.e., pounds per acre per year). It is calculated by dividing the load by the watershed size, which then allows for comparisons of watersheds with different sizes.
- Flow weighted mean concentration (FWMC) is the weighted-average concentration over a period of time, giving the higher flow periods more weight and the lower flow periods less weight. The FWMC is calculated by dividing the total load for a given time period by the total flow volume during that same period, and is typically expressed as mg/l.

#### Nitrogen concentrations

Maximum nitrite+nitrate-N (nitrate) levels in Minnesota rivers and streams (years 2000-2010) exceeded 5 mg/l at 297 of 728 (41%) monitored sites across Minnesota, and exceeded 10 mg/l in 197 (27%) of

these sites. A marked contrast exists between nitrate concentrations in the southern and northern parts of the state. In most southern Minnesota rivers and streams, nitrate concentrations at least occasionally exceed 5 mg/l (Figure 1). Most northeastern and northwestern Minnesota streams have nitrate concentrations which usually remain less than 1 and 3 mg/l, respectively.

Nitrate concentrations in southern Minnesota streams tend to fluctuate seasonally. However, seasonal variability is much less in several southeastern Minnesota streams, where groundwater baseflow provides a continuous supply of high nitrate water to streams throughout the year.

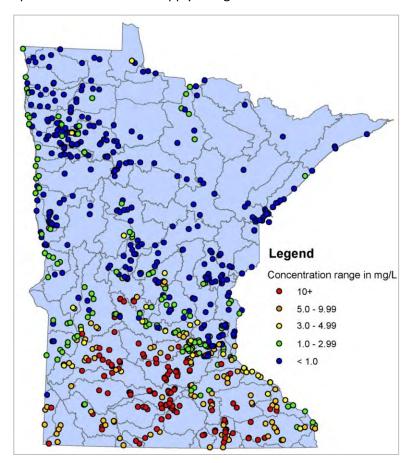


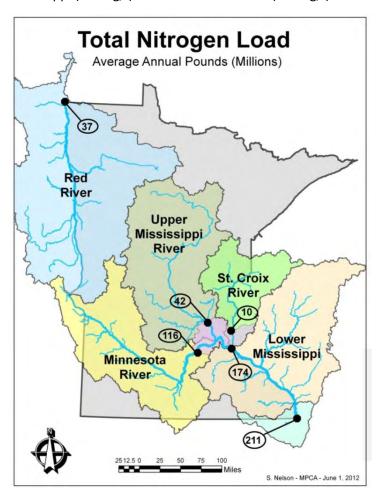
Figure 1. Nitrate concentrations at 728 river and stream sampling sites. Each colored circle shows the 90th percentile concentration from all samples taken at the site between 2000 and 2010.

Total nitrogen concentrations exhibit a similar spatial pattern across the state as nitrate, but are typically about 0.5 to 3 mg/l higher than nitrate-N, since TN also includes organic N and ammonia+ammonium (ammonium). Ammonium concentrations are less than 1 mg/l at 99% of river and stream sites in the state, and median concentrations are mostly less than 0.1 mg/l.

#### Mainstem river loads

Monitoring-based annual TN loads show that most of the state's TN load leaves Minnesota in the Mississippi River (Figure 2). On average, 211 million pounds of TN leaves Minnesota each year in the Mississippi River at the Minnesota-lowa border, with just over three-fourths of this load originating in Minnesota watersheds, and the rest coming from Wisconsin, lowa, and South Dakota. This compares to about 37 million pounds leaving the Red River at the Minnesota-Manitoba border, with about half from Minnesota and half from the Dakotas.

The highest TN-loading tributary to the Mississippi River is the Minnesota River, which adds about twice as much TN as the combined loads from the Upper Mississippi River (at Anoka) and St. Croix River (at Stillwater). The higher TN load in the Minnesota River is mostly due to much higher average TN concentrations in that river (8.2 mg/l flow-weighted mean concentration) as compared to the Upper Mississippi (2.2 mg/l) and the St. Croix River (1.0 mg/l).



South of the Twin Cities, tributaries from Wisconsin and Minnesota contribute additional N to the Mississippi River. Only small fractions of TN are lost in the Mississippi River, except where the water is backed-up for long periods in quiescent waters, allowing nitrate to be converted to N gas through natural processes or to be used by algae. In the river stretch between the Twin Cities and Iowa, some N is lost when river flow slows in Lake Pepin and in river pools behind locks and dams. Monitoringbased loads show that an average 9% TN loss occurs in Lake Pepin. An additional 3 to 13% of the river TN is estimated to be lost in the 168 mile Mississippi River stretch between the Twin Cities and Iowa. The net effect of the TN additions and losses in the Lower Mississippi Basin is an average 37 million pound annual TN load increase between the Twin Cities and Iowa.

Figure 2. Long term (15-20 year) average annual TN loads at key points along mainstem rivers.

Year-to-year variability in TN loads and river flow can be very high. In the Minnesota River Basin, TN loads during low flow years are sometimes as low as 25% of the loads occurring during high flow years. Major river TN loads typically reach monthly maximums in April and May. About two-thirds of the annual TN load in the Mississippi River at the lowa border occurs during the months March through July, when both river flow and TN concentrations are typically highest.

#### Comparing watersheds

Watershed loads, yields and FWMCs were estimated for HUC8 level watersheds throughout the state so that different parts of the state could be compared and geographic priorities established. The two methods used to compare watersheds were: 1) monitoring results from the 2007 to 2009 period, and 2) SPARROW modeling that integrated long-term water monitoring data with landscape information and in-stream losses to estimate long-term average loads.

The monitoring results from 2007-2009 and SPARROW modeling results show similar parts of the state with high and low river N loads (Figures 3 and 4). The highest N yields occur in south central Minnesota, where TN FWMCs typically exceed 10 mg/l. The second highest TN yields are found in southeastern and southwestern Minnesota watersheds, which typically have TN FWMCs in the 5 to 9 mg/l range.

The highest three TN-yielding HUC8 watersheds include the Cedar River, Blue Earth River, and Le Sueur River watersheds, each yielding over 20 pounds/acre/year, on average. The 15 highest TN loading HUC8 watersheds to the Mississippi River contribute 74% of the TN load which ultimately reaches the river. The other 30 watersheds contribute the remaining 26% of the load to the Mississippi.

Total N yield estimated from SPARROW modeling showed that the urban dominated Mississippi River Twin Cities watershed delivered TN yields comparable to many other rural southern Minnesota watersheds (Figure 4).

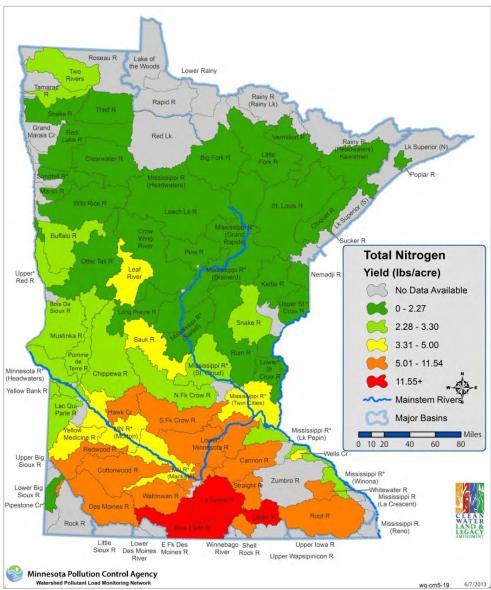


Figure 3. Monitoring-based annual TN yields near the outlet of each watershed. Average of available annual yield information between 2007 and 2009.

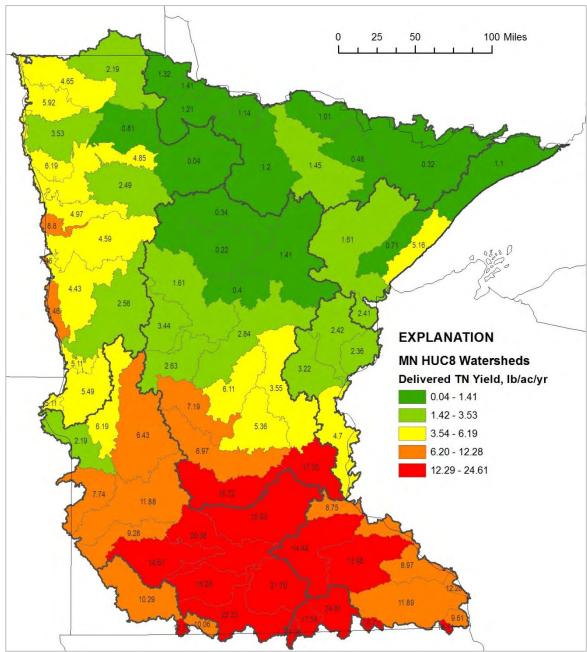


Figure 4. SPARROW model simulated incremental TN yields at the outlet of HUC8 watersheds (or state borders for watersheds cut-off by the state border).

#### **Trends**

Previous studies of N trends in Minnesota rivers and streams showed that *TN loads* increased since the 1970s and 1980s in the Red River of the North, Mississippi River, and Minnesota River. *Nitrate loads* had been found to have increased in the Mississippi and Minnesota Rivers between 1976 and 2005. Previous studies showed that *nitrate concentrations* were increasing in southeastern Minnesota streams and parts of central Minnesota, but that the downstream half of the Minnesota River generally showed no significant trend or a decrease. Previous studies also showed that river ammonium concentrations declined significantly over the 1980s and 1990s, likely in response to municipal wastewater upgrades and possibly also from feedlot and manure management improvements.

For this study, we evaluated flow-adjusted nitrite+nitrate-N (nitrate) concentration trends at 51 mainstem river and major tributary river monitoring sites throughout the state. The statistical trend analyses were performed with the QWTREND model, which was developed to evaluate periods of both increases and decreases which can occur at the same site over the period of record. River flow data was paired with nitrate monitoring results over a timeframe beginning during the mid-1970s and ending between 2008 and 2011.

Long-term (30-36 years) flow-adjusted nitrate concentration changes on the mainstem rivers are shown in Figure 5. The Mississippi River, which has very low nitrate concentrations in the north and less than 3 mg/l in the southern part of the state, showed increasing concentrations between 1976 and 2010 at most sites on the river, with overall increases ranging between 87% and 268% everywhere between Camp Ripley and LaCrosse. During recent years (i.e., 5-15 years prior to 2010), nitrate concentrations were increasing everywhere downstream of Clearwater on the Mississippi River at a rate of 1-4% per year, except that no significant trend was recently detected at Grey Cloud and Hastings in the Metro region.

Increasing nitrate concentration trends were also found in the Cedar River (113% increase over a 43-year period) and the St. Louis River in Duluth (47% increase from 1994 to 2010).

Not all locations in the state, however, are showing increasing trends. While nitrate concentrations remain very high in the downstream stretches of the Minnesota River (FWMC over 6 mg/l), two monitored sites (Jordan and Fort Snelling) showed a slight increase from 1979-2005, followed by a decreasing trend between 2005-06 and 2010-11. During recent years, all sites on the Minnesota River and most tributaries to the Minnesota River evaluated for trends have been either trending downward or have shown no trend (through 2009-11). Additionally, a few tributaries to the Mississippi River have also shown decreasing nitrate trends during the 6-8 year period prior to 2010, including the Rum, Straight, and Cannon Rivers.

Some other rivers have shown no significant trends since the mid-1970s, including the Rainy, West Fork Des Moines, and Crow Rivers. The Red River showed significant increases before 1995, but no significant trends between 1995 and 2010.

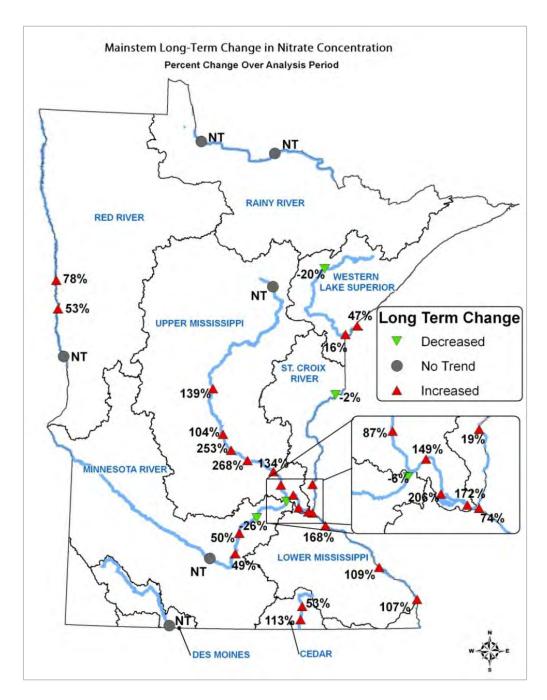


Figure 5. Long-term overall nitrate concentration trends (from mid to late 1970s until 2008-11) at mainstem river monitoring sites. Concentrations were adjusted for flow and changes are statistically significant at p<0.1.

#### Sources and pathways

Nitrogen source contributions to surface waters during average, wet and dry weather periods were estimated for each major basin and statewide. The estimated annual statewide TN (hereafter referred to as N) contributions reaching surface waters during an average precipitation year are shown in Figure 6. Results are intended for broader management planning decisions and should not be used in place of Total Maximum Daily Load (TMDL) studies or detailed local assessments based on site specific water quality monitoring and modeling data.

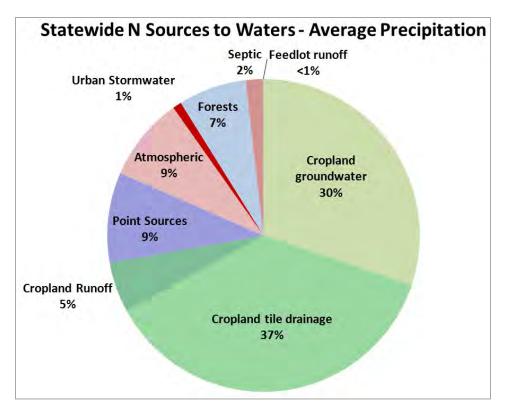


Figure 6. Estimated statewide N contributions to surface waters during an average precipitation year (rounded to whole numbers).

#### **Cropland sources**

Cropland N loads were estimated for three different pathways: surface runoff, tile-line transport, and leaching to groundwater and its subsequent underground movement to surface waters. Cropland sources were estimated by taking published field research results about N losses to water and then using GIS data-bases to extrapolate field-research results to larger scales. Cropland N source estimates were based on available site-specific data and watershed characteristics, adjusted for crops, geologic sensitivity, soils, climate, fertilizer rates, livestock manure availability, agricultural drainage, N losses within groundwater, and several other factors. The amount of N reaching surface waters from cropland varies tremendously, ranging from less than 10 pounds/acre on some cropland and more than 30 pounds/acre on other cropland.

According to the N source assessment conducted for this study, during an average precipitation year cropland sources contribute an estimated 73% of the statewide N load to surface waters. This statewide estimate is similar to SPARROW model simulations, which indicate that 70% of statewide N loading to surface waters is from agricultural sources. The cropland fraction of N load to surface waters varies by watershed, accounting for an estimated 89 to 95% of the N load in the Minnesota portions of the Minnesota River, Missouri River, Cedar River, and Lower Mississippi River Basins, and yet contributing less than 50% of the Upper Mississippi River Basin N (refer to Figure 8 for basin locations).

The emphasis of this study was estimating N loads from specific source categories to *surface waters*. Nitrogen sources to *land* were also estimated, since these sources can provide a general framework of understanding N potentially available for entering waters. Inorganic N becomes available to statewide cropland from several added sources to the soil, including commercial fertilizers (47%), legume fixation (21%), manure (16%), and wet plus dry atmospheric deposition (15%). Soil organic matter mineralization

releases an estimated annual amount of inorganic N comparable to fertilizer and manure N additions combined. Septic systems, lawn fertilizer, and municipal sludge together account for about 1% of all N added to soils statewide.

#### Cropland surface runoff

Cropland N moves from soil sources to surface waters through two dominant pathways: 1) tile-line transport, and 2) leaching to groundwater and subsequent underground flow into surface waters. Compared to these two pathways, cropland surface runoff adds relatively little N to waters. Surface runoff contributes only 1-4% of N loads to waters in all major basins except the Lower Mississippi River Basin and Red River Basin, where runoff from cropland contributes 9-16% of the N load, respectively.

#### Cropland tile drainage

Nitrogen moving through tile-lines and subsequently into ditches and streams was found to be the pathway contributing the most cropland N to surface waters. During an average precipitation year, row crop tile drainage contributes an estimated 37% of the N load to Minnesota's waters overall, and contributes 67% of the N load in the heavily-tiled Minnesota River Basin. During a wet year, the fraction of N to waters from tile drainage increases to an estimated 43% of statewide N load and 72% of the Minnesota River N load. River monitoring results affirmed the importance of tile drainage contributions, showing that the highest N-yielding watersheds in the state are those which are intensively tiled.

#### Cropland nitrate leaching to groundwater

Nitrogen leaching into groundwater below cropped fields, and subsequently moving underground until it reaches streams, contributes an estimated 30% of N to surface waters statewide. Groundwater N can take hours to decades to reach surface waters, depending on the rate of groundwater flow and the distance between the cropland and stream. Nitrogen leaching into groundwater is the dominant pathway to surface waters in the karst dominated landscape of the Lower Mississippi River Basin, where groundwater contributes an estimated 58% of all N. Yet in the Minnesota River Basin, dominated by clayey and tile-drained soils, cropland groundwater only contributes 16% of the N to surface waters, on average.

#### Wastewater point sources

Wastewater point source loads, estimated largely from MPCA discharge permit records, release an annual average 29 million pounds of TN to statewide waters, accounting for 9% of the statewide N load according to the N source assessment. This is slightly more than the 7% point source contribution estimated from SPARROW modeling.

Wastewater point source loads are dominated by municipal wastewater sources, which contribute 87% of the wastewater point source N load discharges, with the remaining 13% from industrial facilities. The 10 largest wastewater point source N loading facilities collectively contribute 67% of the point source TN load. Nearly half (49%) of the wastewater point source N discharges occur within the Twin Cities Metropolitan Area. River monitoring shows that six million pounds of N (on average) is gained in major rivers as they pass through the Twin Cities area, which equates to a 3.5% increase.

Wastewater point source N additions from large urban areas can contribute similar loads as many croplands draining from a similarly sized area. However, the wastewater N delivery to rivers is different than from cropland, as it enters waters at a few specific points as opposed to being dispersed across the watershed.

#### Other sources

Two other source categories, atmospheric deposition and forestland runoff, each contribute cumulative total statewide N loads comparable to wastewater point source N loads. While the N concentrations from atmospheric deposition and forest sources are much lower than wastewater discharges, the aerial extent of these two sources is vast, thereby accounting for the similar overall loads.

Nitrogen falling onto land from wet and dry atmospheric deposition was highest in the south and southeast parts of the state and lowest in the north and northeast where fewer urban and agricultural sources exist. Atmospheric deposition falling into lakes and streams was considered in the source assessment as a direct source of N into waters, contributing 9% of the statewide annual N load to waters. Correspondingly, the areas of the state with the most lakes and streams had the most atmospheric deposition directly into waters. Yet, relatively few other N sources are found in the northern Minnesota lakes regions, and a large fraction of N entering most lakes from atmospheric deposition will not leave the lake in streams. Low river N concentrations and loads are found in the northern lakes regions of the state.

Some N, typically less than three pounds/acre/year, is exported from forested watersheds. Forest N contributions are nearly negligible in localized areas and N levels in heavily forested watersheds are quite low. Yet since such a large fraction of the state is forested, the total cumulative N to waters from forested lands is estimated to be about 7% of the statewide N load.

Other statewide N sources contribute relatively small N loadings, including septic systems (2%), urban/suburban runoff (1%), feedlot runoff (0.2%) and water-fowl (<0.2%).

#### Source load differences among major basins

The load estimates in this study only quantify N source contributions originating in Minnesota portions of basins. Nitrogen source and pathway contributions from Minnesota portions of river basins vary considerably from one major river basin to another, as shown in Figure 7 (see also basin location map in Figure 8). For example, during an average precipitation year, cropland source contributions range between 16% and 95% of the estimated N load to the waters in each basin. Wastewater point source contributions range from 1% to 30% across the different basins, and contribute a higher fraction of the load where cropland sources are relatively low.

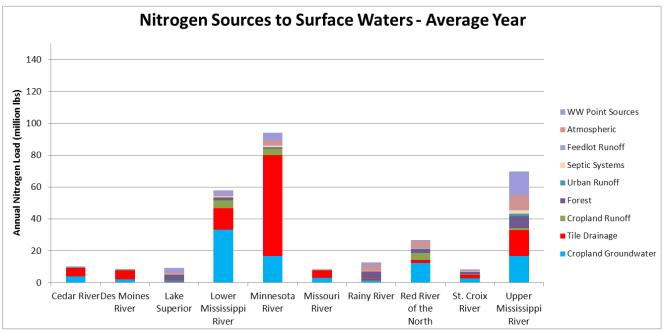


Figure 7. Estimated annual N loads to surface waters from different sources within the Minnesota portions of major basins during an average precipitation year.



Figure 8. Minnesota's major basins and watersheds.

#### Precipitation effects on source loads

Precipitation amounts have a pronounced effect on N loads. During a dry year, statewide N loads drop by 49% from average year loads (Figure 9). During a wet year, overall loads increase by 51%, as compared to an average year (Figure 10). The effects of precipitation are even greater in the Minnesota River Basin, where wet years have an estimated 70% greater N load, and dry years have 65% less N load.

Precipitation also affects the relative contributions from different N sources and pathways. During wet years, the cropland source contributions increase from 73% to 79% of the statewide N loads to waters. Agricultural drainage increases from 37% to 43% of the loads to surface waters during wet years, cropland runoff increases from 5% to 6%, and cropland groundwater remains at 30%. During dry years, the fraction of the load coming from wastewater point sources increases from 9% to 18%, whereas cropland sources are reduced to 54% of the estimated statewide N load.

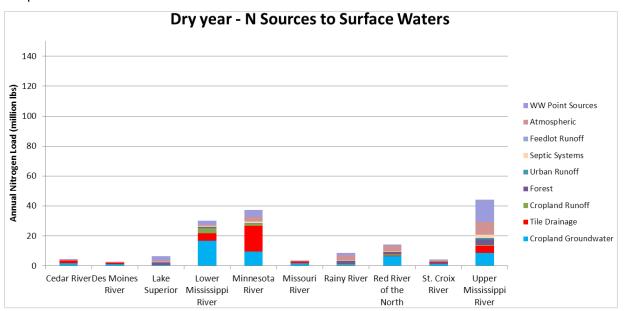


Figure 9. Estimated annual N loads to surface waters from different sources within the Minnesota portions of major basins during a dry year.

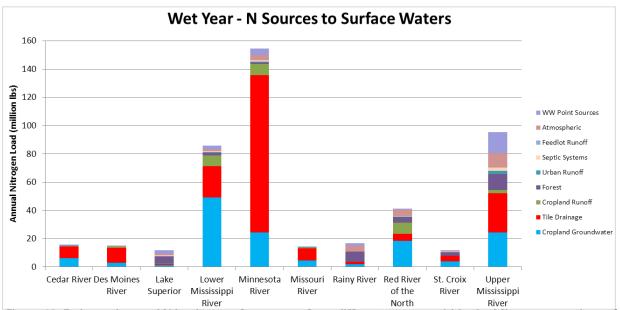
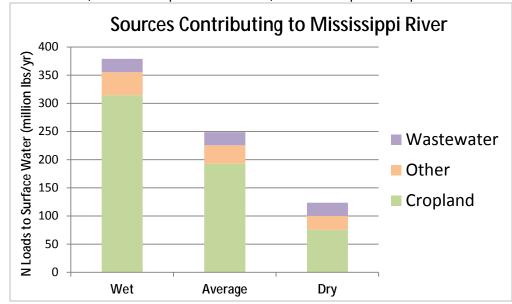


Figure 10. Estimated annual N loads to surface waters from different sources within the Minnesota portions of major basins during a wet year.

#### Sources to the Mississippi River

Just over 81% of the TN load to Minnesota waters is from watersheds which ultimately flow into the Mississippi River. If we look only at those Minnesota watersheds which contribute to the Mississippi River, source contributions during an average precipitation year are estimated as follows: cropland sources 78%, wastewater point sources 9%, and non-cropland nonpoint sources 13% (Figure 11).



Cropland source contributions increase to 83% for these watersheds during wet (high-flow) years, and point sources decrease to 6%. During a dry year, cropland sources represent an estimated 62% of N to waters and point sources contribute 19%.

Figure 11. Sum of N source contributions in watersheds which eventually reach the Mississippi River. The "other" category includes septic systems, atmospheric deposition directly into waters, feedlots, forested land and urban/suburban nonpoint source N. "Wastewater" includes municipal and industrial point sources.

#### Uncertainties and verification of sources

The source assessment conducted by the University of Minnesota and MPCA has some areas of uncertainty. All sources should be treated as large-scale approximations of actual loadings, and each source estimate could be refined with additional research. One particular area of uncertainty is the cropland groundwater component, due to: a) limited studies quantifying leaching losses under different soils, climate and management, and b) high variability in denitrification losses, which can occur as groundwater slowly flows toward rivers and streams.

Because of source assessment uncertainties, we compared the source assessment results with results from five separate approaches, as follows:

- 1) Monitoring results HUC8 watershed and major basin scale monitoring results
- 2) SPARROW modeling major N source categories (statewide)
- 3) **HSPF modeling** Minnesota River Basin modeled estimates of sources, pathways and effects of precipitation
- 4) Watershed characteristics analysis comparing watershed land and hydrologic characteristics with river N yields and concentrations
- 5) Literature review existing studies in the upper-Midwest related to N sources and pathways

Mainstem river monitoring results compared reasonably well to the sum of the sources estimated by the source assessment during dry, average and wet conditions (Figures 12-14). The monitoring results were not expected to be the same as the sum of sources, since the sum of sources do not consider in-stream

N losses or lag times in groundwater N transport from sources to surface waters. Yet the fairly close agreement between the monitoring results and source load estimates provides one line of evidence that the source estimates may be reasonable.

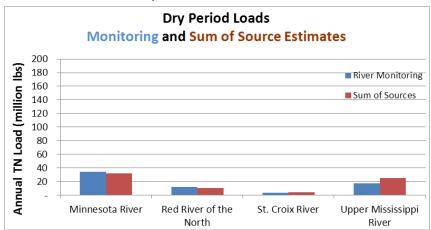


Figure 12. Dry period comparison of river monitoring average annual loads with the sum of estimated source loads.

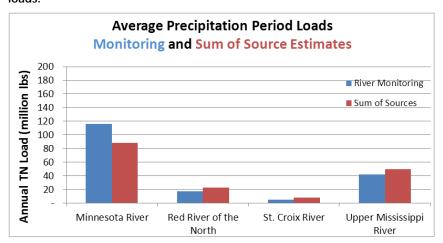


Figure 13. Average period comparison of river monitoring average annual loads with the sum of estimated

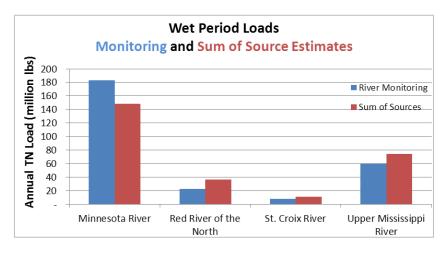


Figure 14. Wet period comparison of river monitoring average annual loads with sum of estimated source loads.

The SPARROW and HSPF model N source estimates were both consistent with the source assessment findings. SPARROW model results showed cropland sources as the dominant statewide N sources to Minnesota rivers, representing 70% of the source loads (Figure 15).

Using a markedly different modeling approach than SPARROW, the HSPF model results showed that the cropland sources represent 96.6% of the Minnesota River Basin nonpoint source inorganic N load to rivers, which was similar to a 97.6% estimate from the source assessment findings. The HSPF model results also showed similar flow pathways and wet weather effects on loads as compared to the source assessment findings.

# Non-Agric NPS 23% Point Source Agriculture 70% Agriculture 70% Do. Do. MN and MPCA Nitrogen Source Assessment Non-Agric NPS 18% Point Source 9% Agriculture 73% Do. Do. Do. MN and MPCA Nitrogen Source Assessment

Figure 15. Comparing N source category contributions to Minnesota surface waters statewide during an average year using a) SPARROW model results, and b) N source assessment conducted for this study.

We also used statistical and non-statistical methods to compare watershed monitoring results with 18 watershed land use and hydrologic characteristics. These checks on the source assessment findings did not show inconsistencies with the source load findings, and they did show several relationships which support the source assessment findings. For example, a distinct pattern was observed between watershed nitrate levels and the percent of watershed with row crops over tile-drainage, sandy soils, and soils with a shallow depth to bedrock (Figure 16).

Statistical models of nitrate and TN concentration suggested that row crops over tile-drained soils and high groundwater recharge areas (sandy soils and/or shallow depth to bedrock) accounted for much of the nitrate concentration variability in the 28 HUC8 watersheds analyzed (r-squared exceeding 0.96). Statistical models also showed a similarly strong correlation between watershed N yields and two variables: 1) the amount of land with row crops over tile drainage, and 2) annual precipitation. For both the concentration and yield statistical models, the tile drainage variable exerted the strongest magnitude of influence, with two to five times the influence of the other explanatory variables.

All five ways of checking the findings corroborate the source assessment results and no major discrepancies were found. This increases our confidence that the source assessment is reasonably accurate and is useful for generally understanding large scale N load sources and pathways to Minnesota surface waters.

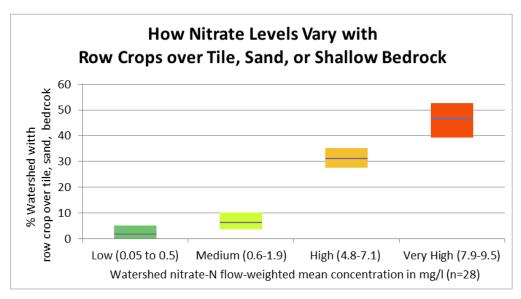


Figure 16. The range (colored bars) and average (dark line) percent of land in row crops underlain by tile-drainage (estimated), shallow bedrock or sandy subsoils. The four watershed nitrate classifications are based on river monitoring averages from two normal flow years within the period 2005-2009.

#### Potential ways to reduce nitrogen in surface waters

Because high N loading is pervasive over much of southern Minnesota, little cumulative large-scale progress to reduce N in surface waters will be made unless numerous large watersheds (i.e., the top 10 to 20 N loading watersheds) reduce N levels. Appreciable N reductions to major rivers and large downstream waters cannot be achieved by solely targeting individual small subwatersheds or mismanaged tracts of land. However, cumulative smaller scale changes repeated across much of the southern Minnesota landscape can make an appreciable difference in N loading.

#### Reducing nitrogen losses from cropland

Based on the N source assessment and the supporting literature/monitoring/modeling, meaningful regional N reductions to rivers can be achieved if Best Management Practices (BMPs) are adopted on acreages where there is a combination of: a) high N sources, b) seasonal lack of dense plant root systems, and c) rapid transport avenues to surface waters (which bypass denitrification N losses common in many groundwaters). These conditions mostly apply to row crops planted on tile-drained lands, but also include row crops in the karst region and over many sandy soils.

Further refinements in fertilizer rates and application timing can be expected to reduce river N loads and concentrations, yet more costly practices will also be needed to meet downstream N reduction goals.

BMPs for reducing N losses to waters can be grouped into three categories:

- 1) In-field nutrient management (i.e., optimal fertilizer rates; apply fertilizer closer to timing of crop use; nitrification inhibitors; variable fertilizer rates)
- 2) Tile drainage water management and treatment (i.e. shallower depth of tile drainage; control structures that let farmers adjust water levels; constructed and restored wetlands for treatment purposes; woodchip trench bioreactors; and saturated buffers)
- 3) Vegetation/landscape diversification (i.e. cover crops; perennials planted in riparian areas or marginal cropland; extended rotations with perennials; energy crops in addition to corn)

Through this study, a tool was developed by the University of Minnesota to evaluate the expected N reductions to Minnesota waters from individual or collective BMPs adopted on lands well-suited for the practices. The tool, called "Nitrogen Best Management Practice watershed planning tool" (NBMP), enables planners to gauge the potential for reducing N loads to surface waters from watershed croplands, and to assess the potential costs (and savings) of achieving various N reduction goals. The tool also enables the user to identify which combinations of BMPs will be most cost-effective for achieving N reductions at a HUC8 watershed or statewide scale.

We used the NBMP tool to assess N reduction scenarios in Minnesota (statewide and in specific HUC8 watersheds). Results from the NBMP tool were also compared to results from an lowa study which used different methods to assess the potential for using agricultural BMPs to achieve N load reductions to lowa waters. Both the Minnesota and lowa evaluations concluded that no single type of BMP is expected to achieve large-scale reductions sufficient to protect the Gulf of Mexico. However, combinations of in-field nutrient management BMPs, tile drainage water management and treatment practices, and vegetation/landscape diversification practices, can together measurably reduce N loading to surface waters.

The N reduction potential varies by watershed (Figure 17). For example, if BMPs were implemented on all land suitable for the BMPs, the NBMP tool predicts a 22% river N reduction in the Root River Watershed and a 39% reduction in the LeSueur River Watershed. The North Fork Crow River Watershed could potentially achieve a 38% N reduction; however, it would need to rely more heavily on taking marginal cropland out of row crop production and replacing with perennials. The total net cost of achieving the reductions shown in Figure 19 is estimated to range from \$22 to \$47 million per watershed per year. The fertilizer BMPs were projected to save money and the majority of the estimated net costs were associated with the vegetation change BMPs.

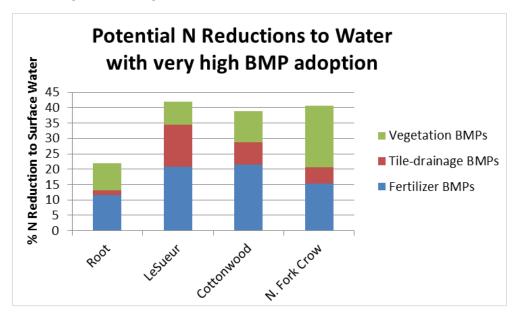


Figure 17 – Potential % N reductions to surface waters estimated with the NBMP tool when adopting BMPs on 100% of lands suitable for the following BMPs: optimal fertilizer rates and timing for corn (fertilizer BMPs), bioreactors and wetland construction/restoration and controlled drainage (tile-drainage BMPs), and plant cover crops and on marginally productive lands replace row crops with perennials (vegetation BMPs).

Statewide, river N loads can potentially be reduced by as much as 13% through widespread implementation of optimal in-field nutrient management BMPs, practices which can reduce fertilizer costs. To achieve 25% N load reductions, high adoption rates of a suite of other BMPs would need to be added to the in-field N management practices, and the net cost per pound of N reduced would increase.

The NBMP tool indicated that a 30-35% statewide reduction of cropland N losses to waters could be achieved if: over 90% of the corn land received optimal fertilizer rates applied in the spring; perennials were planted on 100 feet of either side of most streams; all tile drainage waters were treated in wetlands, bioreactors or otherwise were managed with controlled drainage structures; rye cover crops were planted each year on most row crops; and marginal cropland was retired to perennial vegetation. The projected net cost to install and manage these practices was over a billion dollars per year with recent crop prices and without further improvements in N reduction BMPs. Changes in crop economics and/or improvements to BMPs could reduce this net cost in the future.

lowa predicted a 28% statewide nitrate reduction in water if cover crops were planted on row crops throughout the state. While Minnesota has a cooler climate, cover crops deserve further study in Minnesota due to a combination of desirable potential benefits to water quality and agriculture. If Minnesota can find ways to successfully establish and manage cover crops in row-cropped fields, and then achieve widespread use of cover crops, we could potentially reduce cropland N in Minnesota rivers by as much as 15 to 25% from this practice alone.

Tile-drainage water treatment BMPs are also part of a sequential combination of BMPs which could be employed in many areas to achieve additional N reductions to waters. Constructed wetlands and wetland restoration designed for nitrate treatment purposes remove considerable N loads from tile waters (averaging about 50%) and should be considered for certain riparian and marginal lands. Bioreactors may be an option for treating tile-line waters in upland areas where wetland treatment is less feasible, but they cost considerably more than wetlands for each pound of N reduced. If controlled drainage is used in combination with wetlands and bioreactors on lands well-suited for these BMPs, statewide N loads to streams can be reduced from these practices by an estimated 5-6%, and N loads in heavily-tiled watersheds can be reduced by an estimated 12-14%.

Perennial vegetation can greatly reduce N losses to underlying groundwater and tile drainage waters. When grasses, hay, and perennial energy crops replace row crops on marginally productive lands, N losses to surface waters are greatly reduced on the affected acreage. Under the current economic situation, the crop revenue losses when converting row crops to perennials, makes this practice less feasible on a widespread scale as compared to other practices, according to the results obtained with the NBMP tool. However, if changes occur and new markets develop for perennial crops, the economic picture could make this practice more feasible on larger acreages.

While this study largely focused on N removal BMPs, many BMPs provide additional benefits apart from reducing N. Any evaluation of recommended practices to reduce N should consider the additional costs and benefits of the BMPs. For example, BMPs such as constructed wetlands could potentially help reduce peak river flows through temporary storage of water, which could reduce flooding potential and improve water quality. Wetlands and riparian buffers also have a potential to increase wildlife habitat. Cover crops have added benefits of reducing wind and water erosion and potentially improving soil health and reducing pesticide use.

This study also focused on cost optimization of BMPs, rather than providing a full accounting of the net value of benefits from a reduced hypoxic zone in the Gulf of Mexico and other environmental benefits to Minnesota waters.

#### Wastewater nitrogen reduction

Wastewater point source N discharges can be reduced through two primary methods: 1) Biological Nutrient Removal (BNR), and 2) Enhanced Nutrient Removal (ENR) involving biological treatment with filtration and/or chemical additions.

BNR technologies, if adopted for all wastewater treatment facilities capable of adapting to this technology, would result in an estimated 43-44% N reduction in wastewater point source N discharges to rivers in the Upper Mississippi and Minnesota River Basins, and a 35% reduction in the Red River Basin. Because N loading from wastewater facilities is a relatively small statewide source compared to other sources, these reductions correspond with an estimated overall N reduction to waters of 9.3%, 2.2%, and 0.8% in the Upper Mississippi, Minnesota, and Red River Basins, respectively.

ENR technologies, if adopted for all wastewater treatment facilities capable of adapting to this technology, are estimated to result in a 64-65% N reduction in wastewater point source discharges to rivers in the Upper Mississippi and Minnesota River Basins, and a 51% reduction in the Red River Basin. These reductions correspond with an estimated overall N reduction to waters of 13.5%, 3.2%, and 1.2% in the Upper Mississippi, Minnesota, and Red River Basins, respectively.

#### In conclusion

Surface water N concentrations and loads are high throughout much of southern Minnesota, contributing to the N enriched hypoxic zone in the Gulf of Mexico, nitrate in excess of drinking water standards in certain cold water streams, and a potential to adversely affect aquatic life in a large number of Minnesota rivers and streams. Northern Minnesota has relatively low river N levels, and pollution prevention measures should be adopted in this area as landscapes and land management change.

Since the mid-1970s nitrate concentrations have continued to increase in the Mississippi River, yet they still average less than 3 mg/l (FWMC). The Minnesota River average nitrate concentrations remain high (above 6 mg/l FWMC), but were showing signs of stabilizing or decreasing in the 2005 to 2011 period. Trends are mixed in other rivers in the state, showing increases, decreases and several with no significant trend.

An estimated 73% of statewide N entering surface waters is from cropland sources and 9% is from wastewater point sources, with several other sources adding the other 18%. Most of the cropland N reaches waters through subsurface agricultural tile drainage and groundwater pathways, with a relatively small amount in overland runoff.

Reducing N levels in rivers and streams in southern Minnesota will require a concerted effort over much of the land in this region, particularly tile-drained cropland and row crops over permeable soils and shallow bedrock. Significant cumulative reductions are predicted when multiple practices are implemented over large acreages. Some progress toward reducing N losses to waters can be made by further optimizing in-field N management and temporarily retaining tile-line drainage waters in wetlands, bioreactors and behind controlled drainage structures. Cover crops and strategic establishment of perennial energy crops can greatly reduce N losses to waters, but need further development in Minnesota to make these practices more successful and adopted on more lands.

## A1. Purpose and Approach

#### Purpose

Nitrate has long been a concern for human health when elevated levels reach drinking water supplies. The 10 mg/l nitrate-N drinking water standard established for surface and groundwater drinking water sources and for cold water streams is exceeded in numerous wells and streams. In recent decades, the concern about nitrogen (N) in surface waters has grown due to nitrogen's role in causing a large oxygendepleted hypoxic zone in the Gulf of Mexico, and an increasing body of evidence showing toxic effects of nitrate on aquatic life.

Minnesota has initiated several state-level planning efforts to address N in waters. Effective plans and strategies should be based on an understanding of the scientific data and technical body of knowledge surrounding the issues. The purpose of this study was to provide an assessment of the science concerning N in Minnesota waters so that the results could be used for current and future planning efforts, thereby resulting in meaningful goals, priorities, and solutions.

More specifically, the purpose of this project was to characterize N loading to Minnesota's surface waters, and assess conditions, trends, sources, pathways, and potential ways to achieve nitrogen reductions in our waters. The study results will be used in developing: 1) Minnesota's state-level Nutrient Reduction Strategy, 2) responses to potential river nitrate standard exceedances, and 3) other regional watershed implementation plans for addressing N in waters. Each of these three efforts is summarized below.

The state-level Nutrient Reduction Strategy is a multi-agency effort to establish paths to achieve progress toward meaningful and achievable N and phosphorus reductions. The strategy is being designed to protect and improve Minnesota's own waters, along with reducing cumulative impacts to downstream waters such as the Gulf of Mexico and Lake Winnipeg. In 2008, Minnesota committed to the U.S. Environmental Protection Agency (EPA) and the Gulf of Mexico Hypoxia Task Force to complete the first strategy by 2013. Guidance documents for state strategy development recommend that states conduct assessment work prior to establishing quantitative targets and identifying the needed management practices/strategies. The guidance suggests that each state characterize watersheds, identify sources, prioritize geographic areas, document current loads, and estimate historical trends.

River water quality nitrate standards are being developed by the Minnesota Pollution Control Agency (MPCA) in response to a 2010 Minnesota legislative directive asking the agency to establish water quality standards for nitrate-N and total nitrogen (TN) (2010 Session Laws, Chapter 361, Article 2, Section 4, Subdivision 1). The nitrate water quality standards are being developed based on aquatic life toxicity concerns. Information in this study is not intended to influence the standard, which is established based on strict independent criteria related to toxicity testing, but rather will help us understand the extent of high nitrate water, nitrate sources, and considerations for reducing nitrate in impacted watersheds.

Watershed implementation plans and protection requirements are developed at the local level where water quality standards are exceeded or have the potential to be exceeded. At the time of this writing, 15 streams, mostly in southeastern Minnesota exceed the 10 mg/l standard for nitrate-N.

While N reduction strategies are needed in many watersheds with or without new nitrate standards addressing aquatic life toxicity, the addition of such standards will likely increase Minnesota's efforts aimed at reducing nitrate concentrations. Additionally, because groundwater is a primary pathway of N movement to streams, some of the study results may also be considered for groundwater and drinking water supply protection efforts.

To aid the above efforts, the following information needs were identified and were thus addressed in this study:

- 1. Watershed nitrogen conditions assess how N loads, yields, and concentrations in rivers and streams vary geographically across Minnesota watersheds, and estimate how much N is lost within waters before being delivered to downstream waters.
- 2. *Concentration trends* evaluate how in-stream nitrate concentrations have changed since the mid-1970s and how they have changed during more recent periods.
- 3. *Sources* estimate mass loadings from different point and nonpoint land uses/sources and assess which sources most influence N loading to surface waters.
- 4. *Hydrologic pathways* assess the amount of N delivered to streams by groundwater baseflow, tile drainage, surface runoff, atmospheric deposition, and other hydrologic pathways.
- 5. Solutions for reducing nitrogen evaluate different scenarios for reducing N, considering N reduction potential and costs.

The approaches used to address these areas of study are summarized below and are more specifically described within each chapter.

#### **Approach**

The general approach for this study was to:

- 1. Collaborate with other organizations and MPCA divisions.
  - The MPCA Watershed Division and Environmental Outcomes and Analysis Division worked together with the University of Minnesota and the U.G. Geological Survey (USGS) to complete this study. The University of Minnesota's primary area of focus was determining N contributions to water from nonpoint sources. The USGS assisted with watershed modeling (SPARROW model) and N concentration mapping and trends analyses. The Minnesota Department of Agriculture (MDA) and the Metropolitan Council provided data, assistance, and review. (See acknowledgments for specific authors, co-authors and others who provided assistance.)
- 2. Compile existing information, data, and results, whenever possible, taking advantage of past work from multiple organizations.
  - For many years prior to this study, a tremendous amount of work has been completed by several different organizations to better understand N in Minnesota's surface waters. Our approach was to build on these other efforts, pulling together information from past studies and monitoring results, and combining this information with work conducted specifically for this project. No new monitoring was conducted for this study. Instead we analyzed existing results from the MPCA, Metropolitan Council, USGS, the MDA, and other sources. While new modeling efforts were completed for this project, the models were generally built upon previous modeling efforts by the USGS, University of Minnesota, and the MPCA.

Some of the existing information used in this study includes:

- Recent water N concentration results from over 50,000 water samples collected at over 700 stream sites in Minnesota;
- Water N loads calculated from monitoring over 20 to 30 years at 9 mainstem river sites and 1-10 years near 70 watershed outlets;
- Water chemistry sampling combined with water flow monitoring for 20 to 35 years at over 50 sites around the state (used for time-trend analysis);
- Findings from over 300 published studies;
- · Six previously developed computer models (and two newly developed models); and
- More than 40 existing GIS spatial data mapping efforts.
- 3. Use multiple methods and information sources so that the conclusions do not hinge on one data source or model.

Rather than relying on single models, data sets, or information sources, we used multiple approaches to validate and verify results. In most cases, we had a primary approach along with one or more secondary approaches as verification of the primary approach results. Results from models were verified with recent monitoring results.

4. Focus on the 8-digit HUC (HUC8) watershed scale and larger.

Since the results for this study are intended mostly for helping with larger scale planning efforts, the scale of project results was designed for major watersheds (HUC8s); major basins; and statewide (Figure 1).



Figure 1. Major basins and HUC8 level watersheds in Minnesota.

This report focuses largely on TN since the forms of N which comprise TN can be transformed from one form into another. Since the nitrate form of N affects aquatic life toxicity and drinking water quality and is the dominant form which influences TN in high-yielding watersheds, trends analyses and certain other statistical evaluations were specifically done with the nitrite+nitrate form of N. In some analysis and discussion, we also include the ammonium and organic forms of N.

An overview of the methods used for each of the major study components is described below. More details about the methods are included in the body of the report within each chapter.

#### Nitrogen conditions

Nitrogen conditions across Minnesota were assessed by analyzing monitoring-based calculations of concentrations, loads, and yields, and additionally supplemented with SPARROW model results. All loads and yields in this report are annual loads and yields, unless specified otherwise.

Recent monitoring results at over 700 river and stream sampling sites were used to map and describe concentrations of different forms of N. The resulting maps show concentrations during low N periods (10th percentiles), average conditions (50th percentile) and high N periods (90th percentiles) during the past decade.

Monitoring-based watershed N annual loads were analyzed at two different levels: 1) major (mainstem) rivers, and 2) outlets of HUC8 watersheds. Annual loads were calculated by the MPCA and Metropolitan Council from continuous flow measurements and regular stream sampling. Because loads are largely influenced by the size of the watershed, the area-normalized loads (yields) and flow-weighted mean concentrations (load divided by flow) were mostly used when comparing N loads in watersheds around the state. Monthly loads were assessed at certain mainstem river monitoring points using data from the Metropolitan Council.

A spatial comparison of annual N loads and yields was also evaluated using modeling results from the SPARROW model. This model was developed and calibrated by the U.S. Geological Survey using monitoring-based results that are mostly independent of the other HUC8 watershed monitoring data described in this report. The model is specifically designed to spatially compare nutrient delivery from watersheds within a specific geographic area.

Because N forms transform within waters and are sometimes lost to the atmosphere, an extensive review of literature and data was conducted to evaluate how much N entering waters in one area is lost or transformed as it is transported to downstream waters.

#### Nitrate concentration trends

Stream nitrate concentration trends at 51 monitoring sites in the state were evaluated by the USGS and MPCA for nitrate concentration trends. Water quality monitoring data from the MPCA, USGS and Metropolitan Council was used, along with river flow data from the USGS. Long term trends (30 or more years) were assessed using the USGS QWTREND model. The QWTREND model allowed us to determine which specific periods of time within the entire record had increasing, decreasing, or stable trends. Trend results were mapped so that differences in trends could be observed across the state.

The statistical analyses were compared to several other previous trends studies conducted in Minnesota.

#### Sources and pathways

Total nitrogen inputs to waters from different sources and pathways were estimated as follows:

*Point sources* – MPCA NPDES permit records were used to estimate municipal and industrial point source N discharges directly into surface waters.

Atmospheric deposition – An EPA Model (CMAQ) was used to determine wet and dry atmospheric N deposition. The model is based on results from monitoring combined with N source information. Geographic Information System (GIS) data were used to determine amounts of atmospheric N falling directly onto lakes, streams, and land.

Cropland sources – The University of Minnesota estimated cropland losses for three different pathways: surface runoff, tile-line transport, and leaching to groundwater and its subsequent travel to surface waters. Different methods were used for each pathway, but all three assessments involved taking field research results and then using GIS databases to extrapolate the field-research results to the watershed and basin scales.

For surface runoff, typical N concentrations in cropland runoff were multiplied by runoff volumes that varied for each part of the state.

For tile drainage, field research results from the literature were extrapolated for estimating losses to tile lines under different fertilization rates and precipitation scenarios. Fertilizer rates were estimated from recent farmer surveys.

For leaching to groundwater, field research results from the literature were extrapolated for estimating losses under different soils and geologic sensitivity conditions. Using GIS, the N leaching was estimated for each agro-ecoregion based on geologic sensitivity, soils, climate, fertilizer rates, etc. Recognizing that some N is lost in the groundwater via denitrification before reaching streams, denitrification loss coefficients estimated from research literature were assigned to each agroecoregion. Time lags between leaching to groundwater and delivery to surface waters were not directly accounted for.

All major cropland N inputs and outputs were evaluated in a basin-wide and state-wide N budget assessment. The budget allowed us to estimate the total fraction of cropland N inputs which is lost to waters.

Septic systems – Septic system transport was divided into direct pipe discharges and groundwater discharges. Average N generated per home was multiplied by the number of direct pipe septic systems to represent direct pipe discharges. For leachfields, N generated per home was multiplied by the number of leachfields, and then adjusted to account for denitrification losses within the soil and groundwater that would likely occur prior to N reaching surface waters.

Feedlots – Feedlot runoff N estimates were made using the Minnesota Feedlot Annualized Runoff Model (MinnFARM) and then multiplied by estimates of the size and number of non-compliant feedlots. Land application of manure was incorporated into the cropland source categories, and therefore is not included under the feedlot source category.

Forests – N loss coefficients from published studies of forest land were examined. A coefficient was selected to represent all forested land in the state. This coefficient was multiplied by the forested acreage using GIS.

*Urban stormwater runoff* – N loss coefficients from published studies and Twin Cities monitoring data were examined before selecting a single coefficient to represent typical urban/suburban stormwater runoff N loads. An additional amount of N was added based on a literature search, to represent urban/suburban groundwater contributions. GIS data layers were used to multiply the urban suburban lands by the loss coefficient.

Due to analysis uncertainties, the above source assessment findings were verified using five different approaches, as follows:

Monitoring results – The sum of the individual source estimates were compared with monitoring results from similar geographic areas as the source estimates. This comparison was conducted for the HUC8 and major basin scales.

Watershed land characteristics – Land characteristics in watersheds with more than one year of monitoring during normal-flow conditions were used in non-statistical and multiple regression analyses to assess relationships between the land and river N yields and concentrations. The land characteristics most associated with high and low river N levels were compared with the findings of the N source assessment.

The SPARROW model – The SPARROW model was used to estimate the relative contributions of major source categories of: agriculture, point source, and non-agricultural nonpoint sources. These statewide results were compared with similar groupings from the N source assessment.

*Minnesota River Basin HSPF model* – The HSPF model developed for the Minnesota River Basin was used to compare nonpoint source N delivery pathways and sources for this basin.

*Literature review* – Nitrogen source findings from other studies in the upper Midwest were compared to the findings from the source assessment.

#### Reducing nitrogen loads

The University of Minnesota and Iowa State reviewed existing literature to determine estimates of the expected N reductions which can be achieved from individual agricultural best management practices (BMPs) adopted at both the field and statewide scales. The N reduction estimates, BMP cost estimates, N loss to waters, along with limitations in the landscape for adopting each BMP, were all incorporated into a nitrogen BMP watershed planning spreadsheet (NBMP). We used the tool to estimate the N reduction effects and associated costs from different combinations of BMP adoption rates, and also compared our findings to lowa's results.

This part of the study was intended to provide information and results that could be used for assessing large-scale potential ways to achieve N load reductions. The results are not suited for small scale analysis or individual farmer use.

Estimates of wastewater point source reductions that could be achieved with two types of technologies were developed from existing published information.

## A2. Nitrogen in Waters: Forms and Concerns

Author: Dave Wall, MPCA

Assistance from: Angela Preimesberger (MPCA) and Hillary Carpenter (MDH) on human health and drinking water; Steve Heiskary (MPCA) on lake eutrophication; and Greg Pratt (MPCA) on atmospheric issues

#### Introduction

Nitrogen (N) is one of the most widely distributed elements in nature and is present virtually everywhere on the earth's crust in one or more of its many chemical forms. Nitrate (NO<sub>3</sub>), a mobile form of N, is commonly found in ground and surface waters throughout the country. Nitrate is generally the dominant form of N where total N levels are elevated. Nitrate and other forms of N in water can be from natural sources, but when N concentrations are elevated, the sources are typically associated with human activities (Dubrovski et al., 2010). Concerns about nitrate and total N in Minnesota's water resources have been increasing due to effects of nitrate on certain aquatic life and drinking water supplies, along with increasing N in the Mississippi River and its impact on Gulf of Mexico oxygen depletion. This chapter provides background information on:

- · forms of N found in water
- environmental and health concerns with N in waters
- how N reaches surface waters

Concurrent to this report writing, the Minnesota Department of Agriculture (MDA) is updating the Nitrogen Fertilizer Management Plan. The MDA plan provides a wealth of background information on agricultural N in soils and water, and the reader is encouraged to refer to the plan for additional background information related to N forms, transport to groundwater, health concerns, well-water conditions, N fertilizer sales and sources, and much more:

www.mda.state.mn.us/chemicals/fertilizers/nutrient-mgmt/nitrogenplan.aspx

Additionally, more discussion of N forms and transformations from one form to another is included in Appendix B5-2.

#### Forms of nitrogen in water

#### Overview

Nitrogen enters water in numerous forms, including both inorganic and organic forms (Figure 1). The primary inorganic forms of N are ammonia, ammonium, nitrate, and nitrite. Organic-nitrogen (organic-N) is found in proteins, amino acids, urea, living or dead organisms (i.e., algae and bacteria) and decaying plant material. Organic-N is usually determined from the laboratory method called total Kjeldahl nitrogen (TKN), which measures a combination of organic N and ammonia+ammonium. Since N can transform from one form to another, it is often considered in its totality as total nitrogen (TN). This report most often refers to TN, but also at times focuses more specifically on the dominant form nitrate-N.

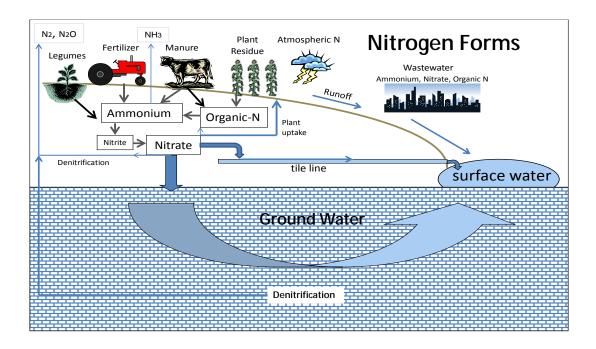


Figure 1. Nitrogen cycle, showing primary N sources, forms and routes to surface waters.

The relative amounts of the different forms of N in surface waters depends on many factors, including: proximity to point and nonpoint pollution sources; influence of groundwater baseflow discharging into the water; abundance and type of wetlands; reservoirs and lakes in the pathway of flowing streams; as

Organic N

Ammonium
Ammonia

Total N

Inorganic N

well as other natural and anthropogenic factors. Temperature, oxygen levels, and bio-chemical conditions each influence the dominant forms of N found in a given soil or water body.

Types of N commonly found in surface waters are depicted in Figure 2. In most surface waters, the dominant forms of N are nitrate and organic-N. Where streams originate in areas of agricultural production, the nitrate form of N is usually substantially higher than organic N. Because nitrate is very low in forested and grassland areas, organic N is typically higher than nitrate in landscapes dominated by these more natural conditions.

Ammonia and ammonium forms of N are usually only elevated near sources of human or animal waste discharges.

Figure 2. Schematic diagram of the relative amounts of different N forms commonly found in Minnesota surface waters with elevated N levels.

An overview of the N forms and their associated health and environmental concerns is provided in Table 1. Each specific form is described in more detail in subsequent sections.

Table 1. Overview of the primary forms of N found in Minnesota waters and associated concerns and standards.

Nitrogen parameter	General description	When found	Sources to surface waters	Health and environmental concerns	Minnesota standards
Nitrate-N (NO3)	Main form of N in groundwater and high-N surface waters. Dissolved in water and moves readily through soil.	Present as a common form of nitrogen, since most other N forms can transform into nitrate in N cycle.	Transformed into nitrate from other N forms found in fertilizer, soil N, atmosphere and human and animal waste.	Methemoglobinemia in infants and susceptible adults. Toxic to aquatic life, especially freshwaters Eutrophication and low oxygen (hypoxia), especially in coastal waters.	Drinking Water: 10 milligrams per Liter (mg/l) in groundwater and Class 2A cold water streams. Standards under development for aquatic life toxicity in MN surface waters.
Nitrite-N (NO2)	Low levels in waters – typically measured in lab together with nitrate	Less stable intermediary form of N found during N transforming processes	Same as nitrate.	Methemoglobinemia in infants and susceptible adults. Toxic to aquatic life.	Drinking Water: 1 mg/l in groundwater and Class 2A cold water streams. Standards under development for aquatic life toxicity in MN surface waters.
Ammonia-N (NH3)	Unionized Ammonia – low levels in most waters.	Most of NH3+NH4 is in the NH4 form. But NH3 increases with higher temps and pH (potential of Hydrogen).	Human and animal waste discharges.	Toxic to aquatic life.	0.016 mg/l in Class 2A cold water streams (trout protection) 0.040 in most other streams (Class 2B).
Ammonium- N (NH4)	Measured in lab together with ammonia – usually higher than ammonia but less toxic	Usually found at low levels compared to nitrate and organic N. Found near waste sources.	Human and animal waste discharges.	Can convert to more highly toxic ammonia in high pH and temperature waters.	
Organic-N	Main form of N in low-N surface waters (where nitrate is low).	Living and dead organisms/algae. Found naturally in waters and is supplemented by human impacts.	Algae; soil; organisms; human and animal waste.	Can convert to ammonium and ultimately nitrate under certain conditions.	
Inorganic N	Sum of Nitrite, Nitrate, Ammonia and Ammonium.			See separate parameters above	See separate parameters above
Total Kjeldahl N (TKN)	Lab measurement which includes organic-N, ammonia and ammonium.	Useful to determine organic-N when ammonia+ammonium is also determined separately and subtracted from TKN.		See separate parameters above	See separate parameters above
Total N	Sum of TKN, nitrite and nitrate.			See separate parameters above	See separate parameters above

## Nitrate (NO<sub>3</sub>) and nitrite (NO<sub>2</sub>)

Nitrate (NO<sub>3</sub>) is very soluble in water and is negatively charged, and therefore moves readily with soil water through the soil profile, where it can reach subsurface tile lines or groundwater. Where groundwater remains oxygenated, nitrate remains stable and can travel in the groundwater until it reaches surface waters. Similarly, nitrate can move downward into tile lines, which then route the drained water to ditches and surface waters. When nitrate encounters low oxygen/anoxic conditions in soils or groundwater it may be transformed to N gasses through a biochemical process called "denitrification." Therefore, groundwater nitrate is sometimes lost to gaseous N before the nitrate-impacted groundwater has enough time to travel to and discharge into streams. Typically a smaller fraction of nitrate reaches streams in stormwater runoff over the land surface, as compared to subsurface pathways.

Nitrite  $(NO_2)$  is typically an intermediate product when ammonium is transformed into nitrate by microscopic organisms, and is therefore seldom elevated in waters for long periods of time. Nitrite is also an intermediary product as nitrate transforms to N gas through denitrification.

Most commonly, laboratories test for a combination of nitrite plus nitrate. When analyzed separately, nitrate is usually much higher than nitrite. Nitrite can be elevated when water samples are taken near sources of organic wastes or sewage, where ammonium is being converted first to nitrite and then to nitrate. Because nitrate is usually so much higher than nitrite, the combined laboratory concentration of nitrite plus nitrate is often referred to in reports as "nitrate." In this report, we use the following terms interchangeably except where it is important to distinguish nitrite from nitrate: nitrite+nitrate-N,  $NO_2+NO_3-N$ , NOx-N and nitrate.

Common additions of nitrate in Minnesota soils and waters include: treated wastewater from municipal or industrial waste, on-site septic systems, fertilizer and precipitation. Much of this nitrate does not initially enter the soils in this form, but results from the biological breakdown of ammonium and organic sources of N which originate as manure, fertilizer and soil organic matter. In the presence of oxygen, moisture, and warm temperatures, other forms of N will tend to transform into nitrate.

Nitrate is the dominant form of N in groundwater, and is also dominant in rivers and streams with elevated TN. In Minnesota lakes, nitrate is nearly always at or below laboratory detection limits (Heiskary and Lindon, 2010). Nitrate is found in reservoirs with short residences times and high inputs of N from upstream sources.

Concerns about nitrate in our water include: human health effects when found elevated in groundwater used for drinking water supplies, aquatic life toxicity in surface waters, and increased eutrophication and correspondingly low oxygen in downstream waters such as the Gulf of Mexico.

#### Ammonia and ammonium

Ammonia (NH<sub>3</sub>) is toxic to fish and other aquatic organisms. Ammonium (NH<sub>4</sub>), the predominant form in the pH range of most natural waters, is less toxic to fish and aquatic life as compared to NH<sub>3</sub>. As the pH increases above 8, the ammonia fraction begins to increase rapidly. In the rare situation that a natural water pH exceeds reaches 9, ammonia and ammonium would be nearly equal.

Sometimes the terms "ammonia" and "ammonium" are used interchangeably in reports and presentations to represent the laboratory-determined concentration of "ammonia plus ammonium-N." The ammonia fraction, often referred to as "unionized ammonia," can be calculated from laboratory reports of ammonia+ammonium if the water temperature and pH are also known. In most Minnesota waters, the ammonium form represents the majority of the ammonia+ammonium.

Common sources of ammonia/ammonium include human and animal wastes, as well as certain fertilizers and industrial wastes. Ammonia and ammonium most commonly enter surface waters through overland runoff or direct discharges from wastewater sources.

Ammonium is also the byproduct when organic matter in soils is mineralized to inorganic-nitrogen (inorganic-N). Once in the soil, ammonium binds onto soil particles such as clay and organic matter. For that reason, ammonium is less likely to move vertically through the soil matrix into groundwater, as compared to nitrate. Yet, ammonium can at times be found in well water at concentrations exceeding 1 mg/l (Razania, 2011). Under the right soil temperature and moisture conditions, ammonium will readily transform into the more mobile form of nitrate-N.

#### Inorganic-nitrogen

Inorganic-N in waters is predominantly the sum of the nitrite, nitrate, ammonia, and ammonium-N. Most inorganic N is typically in the dissolved form in waters. Where sampling or laboratory methods ensure that all of the nitrite, nitrate, ammonia and ammonium is in the dissolved forms, it is referred to as dissolved inorganic nitrogen (DIN).

## Organic-nitrogen

Organic-N includes all substances in which N is bonded to carbon. It occurs in both soluble and particulate forms. Organic-N is found in proteins, amino acids, urea, living or dead organisms (i.e., dead algae and bacteria), and decaying plant material. Soluble organic-N is from wastes excreted by organisms, including livestock manure and human wastes, or from the degradation of particulate organic-N from plants and plant residues.

Some organic-N is attached to soil particles and is associated with sediment losses to water. Different soils have varying amounts of organic-N. For example, soils developed under prairies and prairie wetlands have more organic-N than soils developed in forested areas. Climate, soil particle sizes, age of the land surface, agricultural practices and soil chemistry also affect the amount of organic-N in soils.

Organic-N concentrations in water are typically not measured directly in the laboratory, but are calculated by subtracting the ammonia+ammonium-N (determined separately) from the total Kjeldahl nitrogen (TKN) laboratory analysis (TKN includes N from organic-N and ammonia+ammonium-N). Typically, the organic-N fraction of TKN in surface waters is much higher than the ammonia+ammonium-N fraction.

In nature, organic-N can be biologically transformed to the ammonium form and then to the nitrite and nitrate form. Once in the nitrate or ammonium forms, these nutrients can be used by algae and aquatic organisms and thereby convert back to organic forms of N. Heiskary et al. (2010) and Heiskary and Lindon (2010) found that in high P surface waters, where algae growth is high, TKN is also elevated. Where P and algae are low, TKN is also low. The high algae levels were not believed to be caused by the high TKN, but rather the algae were believed to comprise much of the organic-N in the TKN measurements.

Organic-N sometimes makes up a significant fraction of soluble and particulate N in natural waters, especially in forest and rangeland areas where natural sources of organic matter are found and nitrate concentrations are typically low.

## Total nitrogen

Total nitrogen refers to the combination of both organic and inorganic N. While it can be measured directly in the laboratory, it is also commonly approximated by adding TKN and nitrite+nitrate-N concentrations.

Because N can transform from one form to another in water, TN is often a parameter considered when estimating potential downstream effects of N to receiving waters such as the Gulf of Mexico.

In Minnesota rivers and streams with TN concentrations less than 1.5 to 2.0 mg/l, organic-N comprises most of the TN. As TN increases above 2 mg/l, nitrate-N becomes an important component to TN. When TN concentrations exceed 3 to 4 mg/l, nitrate-N will usually be higher than the organic-N (Heiskary et al., 2010).

#### Environmental and health concerns

Different forms of N in the environment have led to human health and environmental health concerns. Environmental and health concerns with N can be grouped into four general categories:

- 1. human health
- 2. aquatic life toxicity
- 3. eutrophication (resulting in oxygen-deprived or hypoxic waters)
- 4. nitrogen gasses and atmospheric concerns

An examination of the suite of environmental issues together is important so that efforts to reduce N in one area of the environment do not result in unintended problems in other areas, and such that management plans consider more than one N impact at a time.

#### Human health concerns

The N forms of primary concern for human health are nitrite and nitrate. Nitrite is the most toxic form of N to humans, especially infants. Nitrate is of most significance, not because of direct toxicity, but when ingested is converted to nitrite. Exposure to nitrate and in some cases nitrite contaminated well water has notably contributed to methemoglobinemia or "blue baby syndrome" in infants. Cases of methemoglobinemia in infants occurring after consuming formula prepared with drinking water high in nitrate date back to before the 1940s. Early academic research and evaluations by government agencies have led to long-standing regulatory drinking water standards based on methemoglobinemia (described in the next section), with more recent studies examining the potential long-term health effects.

Clinical observations and epidemiological studies in the 1940s and 1950s on methemoglobinemia in infants identified nitrate exposure in well water as an important contributing factor, particularly when well water nitrate concentrations exceeded 10 mg/l nitrate-N (Knobeloch et al., 2000). Later studies determined that bacterial conversion of nitrate to nitrite in the gastrointestinal system was an important determinant in the development of methemoglobinemia (NRC, 1995). Nitrite is a reactive form of N that changes the state of iron in hemoglobin (red blood cells). This altered form of hemoglobin, methemoglobin, has a significantly reduced capacity to bind and transport oxygen. Low oxygen transport leads to the visual indicator of methemoglobinemia (blue-gray skin coloring) and adverse effects, such as lethargy, irritability, rapid heartbeat, and difficulty breathing. It is possible for methemoglobinemia to progress to coma and death if not treated (Knobeloch et al., 2000).

Infants under six months of age are more susceptible to methemoglobinemia than older infants and most adults because of: a) lower acidity (higher pH) levels in their stomachs, creating an environment that favors the growth of bacteria capable of reducing nitrate to nitrite; b) lower levels of an enzyme

that converts methemoglobin back to hemoglobin; and c) greater consumption of drinking water (formula) per unit of body weight (Ward et al., 2005). Additional factors influence the risk of methemoglobinemia in infants ingesting high nitrates, including co-contamination of drinking water with both high nitrate and bacteria, and existing health status (medications and presence of infections or diarrhea).

Besides infants, the Minnesota Department of Health (MDH) also notes that pregnant women and people with reduced stomach acidity and certain blood disorders may also be susceptible to nitrate-induced methemoglobinemia (MDH, 2012).

Minnesota does not require clinicians to report methemoglobinemia cases, but cases are still occasionally identified in states like Wisconsin where reporting is required (Knobeloch et al., 2000). The MDH has conducted studies and extensive public outreach to citizens and medical professionals related to nitrate and bacterial contamination in private well water. Public drinking water is regulated for nitrate, nitrite, and bacterial contamination. With the existing outreach and standards, cases of infant methemoglobinemia from drinking high nitrate well water in Minnesota appear to be very limited.

The MDH and the Centers for Disease Control have also conducted studies on the occurrence of methemoglobinemia in pregnant women in Minnesota (Manassaram et al., 2010). The study did not find elevated levels of methemoglobin, but only a few participants had drinking water concentrations measured above 10 mg/l nitrate-N. In addition, many women were drinking water treated by an inhome device or bottled water. While the authors did not specifically inquire as to the reason for not drinking household tap water, the results suggested awareness by the participants of health concerns associated with potential drinking water contaminants.

Concerns about nitrate have also included possible health effects related to long-term exposure. Studies have suggested association with nitrate exposure and adverse reproductive outcomes, thyroid disruption, and cancer. Evaluations of these potential health effects in 1995 by the National Research Council (NRC) and more recently, by the World Health Organization (WHO) (2007), concluded that human epidemiological studies on nitrate toxicity provide inadequate evidence of causality with these health outcomes. When also considering additional information, such as the internal conversion process of nitrate to nitrite and direct nitrite exposure available from animal studies, risks for reproductive effects and cancer were deemed to be low at environmental concentrations.

Besides contaminated drinking water, other sources of exposure to nitrate and nitrite have been considered for evaluating potential health effects. For older infants and adults, the primary sources of exposure are from diet and internal physiological (endogenous) production. Certain vegetables, as well as cured meat, contain high levels of nitrate and nitrite, respectively. There are added benefits of co-occurring antioxidants and vitamins from vegetable consumption, which can protect against some of the negative health effects associated with nitrate intake (Ward, 2005).

Available information on nitrate and nitrite exposures and adverse health effects continues to center on methemoglobinemia in infants less than six months of age, who have consumed formula with high nitrate concentrations. Older infants, children, and adults, because of differences in both biological processes and exposure sources, are much less susceptible to health concerns. However, both the WHO (2007) and a recent draft report from Health Canada (2012) recommend keeping exposure to nitrate and nitrite concentrations in drinking water below 10 mg/l nitrate-N and 1 mg/l nitrite-N, respectively, for all populations.

#### Drinking water standards for nitrate and nitrite

The U.S. Environmental Protection Agency (EPA) established the Safe Drinking Water Act (SDWA) standard, known as a maximum contaminant level (MCL), for nitrate in drinking water of 10 mg/l nitrate-N (equivalent to 45 mg/l as nitrate) in 1975. The EPA adopted a nitrite MCL of 1 mg/L nitrite-N in 1991. Maximum contaminant levels are regulatory drinking water standards required to be met in finished drinking water provided by designated public drinking water facilities. Both standards were promulgated to protect infants against methemoglobinemia, based on the early case studies in the United States, including Minnesota, which found no cases of methemoglobinemia when drinking water nitrate-N levels were less than 10 mg/L (NAS, 1995). The nitrite MCL is lower than nitrate, because nitrite is the N form of greatest toxicity, and nitrate's risk to infants is based on the level of internal conversion to nitrite. Because the impacts of methemoglobinemia can occur as quickly as a day or two of exposure, the MCLs are applied as acute standards, not to be exceeded on average in a 48-hour timeframe.

The MDH administers the SDWA program. Because nitrate and nitrite are regulated under this program, SDWA facilities must monitor for nitrate and nitrite and inform consumers if MCLs in finished drinking water are exceeded. The MDH reports that exceedances are uncommon (< 1% in 1999 to 2007), but do occur, particularly in systems that use groundwater (MDH, 2009). The MDH notes that users of private wells have more likelihood of having elevated nitrate and bacterial concentrations (MDH, 2012).

The MDH is also responsible for promulgating Health Risk Limits (HRLs) under the Minnesota Groundwater Protection Act (Minn. Stat. ch. 103H). Health Risk Limits are health-protective drinking water standards applicable to groundwater. Health Risk Limits are the principle standards used to evaluate contaminated groundwater not regulated under the SDWA, especially private well water. Health Risk Limits are meant to ensure that consumers of groundwater are not exposed to a pollutant at concentrations that can potentially lead to adverse health effects (Minn. R. ch. 4717). Currently the HRLs for nitrate and nitrite are the SDWA MCLs. The MDH continues to follow ongoing research on these common groundwater contaminants for possible future HRL updates.

#### Surface water standards for drinking water protection

As described, the MDH administers the Federal SDWA standards. The MPCA incorporated these same standards by reference in the State's Water Quality Standards (Minn. R. ch. 7050). The nitrate and nitrite MCLs are applied as Class 1 Domestic Consumption standards. Class 1 standards apply in all Minnesota groundwater and in designated surface waters. Streams upstream of SDWA facilities (e.g., Mississippi River from Fort Ripley to St. Anthony Falls and Red River of the North) are protected as drinking water. Minnesota rules also designate cold-water streams and lakes, primarily trout-waters, as Class 1. Therefore, the MCLs for nitrate-N of 10 milligrams/liter (mg/L) and nitrite-N of 1 mg/L are also regulatory standards in some Minnesota surface waters.

The MPCA and MDA monitor nitrate in surface waters. The MPCA uses this data to determine if all water quality standards are being met. In 2011, 15 cold-water streams in Minnesota were listed as not meeting the nitrate water quality standards (listed as impaired). Twelve of the fifteen were located in southeastern Minnesota. These determinations are based on a limited number of monitoring locations. Surface water nitrate concentrations are discussed further in Chapter B1.

#### Nitrate in groundwater and drinking water: exceedance of standards

A recent national study by the United States Geological Survey (USGS) found nitrate-N concentrations above 10 mg/l in 4.4% of sampled wells (DeSimone et al., 2009). The upper Midwest was noted as one of the areas where concentrations were most commonly elevated. The percent of wells with elevated nitrate depends on the targeted land uses, well depths, well types, and hydrogeologic settings where the well samples are taken.

The MDH and the MDA conduct nitrate monitoring studies in drinking water and groundwater. The MDH Well Water Quality data base for new wells shows that about 0.5% of newly constructed wells exceeded the MCL during the past 20 years. Newly constructed wells target areas and depths where low nitrate waters are more likely to be found, and they have proper grouting and sealing to prevent surficial contamination (MPCA et al., 2012).

In a targeted study of southeastern Minnesota private well drinking water nitrate concentrations, the percent of wells exceeding 10 mg/l nitrate-N ranged between 9.3% and 14.6% during the years 2008 to 2011 (MDA, 2013).

In 1993, the MDA developed a "walk-in" style of water testing clinic with the goal of increasing public awareness of nitrates in rural drinking and livestock water supplies. While the information collected does not represent a statistically random set of data, and is likely biased toward more highly impacted wells, the results verify the broad extent of elevated nitrate in certain Minnesota well water settings. Based on over 52,000 well water samples (1995-2006), 10% of submitted well water samples exceeded the 10 mg/l nitrate-N drinking water standard (MDA, 2012).

When targeting shallow wells in agricultural areas, the national study by DeSimone et al. (2009) found nearly 25% of wells exceeded the drinking water standard for nitrate. The MDA monitoring network designed to assess shallow groundwater in agricultural areas in different regions of Minnesota found that 36% of 208 well water samples collected in 2010 had nitrate-N in excess of 10 mg/l (MDA, 2010) and that 62% of wells had average nitrate-N exceeding 10 mg/l between 2000 and 2010 (MDA, 2013).

#### Minnesota groundwater susceptibility to elevated nitrate

The susceptibility of groundwater to elevated nitrate levels varies tremendously across the landscape and across the state. Groundwater nitrate is more likely to be elevated in areas with a combination of a large nitrate source and more permeable soils and hydrogeologic characteristics, such as sands, shallow groundwater, or shallow soils over fractured or highly permeable bedrock.

Several statewide, regional and county mapping efforts have characterized sensitivity of groundwater to contamination in certain parts of Minnesota. The MDH, working with the counties, has developed numerous nitrate probability maps. These maps show higher and lower probability areas for nitrate reaching groundwater based on geologic sensitivity, land use and water quality results. An example of a nitrate probability map is shown below for Fillmore County (Figure 3). This map and other related maps can be found at: www.health.state.mn.us/divs/eh/water/swp/nitrate/nitratemaps.html.

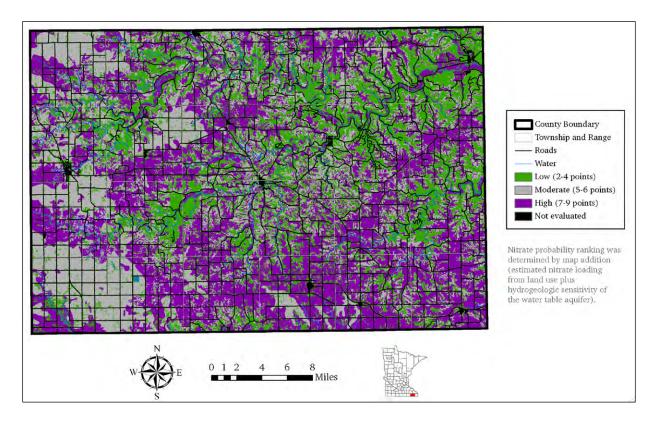


Figure 3. Fillmore County Nitrate Probability Map, showing areas with high (purple), moderate (gray) and low (green) probability of elevated nitrate in the water table aquifer (from MDH).

## Ammonia toxicity to aquatic life

Among the different inorganic nitrogenous compounds ( $NH_4^+$ ,  $NH_3$ ,  $NO_2$ ,  $HNO_2$ ,  $NO_3$ ) that aquatic animals may be exposed to in ambient surface waters, unionized ammonia ( $NH_3$ ) is the most toxic, while in comparison, ammonium and nitrate ions are less toxic. Toxicity from unionized ammonia has long been recognized as a concern, and surface water standards are established in Minnesota to restrict point source discharges of ammonia.

Ammonia is a chemical that occurs in human and animal waste. Ammonia in water readily converts between its highly toxic form (NH<sub>3</sub> or un-ionized ammonia) to its less toxic form ammonium (NH<sub>4</sub>), depending on temperature and pH. The pH and temperature of water samples are required to determine the NH<sub>3</sub> toxicity of a specific stream environment to organisms. As pH and temperature increase, the more toxic unionized ammonia concentrations increase, and there is a corresponding decrease in ammonium. Carmargo and Alonso (2006) found published research indicating that low dissolved oxygen can also increase susceptibility to ammonia toxicity. Conversely, higher salinity and calcium was found to reduce ammonia toxicity.

Plants are more tolerant of elevated ammonia than animals, and invertebrates are generally more tolerant than fish. Toxic effects to fish include reduced blood oxygen carrying capacity, depletion of ATP in the brain, damage to the gills, liver and kidney, and increased susceptibility to bacterial and parasitic diseases (Carmargo and Alonso, 2006). These effects can lead to death and population reductions to aquatic life where concentrations are extreme.

Minnesota has a single chronic standard for ammonia (often referred to as unionized ammonia) of  $16 \mu g/L$  (ppb) for Class 2A waters (primarily trout streams and lakes) adopted in Minn. R. ch. 7050. The standard for all other classes of waters (except class 7) is 40 ppb. No separate standard exists for

ammonia+ammonium-N. Minnesota's 2010 inventory of impaired waters showed a total of six waters assessed as impaired and needing a TMDL for un-ionized ammonia between 1992 and 2010: two in the Minnesota River Basin; two in the Red River of the North Basin; one in the Des Moines River Basin; and one in the St Croix River Basin.

An additional 10 waters were assessed as impaired for un-ionized ammonia between 1992 and 1998, but have since been delisted (2004, 2006, 2008, and 2012 lists). Four delistings were the result of actions taken to upgrade wastewater treatment facilities (new data showed no impairment). One delisting identified septic system upgrades and feedlot/manure management improvements as reasons contributing to water quality standard attainment. The remaining five were delisted based on new and/or more comprehensive data showing no impairment.

In an assessment of water quality in 51 hydrologic systems across the nation, the USGS (Dubrovsky et al., 2010) reported that the chronic criteria for ammonia were exceeded at 4.4% of the sampled sites, a much higher percentage than in Minnesota. Nearly 14% of urban sites and 6% of sites in mixed land use settings exceeded the ammonia chronic criteria. In many cases, treated effluent from wastewater-treatment facilities was known or suspected to be the source of ammonia. Despite large inputs of fertilizer and manure, sampling at 135 agricultural sites found that only 3.7% of the sites exceeded the ammonia criteria, mostly in the western states. This suggests that ammonia from nonpoint sources is typically not reaching or persisting in streams at high concentrations. Rather, ammonia in agricultural watersheds is likely being sorbed onto soils, volatilized, converted to nitrate through the process of nitrification, and (or) rapidly removed from in waters by aquatic plants.

## Nitrite and nitrate toxicity to aquatic life

Nitrite can reduce the oxygen carrying ability in aquatic animals. Hemoglobin in fish is converted into methemoglobin that is unable to release oxygen to body tissues, causing hypoxia and potentially death. Other toxic effects include: electrolyte imbalance; heart function problems; formation of compounds which can be mutagenic and carcinogenic; damage to liver cells and tissue oxygen shortage; increased vulnerability to bacterial and parasitic diseases (Camargo and Alonso, 2006). Nitrite toxicity in natural water systems is typically limited due to the rapid conversion of nitrite into nitrate.

Freshwater fish, invertebrates and amphibians have also been shown to exhibit toxicity effects from elevated nitrate (Camargo and Alonso, 2006). A precise cause of nitrate toxicity is unknown though endogenous conversion to nitrite may be a factor in toxicity to aquatic organisms.

In general, freshwater animals are less tolerant to nitrate toxicity than seawater animals, likely due to the ameliorating effect of water salinity in the seawater. The nitrate concentrations which create toxic effects to aquatic life are substantially higher than those concentrations causing problems with nitrite.

At the time of this writing, the MPCA is studying the toxicity effects of aquatic life under Minnesota conditions, so that water quality standards protective of aquatic life communities can be established in Minn. R. ch. 7050 to be. More information can be found at www.pca.state.mn.us/index.php/view-document.html?gid=14949

#### **Eutrophication in Minnesota waters**

Eutrophication is the process and condition which occurs when a body of water receives excess nutrients, thereby promoting excessive growth of plant biomass (i.e., algae). As the algae die and decompose, decomposing organisms deplete the water of available oxygen, causing harm or death to other organisms, such as fish.

In Minnesota, water quality standards have been adopted to protect lakes from eutrophication, and at the time of this writing Minnesota is drafting standards to protect against eutrophication in rivers. Since phosphorus (P) is considered to be the primary nutrient causing eutrophication in Minnesota lakes and streams and is often referred to as the "limiting" nutrient, eutrophication standards are based on P concentrations rather than N. This does not mean that reducing the supply of N to lakes and streams is unimportant, rather P supplies, relative to aquatic plant and algae requirements, are much lower than N supplies and thus further reduction of P will often lead to reduced algal growth.

When developing the eutrophication standards, monitoring data was examined and compared to responses measured in the fish/biological community. While some sensitive invertebrate populations were lower when TN was elevated in streams, no clear trend was established at that time for the role of N in the biological and eutrophication responses in Minnesota streams (Heiskary et al., 2010). One presumed reason for this is the co-variance of P and N; whereby TP and TKN (mostly organic N) are highly correlated. Also the high TN was the direct result of elevated nitrate-N. These findings and increasing concern about the role of elevated nitrate-N, has caused Minnesota, the EPA, and other states to continue to look for possible relationships between elevated nitrate-N and biological impacts in freshwater lakes and streams.

In lakes, TN to total phosphorus (TP) ratios (TN:TP) have been used as a means for estimating which nutrient may be limiting algal production. Ratios less than 10:1 (molar concentration ratio) have often been used to indicate potential for N being the controlling nutrient for algae growth; while ratios greater than 17:1 have been used as a threshold indicating P as the controlling nutrient. Ratios between 10:1 and 17:1 suggest that either P or N could be limiting. In a recent randomized study of 64 Minnesota lakes, Heiskary and Lindon (2010) noted that five lakes had TN:TP ratios of less than 10:1 (Figure 4). Heiskary (2011 personal communication) indicated that all five lakes are hypereutrophic, with TP concentrations ranging from 140 to 817 ppb. Total nitrogen concentrations in the five lakes were in the normal range of 1.2 to 2.6 mg/l, with most of the N in the organic forms and very low levels of nitrate. Therefore, the low TN:TP ratio is thought to be from the excessively high TP concentrations, rather than indicative of unusually high N levels.

Lake nitrate concentrations in the 64 lakes rarely exceeded laboratory detection limits (Table 2), whereas TN concentrations were generally comparable to stream TN concentrations. Nitrate-N is dissolved and is readily used up by bacteria and macrophytes in lakes, where some of the N may then show up as organic N in TN or TKN laboratory analyses. This is not the case for many streams where it is common to find elevated nitrate-N concentrations.

Table 2. Minnesota lake N concentrations based on 64 lakes (50 random and 14 reference lakes). From Heiskary and Lindon (2010).

Percentile	Nitrate-N (mg/l)	Ammonium-N (mg/l)	Total N (mg/l)
5 <sup>th</sup>	<0.005	0.008	0.288
10 <sup>th</sup>	<0.005	0.011	0.417
25 <sup>th</sup>	<0.005	0.015	0.537
50 <sup>th</sup>	<0.005	0.024	0.807
75 <sup>th</sup>	<0.005	0.045	1.341
90 <sup>th</sup>	0.012	0.182	2.435
95 <sup>th</sup>	0.110	0.276	4.026

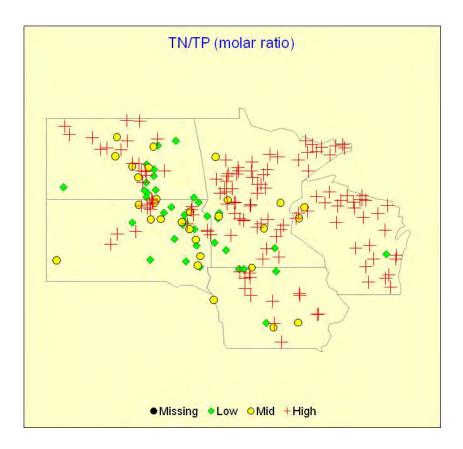


Figure 4. Total nitrogen to TP ratios in Minnesota Lakes, showing locations of "low" (<10:1), "Mid" (10:1 to 17:1) and "High" (>17:1) ratios. From Heiskary and Lindon (2010).

While N is not usually considered to be the nutrient that controls the extent of algae growth in Minnesota lakes or streams, it can contribute to eutrophication of downstream coastal waters. Symptoms of N-driven eutrophication vary, but can include: subtle increases in aquatic plant production; change in the composition of the primary producer communities; rapidly accelerating algae growth; visible discoloration or blooms; losses in water clarity; increased consumption of oxygen; dissolved oxygen depletion (hypoxia); and elimination of plant and animal habitats (EPA, 2011). The EPA reported that coastal water eutrophication is a widespread problem, with one national study showing 78% of the assessed estuarine areas having moderate to high eutrophic conditions (EPA, 2011).

## Gulf of Mexico hypoxia

Nitrogen is considered a limiting nutrient in the Gulf of Mexico, the body of water where much of Minnesota's river and stream waters ultimately discharge. When nutrients in the Mississippi River originating in 31 states reach the Gulf of Mexico, a low oxygen "dead zone" known as hypoxia develops (Figure 5).



Figure 5. Watershed area which drains into the Gulf of Mexico. From Mississippi River/Gulf of Mexico Watershed Nutrient Task Force – Gulf Hypoxia Annual Report 2011.

Hypoxia, which means low oxygen, occurs when excess nutrients, primarily N and P, stimulate algal growth in the Mississippi River and gulf waters. The algae and associated zooplankton grow well beyond the natural capacity of predators or consumers to maintain the plankton at a more balanced level. As the short-lived plankton die and sink to deeper waters, bacteria decompose the phytoplankton carbon, consuming considerable oxygen in the process. Water oxygen levels plummet, forcing mobile creatures like fish, shrimp, and crab to move out of the area. Less mobile aquatic life become stressed and/or dies.

The freshwater Mississippi River is less dense and warmer compared to the more dense cooler saline waters of the gulf. This results in a stratification of the incoming river waters and the existing gulf waters, preventing the mixing of the oxygen-rich surface water with oxygen-poor water on the bottom.

Without mixing, oxygen in the bottom water is limited and the hypoxic zone remains. Hypoxia can persist for several months until there is strong mixing of the ocean waters, which can come from a hurricane or cold fronts in the fall and winter.

Hypoxic waters have dissolved oxygen concentrations of less than about 2-3 mg/l. Fish and shrimp species normally present on the ocean floor are not found when dissolved oxygen levels reduce to less than 2 mg/l. The Gulf of Mexico hypoxic zone is the largest in the United States and the second largest in the world. The maximum areal extent of this hypoxic zone was measured at 8,500 square miles during the summer of 2002. The average size of the hypoxic zone in the northern Gulf of Mexico in recent years (between 2004 and 2008) has been about 6,500 square miles, the size of Lake Ontario. The size of midsummer gulf hypoxic zones from 1985 to 2011 are shown on Figure 6.

A multi-state Hypoxia Task Force (which includes Minnesota) released their first Action Plan in 2001. This plan was reaffirmed and updated in a 2008 Action Plan. The Hypoxia Task Force established a collaborative interim goal to reduce the 5-year running average areal extent of the Gulf of Mexico hypoxic zone to less than 5,000 square kilometers (1,931 square miles). Further information about Gulf of Mexico hypoxia can be found at: <a href="www.gulfhypoxia.net/Overview/">www.gulfhypoxia.net/Overview/</a>

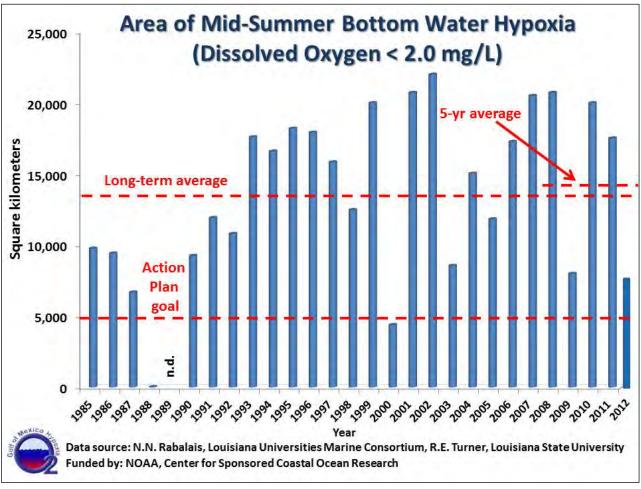


Figure 6. The size of mid-summer bottom water hypoxia areas in the Gulf of Mexico in square kilometers between 1985 and 2011.

A thorough technical discussion of the research associated with Gulf of Mexico hypoxia and possible nutrient reduction options is presented by the US EPA (2007). The report notes that P may be more influential than N in the near-shore gulf water algae growth, particularly in the spring months, when algae and phytoplankton growth are often greatest. In the transition months between spring and summer, the algae and phytoplankton growth are controlled largely by the coupling of P and N. Nitrogen typically becomes the controlling nutrient in the summer and fall months. Based on these more recent findings, emphasis has shifted to developing strategies for dual nutrient removal (P and N). The Science Advisory Board recommends a 45% reduction in riverine TP and TN loads into the Gulf of Mexico (US EPA 2007).

#### Minnesota's contribution to gulf hypoxia

Certain areas of Minnesota release large quantities of N and P to Minnesota streams. Much of the nutrients remain in the Mississippi River system, ultimately reaching the Gulf of Mexico. Alexander et al. (2008) used computer modeling (SPARROW) to estimate the proportion of gulf nutrients originating in different geographic areas. The model accounted for the loss of nutrients in the river, river pools, and backwaters prior to reaching the Gulf of Mexico. This modeling indicated that Minnesota contributed 3% of Gulf of Mexico N and 2% of the P. However, with more recent SPARROW modeling, Minnesota's contribution is estimated to be higher, ranking as the sixth highest state for N contributions behind lowa, Illinois, Indiana, Ohio, and Missouri. The more recent modeling estimates indicate that Minnesota is responsible for about 6% of the N loading and 4% of the P loading into the Gulf of Mexico (Robertson, 2012 personal communication).

Recognizing that it will take a concerted effort by all states which contribute significant amounts of nutrients to the gulf, the MPCA agreed with other top nutrient contributing states to complete and implement a comprehensive N and P reduction strategy. This plan is to be completed in 2013 (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008). The goal of the Action Plan is to reduce nutrients to the Gulf of Mexico while at the same time addressing in-state water protection and restoration.

#### Lake Winnipeg eutrophication

Environment Canada (2011) reported "the quality of Lake Winnipeg waters has deteriorated over time, with particular concern arising over the last few decades in response to the effects of accelerated nutrient enrichment. The frequency and intensity of algal blooms in the lake have increased in association with rising phosphorous and N loading from diffuse and point sources in the Lake Winnipeg watershed."

While the specific role of N in Lake Winnipeg is currently being studied, Manitoba Water Conservation and Stewardship believes there is growing evidence in the literature that N plays a role in eutrophication of many freshwater lakes (Armstrong, 2011).

Minnesota and North Dakota combine to contribute between about 22 and 30% of the N loading to Lake Winnipeg, as exported in the Red River (Environment Canada, 2011; Bourne et al., 2002).

#### Atmospheric concerns

The primary focus of this study is on N in waters, rather than N in our atmosphere. Yet the N cycle is complex and the connections between air, water and land are numerous. It is important to understand atmospheric issues because of the ecological and hydrological linkages between N in atmosphere and N in waters. We need to be careful that our treatment and management to protect waters from N does not create other problems related to N in our atmosphere. Environmental concerns with N in the

atmosphere include: 1) atmospheric deposition of nutrients into waters; 2) acute and chronic toxicity from nitrous oxides in the atmosphere; 3) tropospheric ozone formation; 4) greenhouse gasses, 5) stratospheric ozone depletion; and 6) acid rain (Pratt, 2012).

The form of most N that returns to the atmosphere through various processes is  $N_2$ , a harmless common gas. The atmosphere is approximately 78%  $N_2$  gas. However, relatively small amounts of other forms of N can contribute to environmental problems.

Certain forms of N can be transformed in the atmosphere to nitric acid (HNO<sub>3</sub>), which can create acid rain and lower the pH of surface waters with little ability to buffer the acid rain. The acidification of freshwaters from nitric acid can increase concentrations of aluminum and trace metals, and can have adverse effects on aquatic organisms living in waters which have lower concentrations of calcium, sodium and potassium. In a review of the literature, Carmargo and Alonso (2006) identified numerous adverse effects to plants and animals stemming from fresh water acidification. These effects can include decreased species diversity, delayed egg hatching, disruption of insect and crustacean molting and emergence, respiratory disturbances on a variety of aquatic life, as well as other effects.

In addition to nitric acid deposition, atmospheric N can return to waters in other forms that can add to nutrient-stimulated algae growth and eutrophication. This atmospheric addition is of particular importance where large surface areas of water are found and where the algae growth is largely limited by N, such as coastal waters and estuaries. More information on atmospheric deposition of N to land and waters in Minnesota is found in Chapter D3.

Nitrous oxide (N2O) is a potent greenhouse gas and also contributes to ozone depletion in the stratosphere. Nationally, the highest emissions of nitrous oxide are from the soil processes of nitrification and denitrification (US EPA, 2011). Denitrification mostly results in the release of harmless nitrogen gas (N2) into the atmosphere. However, a small but important fraction of other more harmful gasses from denitrification reaches the atmosphere. The nitrification process also produces nitrous oxides. The Intergovernmental Panel on Climate Change (IPCC) estimates that 1.25% of N that enters agricultural soils and 0.75% of N that reaches rivers is converted to nitrous oxide (Mosier et al., 1998). More research is needed on the release of nitrous oxides from nitrification and denitrification processes, especially as we look at denitrification as a treatment option for nitrate polluted waters.

Lastly, ammonia emissions from such sources as livestock manure and anhydrous ammonia fertilizers combine with sulfate and nitrate to form aerosols (PM2.5), and in most locations ammonium sulfate and ammonium nitrate are the largest components of PM2.5 (Pratt, 2012). These compounds are eventually deposited back to the earth's surface (water and land) and can cause eutrophication and acidification (Pratt, 2012).

## How nitrogen reaches surface waters

Numerous potential sources of N to waters exist, including (in random order):

- · livestock and poultry feedlots
- municipal sewage effluents
- industrial wastewater effluents
- · mineralization of soil organic matter
- cultivation of n-fixing crop species
- · use of animal manure and inorganic N fertilizers, and subsequent runoff/leaching/drainage

- runoff from standing or burned forests and grasslands
- · urban and suburban runoff
- septic system leachate, and discharges from failed septic systems
- emissions to the atmosphere from volatilization of manure and fertilizers and combustion of fossil fuels, and the subsequent atmospheric (wet and dry) deposition into surface waters
- other activities that can mobilize N (from long-term storage pools) such as biomass burning, land clearing and conversion, and wetland drainage

The contributions of the main N sources and pathways in Minnesota were assessed for this study and are described in Chapters D1-D4 of this report.

Nitrogen can take several different pathways to surface waters. Nitrogen can enter waters directly, through direct discharges from municipal and industrial waste sources. Nitrogen can be dissolved in the runoff water, or attached to soil particles in the forms of ammonium-N and organic-N, and runoff during storms or snowmelt. Nitrogen can also be emitted into the atmosphere and return to land and waters in precipitation and dry deposition. The common N sources and pathways to waters are depicted in Figure 7.

The most mobile forms of N in waters are nitrite and nitrate, which easily dissolves in water and moves with the water. Since nitrate moves vertically through the soil with soil water, the primary pathways for nitrate are usually: 1) leaching into groundwater which then moves toward a stream, lake or well; and 2) leaching into tile lines which discharge into drainage ditches and surface waters.



Figure 7. Nitrogen sources and pathways to streams, including direct discharges, runoff, leaching to groundwater, subsurface tile drainage to ditches, and precipitation directly into waters.

Many factors affect the transport of N from source areas to streams. Natural factors, such as soil type, geology, slope of the land, and groundwater chemistry, have a tremendous influence on how much N is transported to streams. Where N sources exist, three Minnesota geologic systems are particularly susceptible to N pollution: 1) karst and other shallow fractured bedrock; 2) unconsolidated sand and gravel aquifers; and 3) alluvial aquifers consisting of sand and gravel deposits interbedded with finer grained deposits.

Human actions, such as irrigation, artificial subsurface drainage, and creation of impervious surfaces, also govern N transport. The result can be varying concentrations of nutrients in streams, even in watersheds with similar land use settings and rates of N additions (Dubrovsky, et al., 2010).

To develop the most effective strategies for reducing N in streams, it is important to understand the combinations of sources and hydrologic pathways resulting in high N levels. That is because strategies and best management practices (BMPs) for preventing surface runoff are often different than those practices used to prevent leaching into ground water and tile waters. And where subsurface tile drainage waters are a dominant pathway, additional BMPs can be considered for treating and managing tile drainage waters.

## Denitrification losses in groundwater prior to reaching surface waters

In order for N on the land to reach waters in appreciable quantities, four things must occur: 1) the presence or addition of a high N source; 2) presence of water to drive the N through or over the soil; 3) the absence of an effective way of removing soil N (such as high density of plant roots); and 4) a transport pathway which circumvents denitrification losses.

The N transport pathway greatly affects the potential for denitrification losses to occur. Where nitrate leaching is the dominant pathway, and the leached water is not intercepted by tile lines, nitrate entering low oxygen groundwater zones can be converted to N gas through a process known as denitrification. Denitrification can remove substantial amounts of N in groundwater systems where oxygen levels are low (Korom, 1992). This can occur either in upland groundwater or subsurface riparian buffer zones. The rate of nitrate losses within groundwater can greatly affect the amount of nitrate which ultimately discharges into streams. For this study, we conducted a literature review on groundwater denitrification for conditions representative of Minnesota aquifers. This review is presented in Appendix B5-1.

Denitrification losses in the subsurface are highly variable and are affected by such factors as: 1) the source and amount of N passing through the root zone; 2) the age of water since entering the subsurface; 3) oxygen state along the subsurface flow pathway; 4) riparian zone processes which potentially remove large amounts of N; and 5) rates of flow.

Most of the nitrate will persist and reach surface waters when the following set of subsurface conditions exist: water age is young (recently entered the ground), rates of flow are high, waters remain oxygenated, and riparian processes are negligible. Such conditions occur in tile-drained lands, sand and gravel aquifers, and karst geologic settings, as well as other settings. In karst, nitrate can rapidly move through the thin layers of soils and reach fractures in bedrock, where fast flow rates can transport nitrate to streams without much opportunity for denitrification losses to occur within the groundwater.

The amount of nitrate entering streams is also influenced by the types of geologic materials that the groundwater encounters on its way to becoming stream baseflow. For example, in shallow subsurface riparian zones that contain organic-rich sediments with low dissolved-oxygen concentrations, bacteria convert dissolved nitrate in groundwater to largely innocuous gaseous forms of N through the process of denitrification (Dubrovsky, 2010). Nitrogen also can be removed by plants in riparian or buffer zones.

USGS researchers concluded, "In some settings, groundwater can flow along relatively deep flow paths beneath riparian zones such that nitrate in the groundwater is unaffected by the riparian zone and can discharge directly to streams. Findings show that riparian zones are most effective for nitrogen removal in settings with thin surficial aquifers underlain by a shallow confining layer, with organic-rich soils that extend down to the confining layer. Groundwater in these types of settings tends to flow through biologically reactive parts of the aquifer, which promotes the removal of nitrate" (Dubrovsky, 2010).

Once N reaches surface waters, it can either remain in the water, be transformed to other forms of N, or be lost to the atmosphere through denitrification. These processes and the factors that affect these processes within Minnesota waters were extensively reviewed for this study, and are discussed in Chapter B5 and Appendix B5-2.

## Overview of nitrogen entering surface waters

In summary, N enters surface waters through groundwater baseflow and from surface and near-surface runoff and tile line transport (Figure 8). Nitrogen can be lost in the groundwater before discharging into streams, and once in the surface waters further losses can occur before reaching downstream waters.

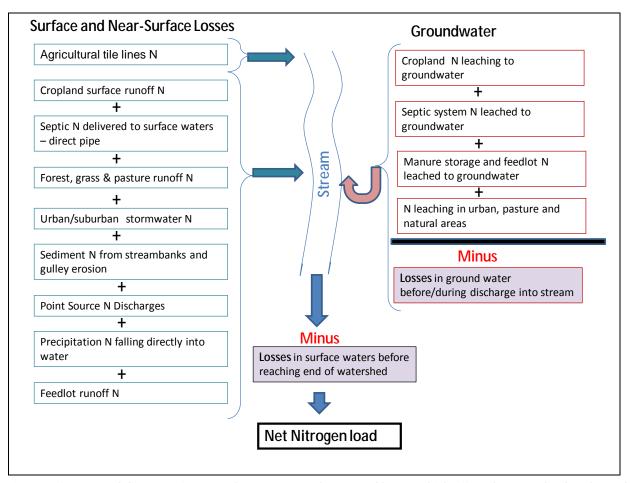


Figure 8. Conceptual diagram of potential N sources, pathways and losses which affect the net N load at the end of the watershed. Denitrification losses are represented by the shaded boxes.

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# **B1. Monitoring Stream Nitrogen Concentrations**

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#### Introduction

River and stream nitrogen (N) concentrations have been sampled by several different agencies during the past decade. The data were primarily collected to characterize ambient river and stream water quality conditions; yet sampling intervals and sampling purposes have varied.

Nitrogen conditions in surface waters are usually characterized in four different ways: 1) concentration, 2) load, 3) yield, and 4) flow weighted mean concentration. Concentrations are determined by taking a sample of water and having a laboratory determine how much N mass is in a given volume of that water sample, typically reported as milligrams per liter (mg/l). Load is the amount of N passing a point on a river during a period of time, often measured as pounds of N per year. Loads are calculated by multiplying N concentrations by the amount of water flowing down the river. Nitrogen loads are influenced by watershed size, as well as land use, land management, hydrology, precipitation, and other factors. Yield is the amount (mass) of N per unit area coming out of a watershed during a given time period (i.e. pounds per acre per year). It is calculated by dividing the load by the watershed size, which then allows for comparisons of watersheds with different sizes. The FWMC is the weighted-average concentration over a period of time, giving the higher flow periods more weight and the lower flow periods less weight. The FWMC is calculated by dividing the total load for a given time period by the total flow volume during that same period, and is typically expressed as mg/l.

This chapter is the first of five chapters on characterizing Minnesota river and stream nitrogen (N) conditions. In Chapter B1, we take a rather simplified look at the ambient concentrations of different forms of N in rivers and streams throughout Minnesota sampled during more recent years (2000-2010). In Chapters B2 and B3, we assess monitoring-based N loads in Minnesota's rivers and streams, with Chapter B2 examining the mainstem river loads during the past few decades and Chapter B3 assessing N loads available for recent years (2005 to 2009) near the outlets of watersheds. Chapters B2 and B3 are different from Chapter B1, since Chapters B2 and B3 incorporate river flow and runoff event-based data and are therefore limited to a smaller number of sites as compared to Chapter B1. Chapter B4 incorporates the results of river load modeling at both the major basin and watershed levels using the SPARROW model results, which were developed using monitoring-based loads throughout the Upper Midwest as adjusted to a detrended 2002 base-year. Chapter B5 examines how much N is transported downstream once it reaches a stream.

The primary objective of work completed for this chapter was simply to observe patterns of how statewide stream N concentrations vary across Minnesota, and to approximate the high, low, and midrange concentrations of different forms of nitrogen. More complex analyses involving flow-weighted mean concentrations are discussed in Chapters B2 and B3.

The steps taken to complete the Chapter B2 simple assessment of N concentrations included:

- a) Compile recent stream N concentration results from multiple agencies into a single file.
  - Nitrogen parameters included: nitrite plus nitrate-N, ammonium plus ammonia-N, total Kjeldahl nitrogen (TKN); and total nitrogen (TN). Total nitrogen was derived by summing TKN and nitrite+nitrate-N.
- b) From combined data sets, calculate concentration statistics for each monitored site which met minimum criteria.
  - Basic statistics calculated include: mean, median, percentiles (10th, 25th, 75th, 90th), maximum and minimum. The 10th percentile is a low-end concentration value for a given river or stream site where 10% of the concentration results are lower and 90% of the results are higher than that value. The 90<sup>th</sup> percentile is higher-end concentration value for a given river or stream site where 90% of the concentrations are lower and 10% are higher than that value.
- c) Plot the concentration statistics results on maps showing the stream sampling sites.
- d) Assess magnitudes of concentration statistics and spatial trends in N concentrations across the state.

#### Data used

We used existing stream N monitoring data from the U.S. Geological Survey (USGS), Minnesota Pollution Control Agency, Metropolitan Council, and Minnesota Department of Agriculture data bases. Only data collected between 2000 and 2010 was considered, so that the results represent more recent conditions, rather than historical conditions.

Some stream sampling efforts are weighted toward higher flow events, whereas other efforts sample at more random times, not necessarily targeting storm/runoff event periods. To make the results more comparable among the sites, data were sorted to eliminate samples which were likely intentionally and specifically sampled during runoff event periods. For example, results were not included in the analyses when samples were taken less than five days apart from another sample at the same site. Most of the data were collected at routine intervals that would inherently include both higher and lower flow periods, and thereby represent a range of flow conditions. Thus the results in this chapter do not represent a flow-weighted analysis, but rather an ambient condition analysis of the concentrations. Flow-weighted analyses are described in subsequent chapters.

The data were sorted to eliminate sites which were not sampled frequently enough to meet minimum criteria. Only those sites sampled at least 15 times during at least two calendar years between 2000 and 2010 were used for calculating "annual" or "all season" concentration statistics. At most river and stream sites, a considerably higher numbers of samples were used than the minimum and the average number of samples per site was 68-69 (Table 1). Because the data for each of monitored stream sites were not all collected during the same months or with the same sampling regularity or methods, the reader is cautioned from drawing distinct comparisons between individual mapped site results. However, we believe that by using the minimum criteria for site selection, the data statistics are sufficient to represent the N concentrations in the broad categorical presentation of the results within this chapter.

Computations for the percentile determinations were completed using the flipped Kaplan-Meier method. Means were calculated using the ROS method (Helsel, 2005).

Four nitrite+nitrate-N concentrations maximum values were considered erroneous data entry errors since they were over 400 mg/l at sites with 90<sup>th</sup> percentile concentrations less than 3 mg/l. All four values were from sampling sites in the Upper Mississippi River Basin. One TKN maximum in this same basin had a similarly erroneous value. These maximums were not used when calculating average maximums for the Upper Mississippi River Basin.

Table 1. The number of stream sampling sites meeting minimum criteria for statistical analysis, and the average number of N chemistry analyses per stream sampling site taken between 2000 and 2010 and which were used to calculate the annual and seasonal medians, means and percentiles.

	Number of sites	Average number of samples per site	Range in number of samples per site
Annual statistics			
Ammonia+ammonium	597	69	15-439
Nitrite+nitrate	728	69	15-393
Total Kjeldahl nitrogen	637	68	15-392

## Results

Statistics calculated using all months of data together is referred to as "annual" or "all season" results. The high-end annual results (90<sup>th</sup> percentile), low-end annual results (10<sup>th</sup> percentile) and mid-range annual results (medians) for each qualifying stream sampling site are described below for each N parameter.

#### Nitrite+nitrate-N

Nitrite+Nitrate-N concentration statistics were calculated for 728 sites meeting the 15-sample annual (all-seasons) criteria. The 90<sup>th</sup> percentile nitrite+nitrate-N concentrations exceeded 5 mg/l throughout most of southern Minnesota, and 31% of sites statewide exceeded 5 mg/l (Figure 1 and Table 2).

Table 2. Comparisons of the number of stream sites with 90<sup>th</sup> percentile and maximums exceeding 5 and 10 mg/l.

Nitrite+nitrate-N concentration	Number (and %) of stream sites with 90 <sup>th</sup> percentile at or above 5 and 10 mg/l	Number (and %) of stream sites with maximums (100 <sup>th</sup> percentile) at or above 5 and 10 mg/l
5 mg/l or higher	225 (31%)	297 (41%)
10 mg/l or higher	125 (17%)	197 (27%)

Nitrite+nitrate-N concentrations exceeded 10 mg/l at times throughout most of south-central Minnesota. Statewide, 17% of river and stream sites had 90<sup>th</sup> percentile concentrations exceeding 10 mg/l. A notable exception to the high southern Minnesota 90<sup>th</sup> percentile nitrate concentrations is the Mississippi River in southeastern Minnesota, which receives much of its flow from tributaries in the northern part of the state where nitrate concentrations are low, thereby diluting the higher nitrate inputs from the southern part of the state.

The northern part of Minnesota has all stream sites with 90<sup>th</sup> percentile concentrations below 5 mg/l, with most streams below 1 mg/l (Figure 1). Even the maximum concentrations over the 11-year period (as shown in Table 3) are low in northern basins such as the Rainey River (1.6 mg/l), the St. Croix River (1.3 mg/l) and Western Lake Superior (0.8 mg/l). The Red River Basin has slightly higher nitrite+nitrate concentrations compared to other northern Minnesota basins, and at many monitoring locations the 90<sup>th</sup> percentile nitrite+nitrate-N concentrations were in the 1-3 mg/l range.

Table 3. Nitrite+nitrate-N concentration statistics for monitoring sites located within various major river basins in Minnesota. Mean 10<sup>th</sup> percentile concentrations for each basin represent typical low nitrate concentrations and mean 90<sup>th</sup> percentiles and maximums represent typical high nitrate concentrations for each basin.

	10th perc	10th percentile (mg/L)			(mg/L)		90th Percentile (mg/L)			Maximum (mg/L)		
	Mean	sd	n	Mean	sd	n	Mean	sd	n	Mean	sd	n
STATEWIDE	0.61	1.32	728	2.2	3.5	728	4.5	6.6	728	7.0	9.1	724
DES MOINES	2.00	3.95	15	8.4	9.6	15	14.9	19.1	15	19.4	21.3	15
MINNESOTA	0.55	0.94	139	4.8	4.3	139	10.2	7.2	139	15.4	11.0	139
UPPER MISSISSIPPI	0.35	0.57	199	1.1	1.8	199	2.7	5.1	199	4.2	6.2	195
MISSOURI - BIG SIOUX	1.44	0.87	10	5.5	3.8	10	8.1	4.5	10	12.9	9.6	10
RAINY RIVER	0.11	0.18	19	0.3	0.4	19	0.8	1.0	19	1.6	1.7	19
RED RIVER	0.03	0.05	168	0.1	0.2	168	0.7	0.6	168	2.1	2.9	168
ST. CROIX	0.22	0.58	42	0.4	0.8	42	0.7	1.0	42	1.3	1.6	42
LOWER MISSISSIPPI	2.40	2.15	74	4.5	2.8	74	7.4	3.8	74	10.6	5.3	74
CEDAR	2.07	1.82	25	5.0	2.1	25	12.1	3.7	25	17.0	4.3	25
WESTERN LAKE SUPERIOR	0.04	0.06	36	0.1	0.1	36	0.3	0.2	36	0.8	1.6	36

Because of the high number of stream sampling sites with nitrite+nitrate-N 90<sup>th</sup> percentiles exceeding 10 mg/l, a separate 90<sup>th</sup> percentile map was created showing multiple nitrate concentration range categories above 10 mg/l (Figure 2). Rivers and stream samples seldom had nitrite+nitrate-N exceeding 20 mg/l, and 90<sup>th</sup> percentile concentrations exceeded 20 mg/l at 15 sites (2% of all sites) statewide. Four sites had 90<sup>th</sup> percentile concentrations exceeding 26 mg/l.

The difference between the maximum nitrate concentrations and the 90<sup>th</sup> percentile concentrations shows the upper-end concentration distribution (Table 2). About 31% of stream sites had 90<sup>th</sup> percentile nitrite+nitrate-N exceeding 5 mg/l; whereas the maximums exceeded 5 mg/l at 41% of the sites. Maximum nitrite+nitrate-N concentrations exceeded 10 mg/l at 27% of sampled stream sites.

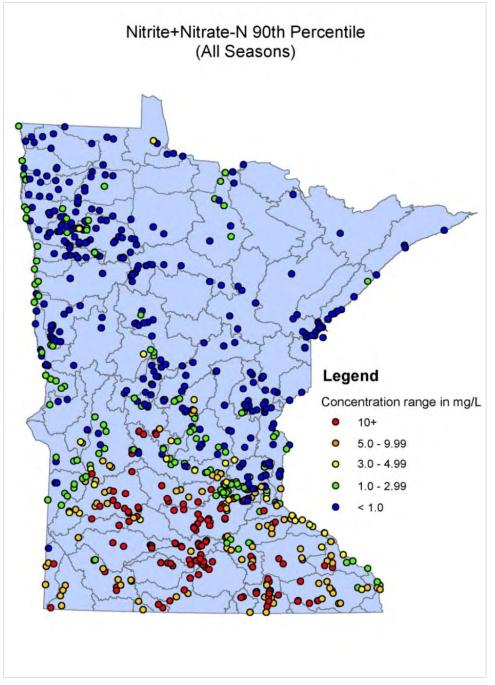
In the 125 rivers and streams where  $90^{th}$  percentile nitrite+nitrate-N concentrations exceed 10 mg/l, the average  $90^{th}$  percentile concentration was 15.9 mg/l. At these same 125 sites, the average maximum concentration was 21.1 mg/l (Table 4). Therefore, the maximum concentrations recorded between 2000 and 2010 at the highest concentration sites (those with  $90^{th}$  percentile concentrations over 10 mg/l) are on average about 5.2 mg/l higher than the  $90^{th}$  percentile concentrations in these same streams.

Table 4. A comparison of the average maximum nitrite+nitrate-N concentrations (mg/l) to the average of 90<sup>th</sup> percentile concentrations for stream site categories with very low (<1 mg/l), low (1-2.99 mg/l), medium (3-4.99 mg/l), high (5-9.99 mg/l), and very high (>10 mg/l) nitrite+nitrate-N concentrations.

	Sites with 90 <sup>th</sup> percentile concentrations	Sites with 90 <sup>th</sup> percentile concentrations	Sites with 90 <sup>th</sup> percentile concentrations	Sites with 90 <sup>th</sup> percentile concentrations	Sites with 90 <sup>th</sup> percentile concentrations
	<1 mg/l	1 – 2.99 mg/l	3 – 4.99 mg/l	5 – 9.99 mg/l	10+ mg/l
Number of sites	315	145	43	100	125
Average of the 90 <sup>th</sup> percentile concentrations	0.35	1.8	3.9	7.6	15.9
Average of the maximum concentrations	1.1	4.1	6.7	11.4	21.1

Median nitrate levels in streams throughout the state are mostly above 3 mg/l in the southern part of the state and below 1 mg/l in the northern part of the state (Figure 3). Median nitrite+nitrate-N levels exceed 10 mg/l in some streams, including streams in the Lower Minnesota River watershed, as well as some scattered sites in other parts of southern Minnesota.

Another way of viewing how nitrate concentrations vary at the same sites is to look at the how the 10<sup>th</sup> percentile map (Figure 4) compares to the median and 90<sup>th</sup> percentile maps. The times of low-nitrate concentrations as represented by 10<sup>th</sup> percentile statistics, show most of streams in the state dropping below 1 mg/l nitrite+nitrate-N. Exceptions to this are the southeast and southwest corners of the state. In southeastern Minnesota, many streams are fed continuously by groundwater with elevated nitrate, so that elevated nitrate continues to discharge into the streams even during drier periods. Table 3 shows that the 10<sup>th</sup> percentile concentrations are high (on average) in the Lower Mississippi Basin



(southeastern Minnesota), followed by the Cedar and Des **Moines River** Basins. The relatively high 10<sup>th</sup> percentile concentrations are thought to be largely due to groundwater baseflow in these regions. Municipal wastewater point source discharges also provide a continuous supply of nitrate to rivers throughout the year and could be contributing to the higher 10<sup>th</sup> percentile concentrations at some sites. It was beyond the scope of this study to research specific sources at specific sites.

Figure 1. Nitrite+nitrate-N 90<sup>th</sup> percentile concentrations for all samples taken at each site between 2000 and 2010.

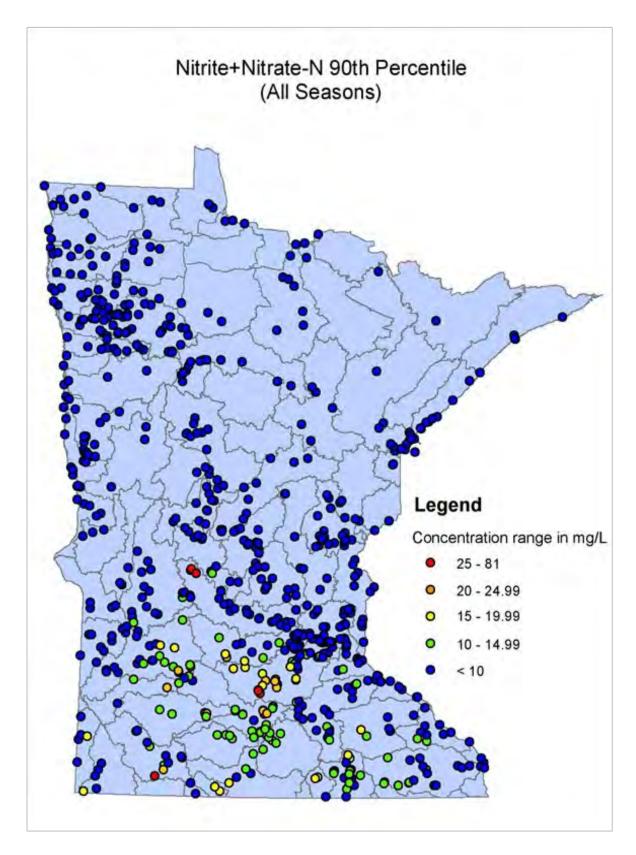


Figure 2. Nitrite+Nitrate-N 90<sup>th</sup> percentile concentrations, showing the magnitude of 90<sup>th</sup> percentile concentrations greater than 10 mg/l. This is the same figure as Figure 1, except that the concentration scale ranges are different, such that all red shaded points in Figure 1 are subdivided into four separate categories.

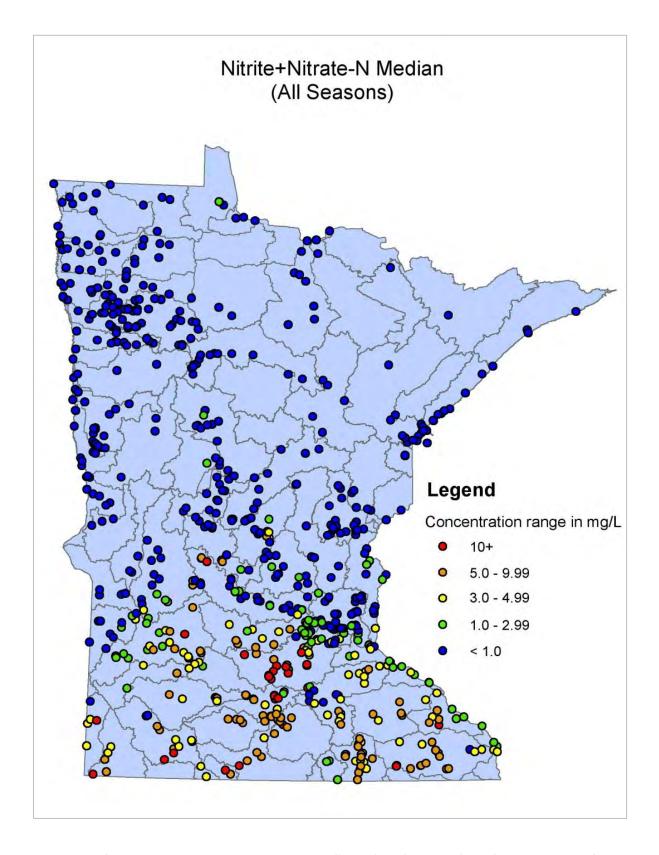


Figure 3. Median nitrite+nitrate-N concentrations for all samples taken at each site between 2000 and 2010.

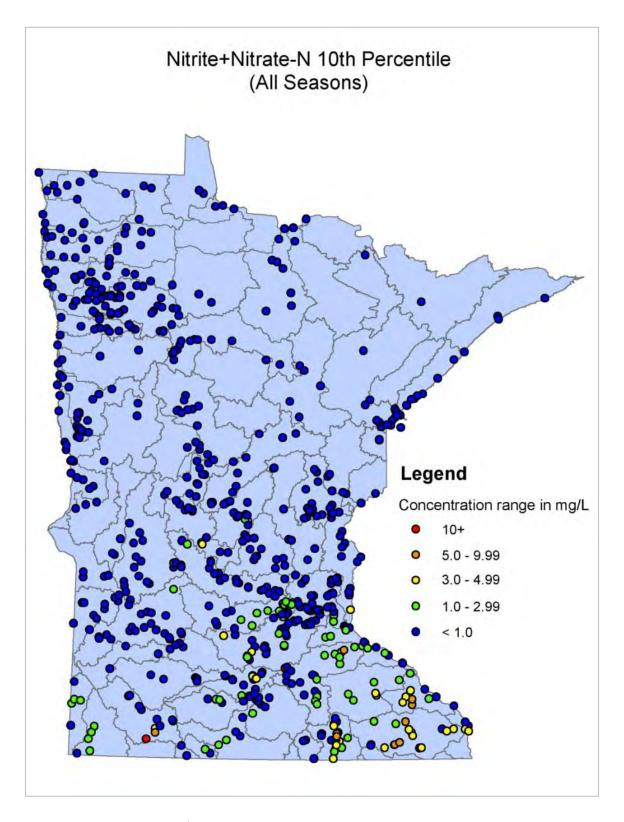


Figure 4. Nitrite+nitrate-N 10<sup>th</sup> percentile concentrations for all samples taken at each site between 2000 and 2010.

#### Ammonia+ammonium-N

Ammonia+ammonium-N (commonly referred to as "ammonium") concentrations are much lower than nitrate concentrations. Ammonia+ammonium-N is quickly converted to nitrite+nitrate-N via nitrification in streams, except during winter months. The 90<sup>th</sup> percentile map shows that the high-end ammonia+ammonium-N levels rarely exceed 1 mg/l (seven sites statewide), and are mostly less than 0.5 mg/l (Figure 5).

The 90<sup>th</sup> percentile concentrations at most Minnesota sites are above the national background ammonia+ammonium-N concentration of 0.025 mg/l (Dubrovsky et al., 2010), suggesting that over much of the state there are certain periods when human impacts cause ammonia+ammonium to increase. However, these impacts are not usually sustained, since median ammonia+ammonium-N levels are less than 0.1 mg/l throughout most the state (Figure 6 and Table 5).

Spatial patterns of ammonia+ammonium-N concentrations are less pronounced compared to nitrite+nitrate-N. The area of the state with predominantly low ammonia+ammonium-N concentrations (<0.1 mg/l) is north-central and northeastern Minnesota. With the exception of the Duluth area streams and two other scattered streams, all northeastern Minnesota streams had 90<sup>th</sup> percentile ammonia+ammonium-N concentrations less than 0.1 mg/l.

During typical conditions (medians) ammonia+ammonium-N concentrations are mostly less than 0.1 mg/l throughout the state. Exceptions to this include some sampling points in the Cedar River, the Twin Cities area, and a few other scattered locations.

The 10<sup>th</sup> percentile concentrations show that almost all monitoring points have less than 0.1 mg/l (Figure 7). An exception is the Cedar River, which has between 0.1 and 0.2 mg/l. The statewide 10<sup>th</sup> percentile is 0.03 mg/l (mean of all 562 sites 10<sup>th</sup> percentile concentrations see table 5), which is essentially the same as the national background concentration.

It was beyond the scope of this study to try and determine reasons why individual sites or clusters of sites had particularly high or low ammonium concentrations.

Table 5. Ammonium+ammonia-N concentration statistics for monitoring sites located within various major river basins in Minnesota. Mean 10<sup>th</sup> percentile concentrations for each basin represent typical low ammonium period concentrations and mean 90<sup>th</sup> percentiles and maximums represent typical high ammonium period concentrations for each basin.

	10th perc	rcentile (mg/L)		Median (mg/L)			90th Pero	centile (mg/L)		Maximum (mg/L		)	
Basin	Mean	sd	n	Mean	sd	n	Mean	sd	n	Mean	sd	n	
STATEWIDE	0.03	0.03	562	0.05	0.07	562	0.26	0.61	562	1.0	1.8	562	
DES MOINES	0.04	0.04	15	0.05	0.04	15	0.18	0.09	15	0.8	0.7	15	
MINNESOTA	0.02	0.02	104	0.05	0.06	104	0.36	0.57	104	1.5	3.1	104	
UPPER MISSISSIPPI	0.03	0.02	200	0.05	0.05	200	0.23	0.22	200	1.0	1.0	200	
MISSOURI - BIG SIOUX	0.04	0.02	4	0.06	0.03	4	0.23	0.14	4	1.2	1.0	4	
RAINY RIVER	0.02	0.01	9	0.02	0.01	9	0.06	0.03	9	0.2	0.1	9	
RED RIVER	0.03	0.03	102	0.05	0.07	102	0.20	0.15	102	0.8	1.3	102	
ST. CROIX	0.03	0.01	42	0.08	0.18	42	0.44	1.68	42	1.0	2.0	42	
LOWER MISSISSIPPI	0.02	0.01	46	0.04	0.02	46	0.32	0.94	46	1.1	1.7	46	
CEDAR	0.12	0.06	15	0.13	0.05	15	0.22	0.11	15	0.5	0.41	15	
WESTERN LAKE SUPERIOR	0.03	0.01	25	0.04	0.02	25	0.10	0.10	25	0.5	0.9	25	

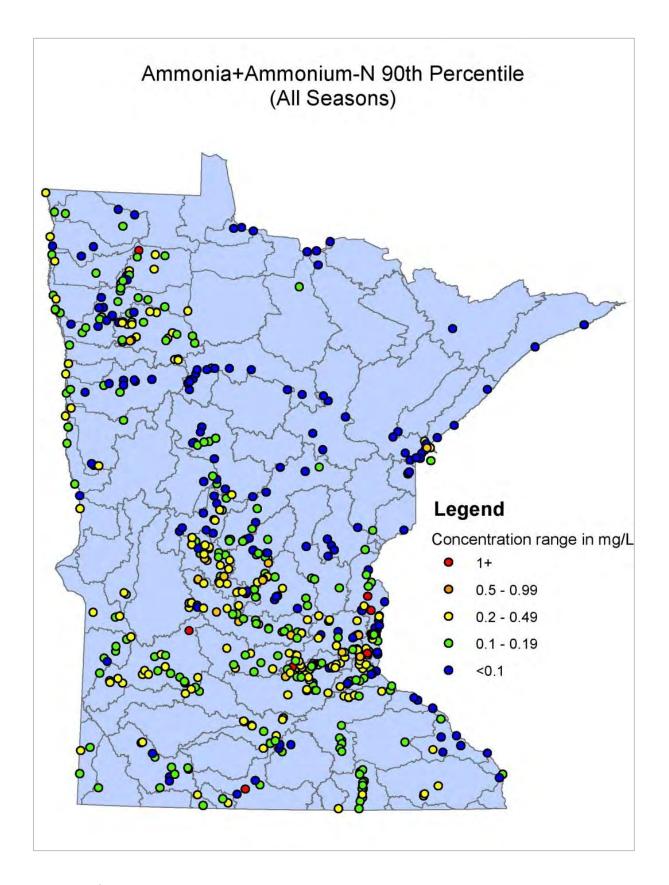


Figure 5. 90<sup>th</sup> percentile ammonia+ammonium-N concentrations for all samples taken at each site between 2000 and 2010.

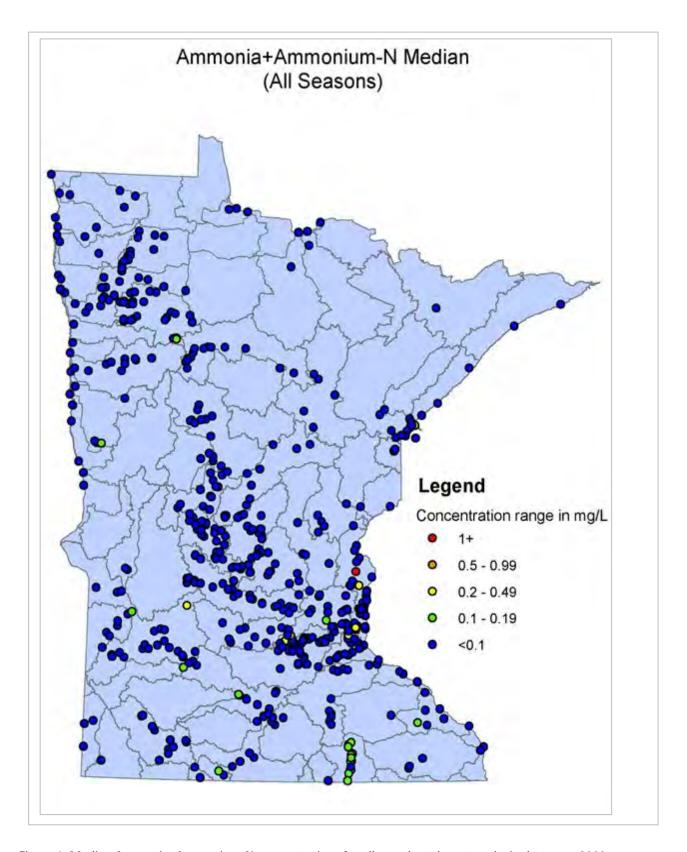


Figure 6. Median Ammonia+Ammonium-N concentrations for all samples taken at each site between 2000 and 2010.

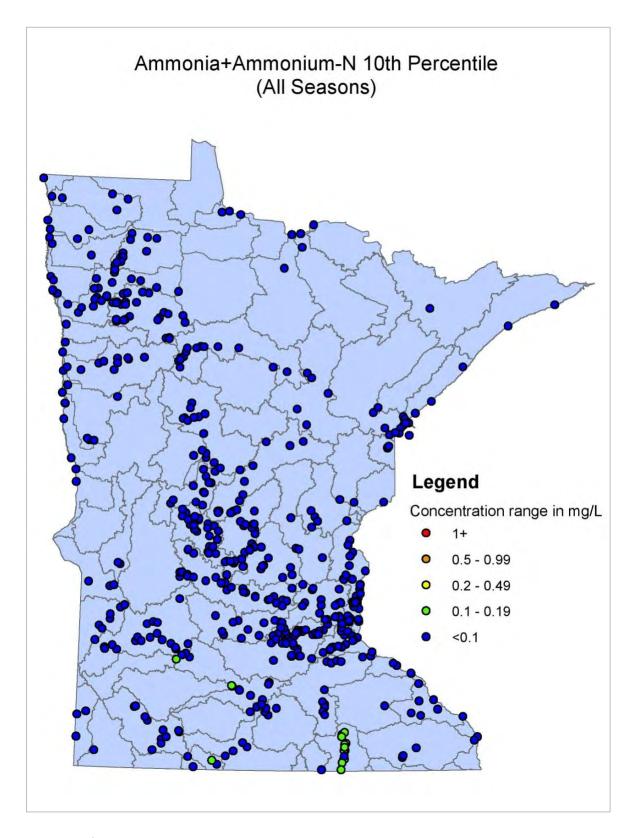


Figure 7. 10<sup>th</sup> percentile Ammonia+Ammonium-N concentrations for all samples taken at each site between 2000 and 2010.

## Total Kjeldahl nitrogen

Total Kjeldahl nitrogen includes both ammonia+ammonium and organic N. Ammonia+ammonium concentrations in surface waters are typically quite low in comparison to TKN concentrations, and at most sites the majority of TKN is organic N.

Total Kjeldahl nitrogen 90<sup>th</sup> percentile concentrations are mostly in the 1-3 mg/l range throughout the state (Figure 8). Several sites in northern Minnesota and a few in southeastern Minnesota had TKN 90<sup>th</sup> percentiles less than 1 mg/l. Five main pockets of elevated TKN (90<sup>th</sup> percentiles over >3 mg/l) are located at various places in the southern half of the state, including clusters northeast and west of the Twin Cities, as well as in central and southwestern Minnesota.

Spatial patterns of TKN concentrations showed that 90<sup>th</sup> percentiles TKN remained less than 1.5 mg/l throughout most of northeastern Minnesota and was between 1.5 and over 3 mg/l in most of southern Minnesota and along the Red River. The statewide mean of all 637 sites 90<sup>th</sup> percentile concentrations is 1.9 mg/l (table 6), and means of 90<sup>th</sup> percentile values for each major river basin did not vary much for most basins of the state.

Total Kjeldahl nitrogen median concentrations did not exceed 3 mg/l at any sites, and were less than 1.5 mg/l at most sites (Figure 9). Medians exceeded 2 mg/l in the Des Moines River and Lower Minnesota River watersheds, in addition to other scattered locations. The statewide mean of all 637 site median concentrations is 1.1 mg/l (Table 6).

Total Kjeldahl nitrogen 10<sup>th</sup> percentile concentrations were mostly less than 1.5 mg/l throughout the state (Figure 10). With the exception of several streams in central and southwestern Minnesota, the 10<sup>th</sup> percentile concentrations were less than 1 mg/l. The statewide mean of all 637 sites 10<sup>th</sup> percentile concentrations is 0.7 mg/l (Table 6).

Table 6. TKN concentration statistics for monitoring sites located within various major river basins in Minnesota. Mean 10<sup>th</sup> percentile concentrations for each basin represent typical low TKN period concentrations and mean 90<sup>th</sup> percentiles and maximums represent typical high TKN period concentrations for each basin.

	10th perc	10th percentile (mg/L)			Median (mg/L)			90th Percentile (mg/L)			Maximum (mg/L)		
	Mean	sd	n	Mean	sd	n	Mean	sd	n	Mean	sd	n	
STATEWIDE	0.7	0.3	637	1.1	0.5	637	1.9	1.0	637	4.2	4.6	636	
DES MOINES	1.4	0.3	12	2.1	0.5	12	3.3	1.1	12	5.4	3.3	12	
MINNESOTA	0.8	0.4	132	1.4	0.5	132	2.5	1.1	132	5.4	2.7	132	
UPPER MISSISSIPPI	0.7	0.3	241	1.1	0.4	241	1.8	0.8	241	3.6	2.7	240	
MISSOURI - BIG SIOUX	0.6	0.2	5	1.0	0.1	5	1.8	0.2	5	3.6	1.3	5	
MISSOURI - LITTLE SIOUX	1.2	0.1	2	1.6	0.1	2	2.3	0.1	2	3.8	0.1	2	
RAINY RIVER	0.6	0.1	17	0.9	0.2	17	1.2	0.3	17	1.7	1.0	17	
RED RIVER	0.7	0.2	91	1.1	0.3	91	1.6	0.5	91	3.8	7.9	91	
ST. CROIX	0.5	0.3	63	0.9	0.4	63	1.9	1.7	63	4.5	6.3	63	
LOWER MISSISSIPPI	0.6	0.3	49	1.0	0.5	49	1.8	0.8	49	5.3	5.8	49	
CEDAR	0.6	0.2	13	1.1	0.2	13	2.1	0.3	13	3.7	1.2	13	
WESTERN LAKE SUPERIOR	0.4	0.1	12	0.6	0.1	12	1.0	0.2	12	1.8	0.6	12	

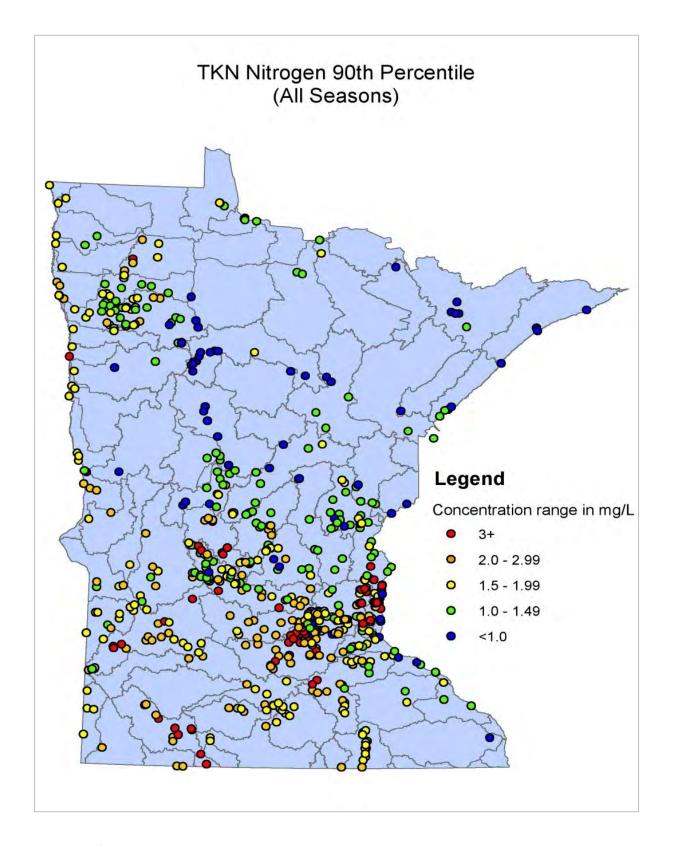


Figure 8.  $90^{th}$  percentile TKN concentrations for all samples taken at each site between 2000 and 2010.

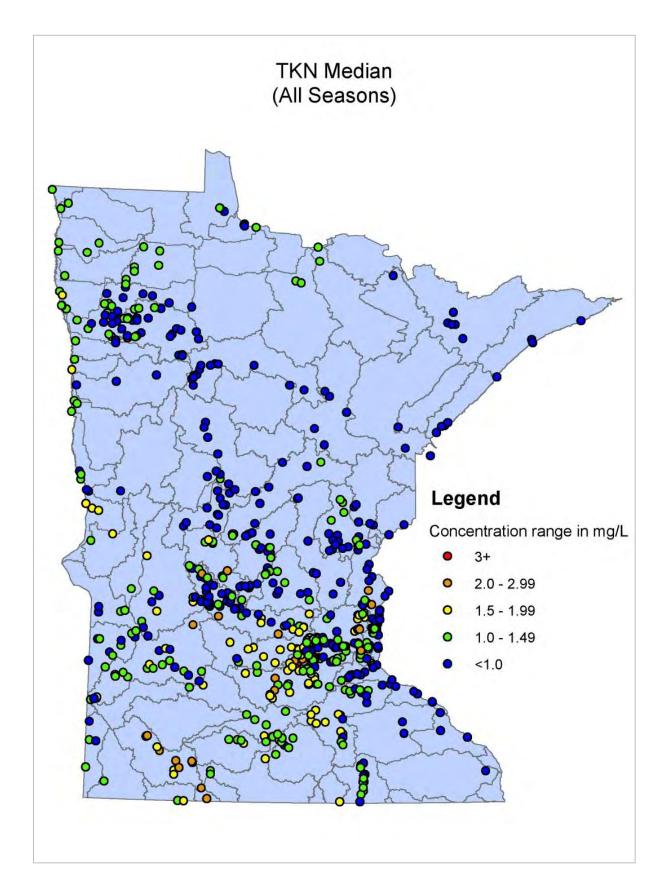


Figure 9. Median TKN concentrations for all samples taken at each site between 2000 and 2010.

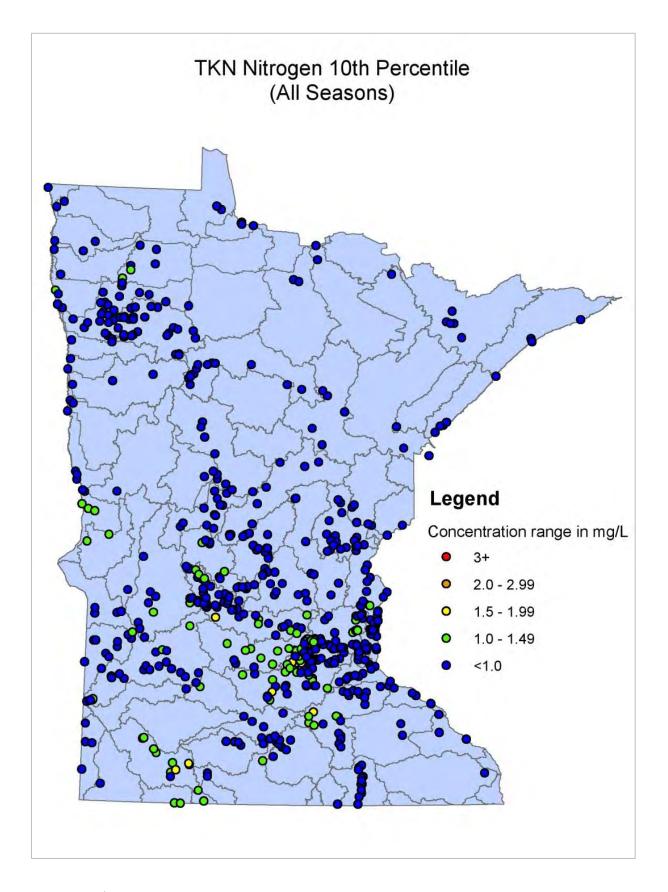


Figure 10. 10<sup>th</sup> percentile TKN concentrations for all samples taken at each site between 2000 and 2010.

## Total nitrogen

Total nitrogen was calculated by summing the laboratory measurements of nitrite+nitrate-N and TKN. While the TN concentrations are slightly higher than nitrite+nitrate-N, the general patterns and concentrations are similar to the nitrite+nitrate-N concentration maps (Figures 11 to 13). The 90<sup>th</sup> percentile concentration map (Figure 10) shows concentrations mostly 1 to 3 mg/l in northern Minnesota and mostly over 5 mg/l in southern Minnesota. The 10<sup>th</sup> percentile map (Figure 13) shows substantially lower TN concentrations than the 90<sup>th</sup> percentile map, with mostly less than 1 mg/l in northern Minnesota and mostly 1-3 mg/l in southern Minnesota.

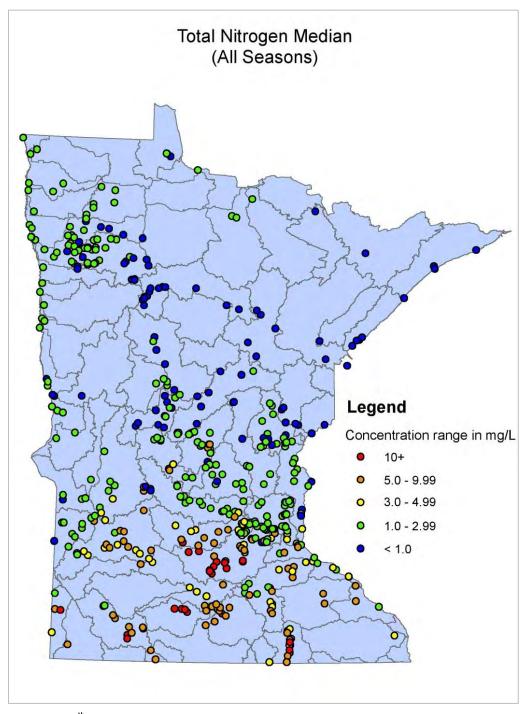


Figure 11. 90<sup>th</sup> percentile TN concentrations for all samples taken at each site between 2000 and 2010.

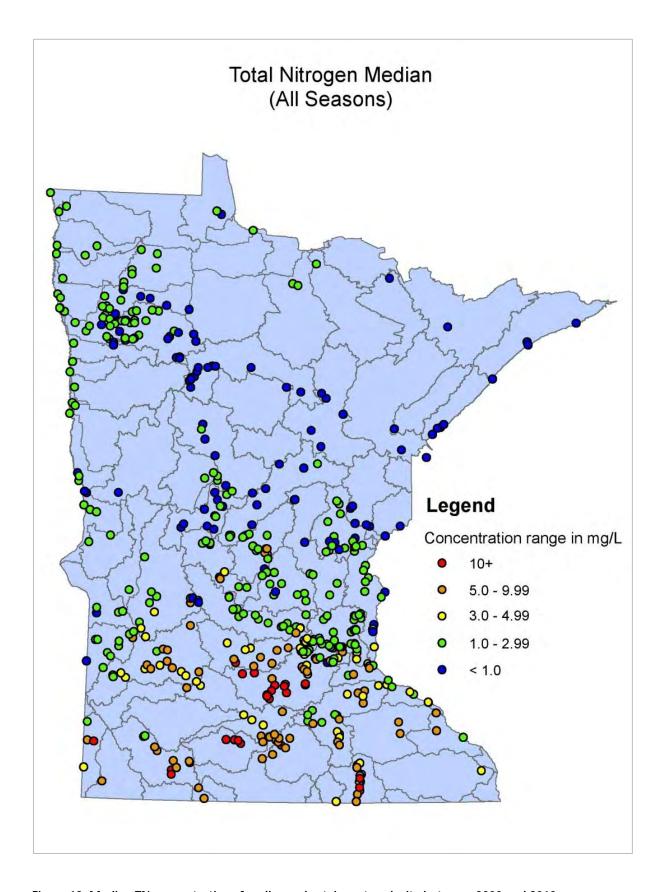


Figure 12. Median TN concentrations for all samples taken at each site between 2000 and 2010.

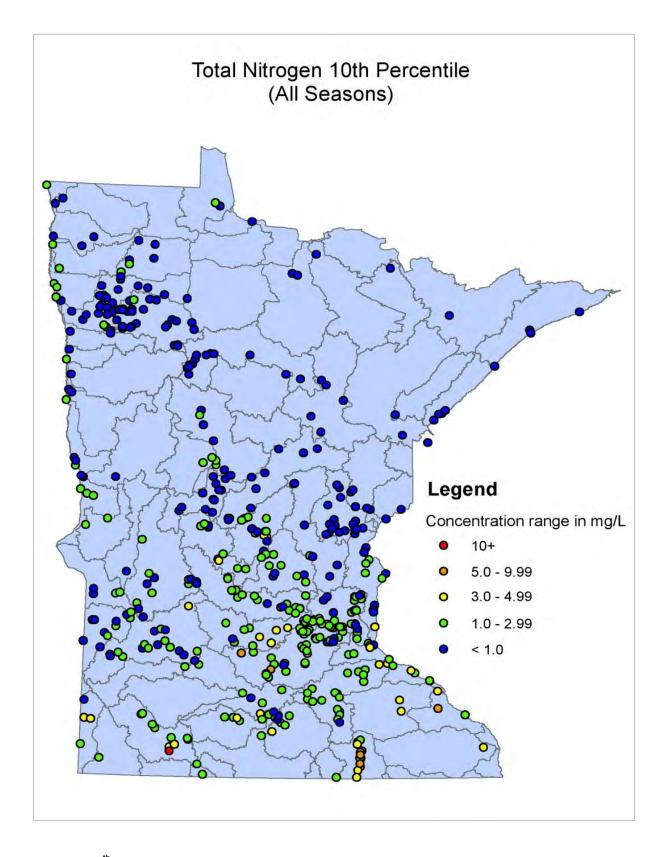


Figure 13. 10<sup>th</sup> percentile TN concentrations for all samples taken at each site between 2000 and 2010.

### Seasonal nitrate concentrations

We analyzed seasonal differences in nitrite+nitrate-N medians at all sites which met a minimum criteria of 12 samples taken during that season. Seasons assessed included: spring (March-May), summer (June-August) and fall (September-November). Results were then separated by the major basin where the streams are located. The seasonal differences in the average of all stream site medians across the basins varied considerably from one basin to another (Figure 14). Streams in the Minnesota River Basin, show a strong seasonal trend of highest nitrite+nitrate-N levels in the spring and the lowest levels in the fall months. Whereas streams in the Lower Mississippi Basin, which are in an area where groundwater baseflow is highly influential, show little change from spring to fall seasons, on average.

Note that each basin has a different number of sampling sites/frequencies, and some basins are large and diverse and others are smaller with less diverse landscapes. Comparisons among basins are limited by these differences. Monthly variability in mainstem rivers are described in more detail in Chapter B3.

# Median Nitrate Conc. by Season

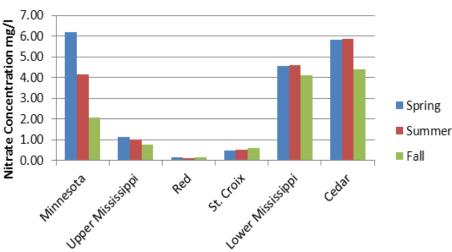


Figure 14. Seasonal nitrite+nitrate-N median concentrations averaged across major river basins in Minnesota. Spring months include March to May, summer months include June to August, and fall months include September to November.

### Summary of findings

### Number of monitoring sites meeting criteria

In Minnesota, 728 river and stream sites have been frequently monitored for nitrite+nitrate-N
during the period 2000 and 2010, with an average of 69 samples analyzed at each site. During
this same period 637 and 597 sites were frequently sampled for TKN and ammonia+ammonium,
respectively.

### Nitrite+nitrate-N

At times, nitrite+nitrate-N concentrations exceeded 5 mg/l throughout most of southern Minnesota, and 90<sup>th</sup> percentile nitrite+nitrate-N concentrations exceeded 5 mg/l at 31% of sites statewide. Nitrite+nitrate-N 90<sup>th</sup> percentile concentrations exceeded 10 mg/l throughout most of south-central Minnesota, and 17% of river and stream sites statewide had 90<sup>th</sup> percentiles

- exceeding 10 mg/l. Rivers and stream samples seldom had nitrite+nitrate-N exceeding 20 mg/l, and 90<sup>th</sup> percentile concentrations exceeded 20 mg/l at 15 sites (2%) statewide.
- Most northern Minnesota streams have nitrite+nitrate-N concentrations which are typically less than 1 mg/l. Yet several northern rivers and streams, particularly along the Red River, have nitrite+nitrate-N between 1 and 3 mg/l.
- The lower range nitrite+ nitrate-N concentrations (10<sup>th</sup> percentiles) are mostly less than 3 mg/l throughout the state. Exceptions to this include about 20 sites in southeastern Minnesota and scattered sites elsewhere with nitrite+nitrate-N which continued to be 3 to 10 mg/l.
- About 31% of stream sites had 90<sup>th</sup> percentile nitrite+nitrate-N exceeding 5 mg/l; whereas the maximums exceeded 5 mg/l at 41% of the sites. Maximum nitrite+nitrate-N concentrations exceeded 10 mg/l at 27% of sampled stream sites, compared to 17% of sites with 90<sup>th</sup> percentile concentrations above 10 mg/l.
- Nitrite+nitrate-N median concentrations vary by season, especially in the Minnesota River Basin, where concentrations are highest in the spring, followed by summer, and then fall.

#### Ammonia+ammonium-N

- The 90<sup>th</sup> percentile ammonia+ammonium-N concentrations exceeded 0.1 mg/l throughout much of the state, but only exceeded 1 mg/l at seven sites.
- Spatial patterns of ammonia+ammonium-N concentrations are less pronounced compared to nitrite+nitrate-N. Most of north-central and northeastern Minnesota have low ammonia+ammonium-N concentrations (<0.1 mg/l). With the exception of Duluth area streams and two other scattered streams, all northeastern Minnesota streams had 90<sup>th</sup> percentile ammonia+ammonium-N concentrations less than 0.1 mg/l.
- Median ammonia+ammonium-N concentrations are mostly less than 0.1 mg/l throughout the state. Exceptions to this include some sampling points in the Cedar River, the Twin Cities area, and a few other scattered locations.

### TKN (mostly organic nitrogen)

- The 90<sup>th</sup> percentile TKN concentrations were between 1 and 3 mg/l throughout much of the state.
- Spatial patterns of TKN concentrations showed that during higher TKN periods, TKN remained less than 1.5 mg/l throughout most of northeastern Minnesota and was between 1.5 and over 3 mg/l throughout most of southern Minnesota and along the Red River. Five main pockets of elevated TKN (90<sup>th</sup> percentiles over >3 mg/l) are all located at various places in the southern half of the state.
- Median TKN levels are predominantly less than 1.5 mg/l throughout the state, and 10<sup>th</sup> percentile levels are predominantly less than 1 mg/l, with only about seven sites in the 1.5 to 2 mg/l range.

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# **B2.** Monitoring Mainstem River Nitrogen Loads

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Load calculations:

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### Introduction

This chapter describes monitoring-based nitrogen results from many of the mainstem rivers in Minnesota, including basin and state outlets and upstream reaches of the Mississippi, Minnesota, St. Croix, and Red Rivers. The following chapter (B3) focuses on a smaller scale, examining monitoring-based results near the outlets of 8-digit Hydrologic Unit Code (HUC8) level watersheds.

Nitrogen (N) load, the amount of N passing a point on a river over a certain amount of time (i.e., pounds per year), can be estimated if river flow is monitored and water samples are collected and analyzed over a range of flow conditions and seasons. In Minnesota, we are fortunate to have numerous monitoring stations where total nitrogen (TN) and nitrite+nitrate (nitrate) loads have been calculated. The primary loads which will be described in this chapter are summarized in Table 1. In this chapter, we describe the results from these monitoring-based loads, yield, and flow-weighted mean concentrations (FWMC) for major rivers and basins.

Table 1. Monitoring programs which provided N load information for this report.

Monitoring program	Lead agency	Watershed/stream locations	Nitrogen parameter(s)	Years	Load estimation methods
Long Term Resource Monitoring Program	US Geological Survey	Mississippi River Upstream and downstream of Lake Pepin; Mississippi River near Iowa at Lock and Dam #7 and 8	Nitrite+Nitrate Total nitrogen	1991- 2010	MPCA used multiple year regressions in FLUX32
Metropolitan Council Major Rivers Monitoring Program	Metropolitan Council Environmental Services	Mississippi River at Anoka and Prescott Minnesota River at Jordan St. Croix River at Stillwater	Nitrite+Nitrate TKN Total Nitrogen	1980- 2010	Met Council used one- year concentration/flow data and a single year's flow to calculate loads in Flux 32.
Red River	Manitoba Conservation and Water Stewardship and Environment Canada	Emerson Manitoba	Nitrite+Nitrate TKN	1994- 2007	Monthly water quality and flow data (average of daily) for full period to estimate monthly and then annual loads
Watershed Load Monitoring Program	MPCA (with support from other organizations)	Outlets of most HUC8 watersheds in Minnesota	Nitrite+Nitrate TKN Total Nitrogen	2007 - 2009	MPCA used single year regressions in FLUX32

### Results overview

Three mainstem rivers (Minnesota River, Upper Mississippi River, and St. Croix River) converge in the Twin Cities Area, where their waters join and continue moving downstream in the Mississippi River along the Minnesota and Wisconsin border. Minnesota and Wisconsin tributaries from the Lower Mississippi Basin add additional N loads into the Mississippi, south of the Twin Cities. At the opposite corner of the state, the Red River flows north along the Minnesota and North Dakota state border into Manitoba.

### Total nitrogen

Long term average TN loads were calculated for these mainstem rivers using monitoring results obtained reasonably close to the outlets of the basins and/or at the state borders (Table 2, Figures 1 and 2). Long-term average loads are mostly used in this chapter, since year-to-year variability can be large due to annual precipitation differences and challenges in perfectly capturing monitoring results during storm events. Averaging loads over a longer period of time reduces the effects of these single year climate influences and load calculation uncertainties.

Table 2. TN loads, yields and flow-weighted mean concentrations (FWMC) for certain major rivers in Minnesota.

	Load avg. million lbs/yr	Yield avg. lbs/acre/yr	FWMC avg. mg/l	Percent of TN in nitrite+nitrate-N form	Period which average is based on
St. Croix River, Stillwater	10	2.3	1.0	37%	1991-2010
Minnesota River, Jordan	116	11.3	8.2	84%	1991-2010
Mississippi River, Anoka (plus Rum R)*	42*	3.3*	2.2	56%	1991-2010
Mississippi River, Prescott	174	6.1	3.8	72%	1991-2010
Mississippi River, Lake Pepin Outlet	145	4.7	3.1	83%	1992-2009
Mississippi River at Minn. – Iowa border	211	5.0	2.6	75%	1991-2010
Lock and Dam #8					
Red River Basin at Emerson Manitoba	37	1.5	2.4	46%	1994-2008

<sup>\*</sup>In this table and the rest of the chapter, loads and yields for the Mississippi River Anoka also include Rum River load averages from 2001 to 2010 calculated by Met Council, combined with the Met Council Mississippi River (Anoka) loads; so that the Mississippi River loads at Anoka include all of the Upper Mississippi River Basin N loads except for the Mississippi River Twin Cities watershed. The Rum River loads represent 6.2% of the total N average load of the Mississippi River at Anoka.

The highest loading tributary to the Mississippi River is the Minnesota River, which contributes an average of 116 million pounds of N per year (1991 to 2010). By comparison, the Upper Mississippi River and St. Croix River add lesser amounts of roughly 42 and 10 million pounds of TN per year, respectively (Figure 1). Moving downstream through the Twin Cities Metropolitan Area, TN increases by about

6 million pounds per year on average from point sources, stormwater and groundwater baseflow in the Twin Cities. Between the south part of the Twin Cities and the Iowa border, TN increases by about another 37 million pounds, with contributions from Lower Mississippi River Basin tributaries. In-stream N losses also occur in this lower stretch of the river, so that the actual additions from Lower Mississippi River Basin tributaries are more than the 37 million pound increase observed in the river loads.

The TN yields and FWMCs are substantially higher in the Minnesota River as compared to the other tributaries and sections of the Mississippi (Table 2). If 12% to 22% of N is lost in the major rivers, pools, and Lake Pepin south of the Twin Cities, then the 116 million pounds of TN measured in the Minnesota River at Jordan (upstream of the Twin Cities) will be reduced to 90 to 102 million pounds at the lowa border, which represents 43% to 48% of the 211 million pounds of TN reaching the Minnesota/lowa border in the Mississippi River.

The Red River TN loads at the Minnesota/Canada border are in the same general range as the Upper Mississippi Basin loads, transporting about 37 million pounds per year, on average.

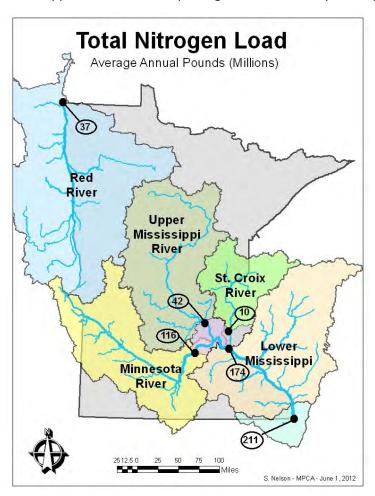


Figure 1. Long term average annual TN loads at key points along major rivers. Time period for long term averages: Red River (1994-2008); Minnesota, Upper Mississippi, and St. Croix Rivers (1991-2010); Lower Mississippi (1992-2009).

### Nitrate-N

Nitrite+Nitrate-N loads are also dominated by the Minnesota River, which contributes an average 97 million pounds per year. The Upper Mississippi River, St. Croix River, Twin Cities Metropolitan Area streams, and the Lower Mississippi River Basin all add lesser amounts of 23, 4, <1 and 34 million pounds of nitrite+nitrate-N, respectively (Figure 2). The Red River nitrate loads are also low compared to the Minnesota River, transporting about 16 million pounds per year, on average.

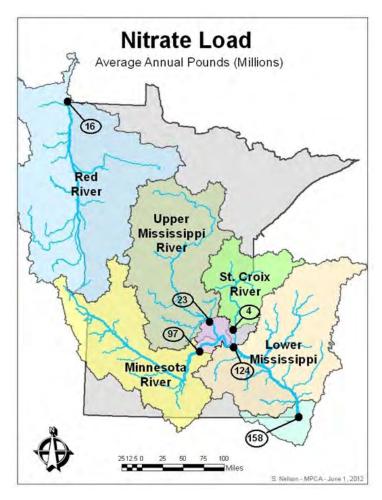


Figure 2. Long term average annual nitrite+nitrate-N loads at key points along major rivers. Time period for long term averages: Red River (1994-2008); Minnesota, Upper Mississippi, and St. Croix Rivers (1991-2010); Lower Mississippi (1992-2009).

For the remainder of this chapter, more specific results are provided for the following rivers:

- the Lower Mississippi River Lake Pepin to Iowa
- the three mainstem rivers converging in the Twin Cities Minnesota River, St. Croix River,
   Upper Mississippi River
- the Red River

### Lower Mississippi River – Lake Pepin to Iowa

### Mississippi River at Minnesota/Iowa border

The U.S. Geological Survey (USGS) has been taking water quality samples (every other week) since 1991 on the Mississippi River near the Minnesota and Iowa border. The U.S. Army Corps of Engineers has been measuring flow at both Lock and Dam #7 and 8 during the same time period. Two of the monitoring locations for the USGS Long Term Resource Monitoring Program (LTRMP) are located at Lock and Dam #7 and 8, near LaCrescent, Minnesota and Genoa, Wisconsin, respectively. Using USGS collected data, the Minnesota Pollution Control Agency (MPCA) calculated annual loads at Lock and Dam #7 and 8 using the FLUX32 model. The load calculations show annual mean total N loads between 1991 and 2010 of 209 and 211 million pounds at Lock and Dam #7 and 8, respectively. Because the average loads are nearly identical at these two monitoring sites, and they are located close to each other, the results and graphs below include only Lock and Dam #8, the more downstream location.

Most of the watersheds contributing water to the Mississippi River at the Minnesota/Iowa border are located in Minnesota. Overall, based on SPARROW model results, we estimate that about 77% of the TN in the Mississippi River at the Iowa border comes from loading in Minnesota catchment areas and the

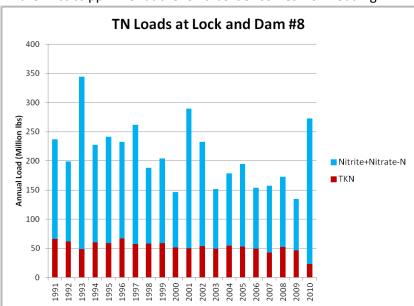


Figure 3. Annual TN loads in the Mississippi river at Lock and Dam #8 (near lowa border), showing a) year to year variability between 1991 and 2010 and b) the proportion of TN which is in the nitrite plus nitrate and TKN (ammonium plus organic-N) form.

other 23% comes largely from Wisconsin, but also lowa and the Dakotas. According to SPARROW model estimates, about 48% and 61% of the St. Croix and Lower Mississippi Basin TN loads are from Wisconsin, respectively. And about 4% of the Minnesota River Basin TN load is from the Dakotas and lowa.

The annual flow-weighted mean TN concentration calculated for Lock and Dam #8 ranged from 2.4 to 3.0 mg/l between 1991 and 2010, averaging 2.6 mg/l. The annual TN loads varied more during this time period (Figure 3), due largely to year-to-year variability in precipitation and river flow. The lowest annual load

occurred in 2009 (135 million pounds) and the highest load occurred in 1993 (344 million pounds). Nitrite+nitrate-N represents approximately 75% of the TN load, with Total Kjeldahl Nitrogen (organic-N + ammonium-N, abbreviated as TKN) making up the other 25% of the TN load (Figure 3).

The average TN and nitrite+nitrate loads peak in April, followed by May and then June (Figure 4). About two-thirds of the annual TN load occurs in the five months between March and July, during periods of spring runoff and early summer storms. Evapotranspiration is high in July through September when the crops are well established, and correspondingly river flow and nitrate loading decreases.

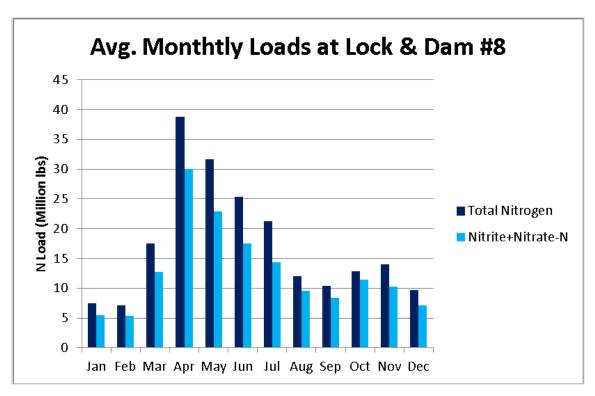


Figure 4. Monthly average (1991-2010) TN and nitrite+nitrate-N loads in the Mississippi river at Lock and Dam #8 (near lowa border).

### Mississippi River at Lake Pepin

Moving upstream on the Mississippi River to another LTRMP site at the outlet of Lake Pepin, the average TN load is 145 million pounds/year (1992-2009), which is about 66 million pounds/year lower than at Lock and Dam #8 for that same time period. During this same stretch of river, TN concentrations (flow-weighted means) drop from an average of 3.1 mg/l at the Lake Pepin outlet to 2.6 mg/l at Lock and Dam #8.

Several rivers from both Minnesota and Wisconsin enter into the Mississippi between Lake Pepin and Lock and Dam #8, including the Cannon, Zumbro, Root, Chippewa, Trempeleau, and Black River, as well as other smaller streams. The SPARROW model results indicate that 76% of the increased N load in the Mississippi River between Lake Pepin and the Iowa border is from Wisconsin tributaries and 24% is from Minnesota tributaries (see Chapter B-4). Estimates further upstream in Red Wing indicate that between Red Wing and the Iowa border in the Lower Mississippi Basin, Wisconsin tributaries contribute 61% of the TN loads and Minnesota 39%.

The average load at the Lake Pepin inlet (1992-2009) is 160 million pounds. Calculated TN loads at the inlet and outlet of Lake Pepin show that the inlet has consistently higher loads than the outlet (Figure 5). Annual N losses within the Lake Pepin section of the river averaged 8.9% per year between 1992 and 2009. The nitrite+nitrate-N fraction of TN is similar at the inlet and outlet, averaging 81.1% at the inlet and 83.4% at the outlet. The N losses within Lake Pepin and on other stretches of the Mississippi are further discussed in Chapter B5 and Appendix B5-2. Total losses in the Mississippi River dam pools and reservoirs are estimated to be between 12 and 22%.

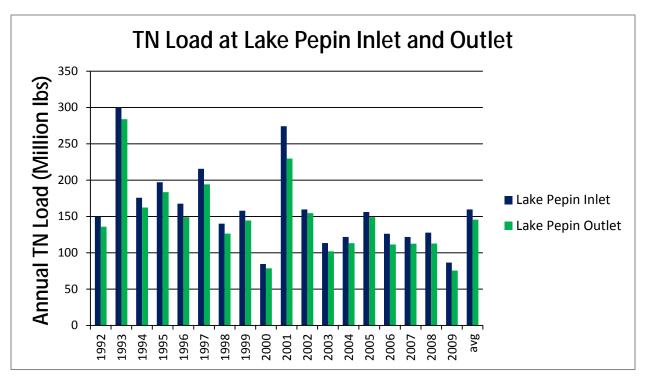


Figure 5. Average TN Loads at the inlet and outlet of Lake Pepin (1992-2009)

### Mainstem rivers entering and leaving the Twin Cities

For several decades the Metropolitan Council Environmental Services (MCES) has maintained monitoring programs that routinely check water quality of the Metropolitan Area rivers, streams, and lakes. At four major river stations, samples have been taken two times per month since 1976, providing one of the best long term nutrient monitoring data sets available in Minnesota. The four monitoring station locations are shown in Figure 6, and include:

- 1. Minnesota River at Jordan with a contributing watershed of 16,023 square miles from southern and southwestern Minnesota, and small portions of Iowa and South Dakota.
- 2. Mississippi River at Anoka with a contributing watershed area of about 17,927 square miles of land in central and north-central Minnesota.
- 3. St. Croix River at Stillwater with a contributing watershed area of about 7,069 square miles along eastern Minnesota and western Wisconsin.
- 4. Mississippi River at Prescott, Wisconsin Lock and Dam #3 reflecting the combination of the above three watersheds along with contributions throughout the Twin Cities Metropolitan Area. The contributing watershed area is about 44,800 square miles.



Figure 6. Locations of four major river monitoring site locations monitored by Metropolitan Council. Map developed by Met Council.

The loads at these four mainstem river monitoring stations were calculated by MCES and provided to the MPCA. The loads were calculated using the U.S. Army Corps of Engineers' software Flux32, from monitored daily average flow and grab sample chemistries taken every other week. Since flow in the four mainstem rivers responds relatively slowly to precipitation events, MCES and MPCA staff had determined, based on the MCES sampling frequency, that using a one-year record of average daily flow and grab sample water chemistry data was adequate to estimate annual loads for the mainstem rivers with acceptable uncertainty. The application of a one-year data set to define an annual river load, rather than multiple years, was viewed as acceptable since river events are typically defined as a multi-day record (three days or greater). The subtle nature of the river system hydrograph, along with consistent frequency of monitoring, allows for a strong statistical relationship when using regressions within Flux.

Loading calculations are an estimate based on monitoring results, and as such are subject to a range of variability. This variability depends on the water quality sampling frequency and regiment, as well as complexities in the watershed hydrologic responses to different runoff events. MCES calculated 95% confidence intervals around each estimated annual load. In a high-confidence year such as 2008 the 95% confidence interval ranged from 11% higher than the estimated load to 11% lower than the estimated load. Yet for certain other years the 95% confidence interval exceeded 50%. While the loads were calculated using single year analyses, in this report we use multiple year averages of those single year load estimates to represent typical loads, reducing the variability associated with single year estimates. The averages and medians were very similar in the Metropolitan Council data sets, typically differing by only 1% to 6% when looking at 20 to 30 year periods. Therefore, the results presented in this chapter would be similar whether using long-term means or medians.

Because the early and late 1980's were relatively dry, the average combined N load during the period 1980-2010 (150,731,000 pounds) is 8.6% lower compared to the 1991-2010 average (164,993,000 pounds). Except where noted, average statistics in this section use the 1991 to 2010 period instead of the complete 30-35 year record, since the 1991-2010 period: a) is more recent and will better represent current loads from more recent land uses, land management and climate, and b) the time period better matches available USGS monitoring data in the Lower Mississippi Basin.

### Year to year load variability

The combined N loads from the Mississippi River (at Anoka), the Minnesota River (at Jordan), and the St. Croix River (at Stillwater) between 1980 and 2010, are represented in Figure 7. The drought years in the late 1980s had low N loads; whereas the wet period between 1991 and 1993 had high loads. The river flows show a somewhat similar, but less pronounced, year to year variability (Figure 8).

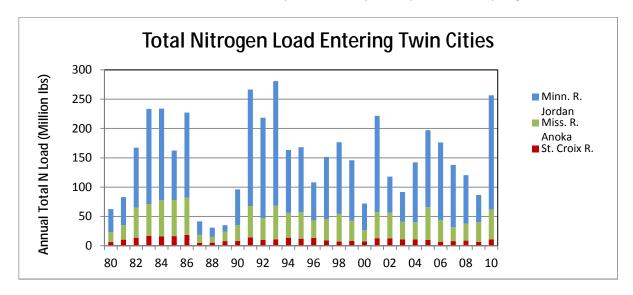


Figure 7. Annual combined total N loads from the three mainstem rivers entering the Twin Cities Area: the Mississippi River in Anoka, the St. Croix River in Stillwater, and the Minnesota River in Jordan. Time period 1980 to 2010.

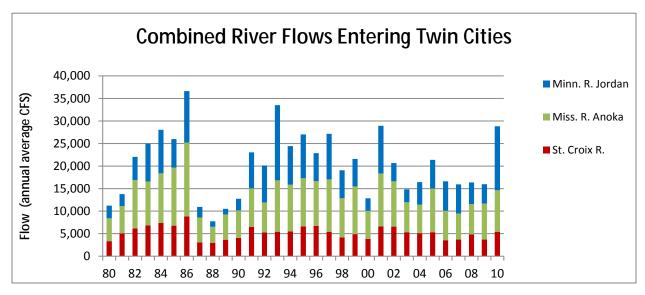


Figure 8. Annual combined TN river flow from the three major rivers entering the Twin Cities: the Mississippi River in Anoka, the St. Croix River in Stillwater, and the Minnesota River in Jordan.

The Minnesota River N loads have been much higher than the loads from the St. Croix at Stillwater and Mississippi at Anoka. The Minnesota River Basin contributes 69% of the total N loads and 78% of the nitrate loads which arrive at the Twin Cities Metropolitan Area in the three mainstem rivers, on average (Figure 9); yet represents only 38% of the total combined land area of the Minnesota, Upper Mississippi, and St. Croix River Basins.

### **Total N Coming into Metro Area**

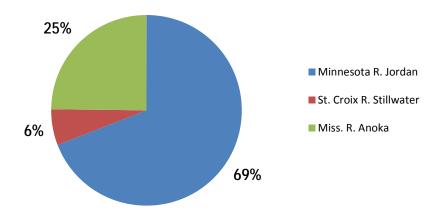


Figure 9. Proportions of TN load flowing into the Twin Cities from the three mainstem rivers, the Minnesota, St. Croix, and Mississippi (average of years 1991-2010).

### **River Flow Coming into Metro Area**

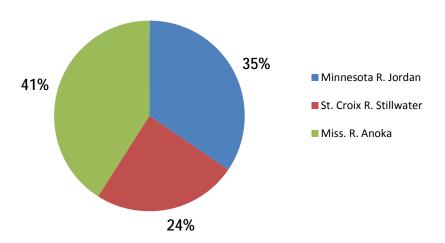


Figure 10. Average annual river flow volumes into the Twin Cities from the three major rivers, the Minnesota, St. Croix, and Mississippi (average of years 1991-2010).

The differences between the Minnesota and Upper Mississippi River N loads cannot be explained by differences in watershed areas or river flow. The catchment area for the Mississippi River at Anoka is 11.5 million acres, compared to a 10.3 million acre catchment area for the Minnesota River at Jordan. And the average flow (1991-2010) in the Mississippi (Anoka) and Minnesota (Jordan) Rivers are similar – 8,762 cubic feet per second (cfs) in the Mississippi and 7389 cfs in the Minnesota. While the flow is 16% higher in the Mississippi River (Anoka), the TN and nitrate loads are both much lower in the Mississippi (Anoka) compared to the Minnesota River (Figure 10).

### Nitrogen forms in the rivers

Most of the N is in the nitrate and organic forms, together representing between 95% and 99% of the TN (Table 3). Ammonia+ammonia-N and nitrite-N tend to convert to nitrate in the presence of oxygenated waters, and concentrations are much smaller than nitrate, together constituting between 1 and 5% of the TN. Therefore, while N parameter results are often reported as nitrite+nitrate-N and TKN (ammonium+organic-N), the nitrate and organic-N forms typically represent most of the N.

The mean organic-N concentrations range from 0.57 mg/l in the St. Croix River to 1.27 mg/l in the Minnesota River. Long term average FWMC of nitrate-N varies more greatly than organic N in the three rivers, ranging from 0.35 mg/l in the St. Croix River to 6.74 mg/l in the Minnesota River (Figure 11 and Table 3).

Table 3. Annual FWMC for different forms of N averaged for years 1991-2010. Calculated from data provided by MCES. Nitrite was calculated by subtracting nitrate from the laboratory results presented as nitrite+nitrate. Organic-N was determined by subtracting NH3+NH4 from TKN.

	Nitrate-N FWMC (mg/l)	Organic-N FWMC (mg/l)	Ammonia + Ammonium-N FWMC (mg/l)	Nitrite-N FWMC (mg/I)	Total N FWMC (mg/l)
Minnesota River Jordan	6.74	1.27	0.09	0.13	8.23
St. Croix River Stillwater	0.35	0.57	0.05	0.01	0.98
Mississippi River Anoka	1.32	0.89	0.07	0.01	2.29
Mississippi River Prescott L&D #3	2.63	0.99	0.09	0.09	3.80

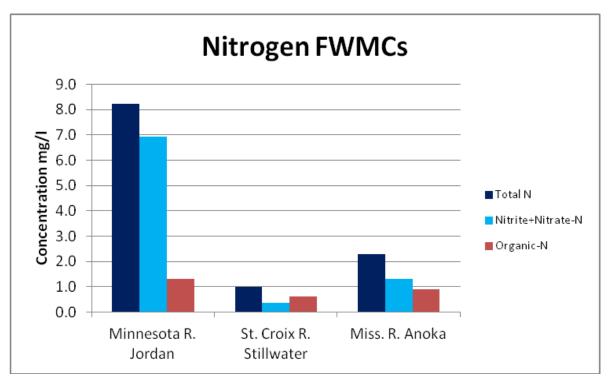


Figure 11. Flow weighted mean concentrations of total N, nitrite+nitrate-N and organic-N in the three mainstem rivers entering the Twin Cities region (average of 1991-2010).

In the Minnesota River at Jordan, nitrite+nitrate-N dominates the load, representing 84% of the TN load (Figure 12). In the lower N loading rivers of the St. Croix and Mississippi at Anoka, the nitrite+nitrate-N fraction is only 37% and 56% of the TN load, respectively.

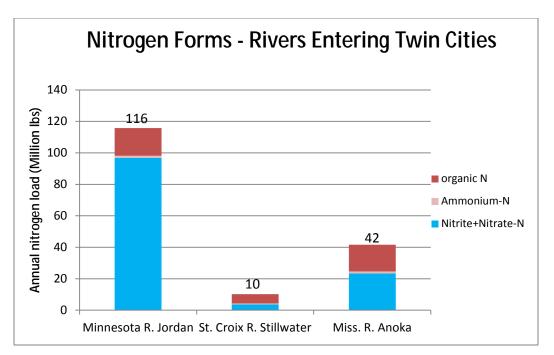
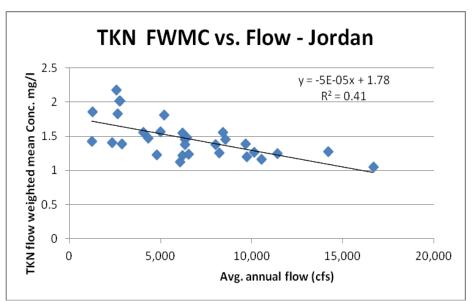


Figure 12. Average annual loads of various N forms in the Minnesota, St. Croix, and Mississippi Rivers entering the Twin Cities Area (1991-2010).

The organic N concentration is similar, but higher, in the Minnesota River as compared to the Upper Mississippi. One reason for this could be a higher amount of algae growth in the Minnesota River. A



negative correlation between TKN concentration and flow in the Minnesota River (Figure 13) suggests that it is unlikely that the elevated TKN is due to the sediment in the river. During the high flow years, TKN concentrations were nearly half of the concentration during very low flow years.

Figure 13. Relationship between long term (1991-2010) annual TKN flow-weighted mean concentrations and annual flow in the Minnesota River at Jordan.

### Month to month variability

Average monthly TN and nitrite+nitrate-N loads were determined for the 20-year period 1991 to 2010. Total nitrogen and nitrate loads are highest in the spring months of April to June in the Minnesota, Mississippi, and St. Croix Rivers (Figures 14-16). The peak N loading month is April at all three rivers. Loads are relatively low from August through February.

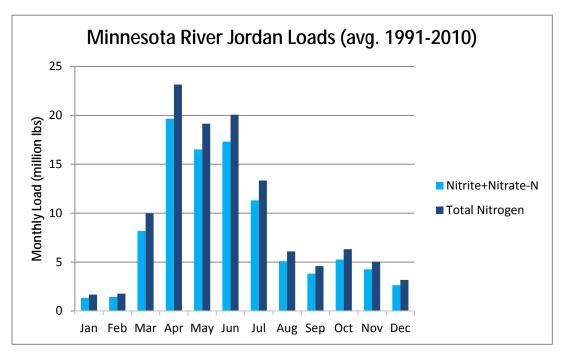


Figure 14. Long term average monthly TN and nitrite+nitrate-N loads in the Minnesota River at Jordan.

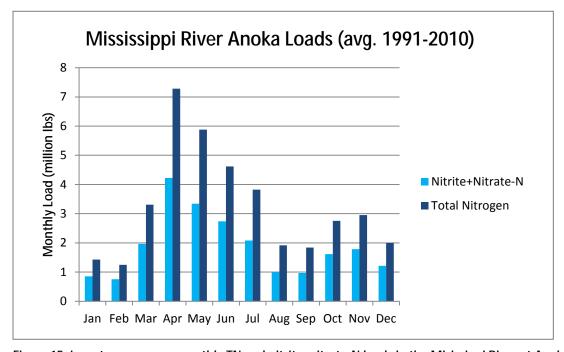


Figure 15. Long term average monthly TN and nitrite+nitrate-N loads in the Misissippi River at Anoka.

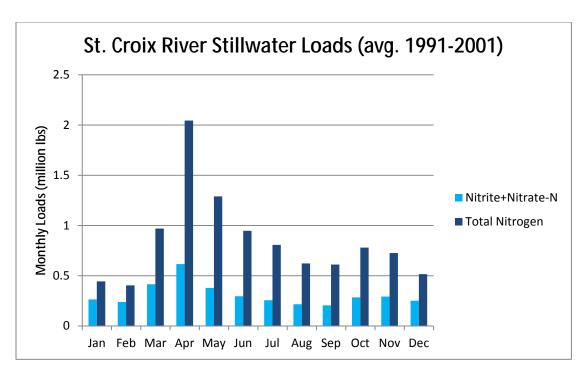


Figure 16. Long term average monthly TN and nitrite+nitrate-N loads in the St. Croix River at Stillwater.

Loads are influenced by both flow and concentration. In the spring months both flow and nitrate concentrations are elevated in the Minnesota River. In the Minnesota River (Jordan) average nitrate concentrations increase from less than 4 mg/l in the winter to about 7 mg/l in May and June (Figure 17). While much less pronounced than in the Minnesota River, an increase in both nitrate and TKN concentrations occurs in the Upper Mississippi River Basin during the spring months (Figure 18). Monthly concentrations in the St. Croix River Basin behave differently, with nitrate concentrations dropping in half during the spring and summer months and peaking in the winter months when flow is dominated by groundwater baseflow and algae production is minimal (Figure 19). In the St. Croix River summer months, organic N increases during the period when algae production increases. Yet, TKN concentrations in the St. Croix remain lower than in the Minnesota River, even during the peak months.

As the three large rivers coming into the Twin Cities Area merge into the Mississippi River south of the Twin Cities (at Lock and Dam #3 near Prescott, Wisconsin), the monthly nitrite+nitrate-N and total N concentration patterns are similar to the patterns observed in the Minnesota River (Figure 20).

The substantial differences in seasonal N concentration patterns among the three mainstem rivers might be explained, in part, by different land uses and flow pathways. The Minnesota River Basin has the highest fraction of tile-drained land. By comparison, the Upper Mississippi River Basin and the St. Croix Basin have less tile drained agricultural lands and more continuously discharging groundwater baseflow inputs (see Chapters D1 and D4).

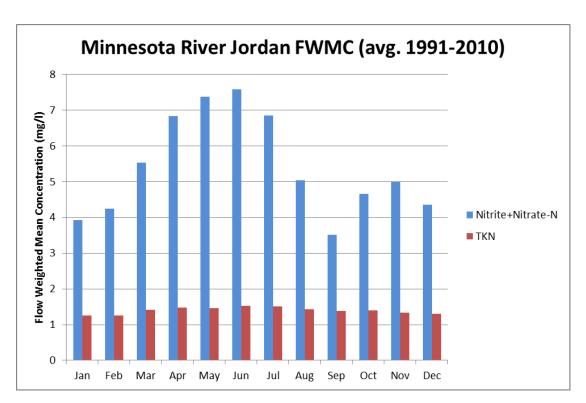


Figure 17. Long term average monthly TKN and nitrite+nitrate-N flow-weighted mean concentrations in the Minnesota River at Jordan.

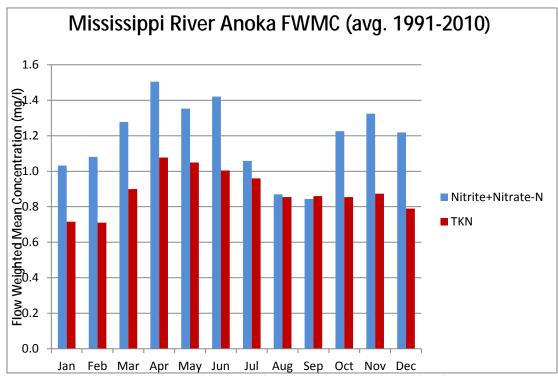


Figure 18. Long term average monthly TKN and nitrite+nitrate-N flow-weighted mean concentrations in the Mississippi River at Anoka.

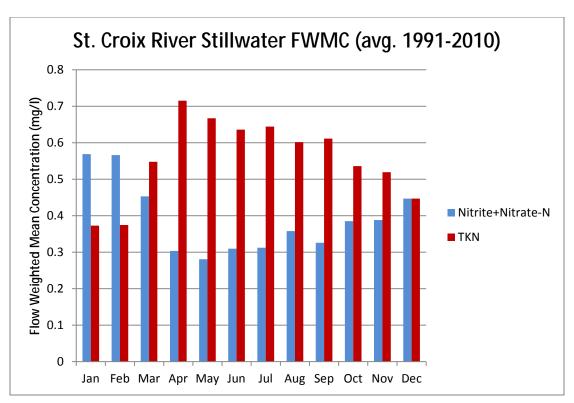


Figure 19. Long term average monthly TKN and nitrite+nitrate-N flow-weighted mean concentrations in the St. Croix River at Stillwater.

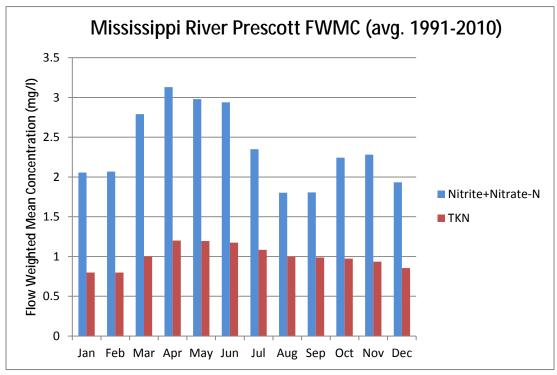


Figure 20. Long term average monthly TKN and nitrite+nitrate-N flow-weighted mean concentrations in the Mississippi River at Prescott, Wisconsin (Lock and Dam #3).

### Twin Cities influence on river nitrogen

Using the 1991-2010 N loading data sets provided by the Metropolitan Council, we compared nitrate loading in the combined three mainstem river sites coming into the Twin Cities with the Mississippi River location flowing out of the Metropolitan Area at Lock and Dam #3 in Prescott, Wisconsin. Differences between the Twin Cities inputs and outputs can potentially be due to: a) uncertainty/error in the estimates; b) N losses through denitrification and other processes within the river; c) stormwater N additions from the urban, suburban, and rural areas; and d) municipal and industrial wastewater discharges in the Metropolitan region.

The 1991-2010 average annual TN was found to be 6 million pounds (3.5%) higher between the combined Jordan/Anoka/Stillwater monitoring points upstream of the Twin Cities, and the Prescott monitoring point downstream of the Twin Cities (Figure 21). This mean TN difference is similar to that found a decade earlier by Kloiber (2004), who looked at the period 1992 to 2001 and found that TN increased by 2.5% through the Twin Cities Metropolian Area. Kloiber reported that the 2.5% difference was within the potential range of uncertainty in the load calculations. Similarly, we found that with the high year-to-year variability in loads, the average 1991-2010 TN loads from rivers into the Twin Cities compared to the average loads out of the Twin Cities was not found to be statistically significant (two-sample t-test, p-value = 0.54).

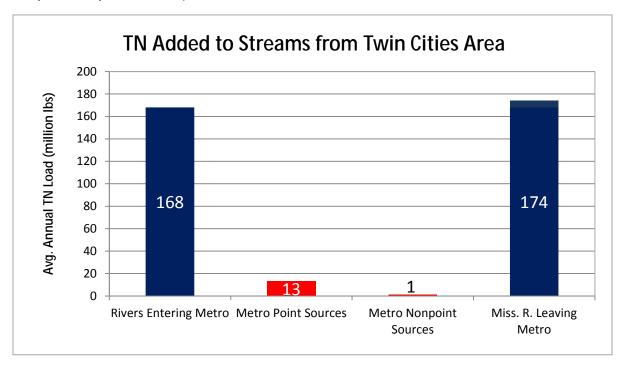


Figure 21. Average annual TN entering the Twin Cities Metropolitan Area in three mainstem rivers: the Minnesota, St. Croix, and Mississippi (average of years 1991-2010), compared to TN leaving the Metropolitan Area in the Mississippi River. The two middle bars represent the added sources of a) estimated point source TN additions to the river in the Twin Cities Area and b) the estimated nonpoint TN sources from stormwater and groundwater in the Metropolitan Area.

We know that some N additions occur in the Twin Cities Area. Point sources plus nonpoint sources add an estimated 13.8 million pounds of N in the Twin Cities Area (12.8 million pounds from point sources and 1 million pounds from stormwater runoff and groundwater contributions – see Chapters D2 and D4). A part of these additions is expected to be offset by in-stream N losses from natural processes as these rivers flow through the Twin Cities. Therefore, while the 6 million pound average increase throughout the Metropolitan Area is not statistically significant, it is within a reasonable range of expected net change considering estimated N inputs and potential N losses within the rivers.

Figure 22 shows the relative amounts of different N forms for the mainstem river inputs into the Twin Cities and the exports out of the Twin Cities. There is a disproportionately higher increase in organic N and ammonium, as compared to nitrate. This could be due to sampling uncertainties, organic N additions and/or in-stream processes where nitrate is used by algae and thereby transformed into organic N.

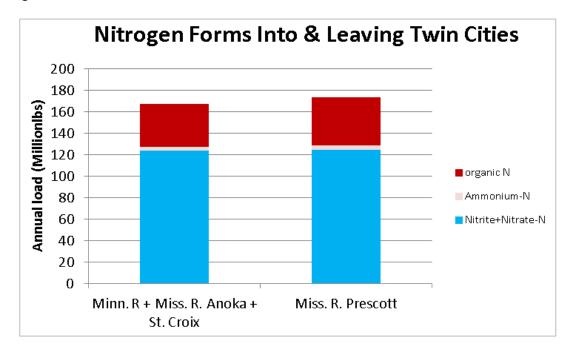


Figure 22. Annual loads of the three different forms of N comprising TN, showing the difference in N forms in the combined mainstem rivers entering the Twin Cities and N forms in the Mississippi River near Prescott downstream of the Twin Cities.

As the Mississippi River continues to flow downstream into southeastern Minnesota, TN loads decrease between Prescott, Wisconsin and the outlet of Lake Pepin. Within this stretch of the river, N inputs are minimal and in-stream losses are measurable (see Chapter B5).

### Nitrogen additions in upstream reaches

Nitrogen increases along the upstream reaches of the Mississippi, Minnesota, and St. Croix Rivers were determined from monitoring results collected during 2007 to 2009. The rivers were sampled near the upstream and downstream points of the mainstem HUC8 watershed boundaries as part of the

Minnesota Watershed Pollutant Load Monitoring network, described in Chapter B3. The results for TN and nitrite+nitrate-N are shown in Figures 23 and 24 as a fraction of load measured in the Mississippi River at Lock and Dam #3 in Prescott Wisconsin, south of the Twin Cities.

The N loads remain a relatively low percentage of the Mississippi River at Prescott loads in most upstream river stretches, and show increasing loads moving downstream. The loads increase dramatically in the Minnesota River between Judson and St. Peter where TN increases from 22% of the Prescott loads to 53% of the loads and nitrite+nitrate-N increases from 23% to 59% of the Prescott loads, as the Minnesota River receives flow from the Blue Earth, Watonwan, and Le Sueur Rivers.

Toward the mouth of the Minnesota River, TN and nitrite+nitrate loads represent 63 and 74% of the loads in the Mississippi River at Prescott, Wisconsin. The Upper Mississippi and St. Croix rivers have TN and nitrite+nitrate loads which remain less than 10% of Prescott loads, except that the Upper Mississippi River loads at Anoka increase to 24% (TN) and 19% (nitrite+nitrate) of the loads in Prescott, downstream of the confluence with the Crow River.



Figure 23. Average TN loads (2007-2009) at different points along the Minnesota, Mississippi and St. Croix Rivers, expressed as a percentage of the load measured at the Mississippi River Lock and Dam #3 near Prescott, Wisconsin (after the convergence of the three rivers).

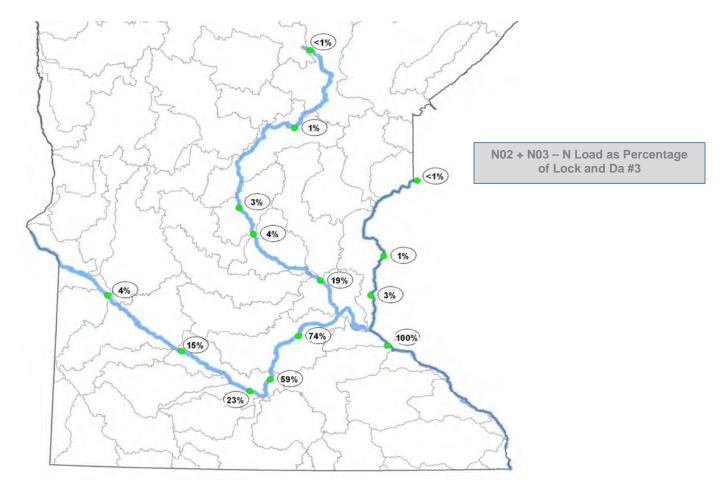


Figure 24. Average nitrite+nitrate-N loads (2007-2009) at different points along the Minnesota, Mississippi, and St. Croix rivers, expressed as a percentage of the load measured at the Mississippi River Lock and Dam #3 near Prescott, Wisconsin (after the convergence of the three rivers).

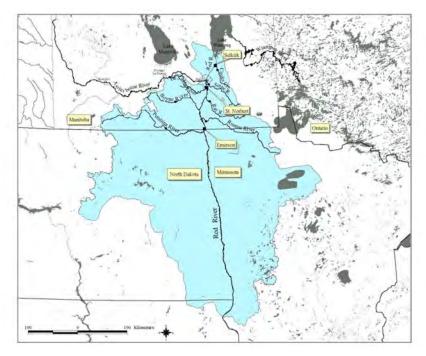
### **Red River**

The U.S. portion of the Red River Basin, depicted in Figure 25, originates mostly in Minnesota and North Dakota, with a small percentage also in South Dakota. After crossing the U.S./Canadian border, additional Manitoba watersheds flow into the Red River before it discharges into Lake Winnipeg.

### Minnesota's contribution to Emerson nitrogen loads

Based on unpublished data provided by Environment Manitoba (Manitoba Water Stewardship and Environment Canada, the average Red River annual TN load between 1994 and 2008 at the Canadian border in Emerson, Manitoba was 37,326,000 pounds/year (Figure 26). Nitrate concentrations are relatively low in the Red River, and only 42% of the TN is in the nitrate form, with the remainder as TKN (organic-N and ammonia+ammonium-N). Most of the Red River load in Emerson originates in the United States, with only 5.5% coming from Canadian watersheds which flow into North Dakota before joining up with the Red River in the United States. Therefore, 94.5% of the 37 million pounds of N reaching the

Canadian border in the Red River is from Minnesota and the Dakotas. Of the United States contributions, SPARROW modeling results indicate that 48% of the United States load is from Minnesota, and 52% is from the Dakotas (see Chapter B4).



Therefore, if we assume 37,326,000 pounds/year of TN at Emerson, of which 94.5% is from the United States and 48% of that amount is from Minnesota, Minnesota's N contribution to the Red River is estimated as 16,931,000 pounds/year, on average.

Figure 25. Red River Basin boundaries. From Bourne et al., 2002.

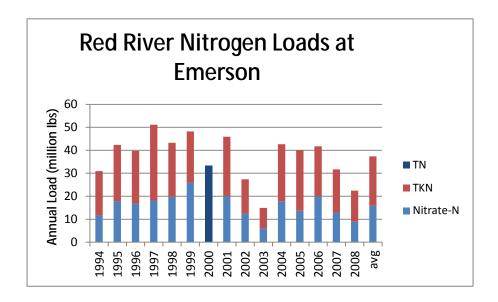


Figure 26. Red River estimated annual N Loads based on monitoring data at Emerson, Manitoba near the U.S./Canadian border. Monitoring and load calculations from Manitoba Conservation Water Stewardship and Environment Canada. Only TN was available for 2000.

### **United States contributions to Lake Winnipeg**

Environment Canada (2011) assessed TN loads from the period 1994 to 2007, including loads from such sources as atmospheric deposition directly into Lake Winnipeg. They concluded that the Red River from the United States and Canada watersheds contributed 34% of the N load to Lake Winnipeg. In an earlier report, Bourne et al. (2002) concluded that 65% of the Red River N comes from the United States. Combining these results, we can assume that approximately 22% of the N load to Lake Winnipeg comes from watersheds in Minnesota and the Dakotas, with about 11% of the Lake Winnipeg TN load from Minnesota.

### **Summary points**

- Long-term (15-30 years) monitoring-based loads, yields and flow-weighted mean concentrations were assessed for the Minnesota River (Jordan), Red River (Emerson), Upper Mississippi River (Anoka), St. Croix River (Stillwater), Mississippi River at Prescott, Wisconsin, Mississippi River at Lake Pepin, and Mississippi River at the Iowa border.
- The Red River is a significant contributor of N to Lake Winnipeg. The United States contributes
  an average of 37 million pounds of N to the Canadian border each year, and approximately 48%
  of that amount (16.9 million pounds) is from Minnesota. This export of N compares to 211
  million pounds, leaving southern Minnesota in the Mississippi River each year, on average, of
  which an estimated 162 million pounds are from Minnesota watersheds.
- The Minnesota River N contributions (average 116 million pounds/year) have the greatest influence on N loads leaving Minnesota in the Mississippi River at the Iowa border. Minnesota River TN loads are about twice as high as the combined loads from the Upper Mississippi River, St. Croix River, and Twin Cities additions. The Minnesota River loads increase greatly between Judson and St. Peter, Minnesota, where the Greater Blue Earth River N loads reach the Minnesota River.
- The Mississippi River TN increases by 37 million pounds between the Twin Cities and the Iowa border. About 9% of all N reaching Lake Pepin is lost in the lake (mostly converted to N gas). An estimated 61% of the loads in the Lower Mississippi Basin tributaries are from Wisconsin and 39% from Minnesota, based on SPARROW modeling.
- Long-term average TN yields and flow-weighted mean concentrations are substantially higher in the Minnesota River, and are between 3.5 and 8 times higher than the Red, St. Croix, and Upper Mississippi Rivers.
- Year-to-year variability in TN loads and river flow can be very high, especially in river systems
  with lower groundwater baseflow contributions and higher tile line contributions. In the
  Minnesota River Basin, TN loads during low flow years are sometimes as low as 25% of the loads
  occurring during high flow years.
- The primary forms of N in the mainstem river systems are nitrate-N and organic-N. Nitrite-N and ammonia+ammonium-N are quite low and together comprise only 1% to 5% of the TN. Organic-N FWMCs are more consistent across the state as compared to nitrate, and range from 0.6 mg/l in the St. Croix to 1.4 mg/l in the Red River. Long-term average nitrite+nitrate-N FWMCs range from 0.3 mg/l in the St. Croix to 6.7 mg/l in the Minnesota River. While organic N is equal to or higher than nitrate in some river basins, nitrate is the parameter which most greatly affects TN loads across the state.

- Nitrite+nitrate-N loads in the Minnesota River (Jordan) are more than three times higher than
  the combined nitrite+nitrate-N loads from the Upper Mississippi, St. Croix, and Twin Cities
  tributary contributions. The Minnesota River's 97 million pounds constitutes a large fraction of
  the 158 million pounds leaving the state in the Mississippi River, and is much greater than the
  16 million pounds leaving the state in the Red River of the North.
- Total nitrogen loads in the Minnesota, Mississippi, and St. Croix Rivers peak in April and May.
   About two-thirds of the annual TN load in the Mississippi River at the lowa border occurs during
   the five months between March and July. This is due to both increased flow and increases in N
   concentrations during these months.
- The Twin Cities Metropolitan Area contributes relatively minor amounts of N to the major rivers. The Twin Cities increase river TN by 3% to 4%, on average, which was not found to be a statistically significant increase. Based on information supported in other chapters, over 90% of the added N from the Twin Cities is expected to be from point sources, mostly human wastewater, with relatively little additions from nonpoint sources such as stormwater.

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## **B3. Monitoring HUC8 Watershed Outlets**

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Load calculations by:

Minnesota Pollution Control Agency: Patrick Baskfield, Dennis Wasley, Andy Butzer, Jim MacArthur,

Tony Dingman, Kelli Nerem, Jerry Flom, Mike Walerak, Stacia Grayson, Stacia Grayson *Metropolitan Council*: Joe Mulcahy, Emily Resseger, Karen Jensen, and Ann Krogman

MSU Water Resources Center: Scott Matteson

GIS analysis and mapping: Tom Pearson and Shawn Nelson

### Introduction

In the previous chapter, monitoring-based nitrogen (N) loads along the Mississippi, Minnesota, St. Croix, and Red Rivers were described. In this chapter, we examine monitoring-based N loads at a smaller watershed scale, mostly looking at the 8-digit Hydrologic Unit Code watershed scale (HUC8 watersheds). The monitoring data analyzed in this chapter was collected between 2005 and 2009, with most of the data collected between 2007 and 2009. The first section describes all results collected through the Minnesota Pollution Control Agency (MPCA) Watershed Pollutant Load Monitoring Network between 2007 and 2009. The second section of this chapter focuses on the results in 28 watersheds which are best suited for making comparisons of watershed N yields and flow weighted mean concentrations (FWMCs) across the state.

### Watershed Pollutant Load Monitoring Network

The Watershed Pollutant Load Monitoring Network (WPLMN) is a multi-agency effort led by the MPCA to measure and compare regional differences and long-term trends in water quality among Minnesota's major rivers including the Red, Rainy, St Croix, Minnesota, and Mississippi and the outlets of major HUC8 tributaries draining to these rivers. The network was established in 2007 following passage of Minnesota's Clean Water Legacy Act with subsequent funding from the Clean Water Fund of the Minnesota Clean Water, Land and Legacy Amendment. Site specific stream flow data from United States Geological Survey (USGS) and Minnesota Department of Natural Resources flow gauging stations is combined with water quality data collected by the Metropolitan Council Environmental Services, local monitoring organizations, and MPCA staff to compute annual pollutant loads at river monitoring sites across Minnesota. The WPLMN is summarized at <a href="https://www.pca.state.mn.us/index.php/water/water-types-and-programs/surface-water/streams-and-rivers/watershed-pollutant-load-monitoring-network.html">https://www.pca.state.mn.us/index.php/water/water-types-and-programs/surface-water/streams-and-rivers/watershed-pollutant-load-monitoring-network.html</a>.

The WPLMN has been collecting water quality at an increasing number of locations since 2007, reaching 79 monitoring sites by 2010. The design scale is focused toward, but not limited to, monitoring HUC8 watershed outlets within the state. Strategic major river mainstem sites are included to determine basin loads and assist with statewide mass balance calculations.

Intensive water quality sampling occurs year round at all WPLMN sites. Thirty to 35 mid-stream grab samples are collected annually at each site, with sampling frequency greatest during periods of moderate to high flow (Figure 2). Because correlations between concentration and flow exist for many of the monitored analytes, and because these relationships can shift between storms or with season,

computation of accurate load estimates requires frequent sampling of all major runoff events. Low flow periods are sampled less frequently as concentrations are generally more stable when compared to periods of elevated flow. Despite discharge related differences in sample collection frequency, this staggered approach to sampling generally results in samples being well distributed over the entire range of flows. Annual water quality and daily average discharge data were coupled in the "Flux32" pollutant load model, originally developed by Dr. Bill Walker and recently upgraded by the U.S. Army Corp of Engineers and the MPCA, to create concentration/flow regression equations to estimate pollutant concentrations and loads on days when samples were not collected. Primary output includes annual and daily pollutant loads and flow weighted mean concentrations (pollutant load/total flow volume). Loads and flow weighted mean concentrations are calculated annually for total suspended solids (TSS), total phosphorus (TP), dissolved orthophosphate (DOP), nitrate plus nitrite nitrogen (NO3+NO2-N) and total Kjeldahl nitrogen (TKN). The NO3+NO2-N is added to TKN to represent total nitrogen (TN).

### Normalizing the loads

Nitrogen loads are influenced by land use, land management, watershed size, hydrology, climate, and other factors. Watershed size greatly influences loads; therefore, when comparing watersheds across a region or state, it is often useful to normalize the results based on watershed size. The "yield" accomplishes this, as the yield is the mass per unit area of a constituent coming out of a watershed during a given time period (i.e., pounds/acre/year). Yield is determined by simply dividing the annual load by the watershed size. In this report all yields are reported in the unit of pounds per acre per year. If all things are equal between two watersheds except flow volume, the watershed recording twice the annual discharge volume will record twice the yield. The yield is a particularly useful parameter when watersheds are being evaluated for their effects on downstream water bodies impacted by high loads.

Another way of normalizing load data for both spatial and volumetric differences between watersheds is by assessing the FWMC. The FWMC is calculated by dividing the total load (mass) for the given time period by the total flow volume. It refers to the average concentration (mg/L) of a particular pollutant per unit volume of water. The FWMC allows for the direct comparison of water quality between watersheds regardless of watershed size or annual discharge volume.

Watershed annual N yields and FWMCs were both used in this study for making comparisons of watersheds across the state.

#### Results

For this report, annual loads, yields, and flow weighted mean concentrations were available for 2007, 2008, and 2009, but data from all three years were not available for all sites. Average annual TKN, TN and nitrite+nitrate-N yields and FWMCs for the period 2007 to 2009 are shown in Figures 1 to 6. The average watershed N levels in each of the Figures 1 to 6 represent a mix of results which include results from:

- one, two, or three years of monitoring
- independent HUC8 watersheds affected only by land and rivers within the HUC8, along with other HUC8s influenced by main stem rivers and other upstream rivers
- low, normal, and high flow conditions as they naturally occurred in this three year period (i.e., some watersheds include mostly dry years;, whereas, other watersheds represent an average of high precipitation years)

The resulting FWMC and yield maps for nitrite+nitrate-N and TN (Figures 1 to 4) show a strong spatial pattern of higher TN and nitrite+nitrate-N in southern Minnesota watersheds, particularly those in south-central Minnesota, and lower N in northern Minnesota watersheds. Some watersheds in southern

Minnesota do not fit the pattern of higher loads or concentrations because they are affected (diluted) by upstream lower N concentration waters (see for example Minnesota River Yellow Medicine, Minnesota River Mankato, Mississippi River Lake Pepin, and Mississippi River Winona).

Total Kjeldahl nitrogen FWMC and yield maps (Figures 5 and 6) at the outlets of all monitored HUC8 level watersheds show generally lower levels compared to nitrite+nitrate-N and are more spatially variable across the state. Sources of organic N can be natural, from human-induced sources and land alterations, or from biological processes (i.e., algae growth) which transform nitrate into organic N.

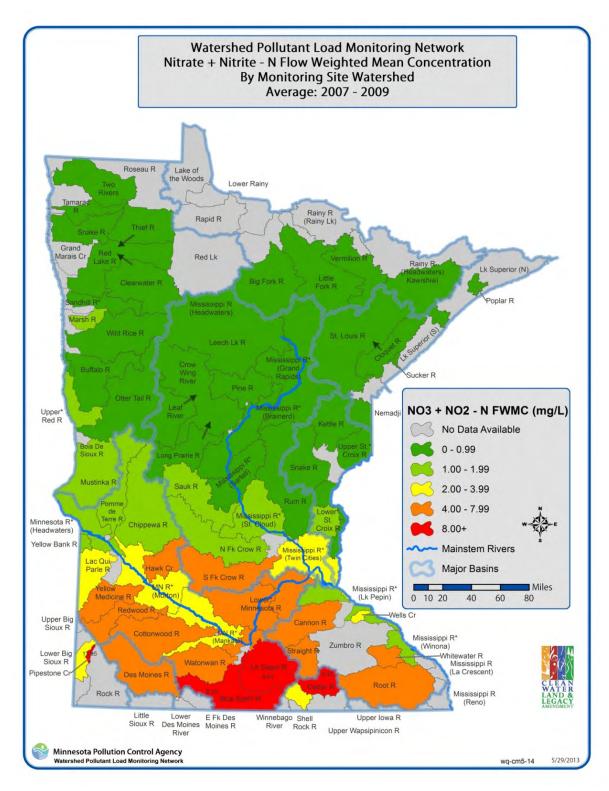


Figure 1. Nitrate+Nitrite-N flow-weighted mean concentrations near the outlet of watersheds. Average of available annual information between 2007-2009 (one to three year average for each watershed).

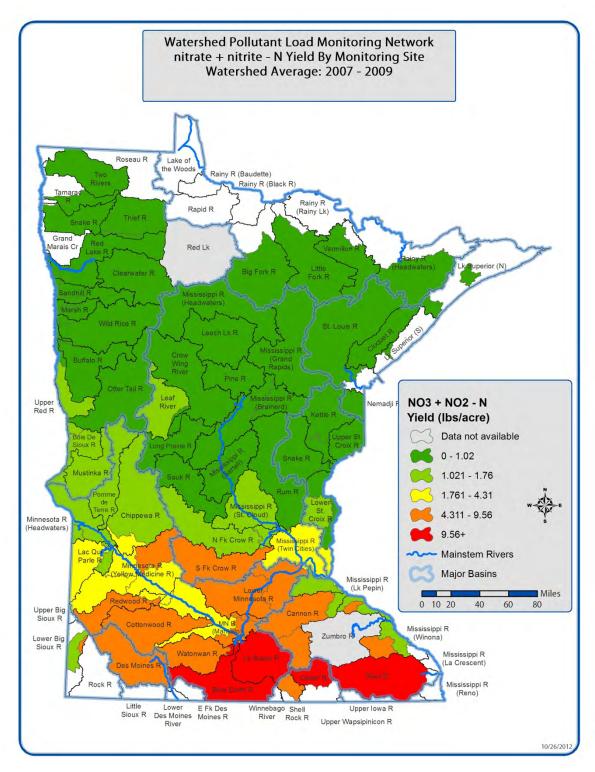


Figure 2. Nitrate+Nitrite-N yields based on monitoring near the outlet of each watershed. Average of available annual information between 2007-2009 (one to three year average for each watershed).

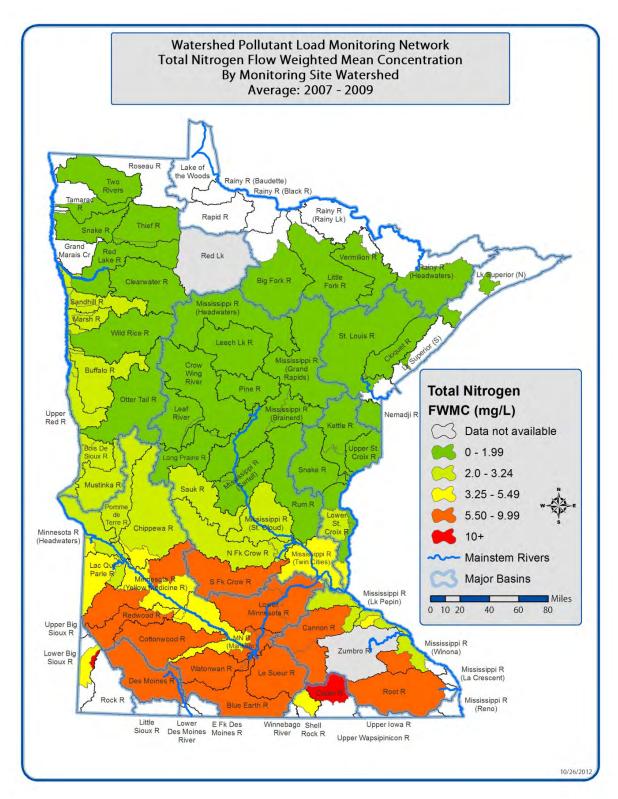


Figure 3. TN flow-weighted mean concentrations near the outlet of watersheds. Average of available annual information between 2007-2009 (one to three year average for each watershed).

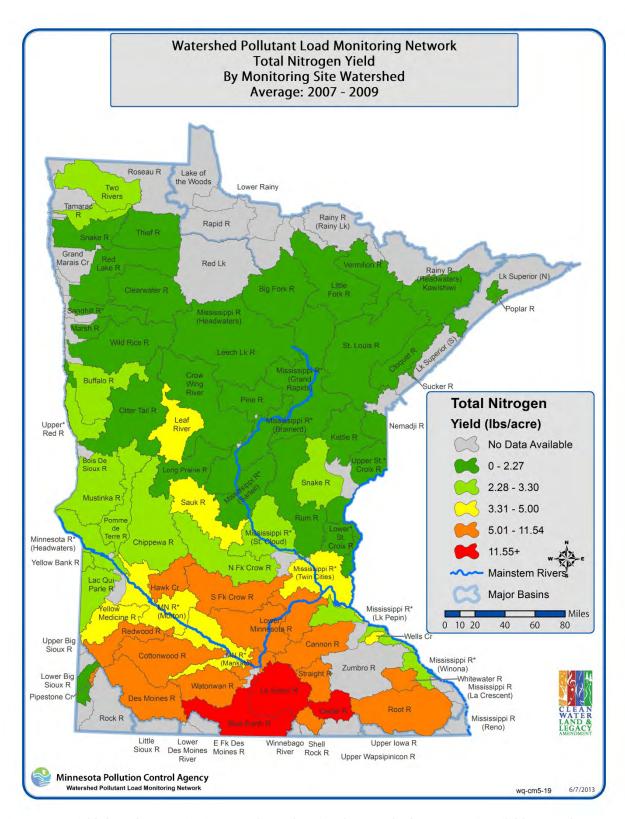


Figure 4. TN yields based on monitoring near the outlet of each watershed. Average of available annual information between 2007-2009 (one to three year average for each watershed).

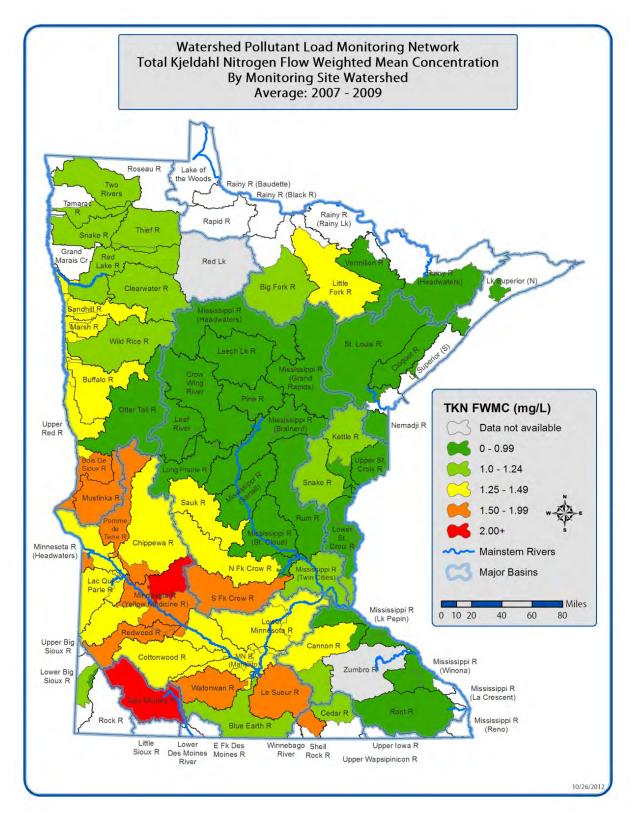


Figure 5. TKN flow-weighted mean concentrations based on monitoring near the outlet of each watershed. Average of available annual information between 2007-2009 (one to three year average for each watershed).

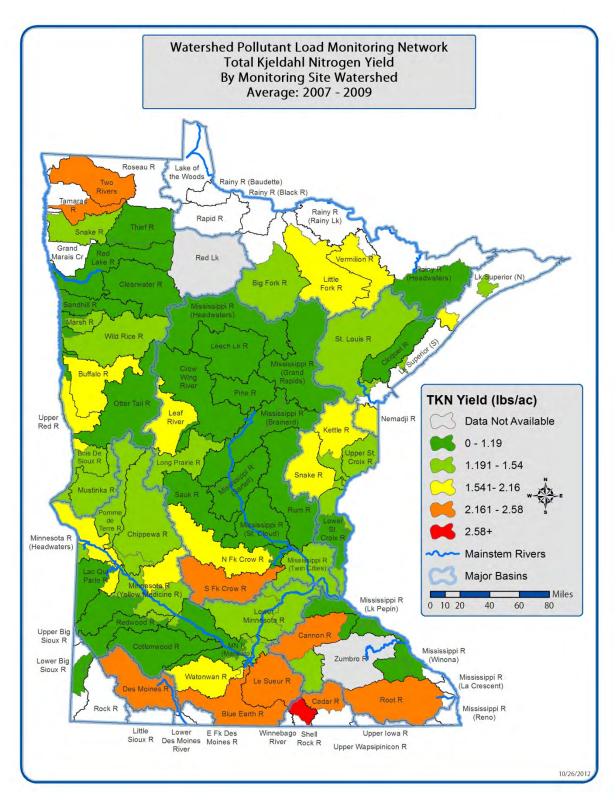


Figure 6. TKN yields based on monitoring near the outlet of each watershed. Average of available annual information between 2007-2009 (one to three year average for each watershed).

Watersheds which are intersected by a main-stem river (shown in Figure 7), such as the Minnesota River (Yellow Medicine), Minnesota River (Mankato), and Mississippi River (Twin Cities), have yields and concentrations influenced by upstream watersheds. Therefore, the results in these watersheds do not reflect N levels from only within the HUC8 watershed, but are a mix of the local inputs and upstream inputs. In many cases, the downstream watersheds along mainstem rivers are diluted by upstream incoming waters and, therefore, show a lower N level as compared to surrounding HUC8 watersheds which are not diluted by upstream waters.

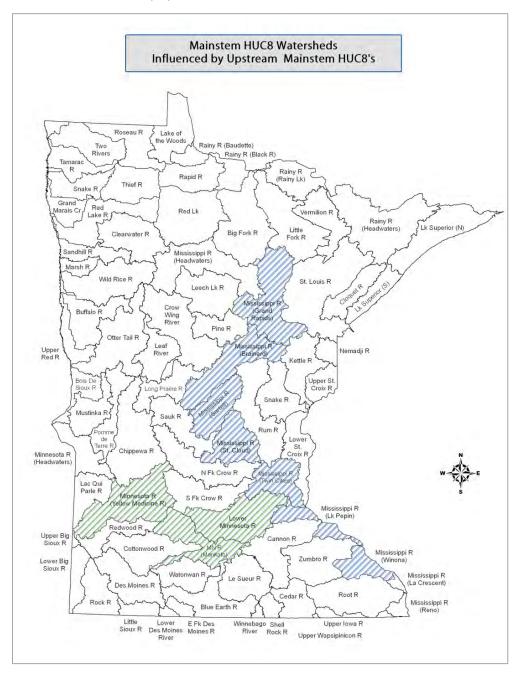


Figure 7. HUC8 Watersheds with Mississippi and Minnesota Rivers flowing through them, and are thereby influenced from land not only within the HUC8 contributing area, but also by additional upstream watersheds. HUC8 watersheds along the Mississippi watersheds and Minnesota River HUC8 watersheds are shown in blue and green, respectively.

#### Independent HUC8 watershed loads (mid-range flow averages)

As noted in the previous section, the yields and FWMCs for Figures 1 to 6 represent results from one to three years of monitoring depending on the availability of data from the developing WPLMN program. To enable a more uniform comparison between watersheds across the state, a subset of watersheds was selected for further analysis. The subset of watersheds was selected to remove variability due to the number of years of data and extreme climatic conditions (extreme low and high flows). The subset of watersheds also excluded HUC8 watershed monitoring sites influenced by upstream watersheds. Yields and FWMCs for this analysis were computed for independent watersheds using two years of data collected during years of mid-range flows within the 2005–2009 timeframe. Normal flows for the South Fork Crow River, Cannon River, and Root River occurred in the 2005-2006 timeframe, prior to the start of the WPLMN and, therefore, data from these three watersheds were used from Metropolitan Council and the USGS.

The years 2005-2009 had some extremely high and low river flow conditions. The year(s) when these high and low flows occurred varied for different regions of the state. When comparing watershed loads and yields measured over shorter periods of time, it is important to reduce the influence of year-to-year climate variability by comparing years with reasonably similar river flow regimes. Thus, the results described below represent monitoring-based loads, yields and flow weighted mean concentrations derived from two-year averages using recent years (2005-2009) when flow was in the normal range (between the 25<sup>th</sup> and 75<sup>th</sup> percentile) and avoiding years of extremes. The two-year periods representing these mid-range flows were as follows for the different regions of the state:

Northwest Minnesota: 2007 and 2008

Southwest and South Central Minnesota: 2007 and 2008

Northeast Minnesota: 2008 and 2009 Southeast Minnesota: 2005 and 2006

We also checked to see how closely the two-year average loads compared to longer term (7-18 year) load averages at 11 sites which had the additional load data available. We found that the two-year averages were closely correlated with the longer term averages, giving us greater confidence that the two-year averages provided representative loads for making geographic comparisons.

The two-year nitrite+nitrate-N and TN average annual yields and FWMCs are shown in Figures 8 to 11 for each independent HUC8 watersheds which were sampled during the two-year normal flow periods between 2005 and 2009. The results show a very similar spatial pattern across the state of high and low N watersheds as Figures 1 to 6, which were developed using one-three year averages during a wider range of river flow conditions. The highest yields and FWMCs were in the southern part of the state, particularly south-central Minnesota, whereas the northern Minnesota watersheds had consistently low N yields and concentrations.

## Nitrite + Nitrate-N Yield

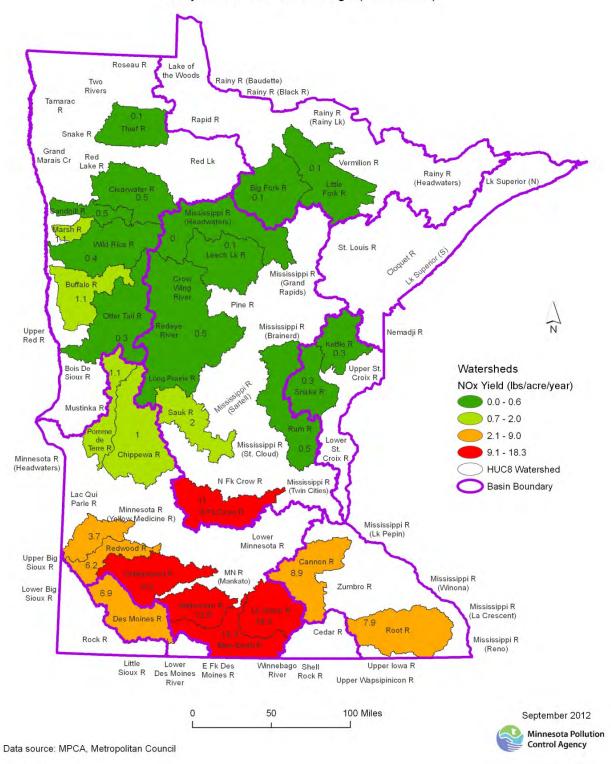


Figure 8. Two-year average Nitrite+Nitrate-N (NOx) yields during normal flow periods between 2005 and 2009.

#### Nitrite + Nitrate-N Flow Weighted Mean Concentration

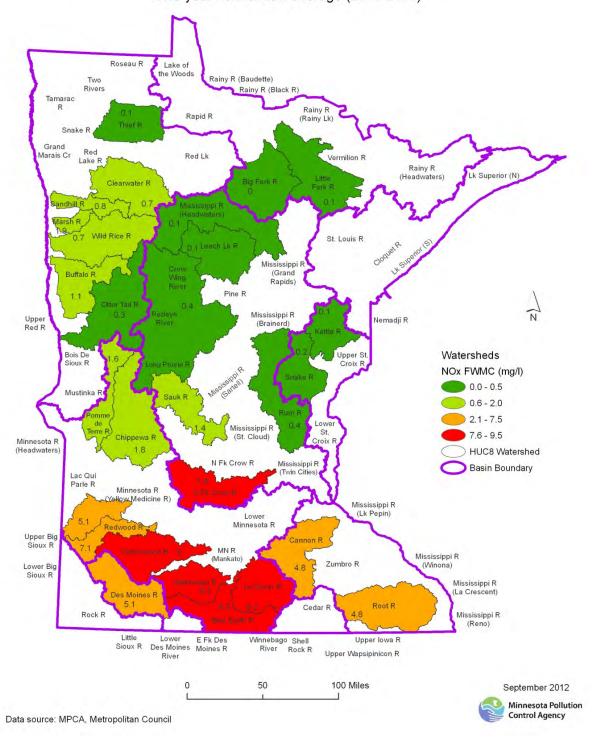


Figure 9. Two-year average Nitrite+Nitrate-N (NOx) FWMC during normal flow periods between 2005 and 2009.

### **Total Nitrogen Yield**

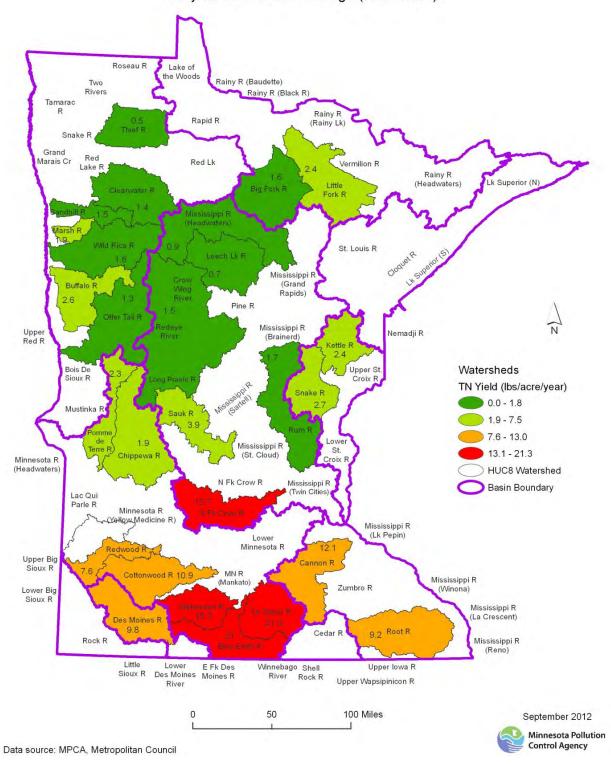


Figure 10. Two-year average TN yields during normal flow periods between 2005 and 2009.

#### **Total Nitrogen Flow Weighted Mean Concentration**

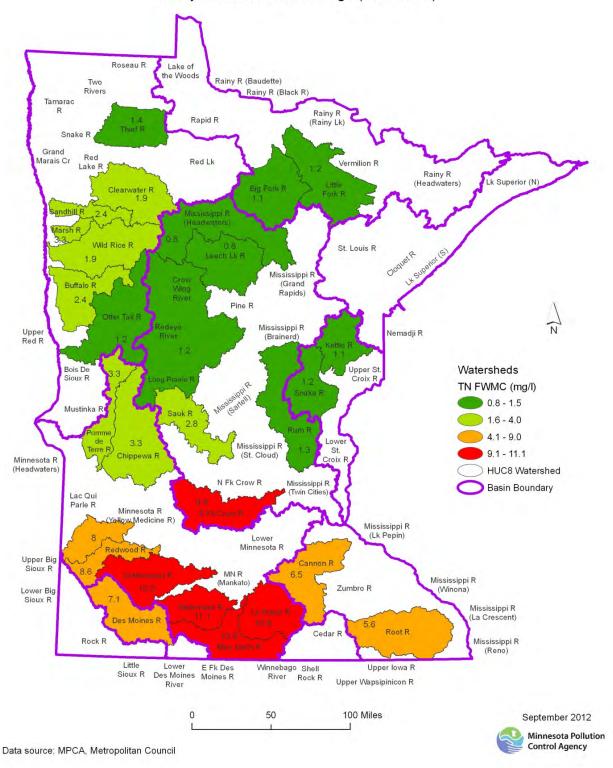


Figure 11. Two-year average TN FWMC during normal flow periods between 2005 and 2009.

## **Summary points**

- Monitoring during recent years is showing that the highest yields and concentrations of both nitrite+nitrate-N and TN are in south central Minnesota, where TN FWMCs generally exceed 10 mg/l and yields range from about 15 to 22 pounds/acre.
- The second highest parts of the state for nitrite+nitrate-N and TN concentrations and yields is southeastern and southwestern Minnesota, which have TN FWMCs in the 5-9 mg/l range and yields ranging from about 8-13 pounds/acre.
- Watersheds north of the Twin Cities have substantially lower nitrite+nitrate-N and TN concentrations, with TN FWMCs in northeastern Minnesota less than 1.5 mg/l and yields less than 2 pounds/acre. Total nitrogen levels are higher in the northwestern part of the state as compared to the northeast, ranging from about 1.5 to 4 mg/l FWMC and 1.5 to 4 pounds/acre yield.
- Exceptions to the high nitrate and TN river concentrations in southern Minnesota occur where river N is diluted by water with lower N coming from northern reaches of the river and flowing into southern watersheds.

## **B4. Modeled Nitrogen Loads (SPARROW)**

Authors: David Wall and Nick Gervino, MPCA

SPARROW model outputs and maps at the major basin and HUC8 watershed scales provided by: Dale M. Robertson and David A. Saad, U.S. Geological Survey, Wisconsin Water Science Center

#### **Purpose**

The SPAtially Referenced Regressions on Watershed attributes (SPARROW) model, developed and maintained by the United States Geological Survey (USGS), was used for this study to estimate Total nitrogen (TN) loads, yields, and flow-weighted mean concentrations (FWMC) in Minnesota 8-digit Hydrologic Unit Code (HUC8) watersheds and major basins. The model was also used to estimate TN contributions from different sources in Minnesota and estimate the effects of reducing specific source contributions.

While Minnesota is fortunate to have an abundance of watershed monitoring data to assess spatial trends in loads around the state, SPARROW modeling results were also included in this study for several reasons, as noted below:

Loads for all watersheds available: Monitoring results are not available for all watersheds in the state. The SPARROW model provides an estimate of loads in all watersheds, including those not directly monitored. Monitoring-based loads which were not used in the model calibration can be used to validate the model, providing greater assurance that model results for non-monitored watersheds are reasonable. By having load estimates for all watersheds, statewide watershed prioritization and spatial comparison efforts are enhanced.

Load estimates are based on many years of sampling: For some watersheds, monitoring results are available for only one or two years. The SPARROW model is developed from longer term monitoring data sets, and therefore represents typical load results for each watershed which are less subject to extreme influences introduced through climate swings or error.

**Incremental loads available**: The SPARROW model allows estimates of incremental river load contributions from individual watersheds, even though the watersheds have other streams flowing into or through the watershed.

**Delivered loads available**: The SPARROW model provides estimates of contributing loads from different watersheds to a selected downstream delivery point such as a state border or confluence with other rivers. In-stream losses are thereby accounted for.

Land use contributions: The SPARROW model provides N categorical load estimates. These results were compared to results from the N source assessment discussed in Chapters D1-D5 of this report to serve as one of several ways to verify the N source assessment results.

#### Overview of SPARROW model

The SPAtially Referenced Regressions on Watershed attributes (SPARROW) watershed model integrates water monitoring data with landscape information to predict long—term average constituent loads that are delivered to downstream receiving waters. The SPARROW models are designed to provide information that describes the spatial distribution of water quality throughout a regional network of stream reaches. SPARROW utilizes a mass-balance approach with a spatially detailed digital network of streams and reservoirs to track the attenuation of nutrients during their downstream transport from each source. Models are developed by statistically relating measured stream nutrient loads with geographic characteristics observed in the watershed [Preston et al., 2011a]. A geographical information system (GIS) is used to spatially describe pollutant sources and overland, stream, and reservoir transport.

The statistical calibration of SPARROW helps identify which nutrient sources and delivery factors are most strongly associated with long-term mean annual stream nutrient loads. The mass-balance framework and spatial referencing of the model provides insight to the relative importance of different contaminant sources and delivery factors. The networking and in-stream aspects of SPARROW enable the downstream loads to be apportioned to the appropriate upstream sources [Preston et al., 2011a]. SPARROW results can be used to rank sub-basins within the larger tributary watersheds and describe relative differences in the importance of nutrient sources among sub-basins.

The process for calibrating SPARROW models is designed to provide an identification of the factors affecting water quality and their relative importance through the combined use of a mechanistic model structure and statistical estimation of model coefficients.

The USGS National Water Quality Assessment program developed 12 SPARROW watershed models for six major river basins in the continental United States. Nutrient estimates for Minnesota were based upon the SPARROW Major River Basin 3 (MRB3) model developed by Robertson and Saad (2011). The MRB3 model for TN was based on data from 708 monitoring stations located throughout North Dakota, Minnesota, Wisconsin, Michigan, Iowa, Illinois, Missouri, Indiana, Ohio, Kentucky, Tennessee, West Virginia, Pennsylvania, and New York. Water quality data from 1970 to 2007 were used to estimate long-term detrended loads (to 2002) at each site. The SPARROW TN model for the Upper Midwest (Robertson and Saad, 2011) incorporates five different nutrient sources, five climatic and landscape factors that influence delivery to streams, and nutrient removal in streams and reservoirs.

More information about the SPARROW model, and specifically the MRB3 modeling effort, can be found in Robertson and Saad (2011) and in Appendix B4-1.

## Delivered total nitrogen load and yield results

#### Major basins

Major basins in Minnesota, as represented by SPARROW model catchments, are depicted in Figure 1. A small fraction of SPARROW catchments extend into neighboring states or Canada. The portion of the Missouri River Basin in the southwestern corner of the state was not part of the MRB3 modeling effort.

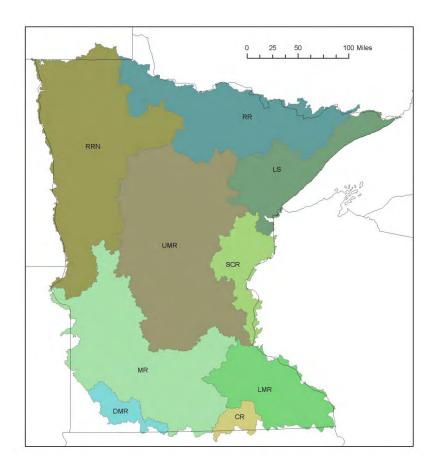


Figure 1. Minnesota Major Basins as represented by SPARROW Catchments. RRN (Red River of the North); UMR (Upper Mississippi River); RR (Rainy River); LS (Lake Superior); SCR (St. Croix River); LMR (Lower Mississippi River); MR (Minnesota River); DMR (Des Moines River); CR (Cedar River).

SPARROW model estimates of TN loads and yields delivered to the outlets of Minnesota's major basins are shown in Table 1 and Figures 2 and 3. In situations where the major river in the basin leaves the state before reaching the outlet of the basin, the SPARROW results in Table 1 and Figures 2 and 3 only include the N loads at the state boundary.

The highest N-yielding basins are the Cedar River and Minnesota River Basins, followed by the Lower Mississippi River Basin in southeastern Minnesota. The Minnesota River Basin had the highest N loads, contributing about half of Minnesota's N load into the Mississippi River. Total nitrogen yield for the entire Minnesota River Basin is 13.3 pounds/acre/year. By comparison, the low-yielding basins, such as the Rainy and Lake Superior Basins had TN loads of 0.8 and 1.8 pounds/acre/year.

Table 1. SPARROW model estimated TN loads and yields at the major basin outlets.

Basin	SPARROW load (lbs) at basin outlet or state border - MN contribution only (TN)	SPARROW <b>yield</b> (lbs/acre) at basin outlet or state border - MN contribution only (TN)
Lake Superior	7,153,338	1.8
Upper Mississippi River	55,451,315	4.3
Minnesota River	127,206,486	13.1
St. Croix River	7,583,476	3.3
Lower Mississippi River	47,264,258	11.7
Cedar River	14,902,044	22.7
Des Moines River	9,887,368	10.4
Red River of the North	37,216,336	3.2
Rainy River	5,737,840	0.80

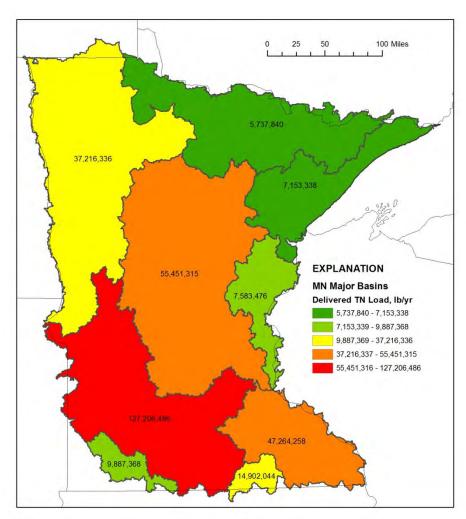


Figure 2. Total nitrogen load from each major basin in pounds/year. The basin loads represent the sum of the delivered incremental loads for each of the SPARROW (MRB3 2002) catchments, where the delivery targets are the basin outlets or state border.

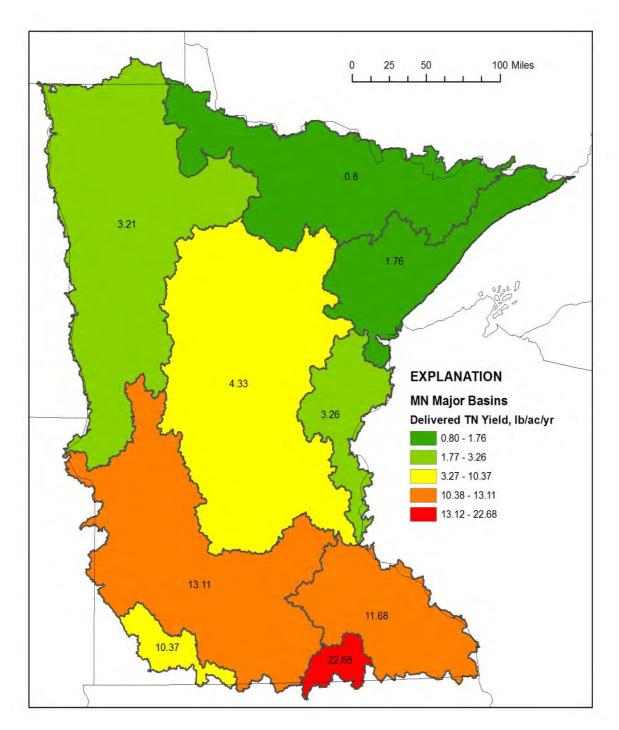


Figure 3. Annual TN yield results by major basin in pounds/acre/year. The basin yields represent the total load delivered to the basin outlet or state border divided by the sum of the SPARROW (MRB3) catchment areas.

Several of the major basins in Minnesota have large areas which extend into neighboring states or Canada. For example, nearly half of the St. Croix Basin lies in Wisconsin and over half of the Red River Basin flowing out of the United States lies in North Dakota. Loads from these areas are not reflected in the model results shown above. The SPARROW mapper tool was used by the MPCA to estimate the amount of N delivered from catchments in these neighboring states (Table 2). The results indicate that St. Croix River TN loads coming into Stillwater, Minnesota, are nearly half from Minnesota (52.2%) and nearly half from Wisconsin (47.8%).

Table 2. Estimated fraction of N coming from Minnesota and neighboring state catchments.

Basin or Watershed	Minnesota Load	Neighboring states load
Minnesota River Basin	96.0%	4.0%
Red River Basin (at Canadian Border)	47.6%	52.4%
St. Croix River Basin (at Stillwater)	52.2%	47.8%
Lower Mississippi River Basin (between Red Wing, MN and Victory, WI at the Iowa Border)	39.3%	60.7%
Blue Earth Watershed at confluence with Watonwan River	81.0%	19.0%

#### **HUC8** watersheds

The SPARROW model was used to estimate HUC8 watershed TN loads at the delivery point of the outlet of the watershed (or near the state boundary where watershed boundaries are cut off by state boundaries). This delivery point only incorporates N losses which occur within the HUC8 watershed. Other model scenarios using different delivery points are discussed later.

The modeled load results at the HUC8 outlets (spacial scheme 1) are shown in Figure 4. The annual loads are directly related to watershed size, with larger watersheds producing higher loads than smaller watersheds with equal yields. If everything else but watershed size is equal, the larger watersheds will have higher loads than the smaller watersheds. Annual yields are a better means to describe the spatial differences in amounts of N being delivered to waters across the state. SPARROW TN yields are shown in Figure 5.

The south-central portion of the state has the highest N yields, with 15-25 pounds/acre/year. The Mississippi River Twin Cities watershed also has a high yield, with 17.4 pounds TN/acre/year delivered to the outlet of the watershed. Most northern Minnesota watersheds yield between 0.1 and 3 pounds/acre, with the exception of watersheds along the Red River, which yield 4-6 pounds TN/acre/year.

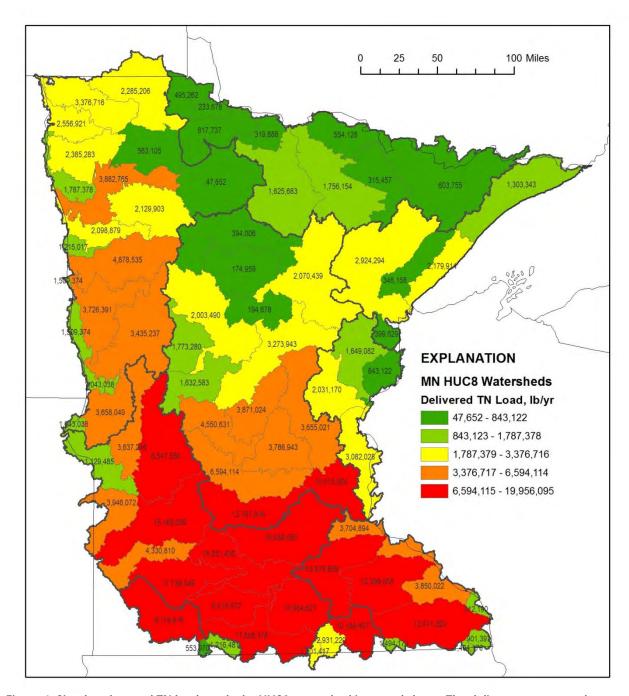


Figure 4. Simulated annual TN load results by HUC8 watershed in pounds/year. The delivery targets are the watershed outlets (or state border where watersheds are divided by a state border).

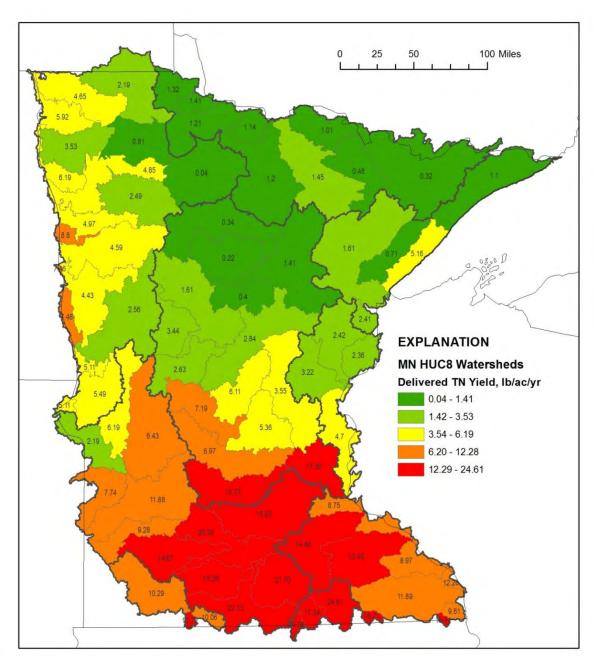


Figure 5. Simulated annual TN yield by HUC8 watershed in pounds/acre/year. Basin yields represent the total load delivered to the watershed outlet (or state border for watersheds straddling the state border) divided by the sum of the catchment area.

The flow-weighted mean TN concentrations generally had a similar pattern as the TN yield map, with the south-central watersheds having the highest concentrations (Figure 6). The FWMC represents the load/flow, whereas yield represents load/area. While the FWMC and yield maps should have many similarities, they are not expected to be identical. The SPARROW FWMC map does not show the FWMCs for the entire HUC8, but rather shows the median of FWMCs of all of the smaller subwatersheds within the HUC8. Therefore, in HUC8 watersheds, such as the Mississippi River Twin Cities, where large loads from the wastewater treatment plant discharge in a single small subwatershed, the median subwatershed FWMC does not accurately portray the true FWMC that would be measured at the HUC8 outlet.

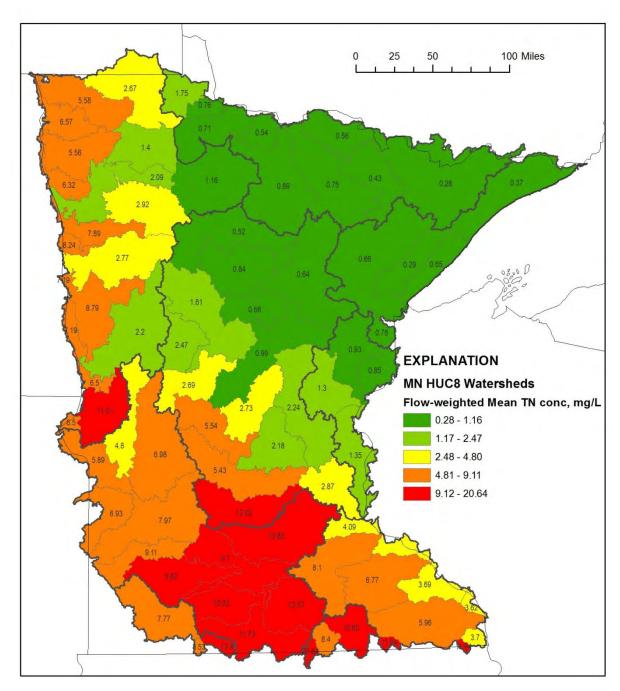


Figure 6. SPARROW flow-weighted mean TN concentration by HUC8 watersheds. The value represents the median FWMC of all subwatershed catchments within the HUC8 watersheds.

#### Subwatershed yields

Total nitrogen yields were also estimated for the SPARROW subwatershed outlets (Figure 7). The results indicate that there can be N yield variability within the same HUC8 watershed. Some subwatersheds stand out as being particularly high N yielding watersheds, surrounded by much lower yielding watersheds. These "islands" of high yields typically reflect metropolitan wastewater discharges from large urban areas such as the Twin Cities, Duluth, and Rochester. When the point sources are removed from the analysis, then the red and orange islands for Minneapolis, Duluth, and Rochester are not visible (Figure 8).

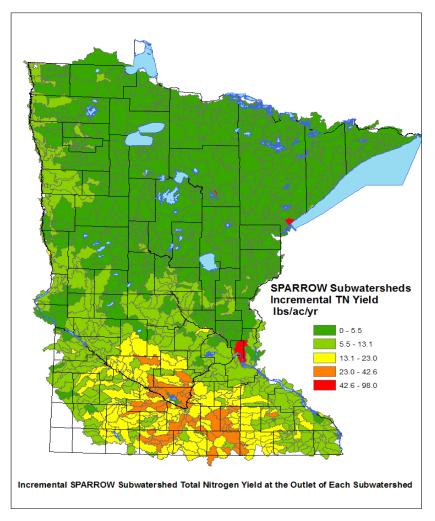


Figure 7. Total nitrogen yield for each SPARROW subwatershed, including both point and nonpoint sources of N delivered to the subwatershed outlet.

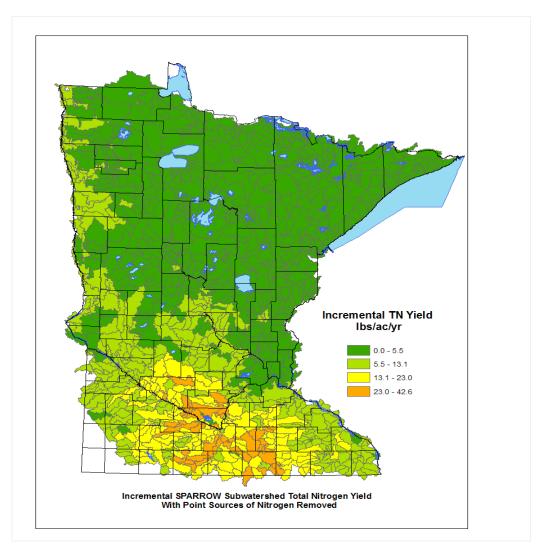


Figure 8. Total nitrogen yield for each SPARROW subwatershed watershed with urban wastewater point sources removed from the analysis. TN delivered to the subwatershed outlet.

## Comparing SPARROW and recent monitoring load estimates

The SPARROW model is developed from monitoring results at numerous long-term monitoring stations, and the model is validated with independent monitoring stations. We decided to further validate the model results by comparing the SPARROW HUC8 load estimates at the watershed outlets to 29 recent monitoring-based load estimates. The monitored loads used for the comparisons were not used in the development of the SPARROW model, and thus provide an independent comparison of the general relationship between SPARROW model and short-term monitoring-based load and yield averages.

The monitoring-based estimates used for the comparisons represent two-year averages from years when flow was not high or low, with neither year in the upper or lower quartile of historical annual river flow. The years used to represent typical flows for the different regions of the state were:

- Northwest Minnesota: 2007 and 2008 (2009 was a high flow year)
- Southwest and South Central Minnesota: 2007 and 2008 (2009 was a low flow year)
- Northeast Minnesota: 2008 and 2009 (2007 was a low flow year)
- Southeast Minnesota: 2005 and 2006 (2007 was high flow; 2008 varied; 2009 low flow)

Plots of the HUC8 monitored loads verses the HUC8 SPARROW loads showed good correlation, with an R-squared of 0.85 (Figure 9). While most of the HUC8 SPARROW and monitored watersheds were in reasonably close agreement, there are a few outliers. The monitoring-based loads have a range of uncertainty largely because the monitoring-based loads represent an average of only two years of data, each year having different annual and seasonal precipitation scenarios.

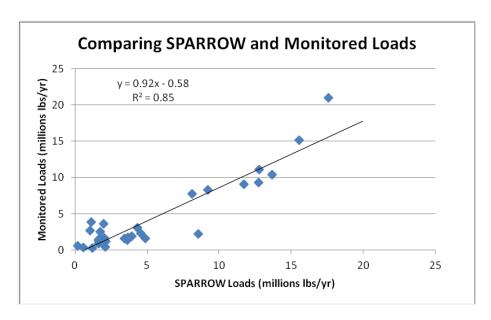


Figure 9. HUC8 watershed outlet SPARROW modeled loads plotted against monitoring-based load estimates developed from the average of two typical flow years between 2005 and 2009.

SPARROW loads were higher in the northwestern part of the Minnesota River Basin than the monitoring-based loads. The Pomme de Terre watershed SPARROW loads were 3.6 million pounds/year, compared to 1.3 million pounds/year from the 2007-08 monitoring-based average.

The Chippewa watershed SPARROW loads were 8.5 million pounds/year, whereas the 2007-08 monitoring average was 2.2 million pounds/year. The 2007-08 monitoring results are somewhat lower for the Chippewa than the estimated loads calculated over the entire period between 2000 and 2008, which averaged 3 million pounds/year. Nonetheless, the SPARROW loads for the Chippewa River remain considerably higher than the monitoring-based loads. The SPARROW model also predicted substantially higher loads in the Red River Basin, as compared to 2007-08 monitoring-based averages. The long-term average SPARROW results for the Buffalo, Wild Rice River, and Sandhill River were more than double the monitoring-based average for the two years.

A comparison of the SPARROW yields with monitoring-based yield averages shows a slightly improved correlation compared to the loading correlation, with an R-squared of 0.90 (Figure 10). The yield correlation is expected to be better than the load correlation, since the monitoring and modeled watershed catchment areas are different for many of the watersheds, and these differences are largely normalized with yields (in pounds per watershed acre per year). Overall, SPARROW yields are higher than the two year monitoring-based average yields.

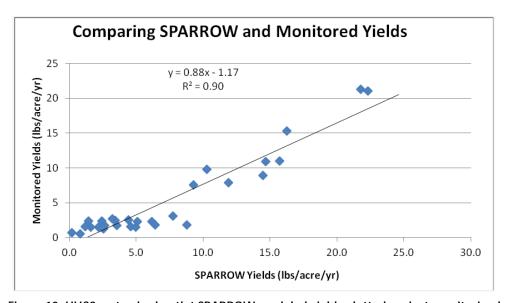


Figure 10. HUC8 watershed outlet SPARROW modeled yields plotted against monitoring-based load estimates from the average of two typical flow years between 2005 and 2009.

In summary, neither the model or two-year monitoring-based results are an exact representation of actual long term loads. However, the fact that these independently derived sources of load information correlate well gives us greater confidence that both the model results and monitoring results are providing reasonable estimates of watershed N loads in most watersheds.

#### Total nitrogen delivery to downstream waters

#### Nitrogen delivery between HUC8 watershed outlets and various downstream delivery points

In addition to examining SPARROW results at the outlet of each HUC8 watershed, the SPARROW model results were determined for two additional delivery points. These downstream points account for TN losses expected to occur as the river flows downstream. Delivery from an upstream reach to a downstream reach in the model (MRB3) is based on in-stream first-order exponential N decay, occurring as a function of three variables: travel time, streamflow (serving as a surrogate for channel depth), and the presence or absence of a reservoir. Stream N decay is not simulated for reach flow rates greater than 70 cubic feet per second. Reservoir loss is based upon the overflow rate of the reservoir (average outflow rate divided by surface area). Only reservoirs listed in the National Inventory of Dams are included in the MRB3 model, which resulted in the inclusion of 136 reservoirs in Minnesota.

The following additional schemes were examined to incorporate estimated N losses occurring after leaving the output point of the HUC8 watershed:

Delivery Scheme 2 -Loads delivered from individual HUC8 watersheds to the state boundaries, including the Canadian border for the Red River and Roseau River, Lake Superior, and the Minnesota/Iowa border (De Soto, Iowa) for watersheds draining through Minnesota into the Mississippi River. Watersheds in the Des Moines and Cedar River Basins were not included because rivers from these areas leave Minnesota before reaching the Mississippi River. This delivery point incorporates all losses within HUC8 watersheds and all losses in rivers between the HUC8 outlets and the state borders.

Delivery Scheme 3 - Loads delivered from individual HUC8 watersheds to the Canadian border and Lake Superior in the northern part of the state and the Mississippi River in southern lowa (Keokuk) for all watersheds draining into the Mississippi River. Keokuck, Iowa is at a point where water from the Des Moines and Cedar Rivers has entered the Mississippi River. Scheme 3 is similar to Scheme 2, but includes a delivery target which is further downstream on the Mississippi River. Since some N losses occur within the Mississippi River between De Soto, Iowa and Keokuk, Iowa, the delivered loads for Scheme 3 will be lower than Scheme 2 for all watersheds draining into the Mississippi River.

Results for all three schemes (different delivery points) are summarized in Table 3. The patterns in loads and yields for Schemes 2 and 3 are generally similar to the loads and yields at the HUC8 outlets. Nitrogen losses between the HUC8 outlet and the state border are between 10 and 16% for a majority of watersheds. Yet, in-river N loss estimates were about 34% for watersheds which have lengthy flow paths between the HUC8 watershed outlets and state border, such as in the Pomme de Terre and Lac Qui Parle in the Minnesota River Basin, and the Mississippi Headwaters and Leech Lake River in the Upper Mississippi River Basin. SPARROW results indicate that the statewide net N loss between the HUC8 outlets and the state borders is 9.7%.

If we only consider those watersheds which drain to the Mississippi River (thus excluding the Red River, Lake Superior, and Rainy River Basins), the net N loss between the outlets and the state border in De Soto, Iowa (near the Minnesota border) is 10.0%, and net loss increases to a total of 20.1% between HUC8 outlets and the Mississippi River in Southern Iowa (Keokuk). Therefore, the SPARROW model results indicate that about an additional 10% of the TN is lost in the Mississippi River along the length of the Iowa border between Minnesota and Missouri.

Table 3. SPARROW modeled delivered loads and yields for Minnesota HUC8 watersheds.

HUC8 Name	HUC8#	SPARROW load at watershed outlet (TN lbs/yr)	Sparrow yield at watershed outlet (TN lbs/acre)	SPARROW delivered load to state border (TN lbs/yr)	SPARROW delivered load. State border in Northern MN and Keokuk, Iowa for Mississippi R. (TN lbs/yr)
Lake Superior - North	04010101	1,303,343	1.1	1,303,343	1,303,343
Lake Superior - South	04010102	2,179,914	5.2	2,179,914	2,179,914
St. Louis River	04010201	2,924,294	1.6	2,924,294	2,924,294
Cloquet River	04010202	346,158	0.7	346,158	346,158
Nemadji River	04010301	399,629	2.4	399,629	399,629
Mississippi River - Headwaters	07010101	394,006	0.3	259,163	235,807
Leech Lake River	07010102	174,959	0.2	115,082	104,710
Mississippi River - Grand Rapids	07010103	2,070,439	1.4	1,774,866	1,614,914
Mississippi River - Brainerd	07010104	3,273,943	2.8	2,875,635	2,616,481
Pine River	07010105	194,678	0.4	166,886	151,846
Crow Wing River	07010106	2,003,490	1.6	1,754,041	1,595,966
Redeye River	07010107	1,773,280	3.4	1,484,104	1,350,356
Long Prairie River	07010108	1,632,583	2.6	1,366,351	1,243,215
Mississippi River - Sartell	07010201	3,871,024	6.1	3,404,125	3,097,343
Sauk River	07010202	4,550,631	7.2	4,001,762	3,641,121

HUC8 Name	HUC8#	SPARROW load at watershed outlet (TN lbs/yr)	Sparrow yield at watershed outlet (TN lbs/acre)	SPARROW delivered load to state border (TN lbs/yr)	SPARROW delivered load. State border in Northern MN and Keokuk, lowa for Mississippi R. (TN lbs/yr)
Mississippi River - St. Cloud	07010203	3,786,943	5.4	3,334,766	3,034,234
North Fork Crow River	07010204	6,594,114	7.0	5,806,749	5,283,441
South Fork Crow River	07010205	12,767,916	15.7	11,243,373	10,230,112
Mississippi River - Twin Cities	07010206	10,015,924	17.4	8,995,296	8,184,634
Rum River	07010207	3,655,021	3.6	3,218,596	2,928,534
Minnesota River - Headwaters	07020001	1,129,485	2.2	997,540	907,641
Pomme de Terre River	07020002	3,637,246	6.2	2,410,134	2,192,932
Lac Qui Parle River	07020003	3,946,072	7.7	2,614,770	2,379,125
Minnesota River - Yellow Medicine River	07020004	15,169,039	11.9	13,397,022	12,189,673
Chippewa River	07020005	8,547,556	6.4	7,549,047	6,868,722
Redwood River	07020006	4,330,810	9.3	3,824,893	3,480,191
Minnesota River - Mankato	07020007	18,251,430	20.4	16,119,333	14,666,648
Cottonwood River	07020008	11,739,549	14.7	10,368,158	9,433,772
Blue Earth River	07020009	17,608,376	22.3	15,551,400	14,149,897
Watonwan River	07020010	9,219,972	16.3	8,142,913	7,409,068
Le Sueur River	07020011	15,564,627	21.8	13,746,398	12,507,563
Lower Minnesota River	07020012	19,956,095	15.9	17,624,863	16,036,499
Upper St. Croix River	07030001	843,122	2.4	753,537	685,628
Kettle River	07030003	1,649,082	2.4	1,473,861	1,341,036
Snake River	07030004	2,031,170	3.2	1,815,350	1,651,750
Lower St. Croix River	07030005	3,082,028	4.7	2,767,967	2,518,516
Mississippi River - Lake Pepin	07040001	3,704,894	8.7	3,397,700	3,091,497
Cannon River	07040002	13,679,859	14.5	12,545,584	11,414,967
Mississippi River - Winona	07040003	3,850,022	9.0	3,719,674	3,384,455
Zumbro River	07040004	12,399,658	13.5	11,774,379	10,713,264
Mississippi River - La Crescent	07040006	912,190	12.3	897,794	816,884
Root River	07040008	12,741,029	11.9	12,539,952	11,409,843
Mississippi River - Reno	07060001	901,397	9.6	901,397	820,162
Upper Iowa River	07060002	1,494,170	16.7	1,487,777	1,353,697
Cedar River	07080201	10,169,407	24.6	10,169,407	9,596,892
Shell Rock River	07080202	2,931,220	17.3	2,931,220	2,818,827
Winnebago River	07080203	1,801,417	24.1	1,801,417	1,732,345
Des Moines River - Headwaters	07100001	8,116,918	10.3	8,116,918	7,079,337
Lower Des Moines River	07100002	553,970	12.8	553,970	483,156
East Fork Des Moines River	07100003	1,216,481	10.1	1,216,481	1,065,658

HUC8 Name	HUC8 #	SPARROW load at watershed outlet (TN lbs/yr)	Sparrow yield at watershed outlet (TN lbs/acre)	SPARROW delivered load to state border (TN lbs/yr)	SPARROW delivered load. State border in Northern MN and Keokuk, lowa for Mississippi R. (TN lbs/yr)
Bois de Sioux River	09020101	1,043,038	5.1	1,025,263	1,025,263
Mustinka River	09020102	3,658,049	5.5	629,665	629,665
Otter Tail River	09020103	3,435,237	2.6	3,376,696	3,376,696
Upper Red River of the North	09020104	1,509,374	7.5	1,491,545	1,491,545
Buffalo River	09020106	3,726,391	4.4	3,682,373	3,682,373
Red River of the North - Marsh River	09020107	1,215,017	8.8	1,204,886	1,204,886
Wild Rice River	09020108	4,878,535	4.6	4,820,908	4,820,908
Red River of the North - Sandhill River	09020301	2,098,879	5.0	2,082,969	2,082,969
Upper/Lower Red Lake	09020302	47,652	0.0	46,853	46,853
Red Lake River	09020303	3,882,765	4.8	3,836,901	3,836,901
Thief River	09020304	563,105	0.8	553,662	553,662
Clearwater River	09020305	2,129,903	2.5	2,104,744	2,104,744
Red River of the North - Grand Marais Creek	09020306	1,787,378	6.2	1,773,828	1,773,828
Snake River	09020309	2,385,283	3.5	2,367,201	2,367,201
Red River of the North - Tamarac River	09020311	2,556,921	5.9	2,556,921	2,556,921
Two Rivers	09020312	3,376,716	4.7	3,376,716	3,376,716
Roseau River	09020314	2,285,206	2.2	2,285,206	2,285,206
Rainy River - Headwaters	09030001	603,755	0.3	164,145	164,145
Vermilion River	09030002	315,457	0.5	90,610	90,610
Rainy River - Rainy Lake	09030003	554,128	1.0	234,682	234,682
Rainy River - Black River	09030004	319,888	1.1	319,888	319,888
Little Fork River	09030005	1,756,154	1.5	1,756,154	1,756,154
Big Fork River	09030006	1,625,683	1.2	1,625,683	1,625,683
Rapid River	09030007	817,737	1.2	817,737	817,737
Rainy River - Baudette	09030008	233,678	1.4	233,678	233,678
Lake of the Woods	09030009	495,262	1.3	495,262	495,262

#### Nitrogen delivery between subwatersheds and the Mississippi River or state borders

Further analysis was conducted to also incorporate losses in streams within the HUC8 and within the subwatersheds. The SPARROW model results indicate that over 90% of the N which leaves most subwatersheds remains in the water and is routed downstream to the Mississippi River (or state borders where subwatersheds are not a tributary to the Mississippi River) (Figure 11). Watersheds which lose more than 10% are typically those where lakes or reservoirs provide substantial N removal between the subwatershed outlet and the Mississippi River (or state border).

When we also consider SPARROW estimated losses within the subwatersheds, the fraction of N reaching the Mississippi River (or state border for non-tributaries to the Mississippi) is further reduced (Figure 12). Figure 12 illustrates the addition of the in-stream N losses occurring within the subwatersheds to the losses occurring after leaving the subwatersheds. The sum of these losses results in a 10 to 40% reduction of the delivery ratio in many of the source subwatersheds. Thus substantial N losses can occur in the smaller order streams within the subwatersheds.

A more thorough discussion of N losses within waters is included in Chapter B5 and associated appendices.

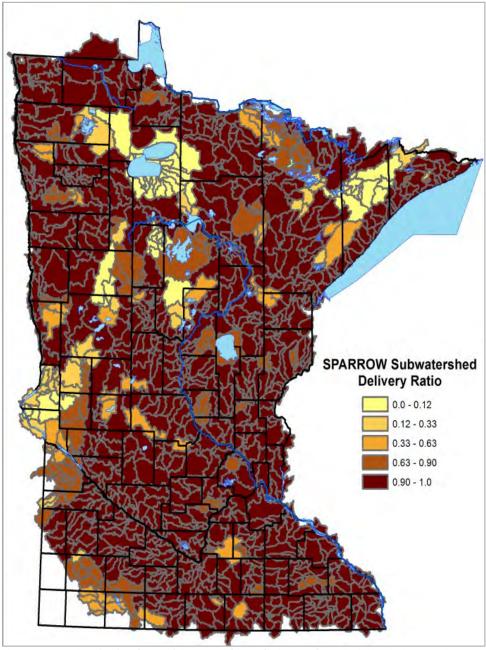


Figure 11. Ratio of N loads reaching state boundaries or the Mississippi River mainstem to N loads in waters leaving the SPARROW subwatersheds.

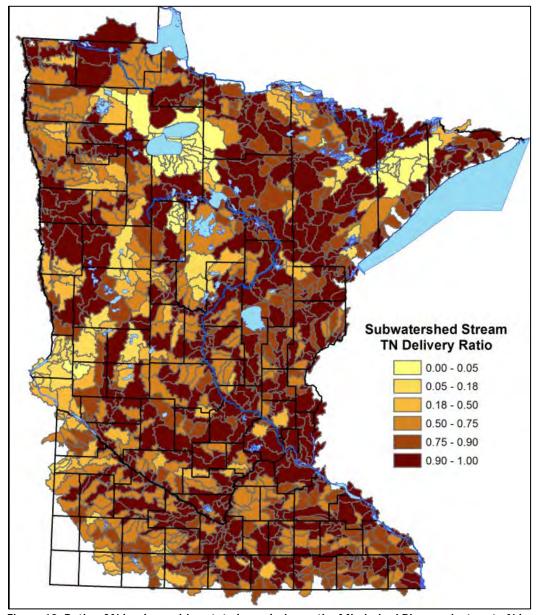


Figure 12. Ratio of N loads reaching state boundaries or the Mississippi River mainstem to N loads entering waters within the SPARROW subwatersheds. This figure includes in-stream losses within subwatersheds and within streams after leaving the subwatershed boundaries.

## Highest contributing HUC8 watersheds to the Mississippi River

The TN load delivered to Keokuk, Iowa, from HUC8 Minnesota watersheds is 219,509,000 pounds/year. Fifteen of the 45 watersheds draining into the Mississippi River from Minnesota each contribute over 3% of the modeled load delivered to the Mississippi River in southern Iowa (Keokuk) (Table 4 and Figure 13). Combined, these 15 watersheds contribute 73.7% of the TN load delivered to Keokuk from Minnesota (Figure 10). The watersheds with the highest loads are mostly located in south-central and southeastern Minnesota. The other 30 watersheds each contribute between 0 and 2.4% of the total load, and are thus considered relatively minor contributors. Note that the watersheds listed in Table 4 show total load and are not the yields which are normalized based on watershed size.

Table 4. Percent contribution of the TN delivered to the Mississippi River in Keokuk, Iowa, from each of Minnesota's HUC8 Watersheds which ultimately drain into the Mississippi River.

Load ranking	WS#	Watershed name	% load contribution
1	33	Lower Minnesota River	7.3
2	28	Minnesota River - Mankato	6.7
3	30	Blue Earth River	6.4
4	32	Le Sueur River	5.7
5	25	Minnesota River - Yellow Medicine River	5.6
6	39	Cannon River	5.2
7	43	Root River	5.2
8	41	Zumbro River	4.9
9	19	South Fork Crow River	4.7
10	48	Cedar River	4.4
11	29	Cottonwood River	4.3
12	20	Mississippi River - Twin Cities	3.7
13	31	Watonwan River	3.4
14	51	Des Moines River - Headwaters	3.2
15	26	Chippewa River	3.1
16	18	North Fork Crow River	2.4
17	16	Sauk River	1.7
18	27	Redwood River	1.6
19	40	Mississippi River - Winona	1.5
20	15	Mississippi River - Sartell	1.4
21	38	Mississippi River - Lake Pepin	1.4
22	17	Mississippi River - St. Cloud	1.4
23	21	Rum River	1.3
24	49	Shell Rock River	1.3
25	10	Mississippi River - Brainerd	1.2
26	37	Lower St. Croix River	1.1
27	24	Lac Qui Parle River	1.1
28	23	Pomme de Terre River	1.0
29	50	Winnebago River	0.8
30	36	Snake River	0.8
31	9	Mississippi River - Grand Rapids	0.7
32	12	Crow Wing River	0.7
33	46	Upper Iowa River	0.6
34	13	Redeye River	0.6
35	35	Kettle River	0.6
36	14	Long Prairie River	0.6
37	53	East Fork Des Moines River	0.5
38	22	Minnesota River - Headwaters	0.4
39	44	Mississippi River - Reno	0.4
40	42	Mississippi River - La Crescent	0.4

Load ranking	WS#	Watershed name	% load contribution
41	34	Upper St. Croix River	0.3
42	52	Lower Des Moines River	0.2
43	7	Mississippi River - Headwaters	0.1
44	11	Pine River	0.1
45	8	Leech Lake River	<0.1
46	47	Upper Wapsipinicon River	<0.1

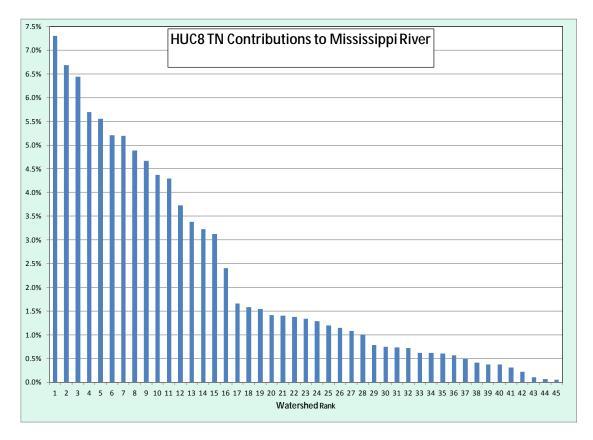


Figure 13. Ranking HUC8 watersheds based upon the contribution of N delivered to Keokuk, Iowa. Each bar represents the percentage of the TN originating from a single HUC8 watershed, from highest contributor (left) to lowest contributor (right).

Statewide, results of the SPARROW model indicate that the top 15 (of 81 total) HUC8 watersheds contribute about 63% of the total load leaving the state in all mainstem rivers (Figure 14). These results indicate that the N exports from the state cannot be solved by only making reductions in a few watersheds; yet substantial progress can be made by focusing on the top 10 to 20 contributing watersheds. The top 10 highest loading watersheds include those in the southern and eastern parts of the Minnesota River Basin and watersheds in the southeastern part of the state.

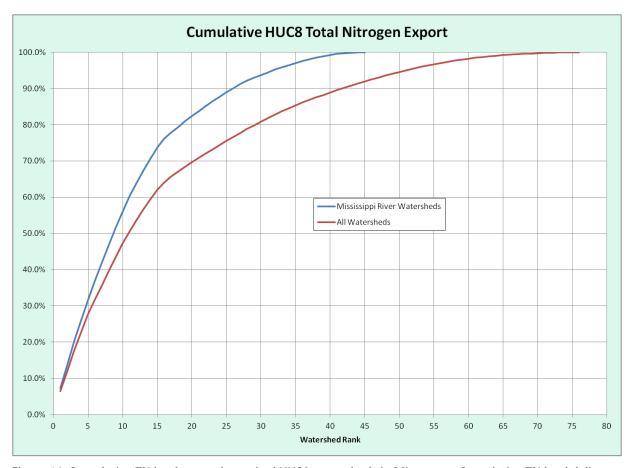


Figure 14. Cumulative TN load export by ranked HUC8 watersheds in Minnesota. Cumulative TN load delivery curves for all HUC8 watersheds in the state (blue line) and only those HUC8 watersheds draining to the Mississippi River (red line). The curves were developed by adding the watersheds in order of highest loaders (left) to lowest loaders (right).

## Nitrogen sources estimated by SPARROW

The SPARROW model was not used for this study as our primary way to estimate nitrogen sources, but was instead used as a check against the source assessment described in Chapters D1 to D4, and as verified in Chapter E1. SPARROW model results were used to estimate broad source categories of contributions of N to the streams (Table 5). Model results indicate that agricultural nonpoint sources (70%), which include a combination of such sources as fertilizer, manure, soil mineralization, legumes and more, are the main contributor. If we only consider the watersheds draining into the Mississippi River, the fraction of N coming from agricultural nonpoint sources is 3% higher as compared to the entire state.

Table 5. SPARROW model estimated TN source contributions to Minnesota streams, including both statewide source estimates and sources in basins reaching the Mississippi River only

Source category	Percent contribution to statewide stream TN loads	Percent contribution to Mississippi River TN loads	
Agricultural nonpoint sources	70%	73%	
Wastewater and industrial point sources	7%	7%	
Other nonpoint sources including atmospheric N	23%	20%	

#### Nitrogen source reduction scenarios

The SPARROW model was used to examine how various TN concentration reduction scenarios may affect the downstream transport of N (Table 6). However, these results were not the primary method of used in the study to evaluate source reduction scenarios, but rather were used as a secondary way of assessing N reduction scenarios. The primary river nitrogen reduction analysis is included in Chapter F1.

The SPARROW modeling results indicated that reducing TN Volumetric Weighted Mean Concentrations (VWMC) in all major rivers and streams with VWMC greater than 5 mg/L down to 5 mg/l would result in a 46.8% TN load reduction in the Minnesota River, 22.9% reduction in the Lower Mississippi loads, a 37% reduction in the Des Moines loads, and a 51.7% reduction in Cedar River Loads.

Note that these scenarios do not directly correspond with the reductions necessary to achieve draft stream nitrate concentration standards. The major differences between these scenarios and scenarios for achieving nitrate toxicity-based standards being considered in Minnesota include: 1) the modeled scenarios are for TN concentrations, whereas the standards being considered are for nitrate-N concentrations; 2) modeled scenarios are for VWMC concentrations during a fairly typical year, whereas the nitrate toxicity standards are expected to be based on four-day average concentrations exceeding the standard twice or more over three years (and current Class 1B/1C water quality standard for nitrate is 10 mg/l for a 1 day average); and 3) this SPARROW model does not consider the smallest reaches of rivers which could exceed standards, even if downstream tributaries included in the model meet the standard.

Table 6. SPARROW model estimates of TN load reduction percentages that correspond with achieving annual mean TN concentrations of 3, 5, 7 and 10 mg/l. NR indicates that the modeled mean concentration is already lower than the targeted concentration.

Basin	Mean Total Nitrogen Conc (mg/L)	10	7	5	3
Cedar River	10.35	-3.4	-32.3	-51.7	-71.0
Des Moines River	7.93	NR	-11.8	-37.0	-62.2
Lower Mississippi River	6.49	NR	NR	-22.9	-53.8
Lake Superior	1.21	NR	NR	NR	NR
Minnesota River	9.39	NR	-25.5	-46.8	-68.1
Rainy River	0.72	NR	NR	NR	NR
Red River of the North	4.52	NR	NR	NR	-33.7
St. Croix River	1.21	NR	NR	NR	NR
Upper Mississippi River	2.46	NR	NR	NR	NR

The SPARROW model was also used to predict statewide delivered TN load reductions with different source reduction scenarios (Table 7). Based on these results, if 30% reductions were made to both point sources and fertilizer sources, the estimated TN load reduction at the state borders would be 11.2%. The agricultural fertilizer category does not include manure sources or any other agricultural N sources except for commercial fertilizer.

Table 7. Estimated effects of statewide reductions in the TN load in streams with source reductions in agricultural fertilizer and urban point sources by 10%, 20%, and 30% as estimated with the MRB SPARROW model.

	10% source reduction	20% source reduction	30% source reduction
Point source	-0.7% TN	-1.2% TN	-2.0% TN
Agricultural fertilizer	-3.1% TN	-6.1% TN	-9.2% TN
Total	-3.8% TN	-7.3% TN	-11.2% TN

#### **Summary points**

- Annual TN modeled yields delivered to the outlets of HUC8 watersheds range from 15 to 25 pounds/acre/year in certain south-central Minnesota watersheds and 0.1 to 3 pounds/acre for most of the northern Minnesota watersheds. Watersheds along the Red River had higher modeled yields than the rest of northern Minnesota, with yields generally ranging from 4 to 6 pounds/acre/year.
- The highest yielding watersheds included the Cedar River, Blue Earth River, Le Sueur River, and Minnesota River (Mankato) HUC8 watersheds, each yielding over 20 pounds/acre/year.
   Modeled yields in the urban dominated Mississippi River Twin Cities were typical of yields in other southern Minnesota watersheds, at 17.4 pounds/acre/year.
- The SPARROW yields compared similarly to monitoring-based yield calculations obtained from recent sampling (2005-2009) results that were not used when the model was calibrated, providing additional confidence in the validity of the model yield results.
- Roughly 10% of the N which leaves the HUC8 watersheds is estimated to be lost between the
  watershed and the state borders. An additional 10% of the N which leaves Minnesota in the
  Mississippi River is lost en route to Missouri.
- The highest 15 contributing HUC8 watersheds to the Mississippi River contribute 74% of the Minnesota TN load which reaches southern Iowa. The other 30 watersheds contribute the remaining 26% of the load.
- SPARROW model results indicate that agricultural nonpoint sources are the largest source category of N to the state's rivers, contributing 73% of TN in the Mississippi River and 70% to all rivers in the state. Point sources contribute 7% of the loads to the Mississippi and statewide, according to SPARROW model estimates.
- If 30% reductions were made to TN losses into surface waters from both fertilizer and point sources, an estimated 11.2% load reduction would be achieved at the state borders.

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# B5. Nitrogen Transport, Losses, and Transformations within Minnesota Waters

Author: Dennis Wasley, MPCA

#### Introduction

Nitrogen (N) losses and transformations can occur at each point along the flow pathway between source and final destination, including within soil, groundwater and surface water.

Nitrogen losses and transformations within the soil system were studied for Minnesota (MN) conditions as part of the agricultural N budget developed by Mulla et al., and which is included in Chapter D4 of this report.

Nitrogen losses can also occur within the groundwater and in the transition zone where groundwater moves into riparian areas and surface waters. A literature review related to denitrification losses of nitrate within groundwater, focusing on upper Midwest studies, is included in Appendix B5-1.

Once in surface waters, N can also be lost through denitrification, converted from inorganic forms (i.e., nitrate) to organic forms (i.e., algae), or transform from organic forms back into inorganic N. Because these processes within surface waters can transform large quantities of N, it is important to understand how these processes can affect N conditions in rivers and streams. For this study, N transformations and losses within surface waters were investigated, through a review of published findings and an analysis of unpublished data. These findings are summarized below and are included in their entirety in Appendix B5-2.

## Summary of nitrogen transformation within Minnesota surface waters

The literature of the past two decades has greatly increased our understanding of N transport in surface waters. Generalizing the movement and transformations of total nitrogen (TN) in surface waters of MN is complicated given the wide range of aquatic systems and N loads delivered to those systems throughout the state. Nitrogen transport in surface waters is spatially and temporally variable, which also makes generalizations difficult.

Nitrogen is present in detectable amounts in most MN surface waters. In surface waters with relatively low N inputs, N is typically present in low concentrations of inorganic forms (often near detection limits), with the majority of N present in organic forms bound in various components of living and dead organisms. As N loading increases to a given surface water beyond its ability to assimilate N inputs, detectable amounts of dissolved inorganic nitrogen (DIN) are measured. In well oxygenated waters, DIN is typically present as nitrate ( $NO_3$ -N) with lesser amounts of nitrite ( $NO_2$ -N) and ammonia/ammonium. Ammonia and ammonium can also make up a portion of DIN in MN waters. It is most common in waters with low dissolved oxygen such as wetlands, the hypolimnion of stratified lakes, and during winter immediately downstream of wastewater treatment plants. Nitrification or uptake of ammonia+ammonium by organisms converts this form of N to other forms in oxygenated surface waters during the other seasons.

Many factors influence the transport of N in surface waters of MN, including N loading, residence time, temperature, nitrate concentration, discharge, depth, velocity, and land use. Some of these factors are inherently different based on the type of surface water. Wetlands and lakes are common in northeast MN along with relatively low N inputs, which both contribute to low N yields. Nitrate concentrations in streams of northeast MN are very low, often near detection limits. Yields of N from watersheds in south-central MN are much higher due to low densities of lakes and wetlands and higher inputs of N, especially during seasonally higher stream discharge. The concentration of TN in streams can drop during low flow periods in mid-late summer due to a combination of lower input loads and in-stream processing where inputs are not excessive. The reduction in mid-late summer TN concentration does not result in substantially reduced annual loads since the majority of TN is transported from late-March to mid-July when stream discharge is typically highest in MN rivers. Watersheds in southeast MN are unique to the other watersheds in the state due to the large inputs of high nitrate groundwater, which maintain elevated TN levels during low flow and, therefore, have less seasonal concentration fluctuations of TN than south-central MN.

Residence time is a key factor for N removal across all aquatic ecosystems. Residence time is basically the time it takes to replace the volume of water for a given surface water. Longer residence time allows for more interaction with biota (including bacteria) within a given aquatic resource. Streams typically have much shorter residence times compared to wetlands and lakes. Consequently, streams generally transport more N downstream than lakes and wetlands. The amount of N removed within streams generally decreases with stream size and N loading.

Special consideration was given to the Mississippi River downstream of the Minnesota River due to the unique rapidly flushed impoundments (navigational pools in the lock and dam system on the mainstem Mississippi) on this river and availability of models and monitoring data. In this river system and other rivers throughout the state, N loading is typically at its annual peak during spring and early summer when streamflow is seasonally higher. Lake Pepin, a natural riverine lake on the Mississippi River, removed only 6% to 9% of the average annual input load of TN during the past two decades. Lake Pepin has the longest residence time of all the navigational pools on the MN portion of the Mississippi River by a factor of at least 5. Upstream removal and loading reductions of N throughout the tributary watersheds is needed to substantially reduce downstream transport of N by the Mississippi River from Navigational Pools 1 to 8 during spring and early summer. Estimates of the collective impact of all the 168 miles of Mississippi River with navigational pools in MN, including Lake Pepin, range from removal of 12% to 22% of average annual input loads. Impressive N cycling has been documented in this system, but the input load simply overwhelms the capacity of the river to remove the majority TN inputs during most years.

Outputs from the SPARROW model are useful to illustrate annual downstream delivery of TN loads in MN streams and rivers. The general findings of this review and the SPARROW modeling indicate that 80% to 100% of annual TN loads to rivers are delivered to state borders unless a large reservoir with a relatively long residence time is located in the stream/river network downstream of a given headwater stream. Large headwater reservoirs such as Lake Winnibigoshish remove a larger proportion of inputs than riverine lakes such as Lake Pepin which has a much larger contributing watershed. Other approaches described in Appendix B5-2 based on mass balances estimated from monitored rivers also showed that the majority of annual TN loads to a given river reach are delivered to downstream reaches.

What is relatively clear from this review and analysis is that larger rivers with high TN loads like the Minnesota River deliver downstream most of the annual N load that reaches the river mainstem. The collective removal rate of N loading in MN's lakes, wetlands, ephemeral streams, and headwaters/streams is less certain. National models such as SPARROW can estimate the collective losses of TN for modeled rivers and streams of a given watershed (see Chapter B4).

Many factors influence the losses in smaller lotic systems (Table 1). Watersheds with extensive lakes and wetlands and modest N loading certainly remove or transform inorganic nitrogen inputs. Watersheds with extensive tile drainage and limited lakes and wetlands often transport large loads of inorganic nitrogen to watershed outlets with some removal in headwaters. The percentage of delivered load typically increases with proximity to large rivers in all watersheds. Weather and precipitation during any given year certainly influence transport dynamics within the watershed. Higher precipitation translates into greater loading and increased stream velocity, which both contribute to increased downstream transport of DIN. Drought conditions lead to reduced loading and lower stream velocities, which contribute to increased losses and transformations of inorganic nitrogen.

Table 1. Positive and negative factors that influence downstream movement of NO<sub>X</sub>-N in MN.

Factor	Conditions that enhance N removal	Example	Conditions that generally reduce N removal	
Streamflow	Low flow	Drought	High flow	Wet periods/spring
Annual Precipitation	Low	Western MN	Moderate	Eastern MN
Depth	Shallow (inches)	Headwater streams	Deep (9 ft)	Impounded portion of Mississippi River
Carbon content of sediment	High organic content	Backwaters, impoundments, wetlands	"Clean" sand with low organic content	Main channel of large rivers
Input loads/concentration	Low	Northern MN watersheds	High	Southern MN watersheds
Season	Late summer	Low flows and high temperature	Early Spring	High flow and cool temperatures
Riparian area	Natural	Forested stream	Rock or concrete	Urban areas
Riparian wetlands	Common	Northern MN	Few	Ditches in southern MN
Temperature	Warm	Summer	Cold/cool	Winter

Lakes, including backwaters of rivers and wetlands, can remove and/or assimilate DIN inputs as long as inputs are not excessive. Long hydraulic residence times in these surface waters along with carbon rich sediments are key to removing inorganic nitrogen inputs. The overall impact of these surface waters on downstream transport of TN from MN is difficult to quantify, but it is certain that existing surface waters of these types currently reduce TN loads to downstream waters.

The comprehensive review of N losses and transformations within surface waters is found in Appendix B5-2.

## C1. Nitrate Trends in Minnesota Rivers

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\*note: At the time this report was being finalized by the MPCA, the USGS review process was mostly complete, but was awaiting final approval. The USGS withholds joint authorship on this chapter until all final approvals have been received.

Statistical Analyses: Directed by Dave Lorenz and conducted by Dave Christopherson and Gary Martin

## Objective

Regular sampling of river and stream water for nitrate began at numerous Minnesota Rivers during the mid-1970s, and many of these sites continued to be monitored through 2008-2011. A few of these sites were previously assessed for nitrogen (N) load and concentration temporal trends, as is reported in Chapter C2. However, most sites have either not been assessed for nitrate trends or have been studied for trends using a shorter period of time and different statistical methods compared to this study.

The objective of this study was to assess long-term flow-adjusted nitrite+nitrate-N (hereinafter referred to as nitrate) concentration trends in a way that would allow us to discern changing trends over a 30 to 35 year record. Recognizing that these trends are commonly different from one river to another river and from one part of the state to another, our objective was to examine as many possible river monitoring sites across the state for which sufficient long term streamflow and concentration data were available.

The nitrate concentration parameter was chosen for the following reasons:

- · Nitrate is the dominant form of N in most streams with elevated total nitrogen levels
- Nitrate can have adverse human and aquatic life impacts at high concentrations (see Chapter A2)
- Nitrate concentrations in Minnesota rivers and streams are mostly influenced by human activities
- The ammonia+ammonium form of N has been consistently shown in previous studies to have decreased substantially since the late 1970's (see Chapter C2) and no further trends study of that N parameter was considered to be needed at this time
- There is less long term data for total nitrogen as compared to nitrate

Nitrate concentration trend analyses can be used to help us understand how human activities and other factors have affected stream nitrate over different time periods. One challenge, however, when interpreting nitrate trend results is a lag time that occurs between changes to the land and the corresponding change to stream N levels, especially where slower moving groundwater is a dominant contributor to streamflow and nitrate loads. In some areas it can take many years for impacted ground water to slowly move into surface waters. In areas where transport to streams is much quicker, such as tile-drained lands and karst lands, the land changes can affect stream water quality within a much shorter period of time.

Nitrate *load* trends were not assessed in this study because the monitoring frequency at most sites was insufficient for load trends analyses, and most of the sites where load trends could be determined were already reported by Lafrancois et al. (2013) for the 1976 to 2005 time period (see Chapter C2).

#### Site selection

We targeted sites that had a long-term (pre-1980) nitrate monitoring record and associated streamflow records corresponding to the same timeframe. We avoided locations that were intentionally sited to evaluate upstream point sources. We also avoided sites where sampling was discontinued prior to 2008 or that had large gaps in the monitoring record.

The primary long-term data set available for Minnesota Rivers is from stations known as "MPCA Minnesota Milestone" sites. MPCA Minnesota Milestone sites were used for 45 of the 51 sites analyzed for long-term trends (Table 1). Most of the Minnesota Milestone sites used for trends analyses had nitrate concentration data over a 30 to 35 year period. The Minnesota Milestone sites were typically sampled 9-10 months per year by taking grab samples; yet occasionally the sampling frequency was reduced to 7-8 months during the year. With only a few exceptions, these sites were sampled every year for nitrate from the mid- to late-1970's until the mid-1990's, at which time the sampling frequency was reduced to two out of every five years, or 40% of the years. Sampling continued at these sites through 2008-2011 at the reduced frequency.

We also conducted trend analyses on a second set of six monitoring sites. The six sites were sampled (grab samples) twice monthly every year since 1976 by the Metropolitan Council Environmental Services. In a few locations, we did not report trends at Minnesota Milestone sites which were located near the Metropolitan Council sites, but instead focused our efforts on the more robust long term data sets obtained by the Metropolitan Council.

To evaluate flow-adjusted trends, only those nitrate monitoring sites which could be paired with nearby streamflow monitoring information for the same years were included in our analysis. The streamflow gauging stations were all within criteria used for other similar studies (i.e. Lorenz et al., 2009). Three sites (198, 003, 975) had nitrate monitoring results from the 1970's, but only had streamflow information since 1991-94. For those sites, our trend analyses began in the early 1990's and continued through 2010.

The location of all monitoring sites used for trends analysis is shown in Figure 1 and are listed along with the number of times each site was sampled in Table 1. The Metropolitan Council monitored sites are denoted with an asterisk in the "Map Number" column in Table 1. The number of samples (observations) taken and used for trends analyses at the six Metropolitan Council monitored sites, range between 778 and 899 (Table 1). The number of samples is much lower for the Minnesota Milestone sites, which were typically sampled from 200 to 300 times.

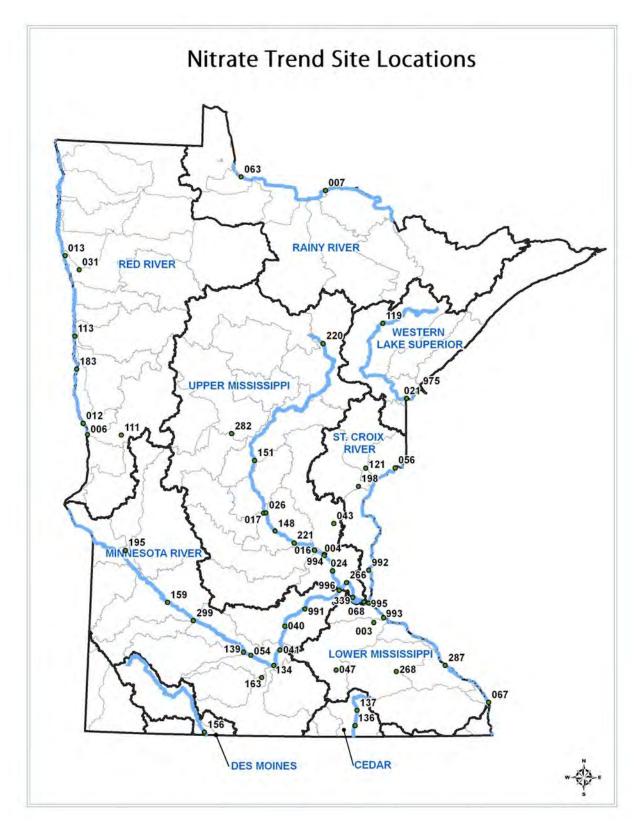


Figure 1. Site locations and associated site numbers for each of the river monitoring sites where trend analyses were completed (refer to Table 1 for more information about each site).

Table 1. Nitrate monitoring site locations/numbers and associated number of observations (nitrate sampling events) and U.S. Geological Survey streamflow gauging station number. An asterisk indicates stations sampled by the Metropolitan Council. All other sites are MPCA Minnesota Milestone sites.

Map Number	Location Code	Nitrate Monitoring Location	No. of Observations	Streamflow Gauging Station No.
Saint Louis I	River			
119	S000-119	St. Louis River, Forbes	223	04024000
021	S000-021	St. Louis River, Fond Du Lac	239	04024000
975	S003-975	St. Louis River Duluth	66	04024000
Red River of	f the North Basin			
111	S000-111	Otter Tail River, Fergus Falls	130	05046000
006	S000-006	Otter Tail River, Breckenridge	247	05046000
012	S000-012	Red River, Brushvale	348	05051000
183	S000-183	Red River, Moorhead	247	05054000
113	S000-113	Red River, Pearley	250	05064500
031	S000-031	Red Lake River, Fisher	211	05280000
013	S000-013	Red Lake River, East Grand Forks	244	05280000
Rainy River	Basin			
007	S000-007	Rainy River, International Falls	250	05133500
063	S000-063	Rainy River, Baudette	254	05133500
Upper Missi	ssippi River Basin			
220	S000-220	Mississippi River, Blackberry	288	05211000
282	S000-282	Long Prairie River, Motley	271	05245100
151	S000-151	Mississippi River, Camp Ripley	227	05267000
017	S000-017	Sauk River, Sauk Rapids	304	05270500
026	S000-026	Mississippi River, Sauk Rapids	244	05270700
221	S000-221	Mississippi River, Monticello	253	05288500
004	S000-004	Crow River, Dayton	152	05280000
994*	UM 871.6	Mississippi River, Anoka	841	05288500
043	S000-043	Rum River, Isanti	289	05286000
016	S000-016	Rum River, Anoka	112	05286000
024	S000-024	Mississippi River, Fridley	243	05288500
Minnesota I	River Basin			
195	S000-195	Pomme de Terre River, Appleton	316	05294000
159	S000-159	Yellow Medicine River, Granite Falls	145	05313500
299	S000-299	Redwood River, Redwood Falls	199	05316500

Map Number	Location Code	Nitrate Monitoring Location	No. of Observations	Streamflow Gauging Station No.
139	S000-139	Cottonwood River, New Ulm	197	05317000
054	S000-054	Minnesota River Courtland	232	05325000
163	S000-163	Watonwan River, Garden City	282	05319500
134	S000-134	Blue Earth River, Mankato	313	05320000
041	S000-041	Minnesota River, St. Peter	226	05325000
040	S000-040	Minnesota River, Henderson	242	05330000
991*	MI 39.4	Minnesota River at Jordan	778	05330000
996*	MI 3.5	Minnesota River at Fort Snelling	915	05330000
Mississippi Ri	ver between the I	Minnesota and St. Croix Rivers		
266	S000-266	Mississippi River, St. Paul Wabasha St.	332	05331000
339	S000-339	Mississippi River, Grey Cloud	329	05331580
068	S000-068	Mississippi River, Hastings Lock and Dam No 2	179	05331580
St. Croix Rive	r Basin			
056	S000-056	St. Croix River, Danbury	309	05333500
121	S000-121	Kettle River, Hinkley	291	05336700
198	S000-198	Snake River, Pine City	190	05338500
992*	SC 23.3	St. Croix River, Stillwater	896	05340500
995*	SC 0.3	St. Croix River, Prescott	899	05340500
Lower Missis	sippi River Basin			
993*	UM 796.9	Mississippi River, Prescott Lock & Dam No 3	870	05331000
047	S000-047	Straight River, Clinton Falls	243	05353800
003	S000-003	Cannon River, Welch	107	05355200
268	S000-268	Zumbro River, South Fork, Rochester	241	05372995
287	S000-287	Mississippi River, Minneiska Loack and Dam No. 5	217	05378500
067	S000-067	Mississippi River, LaCrosse	230	05378500
Cedar and De	s Moines River Ba	sins		
137	S000-137	Cedar River, Lansing	206	05457000
136	S000-136	Cedar River, Austin	300	05457000
156	S000-156	Des Moines River, West Fork, Petersburg	133	05476000

## Statistical analysis methods

The long-term trends in flow-adjusted concentrations (FAC)s were assessed using the QWTREND program (Vecchia, 2003a, 2005). QWTREND was selected because it can describe long-term trends, not just monotonic trends; is insensitive to changes in the variability in streamflow; is also insensitive to unexplained variability in water quality (Lorenz et al., 2009); and it can be used to assess the relation between streamflow and water quality and sampling design. QWTREND uses a time-series model for estimating trends in FAC. The basic form of the model is

FAC = Intercept + Time Series + Long Term + Intermediate Term + Seasonal + Trend + HFV,

#### where

FAC is the log of the flow-adjusted concentration.

Intercept is the intercept term.

Time Series is the collection of autoregressive and moving-average time-series relations

between streamflow and concentration and within the concentration.

Long Term is the 5-year anomaly (5-year moving average log of streamflow).

Intermediate Term is the 1-year and seasonal (3-month) anomaly.

Seasonal is the first- and second-order Fourier terms that describe seasonal variation.

Trend is the user-supplied trend terms that explain long-term deviations not

described by the previous terms.

HFV is the high-frequency variability in the streamflow, which is the daily.

streamflow after the long- and intermediate-term anomalies have been

removed.

Vecchia (2000) describes the estimation of the time-series parameters and Vecchia (2003b) describes the computation of the anomalies.

The suggested minimum data criteria for QWTREND (Vecchia, 2000) are (1) minimum water-quality record length of 15 years, (2) average of at least four samples per year, (3) at least 10 samples within each quarter of the sampled years, (4) less than 10% censored data (i.e. nondetections), and (5) complete streamflow record for the water-quality record for the period of interest plus the preceding 5 years. These criteria were generally met, but exceptions were made for the preceding 5-year part of Criterion 5 when streamflow records were shorter than the water-quality record. Several sites in northern Minnesota had very low nitrate concentrations, often below detection limits, and Criterion 4 was relaxed for those sites. Vecchia (written communication, Dec 14, 2012) stated that QWTREND is accurate on the trend estimates for up to at least 20% censoring, in general, and possibly up to about 35% in some cases. As censoring increases, the trends become progressively less reliable—the magnitude of the slope is decreased and the associated p-values become more significant. Beyond about 35% censoring, QWTREND should be considered only an exploratory tool.

QWTREND was used to determine when changes in the trend during the analysis period (typically 1975–2010) were statistically significant. The critical p-value for a single trend was set at 0.10 compared to the no-trend model. To avoid extraneous trends, the critical p-value for a two-trend model was set at one-half the attained p-value for the single-trend model, the critical p-value for a three-trend model was set at one-third the attained p-value for the single-trend model, and so forth.

The Long Term, Intermediate Term, and High Frequency Variability (HFV) parameters of the model describe the relation between concentration and streamflow and concentration. The HFV parameters include an average response and Fourier terms, the sine and cosine, which describe seasonal differences in the HFV response. Only the average response was included in this analysis. The Long and Intermediate Terms describe the effects of sustained long- and short-term above or below average precipitation; positive parameters suggest a flushing process and negative values suggest a dilution effect and value near zero suggest no effect. The HFV parameter, in general, describes the effect of rainfall or snowmelt events. Again positive parameters suggest a flushing process and negative values suggest a dilution effect and value near zero suggest no effect. Only sites with less than 25% censoring were used in the analysis of streamflow and concentration.

#### Nitrate concentration time trends across the state

An overview of the results is first described for mainstem rivers across the state (Red, Minnesota, Mississippi, St. Croix, Cedar, Des Moines, and St. Louis Rivers). The statewide overview is followed by a more detailed description and discussion of the results for each major basin, including results for many tributary rivers within the basins.

Statistically significant (p <0.1) changes in overall flow-adjusted nitrate concentrations between the mid-1970's and the 2008-2011 timeframe are shown in Figure 2 for Minnesota's mainstem rivers. The magnitude of change over this time period was found to vary greatly across the state. The majority of the mainstem river sites showed increases, ranging from 7% to 268% over the entire analysis time period (30 to 35 years at most sites). Four locations showed slight overall decreases, however, including the two most downstream sites on the Minnesota River and the most upstream site on the St. Croix River and the most upstream site on the St. Louis River.

Because the nitrate concentrations are lower in the Upper Mississippi River, Rainy, and Lake Superior basins, even a very small addition of nitrate over time will result in a relatively high percentage increase. The large percentage increases in the Upper Mississippi River represent a 0.1 to 0.4 mg/l nitrate-N increase (see tables 2-16, ending concentration for more context on understanding the percent change over time).

A commonly asked question is how nitrate concentrations have been changing over more recent years. Results for the most recent years for each major river monitoring site are shown in Figure 3. The number of years encompassing these recent trends varies greatly, and was from 5 to 9 years at seven sites, and 10 years or more at all other sites. The results for these recent periods vary from one part of the state to another. In most northern Minnesota mainstem rivers, nitrate concentrations have not had a statistically significant trend in recent years, with a few exceptions, most notably an average 2% per year increase in the St. Louis River (Duluth) over the past 17 years. Increasing trends during recent periods were found in the Cedar River and at most of the Mississippi River sites south of Sauk Rapids, with the recent rate of change at most sites comparable to the change over the complete period of record. Decreasing trends during recent years were found in the Minnesota River at some locations.

Long term and recent nitrate concentration trends in several major tributaries to mainstem rivers were also assessed and mapped (Figures 4 and 5). Over the entire period of analysis, 11 different tributary rivers showed increases and 3 of those rivers had two monitoring sites on the same river that both showed increases. Four tributaries had no significant trend, and 1 tributary with two sites (Cannon Watershed) showed decreasing trends (Figure 4).

During the more recent years, several tributary rivers have shifted toward showing more sites with decreasing and non-significant trends. Five tributaries showed increasing trends, 4 tributaries had decreasing trends, and 7 have had no statistically significant trend during the most recent trending period (Figure 5).

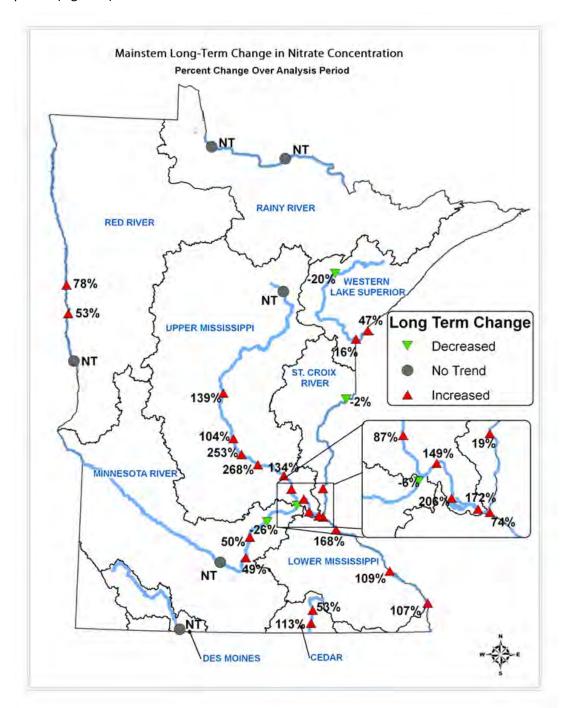


Figure 2. Mainstem river changes in nitrate concentration during the entire period of analysis, which was typically 1976 to 2010, but varied by site (see also tables 2 - 16).

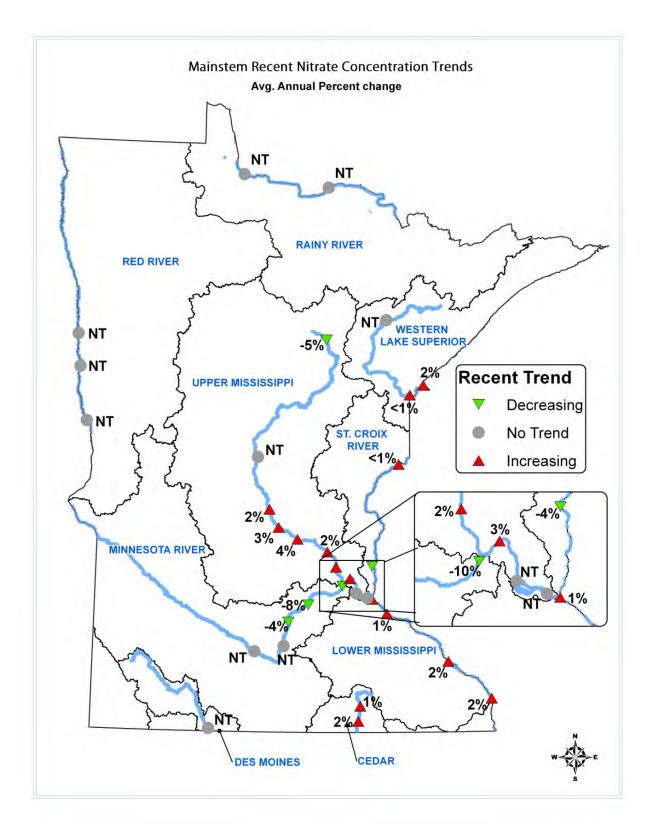


Figure 3. Nitrate concentration trends within past 5-15 years (ending in 2010 for most sites) for mainstem rivers, shown as percent change per year during the most recent trending period.

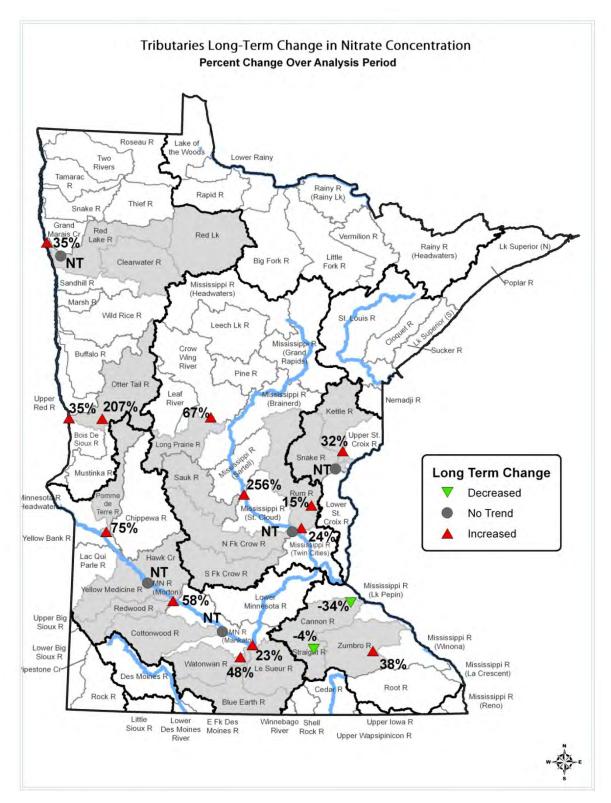


Figure 4. Percent change of nitrate concentrations in tributary rivers during the entire period of analysis (typically 1976 to 2010, but varied by site - see Tables 2 to 16). Watersheds associated with the trend analyses are shaded in gray.

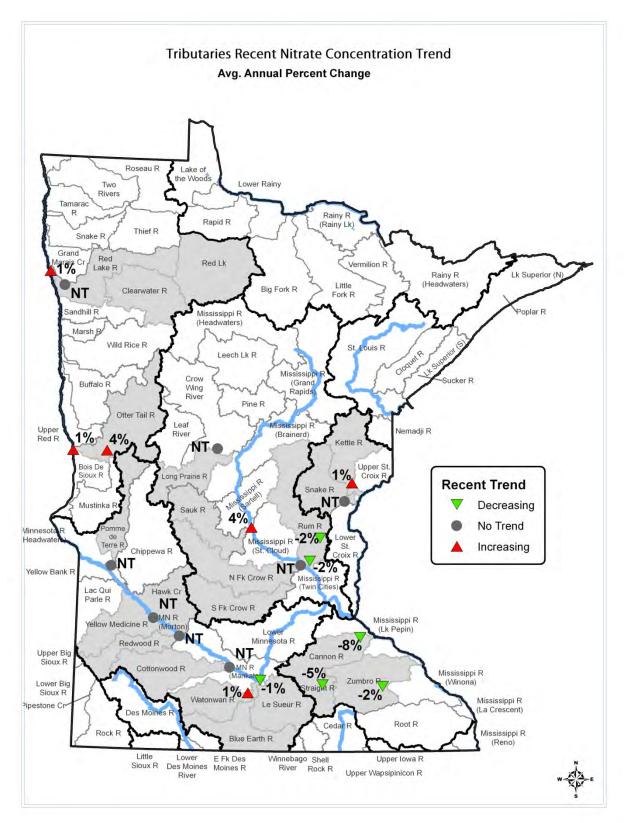


Figure 5. Nitrate concentration trends for tributary rivers within the past 5-15 years (period ending in 2010 at most sites), shown as percent change per year during the most recent trending period. Watersheds associated with the trend analyses are shaded in gray.

At many sites, the long term trends were not constant over the years, and at some river sites there were separate periods of increases, decreases or no trend; and therefore we reported how the trends shifted throughout the 30 to 35-year period of analysis. The next section provides the results of how trends changed during the analysis period at each assessed monitoring site.

## Nitrate concentration trends by basin

Flow-adjusted nitrate concentration trends are shown for major rivers and analyzed tributaries in each major river basin (Tables 2 to 16). Note that for each site there is an overall trend result which represents a calculated change based on all statistically significant trends from the beginning of the trends analysis period to the end. Where trends for specific periods within the overall trend were found to be statistically significant, those specific trend segments are reported below the overall trend. A positive change represents an increasing trend and a negative change represents a decreasing trend. "No trend" indicates that the trend was not statistically significant at the p<0.1 significance level.

Note that where there are two or more separate increasing or decreasing trend segments, the sum of these segmented trends will not add up to the overall trend. That is because the percent of increase or decrease is reported as an increase or decrease from the start of the segment, rather than the start of the entire period of analysis. For example, if a site starts with a concentration of 1 mg/l and for the first decade there is a 100% increase, then the concentration at the end of the first decade is 2 mg/l. If the trend during the second decade is a 25% increase, then the concentration will have increased from 2 mg/l to 2.5 mg/l. Therefore the overall increase over the two decades is 150% (not the sum of the 100% and 25% increases).

The "NO3" concentrations in the graphs and the "ending concentrations" in tables 2 to 16 are annual average "nitrite+nitrate-N" concentrations during the last year of the statistical trend analysis. Because of the way the QWTREND model works, these concentrations represent an annual mean of the log of nitrite+nitrate-N concentrations, corrected for seasonal and streamflow variability which were then translated back into a raw concentration. Therefore, for sites with a high degree of variation in nitrate from season to season, the concentrations reported in the tables and associated graphs are lower than either a flow-weighted mean concentration or an annual arithmetic mean concentration. These concentrations are therefore not comparable to concentrations reported in Section B of this report. Note also that two different y-axis nitrate concentration scales are used in the trend graphics depending on the magnitude of concentrations, typically 0 to 1.0 mg/l and 0 to 10 mg/l.

To find the location of specific site names noted below (often nearby city names), identify the associated site number in Tables 2-16 (left column), and refer to Figure 1. Some secondary site numbers in tables 2-16 are in parentheses, and indicate a Metropolitan Council monitoring site with their associated site number based on the river mile at the sampling location.

#### Mississippi River Basin results

#### **Upper Mississippi River (Blackberry to Fridley)**

The general patterns in the Upper Mississippi River Basin are long-term increases, with flow-adjusted concentrations often more than doubling over the three and a half decades of measurement (Table 2). The only exception to the long term increase is the upper-most Mississippi River site at Blackberry, which showed a decrease between 1997 and 2010. Recent period average annual increases range between 2% and 4% at all Mississippi River sites from Camp Ripley southward to Fridley. At the four most downstream sites, at Sauk Rapids, Monticello, Anoka, and Fridley, the trends show continuous increases since 1976.

Table 2. Flow-adjusted nitrate concentration trends in the Upper Mississippi River between the most upstream site at Blackberry to the most downstream site at Fridley. A positive change represents a statistically significant (p<0.1) increasing trend and a negative change represents a decreasing trend. "No trend" or "NT" indicates that the trend was not statistically significant (p<0.1). Site # refers to site location on Figure 1 and Table 1.

Mississippi River – Blackberry  Overall change 1976-2010  976 - 1997  997 – 2010  10 10 10 10 10 10 10 10 10 10 10 10	*0% +106% -51% +139%	0.05
997 – 2010  1.0 0.8 -220 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015  Mississippi River – Camp Ripley  Overall change 1976-2010	+106%	0.26
997 – 2010  1.0 0.8 -220	-51%	0.26
## 1.0		0.26
0.8 - 220 0.6	+139%	0.26
Overall change 1976-2010	+139%	0.26
=	+139%	
976-1988		
.J/U 1JUU	NT	
989-1995	+139%	
.996-2010	NT	
1.0 0.8 1.51 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
Aississippi River – Sauk Rapids		0.23
Overall change 1976-2010	+104%	
1.0 0.8—026 10.6—		
	verall change 1976-2010	verall change 1976-2010 +104%

<sup>\*</sup>Rounded off to 0% overall change – increase during the first 22 years is nearly balanced by the decrease in the last 14 years. The increase and decrease were statistically significant trends.

Site #	Upper Mississippi River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
221	Mississippi River – Monticello		0.58
	Overall change 1976-2010	+268%	
	1.0 0.8 -221 		
994(871.6)	Mississippi River – Anoka		0.88
	Overall change 1976-2010	+134%	
	1.0 0.8 994 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
024	Mississippi River – Fridley		0.49
	Overall change 1976-2010	+87%	
	1.0 0.8 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

#### **Tributaries of the Upper Mississippi River**

Many tributaries flow into the Upper Mississippi River. Trends in all tributaries, along with trends in point source discharges and groundwater baseflow discharging directly into the Mississippi, affect the Mississippi River trends. Trends in four major tributaries were analyzed for this study. Three of the four tributaries showed an overall increase since 1976 and one tributary (Crow River) had no trend (Table 3). The nature of the increases was different in all three tributaries, with different magnitudes of increases (from 15 to 256%) and different periods of time when these increases occurred. During the past decade, the Long Prairie and Crow Rivers have shown no trend, while the Sauk River nitrate concentrations have been increasing and the Rum River has been decreasing.

The Sauk River is the only analyzed tributary which shows a continuously increasing trend in the past two decades, as is also found in the Mississippi River at Sauk Rapids, Monticello, Anoka and Fridley. We were not able to assess the trend results in the many other tributaries to the upper Mississippi River, and it is possible that those other tributaries also contributed to the increasing trends in the Mississippi River.

Table 3. Flow-adjusted nitrate concentration trends in four tributaries of the Upper Mississippi River. The Rum River had two monitoring sites at different points along the river. "LS" indicates a lower strength trend.

Site #	Tributaries - Upper Mississippi River Basin Site location / trend periods	% change in nitrate	Ending conc. mg/l
282	Long Prairie River – south of Motley		0.43
	Overall change 1976-2010	+67%	
	1976-1991	+67%	
	1992-2010	NT	
	1.0 0.8 0.8 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
017	Sauk River - at Sauk Rapids		0.98
	Overall change 1976-2010	+256%	
	1976-1984	+137%	
	1985-1988	-33%	
-	1989-2010	+123	
	1.0 0.8 0.7 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

Site #	Tributaries - Upper Mississippi River Basin Site location / trend periods	% change in nitrate	Ending conc. mg/l
004	Crow River – at Dayton		1.24
	Overall change 1976-2010	NT	
Note: y-scale 0-2 mg/l	2.0 004 1.5— ——————————————————————————————————		
	1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
043	Rum River - Isanti		0.24
	Overall change 1976-2010	+15%	
	1976-1986	NT	
	1987-1998	+40%	
	1999-2010	-18% (LS)	
	1.0 0.8 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
016	Rum River - Anoka		0.21
	Overall change 1976-2010	+24%	
	1976-1998	+29%	
	1999-2002	+16%	
	2002-2010	-18%	
	1.0 0.8 0.6 0.6 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

#### Mississippi River between the Minnesota and St. Croix Rivers

The three sites in the St. Paul area between the Upper and Lower Mississippi River Basins all show an overall increase in flow-adjusted nitrate concentration over the entire period of record. However, the increases have largely diminished in recent years, with no apparent trend over the last two decades at the two most downstream sites (Table 4).

The Minnesota River, which merges with the Mississippi River upstream of these three sites, has an influence on both the concentrations and trends at these three sites. The nitrate concentrations are substantially higher at these three locations on the Mississippi, as compared to upstream Mississippi River sites at Anoka and Monticello. Another potential influence in these segments of the Mississippi River is the Metro wastewater treatment facility discharge, between sites 266 and 339. This plant services much of the Twin Cities Metropolitan Area.

Table 4. Flow-adjusted nitrate concentration trends in Twin Cities segments of the Mississippi River between the points where the Minnesota River and St. Croix streamflows into the Mississippi.

Site #	Mississippi River – St. Paul area Site location / trend periods	% change in Nitrate	Ending conc. mg/l
266	Mississippi River – St. Paul Wabasha St.		1.9
	Overall change 1975-2010	+149%	
Note: Y-scale 0-10	10 8 - 266 		
339	Mississippi River – Grey Cloud Island		2.4
	Overall change 1975-2010	+206%	
	1975-1991	+206%	
	1992-2010	NT	
	10 8 -339 		

Site #	Mississippi River – St. Paul area Site location / trend periods	% change in Nitrate	Ending conc. mg/l
068	Mississippi River – Hastings L&D 2		2.3
	Overall change 1976-2011	+172%	
	1976-1993	+172%	
	1994-2011	NT	
	10 8 -068 -068 -068 4 - 2 - 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

# Lower Mississippi River - between Prescott (confluence with St. Croix River) and the Iowa border

In the Mississippi River between the Twin Cities and Iowa, flow-adjusted nitrate concentration trends showed a more than doubling since 1976, based on monitoring near Red Wing, Minneiska, and LaCrosse (Table 5). During the last two decades, trends showed a reduced rate of increase at Prescott (Lock and Dam #3) where we have had continuous and more frequent monitoring, but a constant rate of increase further downstream in Minneiska and LaCrosse.

Table 5. Flow-adjusted nitrate concentration trends in the Lower Mississippi River between the confluence of the St. Croix River and the lowa border.

Site #	Lower Mississippi River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
993	Mississippi River – Prescott L&D 3		2.1
	Overall change 1976-2010	+168%	
	1976 - 1991	+117%	
	1992-2010	+24%	
	10 8 993 		

Site #	Lower Mississippi River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
287	Mississippi River – Minneiska L&D 5		1.9
	Overall change 1976-2008	+109%	
	10 8 -287 		
067	Mississippi River – LaCrosse, WI		1.3
	Overall change 1976-2008	+107%	
	10 8 - 067 - 6 6		

#### **Tributaries of the Lower Mississippi River**

The three tributaries analyzed for trends in the Lower Mississippi River Basin all showed decreasing trends in flow-adjusted nitrate concentration between about 2003-05 and 2010 (Table 6). During the decade prior to that, all three sites showed increasing trends. Since 1976, the overall trend in the Zumbro River has been a 38% increase. The Straight River had times of increases and decreases which have amounted to virtually no overall change (-4%). Many tributaries to the Lower Mississippi River from both the Minnesota and Wisconsin side of the basin were not analyzed for trends.

Table 6. Flow-adjusted nitrate concentration trends in four tributaries of the Lower Mississippi River. "LS" indicates a lower strength trend.

Site #	Tributaries - Lower Mississippi River Basin Site location / trend periods	% change in Nitrate	Ending conc. mg/l
047	Straight River – Clinton Falls		3.8
	Overall change 1977-2010	-4%	
	1977-2002	+43%	
	2003-2010	-33%	
	10 8 -047 		

Site #	Tributaries - Lower Mississippi River Basin Site location / trend periods	% change in Nitrate	Ending conc. mg/l
003	Cannon River - Welch		3.2
	Overall change 1991-2010	-34%	
	1991-1994	-29%	
	1994-2005	+42%	
	2005-2010	-35%	
	10 8 -003 		
268	Zumbro River - Rochester		5.71
-	Overall change 1976-2008	+38%	
	1976-2002	+51%	
	2003-2008	-9% (LS)	
	10 8 - 268 10 10 10 10 10 10 10 10 10 10		

#### Minnesota River Basin results

#### Minnesota River

The nitrate trends analyses for Minnesota River sites indicated that flow-adjusted concentrations gradually increased in the Minnesota River for many years, but that there is evidence of amelioration in that trend in more recent years. The upper portion of the basin shows little recent trends in either direction, while sites in the lower portion of the basin, from the Blue Earth to the Minnesota River mouth, show some decreases. In particular, the two sites at Jordan and Fort Snelling, with the most extensive data sets, show decreases of about 40% over the most recent half-dozen years ending in 2010 and 2011 (Table 7).

Sites meeting the long term trends analysis criteria were not available at points on the upper half of the Minnesota River. The most upstream site analyzed is near Courtland, Minnesota, which is just southeast of New Ulm. At Courtland, where nitrate concentrations are still relatively low compared to downstream sites, flow-adjusted nitrate concentrations were not found to be statistically significant.

Between Courtland and St. Peter, the influential tributaries of the Greater Blue Earth and the Watonwan Rivers enter the Minnesota River. At St. Peter and Henderson, concentrations increased from 1976 to 1981 and then decreased between 1982 and 1986, followed by a more stable period of no significant trend at St. Peter and gradual trends at Henderson. Further downstream, in Jordan and Fort Snelling, the River showed increasing trends from 1976 until 2004-05, followed by such large decreases that the overall change since 1976 is a slight reduction in flow-adjusted nitrate concentration.

Table 7. Flow-adjusted nitrate concentration trends at five Minnesota River monitoring locations. "LS" indicates a lower strength trend.

Site #	Minnesota River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
054	Minnesota River - Courtland		1.3
	Overall change 1976-2009	NT	
	10 8 -054 		
041	Minnesota River – St. Peter		2.3
	Overall change 1976-2009	+49%	
	1976-1981	+119	
	1982-1986	-32%	
	1987-2009	NT	
	10 8 -041 		

Site #	Minnesota River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
040	Minnesota River - Henderson		2.1
	Overall change 1976-2009	+50%	
	1976-1981	+129%	
	1982-1986	-31%	
	1987-2000	+33%	
	2001-2009	-28% (LS)	
	10 8 -040 -040 -040 -040 -040 -040 -040 -040		
991(39.4)	Minnesota River - Jordan		1.9
	Overall change 1979-2010	-26%	
	1979-2004	+19% (LS)	
	2005-2010	-38%	
	10 8 991 		
996(3.5)	Minnesota River – Fort Snelling		2.2
	Overall change 1976-2011	-6%	
	1976-2005	+74%	
	2006-2011	-46%	
	10 8 -996 -996 4 2 0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

#### **Tributaries to the Minnesota River**

Four tributaries to the Minnesota River upstream of Courtland had trend analyses performed. All four rivers showed no significant trends since 1993 (Table 8). Prior to 1993, nitrate was increasing in the Pomme de Terre and Redwood Rivers and was stable (no significant trend) at the Yellow Medicine and Cottonwood Rivers.

The Greater Blue Earth River contributes substantial quantities of nitrate to the Minnesota River and therefore has a large effect on Minnesota River nitrate levels in these areas. The Blue Earth River showed an increase from 1976 to 1982, followed by a long gradual decrease. Conversely, the Watonwan River has shown a long gradual increase in flow-adjusted nitrate concentrations. Neither of these trends in the Blue Earth and Watonwan mirrors the trends in the downstream segments of the Minnesota River, suggesting that streamflow and nitrate inputs from additional tributaries have affected nitrate concentration trends in the lower Minnesota River.

Table 8. Flow-adjusted nitrate concentration trends in six tributaries of the Minnesota River.

Site #	Minnesota River Tributaries Site location / trend periods	% change in Nitrate	Ending conc. mg/l
195	Pomme de Terre River - Appleton		0.3
	Overall change 1976-2010	+75%	
	1976 – 1992	+75%	
	1993 – 2010	NT	
	8 — 195 — — — — — — — — — — — — — — — — — — —		
159	Yellow Medicine – Granite Falls		0.5
	Overall change 1976-2009	NT	
	10 8 159 		

Site #	Minnesota River Tributaries Site location / trend periods	% change in Nitrate	Ending conc. mg/l
299	Redwood River – Redwood Falls		2.3
	Overall change 1976-2009	+58%	
	1976-1992	+58%	
	1992-2009	NT	
	10 8 - 299 16: 6 4 - 29 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
139	Cottonwood River – New Ulm		2.0
	Overall change 1976-2009	NT	
	10 8 - 139 		
163	Watonwan River – Garden City		4.2
	Overall change 1976-2009	+48%	
	10 8 - 163 - 163 		
134	Blue Earth River – Mankato		3.1
	Overall change 1976-2010	+23%	
	1975-1982	+70%	
	1982-2009	-27%	
	10 8 -134 		

#### St. Croix River Basin results

#### St. Croix River

Very minor percent changes in nitrate were found at Danbury, Wisconsin, the upper-most monitored reach of the St. Croix River, despite very low (less than 0.1 mg/l) nitrate concentrations at the beginning of the record. Nitrate concentrations remain low throughout the St. Croix River, but are higher at Stillwater and Prescott, as compared to Danbury.

Further downstream at Stillwater and Prescott, nitrate concentrations steadily increased from 1976 to 2005, at which time concentrations began to decrease in Stillwater and continued to rise at Prescott (Table 9).

Table 9. Flow-adjusted nitrate concentration trends at three monitoring sites along the St. Croix River. "LS" indicates a lower strength trend.

Site #	St. Croix River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
056	St. Croix River – Danbury, WI		0.09
	Overall change 1975-2011	-2%	
	1976-1992	-10%	
	1993-2011	+9% (LS)	
	1.0 0.8 0.6 8 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
992/23.3	St. Croix River - Stillwater		0.26
	Overall change 1976-2010	+19%	
	1976-2004	+49%	
	2005-2010	-20%	
	1.0 0.8 992 0.6 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

Site #	St. Croix River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
995(0.3)	St. Croix River - Prescott		0.58
	Overall change 1976-2009	+74%	
	1976-2000	+57%	
	2001-2009	+11%	
	1.0 0.8 995 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

#### **Tributaries to the St. Croix River**

Two tributaries in the upper reaches of the St. Croix River were analyzed for trends. Both the Snake River and Kettle River have very low nitrate, around 0.1 mg/l, similar to the concentrations in the St. Croix River at Danbury. The Kettle River nitrate concentrations showed no trend prior to 1991 and then started to gradually increase after 1991. The Snake River showed no significant trends since 1991 (Table 10). Prior to 1991, flow data were not available for the Snake River to allow for flow-adjusted trends analysis.

Table 10. Flow-adjusted nitrate concentration trends two tributaries of the St. Croix River.

Site #	Tributaries – St. Croix River Basin Site location / trend periods	% change in Nitrate	Ending conc. mg/l
121	Kettle River – Hinkley		0.09
	Overall change 1976-2011	+32%	
	1976-1989	NT	
	1990-2011	+32%	
	1.0 0.8 121 20.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

Site #	Tributaries – St. Croix River Basin Site location / trend periods	% change in Nitrate	Ending conc. mg/I
198	Snake River – Pine City		0.12
	Overall change 1991-2010	NT	
	1.0 0.8 198 0.6 0.9 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

#### **Cedar and Des Moines River results**

The Cedar River is among the highest nitrate concentration rivers in the state. It has steadily shown increasing nitrate levels since 1967 (Table 11), with increases averaging 1% per year at Lansing (1980-2010) and 2% per year at Austin (1967-2009). No statistically significant trend was found on the West Fork Des Moines River near Petersburg (Table 12).

Table 11. Flow-adjusted nitrate-N concentration trends at two sites along the Cedar River.

Site #	Cedar River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
137	Cedar River – Lansing		7.1
	Overall change 1980-2010	+53%	
	10 8 -137 		
136	Cedar River - Austin		6.4
	Overall change 1967-2009	+113%	
	10 8 -136 -136 -136 -136 -136 -136 -136 -136		

Table 12. Flow-adjusted nitrate concentration trends in the West Fork Des Moines River.

Site #	Des Moines River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
156	W. Fork Des Moines River – Petersburg		1.9
	Overall change 1976-2009	NT	
	10 8 -156 -156 -156 -156 -156 -156 -156 -156		

#### Red River of the North results

#### **Red River of the North**

Three sites on the Red River of the North were analyzed for long term trends. All three sites had relatively low nitrate concentrations, although the concentration was higher at the downstream location in Perley. No trends were detected at the upper-most location at Brushvale. At Moorhead, and just downstream from Moorhead at Perley, concentrations showed some increase prior to 1993-95, but had no significant trends detected after the 1993-95 period (Table 13).

Table 13. Flow-adjusted nitrate concentration trends at three locations along the Red River of the North.

Site #	Red River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
012	Red River - Brushvale		0.14
	Overall change 1976-2010	NT	
	1.0 0.8 -012 		

Site #	Red River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
183	Red River - Moorhead		0.21
	Overall change 1976-2010	+53%	
	1976-1987	NT	
	1988-1993	+53%	
	1994-2010	NT	
	1.0 0.8 183 183 180 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
113	Red River - Perley		0.51
	Overall change 1976-2010	+78%	
	1976-1995	+78%	
	1996-2010	NT	
	1.0 0.8 113 0.6 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

#### **Tributaries of the Red River**

Trends were assessed for two tributaries of the Red River, the Ottertail River and the Red Lake River, each with two monitoring locations. Similar to the Red River at Brushvale, nitrate concentrations were very low, mostly between 0.1 and 0.15 mg/l. At these low concentrations, the Ottertail River showed a steady increasing trend since 1982. The percentage increase was greater in Fergus Falls, as compared to the downstream site at Breckenridge (Table 14). The Red Lake River at East Grand Forks showed a very similar trend as the Ottertail River in Breckenridge, both gradually increasing by 35% over the entire time of analysis. Further upstream at Fisher, no trends could be detected.

Table 14. Flow-adjusted nitrate concentration trends in four tributaries of the Lower Mississippi.

Site #	Tributaries – Red River Basin	% change in Nitrate	Ending conc. mg/l
111	Ottertail River – Fergus Falls		0.15
	Overall change 1982-2010	+207%	
	1.0 0.8 -111 		
006	Ottertail River – Breckenridge		0.12
	Overall change 1976-2010	+35%	
	1.0 0.8 0.6 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
031	Red Lake River - Fisher		0.09
	Overall change 1982-2010	NT	
	1.0 0.8 -031 		
013	Red Lake River – East Grand Forks		0.13
	Overall change 1976-2010	+35%	
	1.0 0.8 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

## Rainy and St. Louis Rivers

The Rainy River showed no substantial increases or decreases, with a concentration change at International Falls that rounded to 0%, and no significant trend at Baudette (Table 15). Concentrations have remained very low at both sites since 1976.

Table 15. Flow-adjusted nitrate concentration trends at two locations on the Rainy River.

Site #	Rainy River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
007	Rainy River – International Falls		0.06
	Overall change 1976-2010	*0%	
	1.0 0.8 0.6 8 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
063	Rainy River - Baudette		0.06
	Overall change 1976-2010	NT	
	1.0 0.8 0.6 0.0 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		

<sup>\*</sup> The trend was statistically significant, but was so small that it rounded off to zero.

The St. Louis River, also with very low nitrate concentrations, showed fairly stable trends at Forbes and Fond Du Lac, with a slight decrease at Forbes and a slight increase at Fond Du Lac. In Duluth, nitrate concentrations increased since 1994 by 47% (Table 16).

Table 16. Flow-adjusted nitrate concentration trends at three locations along the St. Louis River.

Site #	St. Louis River Site location / trend periods	% change in Nitrate	Ending conc. mg/l
119	St. Louis River - Forbes		0.11
	Overall change 1978-2010	-20%	
	1978-1986	-20%	
	1987-2010	NT	
	1.0 0.8—119 1.0 0.8—119 1.0 0.0 0.4—119 0.2—110 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
021	St. Louis River – Fond Du Lac		0.10
	Overall change 1976-2010	+16%	
	1.0 0.8 0.6 0.6 0.4 0.2 0.0 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015		
113	St. Louis River - Duluth		0.19
	Overall change 1994-2010	+47%	
	1.0 0.8 975 		

## Discussion

#### Comparison with previous studies

Results of nitrate, total nitrogen and ammonium concentration and load trends from previous Minnesota studies are described in Chapter C2. In this discussion, we will compare only the nitrate concentration trends from previous studies to nitrate concentration trend results reported in this chapter. None of the results are directly comparable because of differences in one or more of the following: trend analysis timeframe; location on the river; and/or statistical analysis/streamflow adjustment methods. Yet, several sites from past studies were close enough in location and timeframe to allow some comparison. In general, the results in this study agreed reasonably well with previous studies where comparisons were possible, except that the magnitude of change was consistently higher in this study as compared to previous studies. Comparisons in specific rivers are described below.

#### Mississippi River

The 76% increase in nitrate concentrations observed by Sprague et al. (2011) in the Mississippi River between 1980 and 2008 at Clinton, Iowa, are reasonably similar to the 107 and 109% increases in the Mississippi River found in this study at the two most downstream Mississippi River sites at LaCrosse and Minneiska (1976 to 2008).

Lafrancois et al. (2013) found increases in the Mississippi River from Anoka to Hastings ranging from 47 to 59% between 1976 and 2006, with one of six sites having no statistically significant trend. Increases were also found in our study, yet the increases were found to be larger during the extended timeframe assessed in this study (1976 to 2010-11). We found increases of 87% to 206% at six Mississippi River sites between Anoka and Prescott.

#### Minnesota River

Previous trend studies in the lower half of the Minnesota River Basin showed that nitrate concentrations either had no significant trend or an overall decreasing trend, with a few exceptions. This study also showed several periods of decreasing trends in the Minnesota River, yet we also found other periods of increases. In the Minnesota River at Jordan, all studies showed little overall change in the Minnesota River nitrate from the late 1970's to the early 2000's (Table 17), although this study indicated a slight increase from 1979 to 2004 and the other studies over slightly different timeframes showed either no trend or a slight decrease. The magnitude of change shown from all studies in the Minnesota River is rather small considering the long period of record.

Table 17. Results of different nitrate concentration trend studies at the Minnesota River Jordan site location, along with the findings in this study.

Timeframe	Nitrate Concentration Change	Author
1979-2004	+19%	This Study
1976-2006	No significant trend	Lafrancois et al. (2013)
1976-2002	-20%	Kloiber, 2004
1979-2003	-10%	Johnson, 2006

#### **Red River**

At the Minnesota/Manitoba border Vechia (2005) found nitrate concentrations to increase in the Red River by 27% from 1982 to 1992, followed by a no-trend period from 1993-2001. Lorenz et al. (2009) found no trend at Grand Forks from 1999-2008. The furthest downstream site evaluated for this study was at Perley. The results we found at Perley were generally similar to what Vechia and Lorenz found further downstream, with an increasing trend through 1995), and no significant trend after that (1996 to 2010).

#### St. Croix River

Kloiber found a 17% nitrate concentration increase in the St. Croix River at Stillwater between 1976 and 2002. This study found a similar increasing trend at this same site between 1976 and 2004, but the magnitude of the increase was slightly higher in this study.

### Lag time with groundwater flow

The average rate of groundwater flow is commonly measured in terms of feet per year. It can take many years to many decades before nitrate leaching through the soil near its source will ultimately move with groundwater until discharging into a river or stream. As described in Appendix B5-1, much of the nitrate can be lost during this groundwater transport process due to denitrification prior to entering surface waters.

The lag time between nitrate leaching through the soil and into groundwater and its subsequent movement to streams depends on many factors, such as soils, geology, topography, and proximity to streams. Groundwater near a stream can enter surface waters within a matter of days or weeks. In parts of the karst region in southeastern Minnesota, water that is further from streams can also travel to streams in shorter periods ranging from less than a day to years. In other areas, the travel time is usually measured in years to decades to centuries. Streams fed by shallow surficial aquifers contain a mix of waters, some of which entered the ground many years earlier and some of which recently entered the groundwater (Puckett et al., 2011). Tesorioro et al. (2013) found decades old nitrate laden water was discharging into a high baseflow stream, suggesting that high nitrate levels may be sustained for decades in some streams regardless of current practices.

This groundwater lag time effect can have a strong influence on observed trends. For example, nearly half of the estimated cropland N sources in the Upper Mississippi River Basin come from groundwater flow; with the rest from tile lines and surface runoff (see Chapters D1 and D4). Because of the long lag time between nitrate entering groundwater and the eventual discharge of the affected groundwater into surface waters in this basin, nitrate pollution which occurred many years to many decades ago may be a large part of the nitrate just now entering streams and rivers. The nitrate concentrations in the Upper Mississippi River integrate the consequences of land use and management in recent years, with that of land use and management occurring years to decades earlier. The complete effects of modern era commercial fertilizer use, crop genetics and management may not yet be realized in Mississippi River nitrate concentrations. Therefore the increasing nitrate levels in the Mississippi River do not necessarily mean that we are currently using practices that are causing higher nitrate loads in the River than a decade or two ago.

The lag-time effect of nitrate moving from groundwater into surface waters is also expected to be a dominant process affecting trends in other basins such as the St. Croix, Red River, and Lower Mississippi Basins, which each have more than half of the estimated cropland nitrate moving into surface waters through groundwater pathways (see Chapter D-1).

In basins with a higher fraction of the nitrate moving through tile drainage, the groundwater lag time will have less of an effect on observed concentration trends in rivers. The Minnesota River Basin has only about 20% of its estimated cropland N transported via groundwater (Chapters D1 and D4), and is dominated instead by the quicker responding tile drainage flow pathway (75% of cropland N estimated). Nitrate concentrations in the downstream sections of the Minnesota River Basin were increasing until the 2001-2005 timeframe, at which time the trends reversed to show declining concentrations through 2009-11. The Des Moines River Basin and Cedar River Basin also have a major nitrate pathway through tile lines (55-70% of cropland N estimated). Nitrate trends in the Cedar show continuous increases. No significant trends were found in the Des Moines River.

#### Changes in land management and precipitation

Many factors potentially affect nitrate concentration trends, including changes in: crops/vegetation; fertilizer management and N use efficiency; human population and wastewater treatment processes; livestock/poultry populations and manure management practices; climate/precipitation; soil mineralization; flow pathways – tile drainage, groundwater, runoff; as well as several other factors.

It was beyond the scope of this study to investigate the relationship between river nitrate concentration trends and changes in land use and hydrologic factors expected to influence nitrate concentrations. Changes in certain variables which have the potential to affect river N levels are summarized below. Future studies that more thoroughly explore possible reasons for nitrate concentration changes could be useful for understanding the key driving factors affecting nitrate increases and decreases.

#### Fertilizer use

Minnesota N fertilizer sales have followed a similar pattern as national fertilizer sales (Figure 6). Fertilizer sales increased markedly between 1965 and 1980, followed by leveling off of sales and a gradual long-term overall increasing trend between 1980 and 2011. The average statewide N rate per acre on corn cropland started leveling off in the early 1970's, with a gradual increasing trend from 1972 until the early 1980's (Figure 7). Fertilizer rates per acre of corn cropland appear to have been relatively stable to slightly increasing from the late 1980's until about 2010, according to information provided by the Minnesota Department of Agriculture.

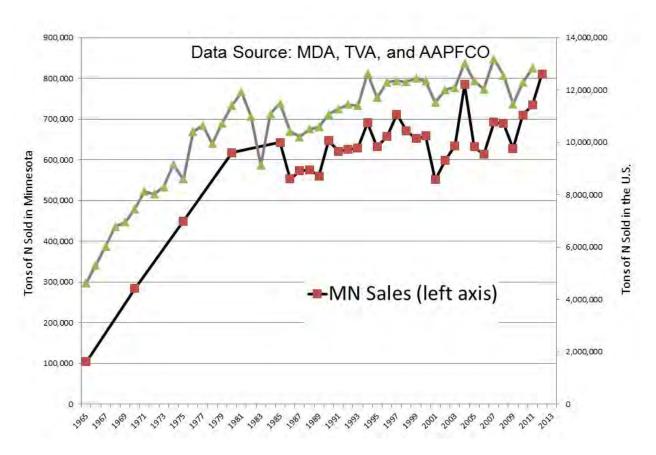


Figure 6. Commercial N fertilizer sales trends from 1965 to 2011 in the U.S. (green) and in Minnesota (red). Graph from MDA (2013). Data sources include: MDA, TVA, and AAPFCO.

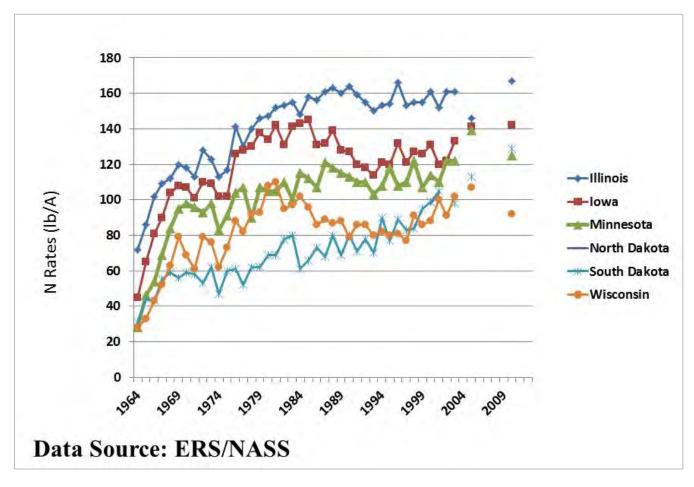


Figure 7. Midwest states' N fertilizer rates for corn from 1964 to 2010. Graph from MDA (2013). Data sources: ERS/NASS.

#### Crop nitrogen fertilizer use efficiency

An estimated 31% of statewide N outputs from agricultural lands go into the atmosphere, mostly through the three processes of senescence, denitrification in soil, and volatilization, and an estimated 6% of N outputs go into groundwater and surface waters (see Chapter D4 - Mulla et al., 2013). The remaining 63% of N from agricultural lands goes into crops and food products. As N fertilizer use becomes more efficient through plant genetics and improved management practices, more of the N goes into crops and potentially less is lost into the atmosphere and into waters. The N fertilizer use efficiency has been increasing over the past decades according to information assembled by the Minnesota Department of Agriculture. The bushels of corn produced per pound of N fertilizer input (crop N use efficiency) has increased from about 0.8 in 1992 to about 1.3 in 2011 (Figure 8; MDA, 2013). More N is now used by the crop and less N may therefore be available in the soil for potential losses to the air and water for each bushel of corn produced. The potential benefits of this trend to water quality, however, may be offset somewhat as corn protein content decreases and as more corn is grown per acre. Further study is needed of the water quality effects from such changes.

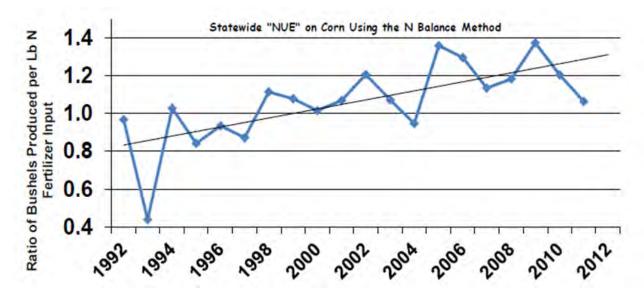


Figure 8. Bushels of corn produced per pound of N fertilizer applied to corn cropland, 1992 to 2011. Graph from MDA (2013).

### Livestock/poultry manure

Based on U.S. Department of Agriculture National Agricultural Statistics Service inventories between 1974 and 2007, Minnesota cattle and calf numbers have declined by 35% (most influenced by dairy declines), while swine numbers have more than doubled and turkeys have more than tripled. The total number of animal units in the state, as animal units are defined in Minn. R. ch. 7020, has generally remained constant since 1974 (Figure 9). Decreasing cattle were offset by the increasing swine and turkey numbers.

The estimated amount of manure N being applied onto cropland from livestock and poultry did not vary by more than 12% between 1974 and 2007, and estimated manure N amounts applied statewide in 2007 were only 1% more than applied in 1974. It is also possible that even though the amount of manure N being generated and applied to lands has not changed much, the amount of manure N entering waters may have changed (i.e. less manure N entering waters).

Manure management changed considerably throughout this period (1974 to 2007) as more liquid manure storage pits and basins were constructed, replacing solid manure handling systems. Methods of application correspondingly changed, and injection of liquid manure below the ground surface became more popular. We expect that these changes should have resulted in more predictability in crop available N from manure, and therefore improved manure management and less N losses to waters.

During 2000, Minnesota changed its Feedlot Regulations related to manure spreading. The effects of these regulations on N management have not been researched. It is possible that the new regulations resulted in improved N management and less N losses to waters. The rule changes affecting N management included requirements for: nutrient management plan development, record-keeping of manure spreading, and laboratory testing of manure N content, among others.

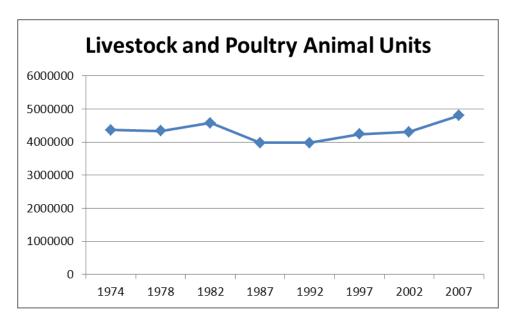


Figure 9. Trends of total animal units (AUs) in Minnesota based on USDA National Agricultural Statistics Service data and the following conversion factors: dairy cow - 1.4 AUs; beef cow - 1 AU; other cattle and calves avg. - 0.7 AU; swine and hogs - 0.3 AU; turkeys - 0.018 AU; chickens - 0.003 AU.

### **Human population**

The Minnesota population has been growing steadily from 4 million people in 1980 to 5.4 million in 2012. The increased population would be expected to have a corresponding increase in human wastewater N discharges from municipalities and septic systems. Because of wastewater treatment system upgrades at many facilities in the 1980's and 1990's, the form of N released to waters changed from ammonium to nitrate.

### Cropping changes

Since the mid-1960's, row crop acreages have increased substantially in Minnesota. Corn acreage has increased by over 30% (Figure 10) and soybean acreage has more than doubled (Figure 11). At the same time, alfalfa and clover, which contribute low levels of N to waters, have decreased by more than 40%. Between 2006 and 2011 Minnesota's net loss of grasslands converted to corn/soybeans was 196,000 acres (Wright and Wimberly, 2013).

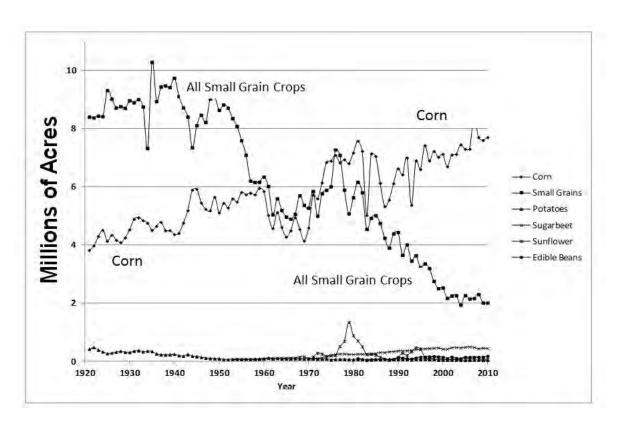


Figure 10. Trends in acreage planted to corn and small grain crops in Minnesota between 1920 and 2011. From MDA (2013).

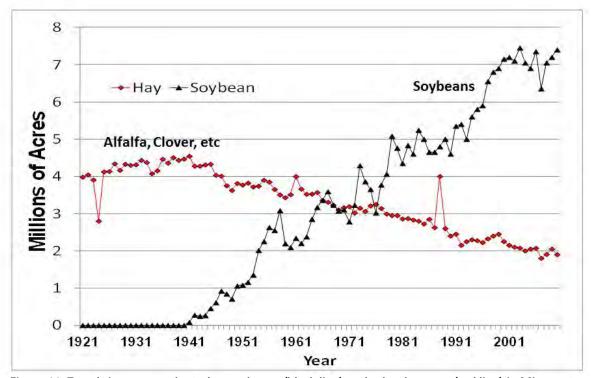


Figure 11. Trends in acreage planted to soybeans (black line) and other legumes (red line) in Minnesota between 1921 and 2011.

### Tile drainage changes

Tile drains continue to be installed and replaced in Minnesota soils. The rate of increasing tile drainage is not well documented in the state and was not quantified for this study. The Red River Valley is one area of the state which historically had minimal tiling, but during recent years has had millions of feet of drain tile installed on cropland soils.

### **Precipitation changes**

Between 1975 and 1995, the statewide annual average precipitation trends showed huge swings of wet and dry periods. Since 1995, statewide seven-year moving average precipitation has remained relatively high compared to historical levels, with a fairly stable trend compared to other times in history (Figure 12).

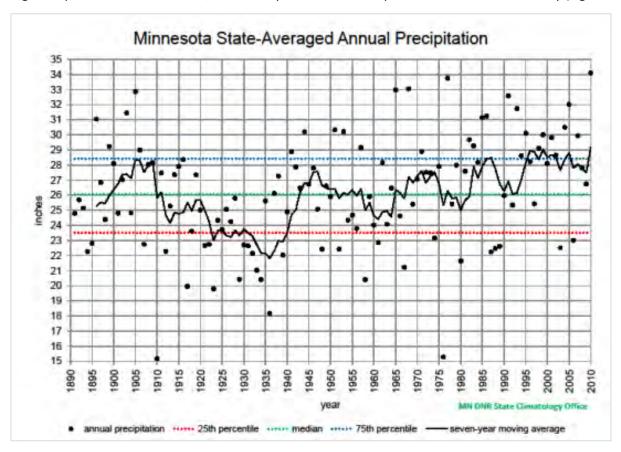


Figure 12. Long term precipitation patterns in Minnesota since 1890. From MN DNR State Climatology Office.

Figures 13 to 20 show spatial average annual precipitation amounts across HUC8 watersheds in different regions of the state from 1980 to 2009, developed from precipitation data provided by the Minnesota Department of Natural Resources. Overall, the precipitation trends in this timeframe did not show major overall changes, although slight increases or slight decreases are evident in some watersheds (Figures 13-19). A region of the state with a more consistent increasing trend over this period is northwestern Minnesota in the Red River Basin (Figure 20).

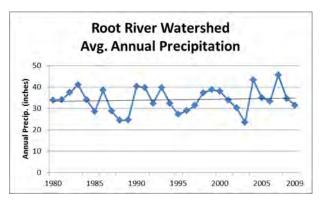


Figure 13. Spatial average annual precipitation amounts for the Root River Watershed from 1980 to 2009.

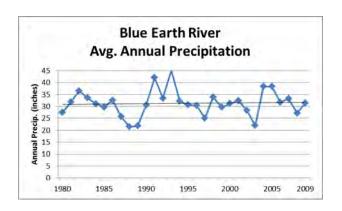


Figure 14. Spatial average annual precipitation amounts for the Blue Earth River Watershed from 1980 to 2009.

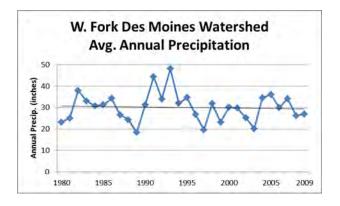


Figure 15. Spatial average annual precipitation amounts for the West Fork Des Moines River Watershed from 1980 to 2009.

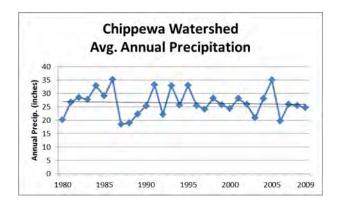


Figure 16. Spatial average annual precipitation amounts for the Chippewa Watershed from 1980 to 2009.

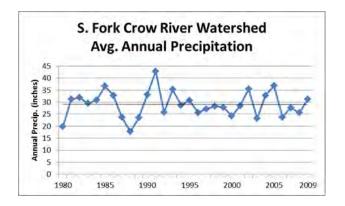


Figure 17. Spatial average annual precipitation amounts for the South Fork Crow River Watershed from 1980 to 2009.

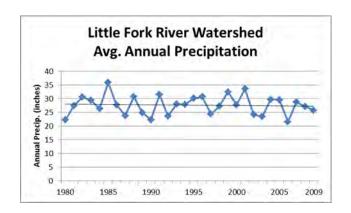


Figure 18. Spatial average annual precipitation amounts for the Little Fork River Watershed from 1980 to 2009.

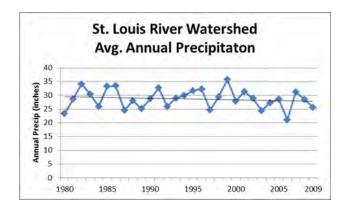


Figure 19. Spatial average annual precipitation amounts for St. Louis River Watershed from 1980 to 2009.

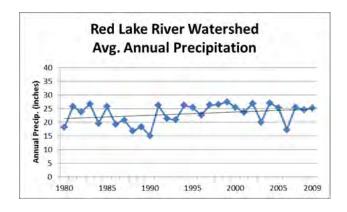


Figure 20. Spatial average annual precipitation amounts for the Red Lake River Watershed from 1980 to 2009.

## Relationship between streamflow and nitrate concentration – a QWTREND analysis

The QWTREND model was used to evaluate the relationship between streamflow and nitrate concentrations using four different time period assessments: 1) seasonal – 90 day periods, 2) annual, 3) five-year and 4) HFV – short-term events. A positive streamflow anomaly coefficient indicates a direct relationship between streamflow and nitrate concentrations, such that nitrate concentrations are statistically higher during high flow periods. A negative coefficient indicates a negative relationship between flow and nitrate concentration. A higher magnitude coefficient represents a stronger relationship, such that coefficients in the 0.4 to 0.8 range represent a very strong relationship between streamflow and nitrate levels.

Most of the rivers had a positive coefficient for the seasonal, annual and HFV periods of time, indicating that the average nitrate concentrations over the 90 day, annual and short-term event time periods are typically higher when streamflows are higher. One exception was the Rainy River, which had such low coefficients that essentially no relationship was evident between streamflow and nitrate. In general, the coefficients are larger for the southern part of Minnesota than in the northern part, indicating a stronger relationship between streamflow and nitrate levels in parts of the state where nitrate concentrations and effects of human activities on nitrate levels are higher.

The streamflow anomaly coefficients are larger for the 90-day and annual averages as compared to the five- year average (Table 18), indicating that nitrate variation from season to season or year to year is more highly correlated to streamflow than five-year average streamflow and nitrate relationships.

The Minnesota River Basin shows a strong direct correlation between streamflow rate and nitrate concentrations for all types of time periods evaluated, but was highest for the seasonal averages. By comparison, the Upper Mississippi River Basin, which has a greater influence from groundwater baseflow and less influence from tile drainage, had lower coefficients and thus a weaker relationship between concentration and streamflow.

Some of the coefficients for the five-year anomaly are negative, although the negative relationships are weak at all sites (low coefficient magnitude), except the Mississippi River between the Minnesota and the St. Croix Rivers. The negative long-term (five-year) coefficients may be at least partly attributable to the dilution of wastewater, since the strongest negative signal for those coefficients is downstream of the Twin Cities.

Overall, the pattern of the coefficients suggests that surplus nitrate is flushed through the soil or off the soil by both rainfall/snowmelt events and by sustained wet periods, particularly in the agricultural areas of the state.

Table 18. Mean model coefficients for the streamflow anomalies by basin. Coefficients greater than 0.2 are highlighted in yellow.

Seasonal (90 day average streamflow)	Annual	5-Year	HFV (event flushing – seasonal component)					
Upper Mississippi River Basin								
0.197	0.197	-0.121	0.082					
	Mississippi River between M	linnesota and St. Croix Rivers						
0.569	0.768	-0.205	0.250					
	Lower Miss	issippi River						
0.988	0.768	-0.056	0.100					
	Tributaries to the Lo	wer Mississippi River						
0.226	0.178	0.046	0.075					
	Minnesota River Basin							
0.703	0.649	0.453	0.269					
	St. Croix F	River Basin						
0.041	0.014	-0.008	0.002					
	Cedar and Des M	oines River Basins						
0.521	0.521	0.240	0.233					
	Red River of the	ne North Basin						
0.133	0.026	0.011	0.178					
	Rainy Ri	ver Basin						
-0.0001	0.018	-0.075	-0.003					
	Saint Louis River Basin and	Lake Superior Tributaries						
0.120	0.287	0.011	0.001					

### Summary of nitrate trends results

Flow-adjusted nitrate concentration trends in the Mississippi River increased between 1976 and 2010 at most sites on the river, with overall increases ranging between 87% and 268% everywhere except the most upstream location at Blackberry (0% change). Three of the 10 sites with increases showed a leveling off of the increase or no-trend starting in the mid to late-1990's (Camp Ripley, Grey Cloud and Hastings). The other 7 sites showed a continuous increase over the analysis period. During recent years, the annual increases everywhere downstream of Clearwater have ranged from 1% to 4% (except that no significant trend has been detected at Grey Cloud and Hastings). The two most upstream locations at Blackberry and Camp Ripley have recently shown a decreasing trend and no trend, respectfully. Trend results from a limited number of tributaries to the Mississippi River showed trends which did not always match the Mississippi River trends. For example, during recent years several tributaries, including the Rum, Straight, Cannon, and Zumbro Rivers, have shown decreasing trends.

Flow-adjusted nitrate concentration trends in the Minnesota River were somewhat different at different points along the River. The two most upstream sites at Courtland and St. Peter showed no trend after 1987. St. Peter and Henderson showed an increase from 1976 to 1981, followed by a decrease between 1982 and 1986. After 1986, the Henderson site showed a similar pattern as the Jordan and Fort Snelling sites. All three downstream sites (Henderson, Jordan and Fort Snelling) showed a steady gradual increase through 2004, followed by a decrease between 2005 and 2010. The overall long term net change at the three downstream sites was +50%, -26% and -6%. During recent years, all sites on the Minnesota River and most tributaries to the Minnesota have been trending downward or have shown no trend. The only exception is the Watonwan River, which has been showing a slight increase of about 1% per year.

In a couple of the smaller upstream stretches of mainstem rivers originating in Minnesota, the Cedar River showed a steady increase of 113% over a 43-year period; whereas The West Fork of the Des Moines River showed no trend.

In northern Minnesota, the major rivers showed either no trend or a slight increase. All of these rivers had very low nitrate concentrations throughout the period of analysis. The Red River showed significant increases before 1995, but no trends since about that time. The St. Louis River at Duluth changed the most, showing a 47% increase between 1994 and 2010.

Overall, the findings showed generally similar trend patterns as previous trend studies conducted at the same or nearby locations, although there were some differences. The magnitude of change was typically larger in this study as compared to previous studies. Additionally, the slight increase in nitrate at the Minnesota River Jordan site from 1976 to 2003 was different from other studies which showed no significant trend or a decreasing trend.

The reasons for the nitrate concentration changes were not determined. However, we noted several concurrent statewide land use trends during the period of analysis. Acres planted to corn and soybeans increased, while small grain and alfalfa/clover acreages decreased. Fertilizer application increased, mostly prior to 1980, and has increased at a much slower rate since 1980. Manure N generation was essentially the same in 1974 and 2007. And overall corn N use efficiency has increased steadily since 1992, resulting in more corn grown for each pound of fertilizer used. Human population has increased from 4 to 5.4 million people. No strong trends in annual precipitation were evident during recent decades, except in northwestern Minnesota where annual precipitation has been increasing.

### **Future studies**

Studies that might add to the understanding of nitrate trends include:

- Further explore the causes of nitrate concentration trends, particularly the decreases observed in downstream parts of the Minnesota River after 2005, and several periods of increases in other rivers between 1990 and 1995.
- As more total nitrogen and nitrate load results become available, analyze trends in loads.
- Assess typical lag times between BMP adoption and river nitrate response in watersheds where groundwater is the dominant pathway for nitrate to rivers.
- Re-evaluate trends periodically to see if recent short-term trend patterns continue, such as the decreasing trends in the Minnesota River Basin.
- Use alternative statistical trend methods to compare against QWTRND methods used in this analysis.
- Assess nitrate load changes over time where monitoring is sufficient and land use changes have been made.

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# C2. Nitrogen Trend Results from Previous Studies

Author: Dave Wall, MPCA

### Overview

Several statistical trend analyses of Minnesota's river and stream nitrogen (N) levels have been investigated during recent decades. We reviewed the results of these previous studies to: 1) compare past results to the nitrate concentration trend analyses developed for this study and reported in Chapter C1; 2) review trends of N forms not evaluated in Chapter C1, such as ammonium and total nitrogen (TN); and 3) review river N *load* trends which are not assessed in Chapter C1. Because trend results depend on the watersheds studied, the timeframe analyzed, monitoring design, parameters assessed, and statistical procedures, the studies are not directly comparable. Yet collectively, these trends analyses provide useful information for understanding possible trends in Minnesota's rivers and streams over the past several decades.

An overview of results from previous studies is shown in Table 1. The specific studies noted in Table 1 are described in more detail in the remainder of Chapter C2.

Table 1. Summary of past trend results assessed for rivers in Minnesota. "Nitrate" refers to nitrite+nitrate and "ammonium" refers to ammonia+ammonium.

Study area	Timeframe considered	Trends results summary	Organization (author)
Mississippi River			
Mississippi River in Clinton Iowa	1980 - 2008	Nitrate concentration - increased 76%	USGS
<ul> <li>drainage area includes much</li> </ul>		Nitrate load - increased 67%	(Sprague et al.,
of southern MN, NE Iowa and			2011)
western Wisconsin			
Mississippi River in Clinton Iowa	1975-2005	Total Nitrogen flow adjusted conc. increased	USGS
<ul> <li>drainage area includes much</li> </ul>		from 1975-82, then remained stable from	(Lorenz et al.,
of southern MN, NE Iowa and		1983 to 2005.	2008)
western Wisconsin			
Mississippi River – Twin Cities	1976 - 2005	Total Nitrogen conc. – no trend at all six sites	Natl. Park
Area		Total Nitrogen loads – No trends at four	Service, Science
		sites; 18-24% increase at two sites;	Museum and
		Nitrate-N conc. – no trend at one site; 47-	Met Council
		59% increases at five sites; Nitrate-N loads	(Lafrancois et
		- 37 to 68% increase at all six sites	al., 2013)
		Ammonium loads and conc. – all sites	
		decreased by 129 - 353%	
Mississippi River at Anoka and	1976 – 2002	Nitrate conc increased 31% at Anoka and	Met Council
Red Wing		12% at Red Wing Ammonium conc	(Kloiber, 2004)
		decreased 91% and 78%	

Study area	Timeframe considered	Trends results summary	Organization (author)
Minnesota River			
Minnesota River at Jordan	1976-2005	Total Nitrogen conc. – No Trend Total Nitrogen load – Increased 18% Nitrate conc. – No Trend Nitrate load – Increased 27% Ammonium conc. – Decrease 221% Ammonium load – Decrease 142%	Lafrancois et al., 2013
Minnesota River at Jordan	1976 – 2002	Nitrate conc decreased 20% Ammonium conc decreased 72%	Met Council (Kloiber, 2004)
Minnesota River and Greater Blue Earth River	Starting in Late 1970's to mid 1980s; ending 2001- 2003	Nitrate conc. – decreasing trends in the Minnesota River Jordan and the Greater Blue Earth River; Increasing trend in the Minnesota River at Fort Snelling	U of MN (Johnson, 2006)
Minnesota River Basin – multiple locations	1999 - 2008 (some exceptions)	Nitrate conc Western end of basin (upper parts of basin) had mostly stable and increasing trends; Eastern end of basin (lower parts of basin) had mostly stable and mixed trends, with several sites showing decreasing trends.	Minnesota State Univ. at Mankato (Sanjel et al., 2009)
St. Croix River			
St. Croix River at Stillwater	1976 – 2002	Nitrate conc Increased 17% Ammonium conc Decreased 81%	Met Council (Kloiber, 2004)
Red River of the North			
Red River at Emerson (near Canadian border) and Halstad, MN Red River at Canadian Border	1975 - 2001 1978 - 1999	Nitrate conc. increased (23-27%) from 1982 to 1992 at both sites, and had no trend before 1982 and after 1992.  Total nitrogen conc increased 29%	USGS (Vecchia, 2005) Manitoba WQ Mgmt (Jones et al., 2001)
Southeastern Minnesota			
25 rivers in SE Minnesota	1984 – 1993	Nitrate conc stable, except for slight increase in St. Croix River at Prescott Ammonium conc decreased at 24/25 sites	USGS (Kroening & Andrews, 1997)
Southeastern Minnesota Springs	Early 1990's to 2010-11	Nitrate conc. – increased at two springs by 15% and 100%.	MPCA (Streitz, 2012)
Mississippi River Winona Watershed	Varied 16 to 35 yrs ending 2008-11	Nitrate conc. – All six sites had increasing trend	Olmsted Co. Env. Res., 2012 (Crawford et al)
Twin Cities area streams	Mostly 1999 to 2010; some sites 1990-2010	Nitrate conc varied trends, with 6 sites decreasing, 3 sites increasing and 9 sites having no trend or mixed trends.	Met Council (Jensen, 2013)

# Mississippi River south of the Minnesota border

The U.S. Geological Survey (USGS) has been measuring flow and nutrient concentrations in the Mississippi River at Clinton Iowa since the mid-1970s. The contributing watersheds for this site include basins primarily in Minnesota, Wisconsin, and northeastern Iowa (Figure 1). Trend results were reported in two recent USGS reports.

Using the QWTREND model, Lorenz et al. (2009) found TN flow-adjusted concentrations to increase between 1975 and 1982 from 1.60 to 2.38 mg/l. Between 1983 and 2005, the concentrations remained largely stable, decreasing slightly from 2.38 to 2.30 mg/l (Figure 2). Total nitrogen *loads* also increased in the 1975 to 1982 time period, and then generally remained stable between 1983 and 2004.



Figure 1. Location of the Clinton, Iowa USGS monitoring site and the contributing drainage area (from USGS).

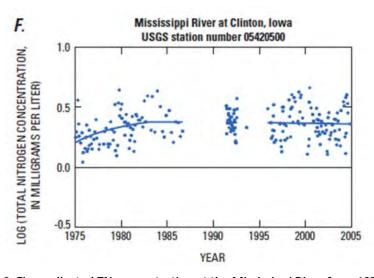


Figure 2. Flow adjusted TN concentration at the Mississippi River from 1975 to 2005. (from Lorenz et al., 2009).

Sprague et al. used the WRTDS model to evaluate nitrite+nitrate (nitrate) concentration changes at the Mississippi River Clinton, Iowa site (Sprague et al., 2011). The period of trends analysis began in 1980 and ended in 2008. Concentrations were normalized to remove variation due to random streamflow differences from one period of time to another. Results showed a nitrate increase, with the annual flow-normalized mean concentration increasing from 1.13 mg/l in 1980 to 1.99 mg/l in 2008. The increases were found at all categories of streamflow, but were largest during high and moderate streamflows at this monitoring location. Annual flow-normalized nitrate loads increased 67% during this same time period. The year-to-year load increases were found to be generally consistent, whether evaluated just for the spring months or for the entire year. One of the reasons for the difference in findings between the Lorenz et al. (2009) study and the Sprague et al. (2011) study was the assessed timeframe. Nitrate levels spiked in 2008, a year that was included in the Sprague study, but was after the Lorenz analysis period. Different statistical methods and different parameters (TN vs. nitrate) may also explain the differences in findings. Both studies showed fairly level concentrations between 1983 and 2005.

# Minnesota, Mississippi, and St. Croix Rivers near the Twin Cities

### Nitrogen concentration trends 1976-2005

Using data collected every other week from 1976 to 2002, the Metropolitan Council (Kloiber, 2004) assessed temporal trends at four large river monitoring sites, including the: 1) Minnesota River at Jordan; 2) St. Croix River at Stillwater; 3) Mississippi River at Anoka; and 4) Mississippi River at Red Wing (Figure 3). Using a flow-adjusted Seasonal Kendall Trend test, Kloiber found that ammonium concentrations decreased between 72 and 91% during the 1976 to 2002 timeframe at the four monitoring points. This decrease was thought to be due to improvements in point source controls which occurred during this same period. Total Kjeldahl nitrogen (TKN) decreased between 20 and 34% at the three monitored sites. Nitrate was found to have increased in the St. Croix River (+17%) and Mississippi River Anoka (+31%). Nitrate concentrations at the Minnesota River monitoring site near Jordan decreased by 20% (Table 2).



Figure 3. Location of Metropolitan Council major river load monitoring stations (from Met Council)

Table 2. Nitrogen parameter concentration medians, means and trends as determined by Metropolitan Council at their major river monitoring sites between 1976 and 2002. From Kloiber 2004.

	Median nitrate- N mg/l	Mean nitrate- N mg/l	Trend nitrate-N	Median NH4-N mg/l	Mean NH4-N mg/l	Trend NH4-N	Median TKN mg/l	Mean TKN mg/l	Trend TKN
MN River at Jordan	4.4	4.9	Decrease 20%	0.05	0.12	Decrease 72%	1.4	1.4	Decrease 20%
St. Croix River at Stillwater	0.3	0.4	Increase 17%	0.05	0.08	Decrease 81%	0.6	0.6	Decrease 33%
Mississippi River at Anoka	0.6	0.8	Increase 31%	0.05	0.11	Decrease 78%	0.9	0.9	NM
Mississippi River at Red Wing	2.2	1.4	Increase 12%	0.13	0.26	Decrease 91%	1.2	1.1	Decrease 34%

### Loads and concentration trends 1976-2005

The National Park Service, working together with the Science Museum of Minnesota and Metropolitan Council Environmental Services, recently assessed flow-adjusted load and concentration trends at six Mississippi River locations between Anoka and Hastings, along with the Minnesota River near Fort Snelling. Using the Seasonal Kendall Trend test and Sen's slope estimator, long-term trends were determined for three N parameters analyzed at least twice monthly throughout each year of the 1976 to 2005 timeframe (Lafrancois et al., 2013). Percent changes over the 1976-2005 period are shown in Table 3.

Table 3. Percent increases (+) or decreases (-) in three N parameters measured at least twice monthly between 1976 and 2005. Red indicates increasing trends; blue indicates decreasing trends and white "n.s." boxes indicate no statistically significant trend. From Lafrancois et al. (2013).

Sites	TN conc.	TN load	NO2+NO3-N	NO2+NO3-N	NH3+NH4-N	NH3+NH4-N
			conc.	load	conc.	load
Miss R. UM872	n.s.	+22%	+49%	+62%	-214%	-129%
(Anoka)						
Miss R. UM 848	n.s.	+24%	+58%	+68%	-234%	-133%
(Mpls)						
Miss R. UM839	n.s.	n.s.	n.s.	+37%	-230%	-182%
(St. Paul)						
Miss R. UM831	n.s.	n.s.	+59%	+53%	-303%	-238%
(S. St. Paul)						
Miss R. UM827	n.s.	n.s.	+53%	+55%	-284%	-251%
(Inver Grove						
Heights)						
Miss R. UM816	n.s.	n.s.	+47%	+51%	-353%	-271%
(Hastings)						
Minn. R.	n.s.	+18%	n.s.	+27%	-221%	-142%
MI4						
(Fort Snelling)						

In summary, this study showed that ammonium concentrations decreased dramatically between 1976 and 2005, while nitrate concentrations increased at most Mississippi River sites. Total nitrogen concentrations did not have a statistically significant trend at any of the sites. Total nitrogen loads increased slightly (18-24%) in the north Metro part of the Mississippi River and Minnesota River Fort Snelling, and were not significant at the four Mississippi River sites downstream of Minneapolis. Nitrate loads increased by 27 to 68% at all sites.

### Minnesota River Basin

### Multiple sites 1998 - 2008

Nitrate concentration trends over a 10-year period (1999-2008) were evaluated in the Minnesota River Basin by Sanjel et al. (2009). For this relatively short period of time, the Seasonal Kendall test method generally showed that watersheds in the western part of the basin had either no statistically significant trend (seven sites) or an increasing trend (four sites). Watersheds in the eastern (lower) part of the

basin had sufficient data to use the more robust QWTREND model. All three tributaries in the southeast part of the Basin had decreasing trends, and the Minnesota River had a decreasing trend at Judson and no statistically significant trend at St. Peter.

Of the nine sites evaluated in the Cottonwood River and eastward, the results were mixed. With the Seasonal Kendall test, six sites showed no trend, one site showed a decreasing trend (Little Cobb River), and two sites showed increasing trends (Cottonwood River and Minnesota River at Judson). The two most downstream sites (Minnesota River at St. Peter and at Jordan) showed no statistically significant trend.

### Fort Snelling, Jordan, and Greater Blue Earth - various timeframes between 1976 and 2003

Nitrate-N flow-adjusted concentration trends were evaluated by Johnson (2006) for two Minnesota River sampling locations (Fort Snelling and Jordan) and the Greater Blue Earth River, which is the largest tributary to the Minnesota River. The trend results, which extended for at least 10 years and ended between 2001 and 2003, are shown in Table 4. Both the Minnesota River Jordan and Greater Blue Earth River had decreasing trends during this timeframe. However, the Minnesota River Fort Snelling site showed an increasing trend between 1976 and 2003 with the QWTREND method. A direct comparison over this same timeframe using the Seasonal Kendall method at Fort Snelling was not performed, yet the Seasonal Kendall test showed a 63% increase in the relatively short interval from 1995 to 2003.

Table 4. Flow-adjusted nitrate concentration trends during varying time periods and statistical methods (from Johnson, 2006).

	Nitrate-N mg/l	Nitrate-N mg/l
	QWTREND	Seasonal Kendall
MN River at Jordan		
1979-2003	-10%	-28%
MN River at Fort Snelling		
1976-2003	+89%	
Greater Blue Earth River		
1986-2001	-17%	
1990-2001		-40%

### Southeastern Minnesota

Twenty-five sites in the southern half of the Mississippi River Basin, and the Cannon, Vermillion, and St. Croix River watersheds 1984 - 1993

Using data collected between 1984 and 1993, the USGS conducted an in-depth study of stream nutrients in large parts of Minnesota, including the southern half of the Mississippi River Basin, the Cannon and Vermillion River watersheds, and the St. Croix River Basin in Minnesota and Wisconsin (Kroening and Andrews, 1997).

Seasonal Kendall tests were conducted to determine temporal trends for water years 1984 to 1993. Most stream sites outside of the Twin Cities Metropolitan Area showed no increases in nitrate or TN during the 10-year period. The only site showing a slight increase in nitrate concentrations was the St. Croix River near Prescott, Wisconsin. In the Metro Area, nitrate increased, which was thought to be due to the modified wastewater treatment systems, converting ammonium into nitrate. Many upgrades

to municipal wastewater treatment facilities were made during the 10-year analysis period (131 upgrades out of 292 municipal systems). Additionally, most of the combined sanitary and storm sewers in Minneapolis and St. Paul were separated. Correspondingly, ammonium concentrations decreased at 24 of 25 stream sites, based on available data from water years 1984 to 1993.

### Southeastern Minnesota springs

Nitrate trends assessed in two springs feeding fish hatcheries in southeastern Minnesota's Root River watershed both showed statistically significant (p=0.001) increasing trends over the past two decades (Streitz, 2012). The springs were monitored approximately monthly at Peterson and every other month at Lanesboro by the Minnesota Department of Natural Resources (DNR). Average annual nitrate-N concentrations in the Lanesboro spring increased from about 5.2 mg/l to 6 mg/l between 1991 and 2010 (Figure 4). Nitrate increased by a larger amount in the spring at the Peterson, Minnesota, fish hatchery, with average annual concentrations rising from less than 2 mg/l in 1989 to 4 mg/l in 2011 (Figure 5).

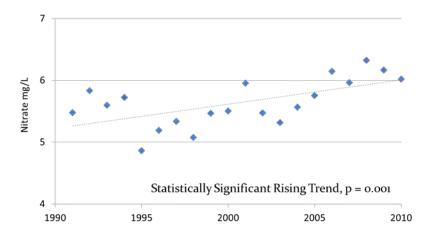


Figure 4. Lanesboro spring (DNR Fish Hatchery) average annual nitrite+nitrate-N concentrations from 1991 to 2010 (Streitz, 2012)

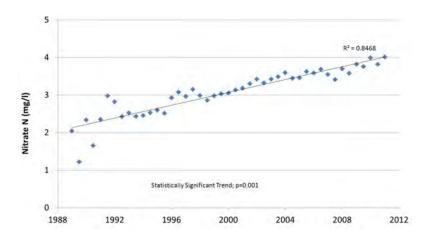


Figure 5. Peterson spring (DNR Fish Hatchery) average semi-annual nitrite+nitrate-N concentrations from 1989 to 2011 (Streitz, 2012)

### Mississippi River - Winona Watershed

Nitrate concentration trends were assessed by Olmsted County Environmental Resources (2012) at six sites for periods of analysis ranging from 16 to 35 years at five sites on various branches of the Whitewater River and one site on Garvin Brook. Nitrate concentrations were not adjusted for flow; however, little relationship was found between flow and nitrate concentrations at these highly groundwater influenced streams. All six sites showed an increasing trend. The South Fork Whitewater Watershed near Utica increased from 4.2 to 11 mg/l between 1974 and 2011. The North Fork Whitewater River near Elba increased from <1 mg/l in 1967 to 6 mg/l in 2010.

### Twin Cities area stream trends

The Metropolitan Council has been regularly sampling 18 stream and river sites in and around the Twin Cities Metro Area. The starting year for sampling varied between sites, ranging from 1989 to 1999. Nitrate concentration trends analyses were conducted by the Metropolitan Council from the starting year through 2010 using QWTREND (Jensen, 2013). The results provided to the MPCA showed no consistent patterns in trends. More streams showed decreases as compared to increasing trends (6 vs. 3). Four streams had no trends, and five streams had trends that were significantly increasing during certain time periods and significantly decreasing during other periods.

# Summary

Nitrogen trends have varied across the state, depending on the N parameter, the location, and timeframe assessed. Ammonia+ammonium-N concentrations have consistently decreased between the mid-1970s and early 2000s, and also decreased during the shorter interval between 1984 and 1993. Improvements to both municipal wastewater treatment plants and feedlots occurred during this same time period.

Total nitrogen *concentrations* have shown few significant trends from the mid-1970s through 2005, although one study showed a few decreasing trends between 1976 and 2002. However, TN *load* trends have shown increases at some sites, with non-significant trends at other sites.

Nitrite concentrations and loads were generally increasing in the Mississippi River from the time beginning around 1976-1980 and ending 2002-2008. The St. Croix River also showed some evidence of nitrate increases. The Minnesota River showed either decreasing or non-significant nitrate concentration trends during these years at most sites, with a possible increase at Fort Snelling, as shown in one study. Nitrate *loads* in the Minnesota River at Jordan showed a slight increasing trend from 1976-2005, at the same time that nitrate concentration trends were stable or decreasing.

In the Red River, nitrate concentrations increased between 1982 and 1992, and then remained stable for the subsequent decade.

Other various rivers and stream sites sampled for nitrate showed some sites with increasing concentration trends, but several others with stable, decreasing, or mixed trends.

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# D1. Sources of Nitrogen – Results Overview

Author: Dave Wall (MPCA), incorporating results from Chapters D4 by David J. Mulla et al. (UMN), Chapter D2 by Steve Weiss (MPCA), and Chapter D3 by Dave Wall and Thomas Pearson (MPCA)

### Introduction

The previous chapters focused on river monitoring results and nitrogen (N) transport within waters. In this chapter and the other chapters in Section D, we assess sources and pathways of N entering Minnesota surface waters. Section D is divided into four chapters: D1) all N source results overview, D2) wastewater point sources, D3) atmospheric deposition and D4) nonpoint sources. This chapter incorporates results from Chapters D2, D3, and D4, so that the point sources, nonpoint sources and atmospheric deposition sources can be compared together. All source estimates should be viewed as large-scale approximations of actual loadings.

In this chapter, N sources were categorized as:

- 1. Sources to the land
- 2. Sources to surface waters

The emphasis of this study was estimating N loads from specific sources to *surface waters*. Nitrogen sources to *land* are also estimated, since these sources can provide a general understanding of N potentially available for being transported to waters. A certain fraction of all N to land will enter surface waters. However, the N additions to land/soils cannot be proportionally attributed to delivery into waters, as many factors affect transport of soil N from the land into waters. These factors include: timing of the additions, form of N, climate and soils where N is introduced, potential for plant uptake and removal, potential for denitrification, along with several other variables.

### Sources to the land

Statewide estimated amounts of inorganic N from primary sources added to the land and from biological processes within soils are shown below (Table 1 and Figure 1).

When considering the N additions to all soils statewide apart from mineralization, cropland commercial fertilizers account for 47% of the added N, followed by cropland legume fixation (21%), manure (16%), and wet +dry atmospheric deposition (15%). Atmospheric deposition contributes nearly the same fraction of statewide N to cropland and non-cropland soils. The combination of septic systems, lawn fertilizer, and municipal sludge account for about 1% of all N added to soils statewide.

Soil organic matter mineralization also contributes a large amount of annual inorganic N to soils, yet the precise amount is more difficult to determine than other sources. Estimates of net mineralization from Mulla et al. reported in Chapter D4 suggest that average cropland soil mineralization releases an annual amount of inorganic N that is comparable to inorganic N from fertilizer and manure additions combined. Mineralization is a complex process affected by climate, soil type and conditions, fertilization, cropping, soil tillage practices and more.

The soil N mineralization estimates were not used to calculate N transport to waters in this study. However, the N transport to waters (as discussed in the next section) accounts for differences in soil types around the state, while additionally considering fertilizer rates, precipitation, crop types, and other variables described in Chapter D4.

Table 1. Estimated annual inorganic N amounts 1) added to land (including legume N fixation), and 2) released from soil organic matter mineralization.

	Inorganic nitrogen (million pounds)	Notes and sources:
1. Added to land		
Commercial fertilizer to cropland	1359	From Chapter D-4 by Mulla et al. Derived from farmer surveys and GIS crop information. Average state fertilizer sales from 2005-2010 are similar (1321 million lbs), as reported by MDA.
Manure application to cropland	446	Crop available N during 1 <sup>st</sup> and 2 <sup>nd</sup> year after application. From Chapter D-4 by Mulla et al. Derived from MDA and MPCA data, and Midwest Plan Service and Univ. of MN N availability information.
Atmospheric deposition statewide	427	See Chapter D-3. Includes all wet and dry deposition onto all land and marshes/wetlands.
Lawn Fertilizer	12	MDA 2007 Report to the Minnesota Legislature "Effectiveness of the Minnesota Phosphorus Lawn Fertilizer Law"
Septic system drain fields	9	See Chapter D-4. Includes runoff from failing systems and leaching to groundwater from all drainfields.
Municipal sludge	2	From MPCA permit reports of acreages/crops in 2009 and 2010 cropping years, multiplied by N rates.
Cropland legume fixation	612	From Chapter D-4 by Mulla et al.
Total additions	2867	
2. Soil mineralization		
Cropland soil mineralization	*1728	Net mineralization from Chapter D-4 by Mulla et al. 2013
Forest soil mineralization	*830	Assumed 51 lbs/acre, based on ranges of mineralization amounts in Reich et al. (1997) and 16.3 million acres of forest.
Total mineralization	2558	
Total of all sources	5425	

<sup>\*</sup>More uncertainty exists with estimates of soil mineralization N as compared to other sources to soils.

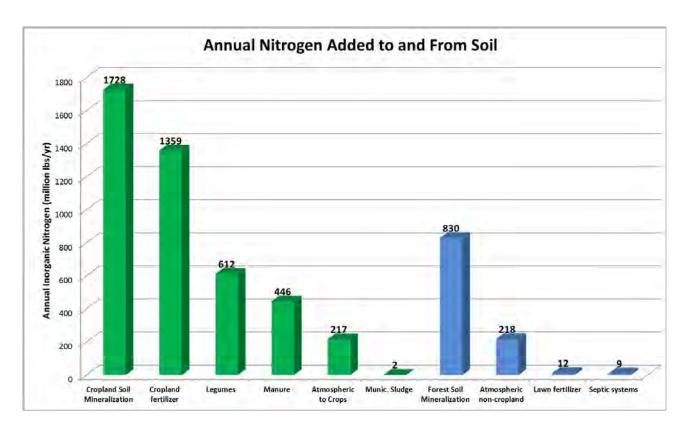


Figure 1. Estimated annual amount of inorganic N to and from cropland soils (green) and non-cropland soils (blue), in millions of pounds per year. Note: these amounts only reflect soil N and they are not proportionately delivered to surface or ground waters from each source.

### Sources to surface waters: statewide

A fraction of the N added to soils reaches surface waters. Most of the soil N is either taken up by the crops or lost to the atmosphere through senescence, volatilization, or denitrification. Yet, because the N inputs and mineralization are high in many regions of the state, even a small percentage of these inputs lost to waters can cause concerns for in-state and downstream waters, as described in previous chapters.

The percentage of soil N lost to waters is expected to vary greatly from one region to another, depending on soils, climate, geology, cropping practices and other factors. In Chapter D4, Mulla et al. calculated the *statewide* fraction of cropland soil N lost to waters as a percentage of all added and mineralized N estimates. They estimated that about 6% of all cropland N additions/sources reach waters during an average precipitation year. If the N losses to surface waters are calculated as a fraction of only the added N (not including the mineralized N), then the *statewide* fraction of added cropland soil N reaching surface waters is about 8%. These estimates should not be applied at the local or regional scale, as N delivery to waters varies considerably by region.

The rest of the discussion in this chapter focuses on N source contributions to surface waters, rather than additions to soil/land. Different N source categories are used to represent contributions to *surface* waters as compared to source categories of *soil* N because: a) the pool of N sources get mixed in the soil and distinct N sources of fertilizer, manure, mineralization or atmospheric deposition to cropland

were not differentiated in groundwater or tile-line drainage waters in this study, and b) some sources to waters never reach the soil but instead go directly into water (i.e. wastewater point sources and atmospheric deposition directly into lakes and streams).

The estimated annual amounts of N which reach surface waters from primary source categories are shown in Table 2 and Figure 2, and are described in more detail in chapters D2, D3, and D4 of this report. Cropland sources are estimated to contribute 72.9% of the statewide N load to streams and lakes during an average year, increasing to 78.9% during wet years when N exports to the Gulf of Mexico are highest. The cropland estimates are divided into three transport pathways: 1) surface runoff, 2) tile drainage, and 3) leaching to groundwater and subsequent travel to surface waters through groundwater baseflow. Surface runoff contributes relatively little N compared to the other pathways. Tile drainage is the largest pathway, contributing an estimated 37% of the statewide N load from all sources during an average year, and 43% during a wet year. Tile drainage contributions vary tremendously from one area of the state to another, being negligible in several basins and yet contributing about 67% of all N load in the Minnesota River Basin. Cropland leaching to groundwater and its subsequent transport to surface waters is also a major source/pathway, although it can take a long time to reach surface waters after initially entering the groundwater.

Wastewater point sources represent an estimated 9% of the N load during an average year, 6% during a wet year, and 18% of the load contribution during a dry year. Direct atmospheric deposition into lakes and streams contributes a comparable amount of statewide N load as point sources, but has a different geographic distribution compared to point sources. All forested lands together contribute an estimated 7% of the statewide N load.

Urban stormwater/groundwater, combined with septic systems and feedlot runoff contribute to less than 3% of the statewide N load to surface waters during an average precipitation year. Other sources with contributions less than an estimated 0.2% of statewide loads to surface waters are not included. An example of a very low N contributor is duck and geese excrement, which add an approximate 0.1% of the statewide N load to waters (assuming bird numbers from U.S. Fish and Wildlife Service waterfowl population reports (2012), all droppings directly enter waters, and loadings of roughly 0.4, 0.3 and 1.2 pounds N/year/bird for mallards, other ducks and geese, respectively).

Table 2. Estimated statewide annual amounts of N reaching surface waters (from chapters D2-D4). Wet years represent the 90<sup>th</sup> percentile annual precipitation years and dry years represent the 10<sup>th</sup> percentile years.

N reaching surface waters (million pounds per year)

	N reaching su	irface waters (million pou	nds per year)
	Avg. precip. year	Wet year	Dry year
1. Cropland nonpoint sources			
Leaching to groundwater*	93.3*	137.6*	49.2*
Tile drainage	113.9	199.6	31.9
Runoff from cropland	16.2	28.7	7.3
Total	223.4	365.9	88.4
	72.9%	78.9%	56.5%
2. Non-cropland nonpoint sources			
Atmospheric deposition to lakes and streams	23.8	26.2	21.4
Urban/suburban runoff and leaching**	2.8	4.3	1.4
Forests runoff/leaching	21.8	32.8	10.9
Septic system runoff/leaching	5.5	5.5	5.5
Feedlot runoff (barnyards)	0.2	0.27	0.13
Total	54.1	69.1	39.3
	17.7%	14.9%	25.1%
3. Point sources			
Municipal Point Sources	24.9	24.9	24.9
Industrial Point Sources	3.9	3.9	3.9
Total	28.8	28.8	28.8
	9.4%	6.2%	18.4%
Grand total	306.3	463.8	156.5
	100%	100%	100%

<sup>\*</sup>This number represents the N amount which reaches surface waters from cropland ground water sources. It is substantially lower than the amount which initially reaches groundwater, since this number subtracts assumed denitrification losses which occur along the course of groundwater flow between the field and discharge into streams.

<sup>\*\*</sup>Urban and suburban nitrogen amounts reaching waters include both stormwater and snowmelt runoff, and a relatively small amount which also leaches to groundwater and is transported to surface waters via groundwater (also accounting for denitrification losses within groundwater).

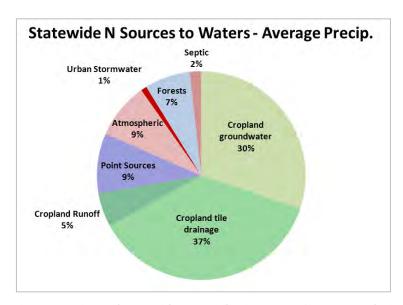


Figure 2. Estimated statewide N contributions to surface waters during an average precipitation year (rounded to the nearest percent).

Annual precipitation has a pronounced effect on N loads. During a wet year, overall estimated loads increase by 51%, as compared to an average year. During a dry year, N loads drop by 49% from average year loads. The effects of precipitation are even greater in certain basins, such as the Minnesota River Basin. In the Minnesota River Basin, wet years have 70% more N load, and dry years have 65% less N load, as compared to average years.

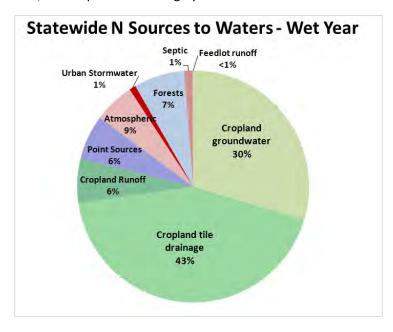


Figure 3. Estimated statewide N contributions to surface waters during a wet year.

High precipitation periods are of particular interest, since higher precipitation increases the N load transport to downstream waters such as the Gulf of Mexico. In addition to overall increasing loads, climate influences the relative source contributions from different sources and pathways. During wet years (Figure 3), the cropland sources increase to 79% of the estimated N loads to waters statewide.

Agricultural drainage increases to 43% of the loads to surface waters during wet years, cropland runoff increases to 6%, and cropland groundwater remains at 30%. The absolute loading of wastewater point source contributions remain unchanged during wet and dry years, but their relative contribution changes as the overall total annual load from all sources increases or decreases.

# Sources to surface waters: by major basins

Nitrogen source contributions vary considerably from one major basin to another (Figures 5-17 and Tables 3-5). For example, during an average precipitation year, the estimated cropland sources (cropland groundwater, cropland tile drainage and cropland runoff) contribute between 89% and 95% of the load in several basins, including the Minnesota parts of the Minnesota River, Missouri River, Cedar River, and Lower Mississippi River Basins. Cropland contributes a much lower percentage of N to waters (49%) in the Upper Mississippi River Basin, and even less in the Red River (see Figure 4 for major basin locations). Point source contributions range from 1% to 30% across the different basins, generally representing a higher fraction of the load where cropland sources are relatively low and where major metropolitan areas are found (i.e. Twin Cities are largely in the Upper Minnesota River Basin). In the lower N yielding basins dominated by forests and lakes, such as in the Rainy River and Lake Superior Basins, forest and atmospheric sources contribute a higher fraction of the N.

# Map of Minnesota Basins Basins Cedar River Des Moines River Lake Superior Lower Mississippi River Minnesota River Rainy River Red River of the North St. Croix River Upper Mississippi River

Figure 4. Location of major river basins in Minnesota.

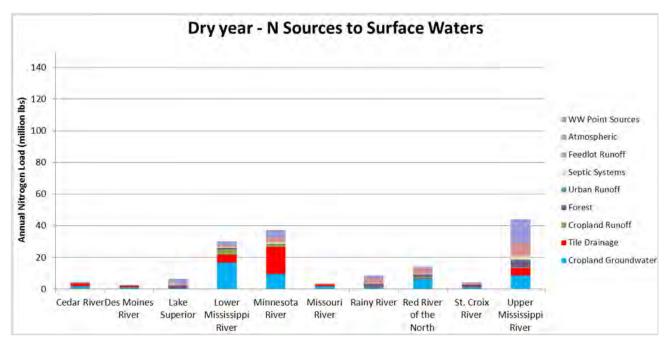


Figure 5. Estimated N loads to surface waters from different sources within the Minnesota portions of major basins during a dry year (10<sup>th</sup> percentile precipitation year).

Table 3. Estimated N loads to surface waters from different sources within the Minnesota portions of major basins during a dry year (10<sup>th</sup> percentile precipitation year).

	Cropland	Cropland	Cropland	_	Urban				Point	
Basin	Groundwater	Drainage	Runoff	Forest	NPS	Septic	Feedlot	Atmospheric	Sources	Total
Cedar River	1,838,932	1,870,122	94,791	10,705	19,508	87,875	5,240	125,081	635,348	4,687,602
Des Moines River	1,173,366	888,502	76,405	11,038	5,971	69,203	3,368	299,546	284,353	2,811,752
Lake Superior	448,753	115,893	126,699	1,762,240	57,197	382,620	8	818,578	2,870,456	6,582,444
Lower Mississippi River	16,875,018	4,744,251	3,657,868	664,031	171,895	520,672	70,456	910,326	2,643,750	30,258,267
Minnesota River	9,587,169	17,172,963	1,410,743	285,815	281,171	888,027	41,709	2,874,636	4,717,144	37,259,377
Missouri River	1,695,077	1,387,158	62,703	8,535	9,643	84,618	6,586	175,796	98,436	3,528,552
Rainy River	772,685	238,187	107,451	2,346,796	13,525	141,823	58	3,447,922	1,689,520	8,757,967
Red River of the North	6,593,744	169,422	1,044,099	1,357,406	63,190	479,149	8,638	3,873,237	617,872	14,206,757
St. Croix River	1,396,201	732,743	60,944	764,478	53,368	434,357	766	499,943	441,629	4,384,429
Upper Mississippi River	8,795,966	4,555,276	705,877	3,711,788	744,258	2,392,008	48,354	8,420,932	14,817,420	44,191,879
Grand Total	49,176,911	31,874,517	7,347,580	10,922,832	1,419,726	5,480,352	185,183	21,445,997	28,815,928	156,669,026

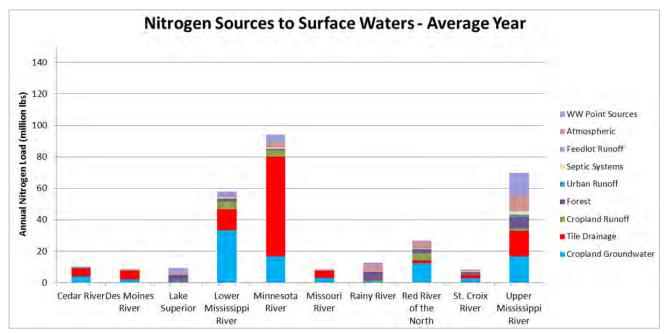


Figure 6. Estimated N loads to surface waters from different sources within the Minnesota portions of major basins during an average precipitation year.

Table 4. Estimated N loads to surface waters from different sources within the Minnesota portions of major basins during an average precipitation year.

Basin	Cropland Groundwater	Cropland Drainage	Cropland Runoff	Forest	Urban NPS	Septic	Feedlot	Atmospheric	Point Sources	Total
Cedar River	3,998,333	5,246,863	170,842	21,410	39,013	87,875	6,239	138,979	635,348	10,344,902
Des Moines River	2,034,489	5,672,975	355,036	22,076	11,943	69,203	4,009	332,829	284,353	8,786,913
Lake Superior	813,293	446,889	224,736	3,524,480	114,394	382,620	9	909,531	2,870,456	9,286,408
Lower Mississippi River	33,190,774	13,496,944	5,160,896	1,328,062	343,788	520,672	83,876	1,011,473	2,643,750	57,780,235
Minnesota River	16,875,469	63,106,270	4,034,140	571,629	562,341	888,027	49,653	3,194,040	4,717,144	93,998,713
Missouri River	3,095,517	4,642,270	358,054	17,068	19,285	84,618	7,840	195,329	98,436	8,518,417
Rainy River	1,379,430	876,724	191,282	4,693,593	27,053	141,823	69	3,831,024	1,689,520	12,830,518
Red River	12,427,316	1,945,435	4,156,273	2,714,812	126,383	479,149	10,285	4,303,597	617,872	26,781,122
St. Croix River	2,734,879	2,340,243	112,083	1,528,955	106,737	434,357	912	555,492	441,629	8,255,287
Upper Mississippi River	16,717,357	16,145,270	1,415,241	7,423,577	1,488,515	2,392,008	57,563	9,356,591	14,817,420	69,813,542
Grand Total	93,266,857	113,919,883	16,178,583	21,845,662	2,839,452	5,480,352	220,455	23,828,885	28,815,928	306,396,057

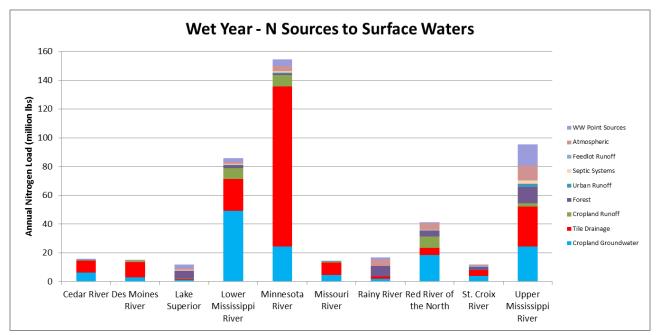


Figure 7. Estimated N loads to surface waters from different sources within the Minnesota portions of major basins during a wet year (90<sup>th</sup> percentile precipitation year).

Table 5. Estimated N loads to surface waters from different sources within the Minnesota portions of major basins during a wet year (90<sup>th</sup> percentile precipitation year).

Basin	Cropland Groundwater	Cropland Drainage	Cropland Runoff	Forest	Urban NPS	Septic	Feedlot	Atmospheric	Point Sources	Total
Cedar River	6,123,057	8,535,764	295,660	32,116	58,521	87,875	7,611	152,877	635,348	15,928,829
Des Moines	0,123,037	0,555,701	233,000	32,110	30,321	07,075	7,011	132,077	033,3 10	10/720/027
River	2,896,958	10,657,787	828,794	33,115	17,914	69,203	4,892	366,112	284,353	15,159,128
Lake Superior	1,180,848	769,625	329,261	5,286,720	171,591	382,620	12	1,000,484	2,870,456	11,991,617
Lower Mississippi River	49,356,821	21,943,782	7,559,105	1,992,091	515,683	520,672	102,330	1,112,620	2,643,750	85,746,854
Minnesota River	24,393,974	111,213,311	8,199,383	857,443	843,513	888,027	60,576	3,513,444	4,717,144	154,686,815
Missouri River	4,497,544	8,621,258	872,115	25,604	28,928	84,618	9,565	214,862	98,436	14,452,930
Rainy River	1,987,456	1,496,321	282,240	7,040,390	40,580	141,823	85	4,214,126	1,689,520	16,892,541
Red River of the North	18,553,349	4,907,556	7,829,840	4,072,215	189,569	479,149	12,547	4,733,957	617,872	41,396,054
St. Croix River	4,048,735	3,787,514	168,774	2,293,431	160,106	434,357	1,112	611,041	441,629	11,946,699
Upper Mississippi River	24,544,775	27,685,025	2,305,990	11,135,361	2,232,772	2,392,008	70,230	10,292,250	14,817,420	95,475,831
Grand Total	137,583,517	199,617,943	28,671,162	32,768,486	4,259,177	5,480,352	268,960	26,211,774	28,815,928	463,677,299

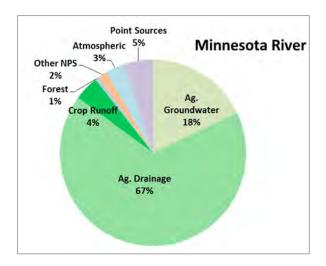


Figure 8. Estimated N sources to surface waters from the Minnesota contributing areas of the Minnesota River Basin (average precipitation year).

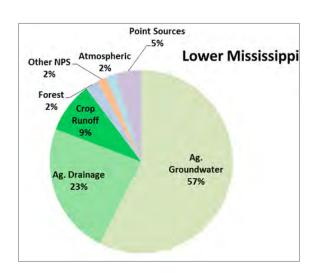


Figure 9. Estimated nitrogen sources to surface waters from the Minnesota contributing areas of the Lower Mississippi River Basin (average precipitation year).

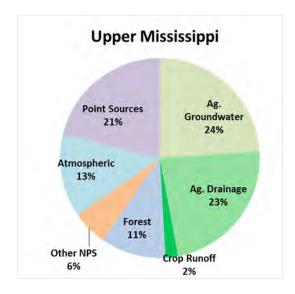


Figure 10. Estimated N sources to surface waters from the Upper Mississippi River Basin (average precipitation year).

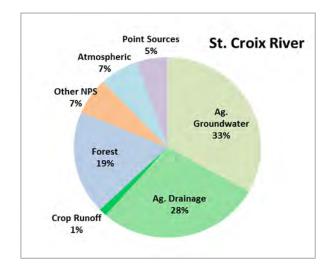


Figure 11. Estimated N sources to surface waters from the Minnesota contributing areas of the St. Croix River Basin (average precipitation year).

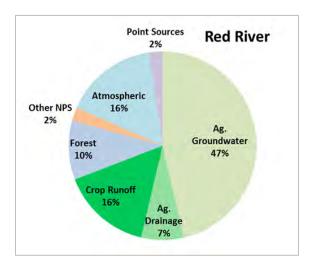


Figure 12. Estimated N sources to surface waters from the Minnesota contributing areas of the Red River Basin (average precipitation year).

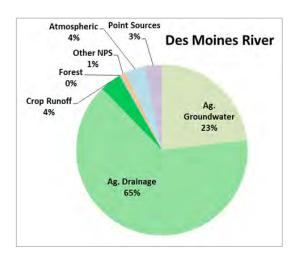


Figure 14. Estimated N sources to surface waters from the Minnesota contributing areas of the Des Moines River Basin (average precipitation year).

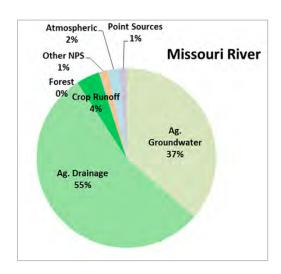


Figure 13. Estimated N sources to surface waters from the Minnesota contributing areas of the Missouri River Basin (average precipitation year).

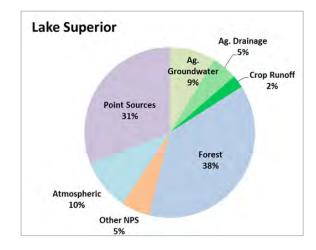


Figure 15. Estimated N sources to surface waters from the Minnesota contributing areas of the Lake Superior Basin (average precipitation year).

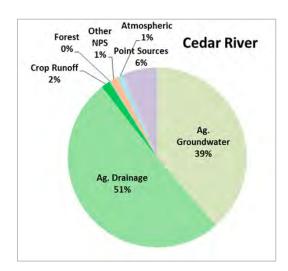


Figure 16. Estimated N sources to surface waters from the Minnesota contributing areas of the Minnesota River Basin (average precipitation year).

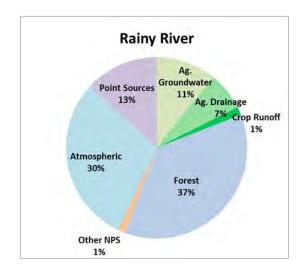


Figure 17. Estimated N sources to surface waters from the Minnesota contributing areas of the Rainy River Basin (average precipitation year).

# Contributions to the Mississippi River

Because of the goal to reduce N loads going to the Gulf of Mexico in the Mississippi River, we also assessed the loads going just to the Mississippi River. About 81% of the total N load to Minnesota waters is from basins which end up flowing into the Mississippi River (including all basins except the Lake Superior, Rainy, and Red). If we look only at those Minnesota watersheds which contribute to the Mississippi River, source contributions during an average precipitation year are estimated as follows: cropland sources 78%, point sources 9%, and non-cropland nonpoint sources 13% (Figure 18). Cropland source contributions increase to 83% for these watersheds during wet (high-flow) years, while point sources decrease to 6% during wet years. During a dry year, cropland sources represent an estimated 62% of N to waters headed toward the Mississippi River and point sources contribute 19%.

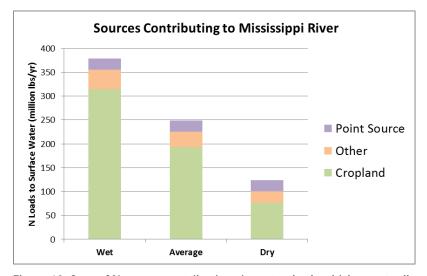


Figure 18. Sum of N source contributions in watersheds which eventually reach the Mississippi River. The "other" category includes septic systems, atmospheric deposition directly into waters, feedlots, forested land and urban/suburban nonpoint source N.

# Source contributions to waters on a per-acre basis

Some sources contribute elevated N to waters on a per acre basis, but they do not represent enough cumulative acres to create an environmental threat at the statewide or regional level. Thus, sources that are relatively minor at the state-level scale can sometimes still contribute significantly to N loads at the local-level.

One way of comparing contributions from different land uses and understanding the potential for affecting local water bodies is to consider the yield, represented in pounds per acre per year delivered to surface waters. Yields from source categories are shown in Table 6 and Figure 18, for average precipitation conditions. The estimates are presented as a range, showing both the lower and higher ends of estimated yields for each source category.

Note that the yield within a single field can be larger than the yield ranges in Table 6 and Figure 18, which are based on averages across larger areas, such as subwatersheds, agroecoregions, and other monitored areas. Also, it is important to note that some source contributions to waters are not dispersed throughout the land, but enter waters at specific locations. For example, wastewater point sources from an urban area enter waters at specific points, and can therefore have a more noticeable impact in the immediate area of discharge as compared to more dispersed sources spread out over the same size area. Even though the overall loads and yields can be the same, the point source nature of discharges can affect localized water resources in different ways than more dispersed nonpoint source discharges.

The yield ranges show that N is relatively low on a per-acre basis from the following source categories: forests, urban stormwater, atmospheric deposition, and mixed crops in less geologically sensitive non-tiled regions. Row crops in sensitive areas (tile-drained, sandy, karst) have the highest yields. Point sources are a relatively small N source statewide compared to cropland sources, yet they can potentially impact localized stretches of rivers. High densities of septic systems in geologically sensitive areas can also potentially contribute moderately high N yields to surface waters, yet most areas with septic systems have yields to surface waters comparable to the lower yielding sources.

Table 6. Total nitrogen yields from various N source categories (average precipitation conditions). The estimates are presented as a range, showing both the lower and higher-end estimated yields for each source category.

Source category	Low-end	High-end	Assumptions and sources for yields
	lbs/ac/yr	lbs/ac/yr	
Row crops in sensitive areas (i.e. tiled, sandy soils, or karst regions)	20	37	Average precip cropland losses to waters based on Mulla et al. (2013) analyses presented in Chapter D4 for the following Agro-ecoregions: Rochester Plateau 37; Anoka Sand Plain 35; Level plains 33; Blufflands 20.
Mostly row crops in less sensitive areas	15	23	Average precip cropland losses to waters based on Mulla et al. (2013) analyses presented in Chapter D4 for the following Agro-ecoregions: Undulating Plains 23; Wetter clays and silts 19; Rolling moraine 15.4.
Mixed crops in less sensitive areas	5	10	Average precip cropland losses to waters based on Mulla et al. (2013) analyses presented in Chapter D4 for the following Agro-ecoregions: Cotoeu and Inner Coteau 9; Central Till 8; Steep Dryer Moraine 7; Drumlins 6
Municipal and Industrial Point Sources	8	20	From Point Source Chapter D2 by Weiss (2013). The lower density development in the Blue Lake wastewater treatment sewershed had an average of 7.8 lbs/acre/yr from both municipal and industrial wastewater, and the higher density development within the Metro sewershed had 19.7 lbs/acre/yr. Note: this N is not released in a diffuse manner – so the immediate impact to waters will be most noticeable near the points of discharge.
Urban/suburban stormwater + groundwater	2	10	Metropolitan Council monitoring of Bassett Creek and Battle Creek yielded approx. 2.5 lbs/acre/yr (from data provided by Karen Jensen); Hennepin County Three Rivers Park monitoring of subwatersheds showed industrial areas averaging 3.7 lbs/acre/yr; residential 1.9; mixed 3.9 (from data provided by Brian Vlach); Minneapolis Park Board average watershed yields in 2002-04 was 5.6 lbs/acre/yr and in different Mpls. watersheds averaged 9.7 lbs/acre/yr between 2005-2010 (data provided by Mike Perniel). All literature review results as referenced in chapter D-4 fall within these ranges, mostly averaging between 2.5 and 6 lbs/acre/yr.
Septic Systems	4	17	Low end assumes 4 person households, 7 lbs per person per year, on 3.5 acre lots, and half of N lost in groundwater through denitrification. High end assumes 4.5 person households, 8 lbs per person, on 1.5 acre lots, and 30% N lost in groundwater through denitrification.
Atmospheric	4	14	Wet plus dry deposition as shown in Chapter D-3 by Wall and Pearson (2013). Low end are estimated loads from northeastern Minnesota watershed spatial averages and High end estimates are from southeastern Minnesota watershed spatial avgs.
Forest	0.4	5	See Chapter D4. Wisconsin forested watersheds yielded 3.1 and 3.6 lbs/acre (from Clesceri, et al. (1986). USGS report showed forested watershed N yields of 0.41 lbs/acre in Namekogen and 0.25 lbs/acre in the St. Croix River (Graczyk, 1986).

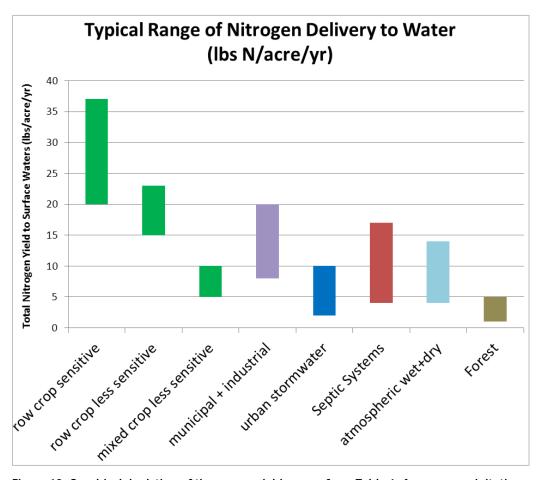


Figure 19. Graphical depiction of the source yield ranges from Table 6. Average precipitation year.

# Flow pathways from all sources combined

The dominant N flow pathways between all sources and receiving surface waters vary from basin to basin and sometimes with climate. Four categories of flow pathways were estimated based on the following categorizations and assumptions:

**Groundwater**: The groundwater flow pathway was calculated from the source assessment information by adding 100% of the cropland groundwater that reaches surface waters, 80% of septic system N reaching surface waters, 20% of the urban/suburban nonpoint N, and 50% of forest N.

**Surface runoff:** The surface runoff flow pathway was calculated from the source assessment information by adding 100% of the cropland surface runoff, 20% of the septic system N reaching surface waters (direct pipe losses), 80% of the urban/suburban nonpoint N, 50% of forest N, and 100% of feedlot runoff N.

Tile line drainage: The tile drainage includes all cropland tile line drainage N.

**Direct Discharge**: The direct discharge pathway was calculated by adding 100% of point source discharge N and 100% of direct wet+dry atmospheric deposition into lakes and streams.

The estimated statewide N load from each N transport pathway to surface waters for average and high precipitation periods are depicted in Figures 20 and 21. Tile line and groundwater are the two dominant

N pathways to surface waters statewide. The influence of tile lines increases from 37% of the load to surface waters during and average precipitation year to 43% of the N load to surface waters during the highest loading years (wet years). The groundwater pathway is the second largest pathway in both average and wet years, representing just over one-third of the load.

The fraction of forest N delivered to surface waters via surface runoff and groundwater flow pathways was not found in the literature, and the above results assume that half is transported in surface runoff and the other half through groundwater. Because forestland only contributes an estimated 7% of the statewide N load, errors in pathway assumptions for forestland will not have an appreciable effect on the statewide pathway characterization in Figures 20 and 21.

While all the sources/pathways represent annual estimated N loads, the arrival time to surface waters varies considerably depending on the travel pathway. Much of the N from the groundwater pathway will take many years to reach surface waters. Other pathways have much shorter travel time to waters. Therefore, in areas where groundwater is an important pathway, the N concentrations in surface waters may not completely represent modern land uses and management. The N source assessment in this study attempted to account for estimated denitrification losses within the groundwater flow pathway, but did not address the time lag for groundwater flow. In other words, while the source assessment is the best estimate of source contributions to surface waters, the point in time when these sources actually reach surface waters will vary from source to source and from basin to basin, depending on how much of the N load is coming from groundwater sources and the rate at which groundwater flows.

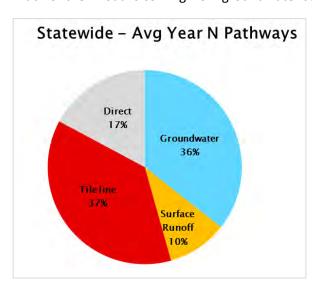
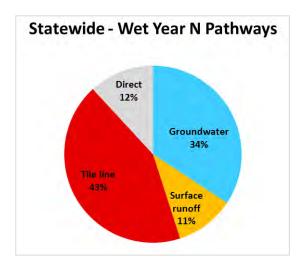


Figure 20. Statewide N pathways to surface waters during an average precipitation year, as estimated by UMN/MPCA. Direct includes both point sources and atmospheric deposition into waters.

Figure 21. Statewide N pathways to surface waters during a wet year, as estimated from UMN/MPCA.



Nitrogen pathways vary by basin (Figure 22). Groundwater is a dominant pathway in the Lower Mississippi, Upper Mississippi, and St. Croix River Basins; whereas tile line flow is the dominant pathway in the Minnesota River Basin.

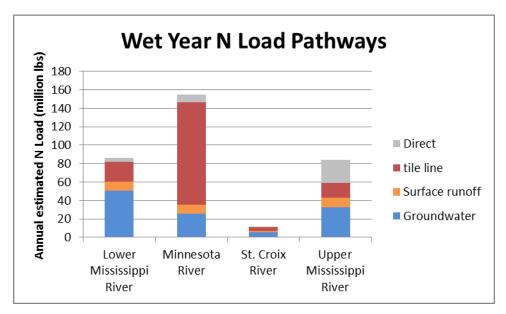


Figure 22. Basin N pathways to surface waters during a wet year for each of the four largest basins which drain into the Mississippi River system. Results are only for Minnesota land within the basins.

## Uncertainty

The source contributions to surface waters conducted by the University of Minnesota and MPCA (UMN/MPCA) as described in Chapters D1 to D4 have areas of uncertainty. One particular area of uncertainty is the cropland groundwater component due to: a) limited studies quantifying leaching losses under different soils, climate and management, and b) high variability in denitrification losses which can occur as groundwater slowly flows toward rivers and streams.

Because of source assessment uncertainties, we compared the source assessment results with other related findings, using five different methods. These verification methods, as reported in Chapters E1 to E3, showed results which generally support the source assessment findings. However, all sources should be treated as large-scale approximations of actual loadings, and each source estimate could be refined with additional research.

# Summary

Soil N comes from a variety of sources. Of the added sources, cropland fertilizer represents the largest source. Manure, legumes, and atmospheric deposition are also significant sources, and when added together provide similar N amounts as the fertilizer additions. Soil organic matter mineralization releases large quantities N annually, which were estimated to contribute about the same amount of N as cropland fertilizers and manure combined. Septic systems, lawn fertilizers and municipal sludge add comparatively small amounts of N to soils statewide (less than 1% of added N).

Cropland agricultural sources contribute an estimated 73% of the N load to Minnesota surface waters during a normal precipitation year, with the rest contributed mostly by wastewater point sources, atmospheric deposition and forestland. Feedlot runoff, urban stormwater and septic systems combined contribute less than 3% of the N load to surface waters. The sources and loads vary considerably from one major river basin to another.

The dominant pathway to surface waters is through the subsurface, with about 73% of the N load from all sources entering surface waters on an average year through groundwater pathways combined with cropland tile drainage. Surface runoff from all sources combined contributes a relatively small amount (10%) of the N loading to surface waters, and direct deposits into waters (point source discharges and atmospheric deposition) represent 17% of N to surface waters during an average year. During the highest loading years (wet weather), the tile drainage pathway contributions increase to 43% of the estimated N load, and all cropland pathways combined contribute an estimated 79% of the N load.

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# D2. Wastewater Point Source Nitrogen Loads

Author: Steve Weiss, MPCA

#### Introduction

Nitrogen, in its various forms, functions as both a nutrient with the potential to contribute to eutrophication (i.e. in coastal waters), and as a toxic pollutant with the potential to affect aquatic life and human health. In circumstances where excess nitrogen (N) loading may preclude the attainment of designated uses, loading from point sources is of particular importance because it can be controlled with nutrient removal technology through permit limits. This chapter provides estimates of N loading from municipal and industrial point source dischargers with National Pollution Discharge Elimination System (NPDES) permits; hereafter referred to as point sources. Load sources not covered in this chapter include: permitted industrial or municipal stormwater, concentrated animal feeding operations, large subsurface treatment systems, individual subsurface treatment systems, spray irrigation facilities where measured drain tile flow data are unavailable, and the land application of wastewater treatment biosolids. Significant sources from this list are generally covered in other chapters. Loads from individual point sources are aggregated and presented by basin and major watershed. Seasonal patterns, yield per unit area, yield per capita, and the distribution of load between municipal and industrial sources are examined in greater detail. Although this chapter primarily focuses on total nitrogen (TN), estimates of ammonia (NHx), total kjeldahl nitrogen (TKN), and nitrite and nitrate nitrogen (NOx) are also presented in various tables and appendices.

Project results are presented first, followed by a discussion of the methods used to determine the estimated point source loads.

#### Statewide totals

Currently, Minnesota has over 900 wastewater point sources that actively discharge to surface waters. Of these point sources, 64% are domestic wastewater treatment plants (WWTPs) and 36% are industrial facilities (Appendix D2-1). In total, it is estimated that wastewater point sources discharge an average annual TN load of 28,671,429 pounds statewide (Table 1). Most of this load is from municipal dischargers (24,929,970 pounds/year TN, 87%); the remainder is from industrial facilities (3,741,459 pounds/year TN, 13%). Within most basins, municipal facilities account for over 90% of the point source load (Table 1). The few exceptions include basins like the Rainy River and St. Croix River which have large, water-using industrial facilities.

Despite the large number of individual permits in Minnesota, the majority of wastewater point source TN loading comes from a small number of large facilities. The 10 largest point sources, as measured by average annual TN load, collectively amount to 67% of the point source TN load. The single largest facility is the Metropolitan Council Environmental Service (MCES) Metro WWTP which discharges an annual average TN load of 10,363,151 pounds/year. The Metro WWTP, by itself, amounts to 36% of the overall point source TN load. The remaining MCES facilities within the top 10 include the Blue Lake, Seneca and Empire WWTPs which collectively discharge 12% of the point source TN load. Other

notable large municipal TN load sources include the Western Lake Sewer and Sanitary District (WLSSD) WWTP in Duluth, Rochester WWTP and St. Cloud, which are estimated to discharge 7%, 3%, and 2% of the overall municipal TN load, respectively. Following the 10 largest dischargers, no single facility amounts to over 1% of the state wide point source TN load. It should be noted that the industrial load only includes estimates from industrial facilities that have individual NPDES permit and not facilities considered significant industrial users (SIUs), which discharge to municipal WWTPs for further treatment. Insufficient data are available from which to estimate SIU flow and loading to municipal WWTPs statewide.

Table 1. Estimated wastewater point source TN loading per basin from industrial and municipal dischargers (2005-2009).

	Industrial		Municipal		Total
Basin	Load (lbs/yr)	%	Load (lbs/yr)	%	Load (lbs/yr)
Upper Mississippi River	1,132,842	8%	13,609,734	92%	14,742,576
Minnesota River	273,539	6%	4,443,605	94%	4,717,144
Lake Superior	256,035	9%	2,614,346	91%	2,870,381
Lower Mississippi River	257,372	10%	2,386,378	90%	2,643,750
Rainy River	1,576,132	93%	113,388	7%	1,689,520
Cedar River	14,219	2%	621,129	98%	635,348
Red River of the North	63,066	10%	554,806	90%	617,872
St. Croix River	84,148	23%	287,900	77%	372,049
Des Moines River	84,062	30%	200,291	70%	284,353
Missouri River	44	0%	98,392	100%	98,436
Total	3,741,459	13%	24,929,970	87%	28,671,429

# Major basin wastewater point source loads

#### **Upper Mississippi River Basin**

On average, more TN is discharged annually by wastewater point sources in the Upper Mississippi River Basin (UMR) than in all other basins state-wide (14,742,576 pounds/year, 51%, Figures 1 and 3). Although there are numerous domestic and industrial dischargers within this basin, (142 and 118, respectively) the majority of the flow and loading is discharged by a few large municipal sources in the Twin Cities Metropolitan Area (TCMA). Industrial point source loading is generally estimated to be small (8%) as compared to municipal (92%). The few exceptions include high protein industries like food, rendering, and paper, the latter of which adds nutrients to feed bacteria and thereby reduce biological oxygen demand (BOD). Within the UMR, the two highest loading major watersheds are the Mississippi River Twin Cities and St. Cloud which generate annual TN loads of 10,972,760 and 864,231 pounds, respectively (Figure 2, 4, Appendix D2-2). Municipal wastewater accounts for the majority of point source loading within these watersheds (Figure 3).

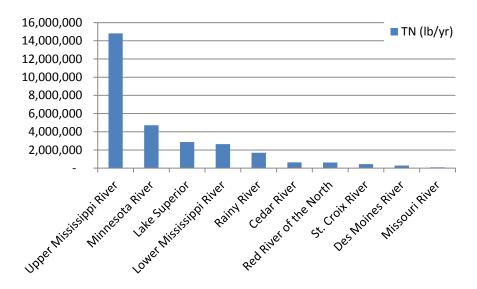


Figure 1. Comparison of watershed basin annual TN load estimates from permitted point sources.

#### Minnesota River Basin

The Minnesota River Basin (MRB) is estimated to have the second highest annual wastewater point source TN load (4,717,144 pounds). This equates to 16% of the total statewide point source TN load. Unlike the UMR, loading in the MRB is more evenly distributed among its 155 municipal and 81 industrial facilities in most sub basins. The Minnesota River (Shakopee) has the highest point source TN load within the MRB (3,170,968 pounds/year) and is the second highest loading major watershed in the state. Point source TN loading in the MRB Shakopee primarily comes from larger municipal facilities.

#### Lake Superior, Lower Mississippi, and Rainy River Basins

The Lake Superior, Lower Mississippi River, and Rainy River Basins have the third, fourth, and fifth highest annual wastewater point source TN loads at 2,870,381 pounds, 2,643,750 pounds, and 1,689,520 pounds, respectively. Like other basins, the point source TN loading in the Lake Superior and Lower Mississippi River Basins is primarily from municipal sources. Point source TN in the Rainy River, however, is estimated to be mostly from one large paper manufacturer. Industrial TN loading is estimated to be 93% of the total point source load. Paper facilities typically have a carbon rich pulp influent which requires that nutrients (i.e. phosphorus and N) be added to feed bacteria and thereby reduce BOD. Given the tremendous flow from the paper industry, moderate to high effluent TN concentrations can result in large loads.

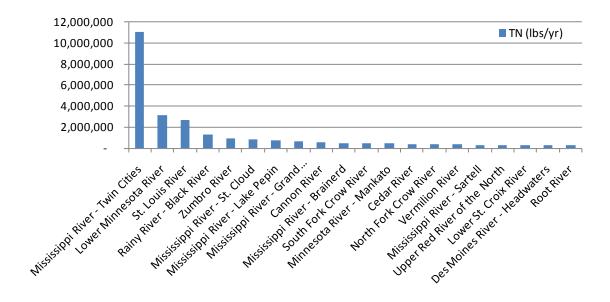


Figure 2. Annual N load estimates from permitted point source dischargers within the top 20 major watersheds in Minnesota.

#### Cedar, Red, St. Croix, Des Moines, and Missouri River Basins

The remaining basins of the state, including the Cedar River, Red River, St. Croix River, Des Moines River, and Missouri River, are estimated to collectively generate less than 7% of the wastewater point source TN load. The major watersheds within these basins generate annual TN point source loads in the range of less than 100 pounds to roughly 400,000 pounds.

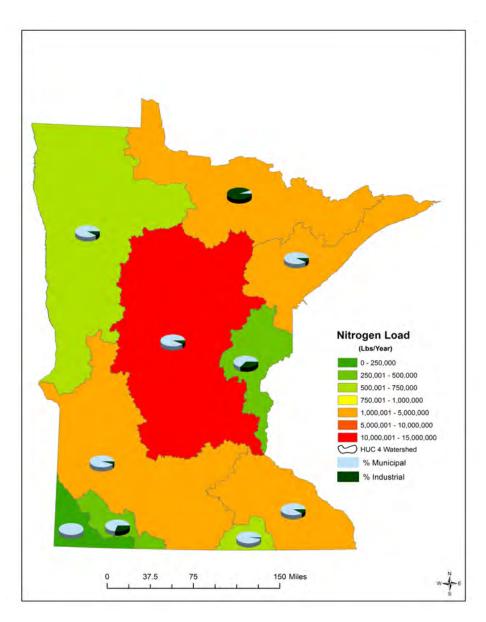


Figure 3. Total nitrogen load by basin from municipal and industrial NPDES point sources (2005-2009). Pie charts represent the percent load distribution among municipal and industrial facilities within each basin.

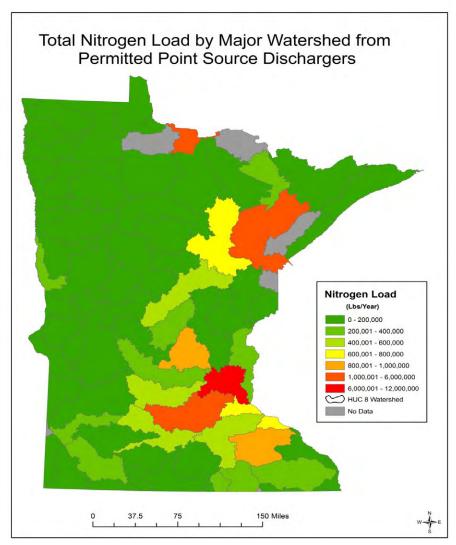


Figure 4: Total nitrogen annual load by major watershed from municipal and industrial NPDES point sources (2005-2009).

# Wastewater point source yield

Nonpoint pollutant load sources are commonly assessed by a yield or per unit area basis. For means of comparison, TN point source yield values were also calculated for basins (Appendix D2-1), major watersheds (Figure 5, Appendix D2-1(B)), and in a few select cases by the land area contributing to a specific wastewater treatment facility (sewershed) (Figure 6, Table 2). Wastewater point source yields are intended to represent the TN loading potential from low to high density residential landcover. Basin and watershed yields might best be used to rank or compare watersheds or basins with each other. In contrast, sewershed yields are a more direct measure of urban point source load potential because the land area directly represents the extent of the collection system area. Yield on a per capita basis was also examined for a few select urban watersheds where sufficient user data were available (Table 2). Note that the nature of yields from wastewater point sources is different than yields from nonpoint sources, since all of the load from point source contributing areas is released at specific points in the rivers, instead of being a more diffuse discharge occurring over a larger geographic area. Yield

comparisons between point and nonpoint sources are more appropriate for assessing the relative effects on downstream waters. However, the localized effects from point and nonpoint source discharges can potentially be different from similarly N yielding areas.

#### Basins and major watersheds

The Mississippi River Twin Cities major watershed has, by far, the highest wastewater point source TN yield (17.0 pounds/acre, Figure 5, Appendix D2-1(B)). Other major watersheds with notable yields include the Rainy River – Manitou (3.8 pounds/acre), the Minnesota River – Shakopee (2.7 pounds/acre) and the Mississippi River – Lake Pepin (1.9 pounds/acre). High point source yields typically result from a large volume of wastewater discharged within a given area. However, in some cases like the Cedar River Basin, the comparatively high point source yield is the result of a small overall basin area. Major watershed yields, especially in the Metro Area, may be distorted due to sewersheds that overlap defined watershed boundaries (Figure 6). For Example, the Metro WWTP receives wastewater from developments within the Lower Minnesota River; this amplifies the overall yield within the Mississippi River - Twin Cities watershed. Conversely, the Blue Lake WWTP serves developments within the Mississippi River – Twin Cities watershed. It is difficult to predict the difference in volume and pollutant loading received from sewersheds that extend beyond the watersheds that they discharge within.

#### Sewersheds

Sewershed yield was examined for seven metro area WWTPs to better understand the range in sewershed nitrogen yield. The Twin Cities metro area was selected for yield analysis because of the good availability of wastewater data, its dominance statewide in wastewater treatment volume, and the wide range of population densities within the sewersheds. Three primary aspects were analyzed; 1) point source yield per sewershed area, 2) sewershed population density, and 3) yield per capita (Table 2). Sewersheds are defined as the estimated perimeter surrounding a collection system of interest (Figure 6). It should be noted that sewersheds inevitably contain features such as parks, wetlands, and lakes which may not be characteristic of urban land cover or significantly contribute to TN loading. Area-based yields were calculated in consideration of both municipal and industrial point source loading. Industrial yield contributions included those industries with outfalls either located within or directly adjacent to sewershed boundaries. Finally, population density, yield per capita, and their relationship to area-based yield were also examined.

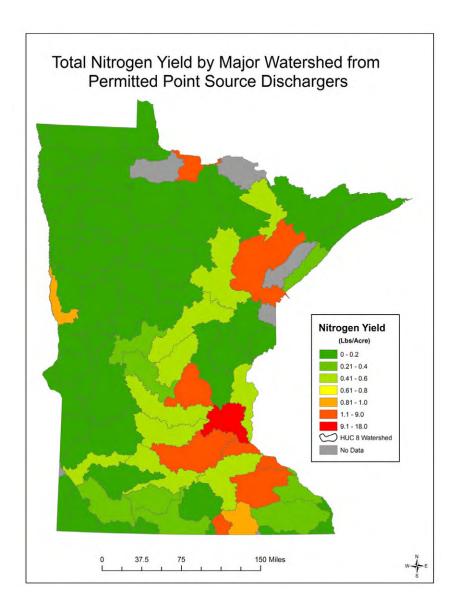


Figure 5. Total nitrogen yield by major watershed from municipal and industrial NPDES point sources (2005-2009).

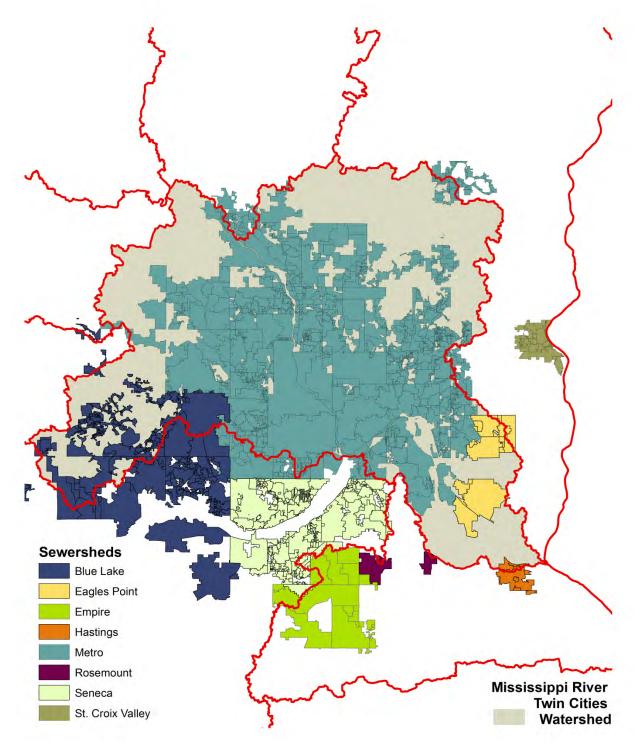


Figure 6. Municipal sewer drainage areas (sewersheds) within the TCMA in relationship with major watershed boundaries. It should be noted that effluent discharged in one watershed may contain drainage from adjacent watersheds given that sewershed and watershed boundaries overlap.

Table 2. Total nitrogen wastewater point source yield data from seven sewersheds (2005-2009).

Area and Population				Average Annual Load			Average Annual Yield			
Sewershed	Area <sup>1</sup> acres	Population <sup>2</sup>	Population Density persons/ acre	Municipal pounds/ year	Industrial pounds/ year	Total pounds/ year	Municipal pounds/ acre	Industrial pounds/ acre	Total pounds/ acre	Per Capita pounds/ person
Metro	512,941	1,846,185	3.6	9,971,974	115,180	10,087,154	19.4	0.2	19.7	5.5
Blue Lake	174,126	285,162	1.6	1,308,553	50,248	1,358,801	7.5	0.3	7.8	4.8
Seneca	79,569	244,996	3.1	1,270,979	42,828	1,313,807	16.0	0.5	16.5	5.4
Empire	95,999	149,509	1.6	656,614	101	656,715	6.8	0.0	6.8	4.4
Eagles Point	25,140	71,741	2.9	270,448		270,448	10.8	0.0	10.8	3.8
Stillwater	13,070	27,787	2.1	164,470	33,331	197,801	12.6	2.6	15.1	7.1
Hastings	5,079	20,572	4.1	103,254		103,254	20.3	0.0	20.3	5.0
Average	129,418	377,993	2.7	1,963,756	48,338	1,998,283	13.3	0.5	13.9	5.1

Note: Sewershed area and population data provided by Metropolitan Council (pers. comm. K. Jensen, E. Resseger, 3/16/2012)

<sup>&</sup>lt;sup>1</sup>WWTP service areas are derived from the Metropolitan Council sewersheds GIS layer. <sup>2</sup>Population data derived from the Metropolitan Council Research Group's draft 2010 population data, which is based on 2010 census data.

The estimated sewershed area ranges from 5,079 acres (Hastings) to 512,941 acres (Metro) and averages 129,418 acres (Table 2). Overall, sewershed population ranges from 20,572 to 1,846,185 people. The population density of these sewersheds ranges from 1.6 (Blue Lake and Seneca) to 3.6 capita per acre. Of note, the smallest sewershed, Hastings, had the second highest population density. As such, sewershed size does not correlate well with population density.

Wastewater point source TN loading in select sewersheds ranged from approximately 100,000 pounds/year to nearly 10,000,000 pounds/year, most of which was estimated to be from municipal sources (Table 2). The range of loading closely relates to both the size and population of a given sewershed. Total sewershed yield per unit area ranged from 6.8 to 20.3 pounds/acre with an average of 13.9. In most sewersheds the industrial component was minor (0-4%). However, in Stillwater, estimated TN loading from a power plant amounted to 17% of the total area-based sewershed load. Given that the power users extend far beyond the boundaries of the Stillwater sewershed, addition of this industrial load results in an elevated area-based yield that may not accurately depict the urban activity of that particular sewershed area. Nonetheless, the average municipal area-based yield (13.3 pounds/acre) closely resembles that of the average total area-based yield (13.9 pounds/acre), which includes individually permitted industrial dischargers.

Sewershed per capita yield and population density are also important components to consider. TN yield per capita ranges from a minimum of 3.8 pounds/capita (Eagles Point) to a maximum of 7.1 pounds/capita (Stillwater) with an average of 5.1 pounds/capita (Table 2). There were no strong relationships between per capita yield and either total area-based yield ( $R^2 = 0.21$ , Figure 7) or municipal area-based yield. This is due, in some part, to Stillwater's high per-capita yield yet moderate area-based yield. In contrast, strong relationships were observed between population density and both total area-based yield ( $R^2 = 0.80$ , Figure 8) and municipal area-based yield ( $R^2 = 0.89$ , Figure 9).

Sewershed areas may not be readily available for many urban communities, and yet population density data often is. One may estimate municipal area-based yield with population density data of the desired scale. The linear relationship between population density and municipal area-based yield is defined below (Figure 9):

Equation 1:

$$y = 5.3164x - 1.0084$$

Where:

y = municipal point source average annual TN yield (pounds/acre), and x = population density (capita/acre)

For example, if a community served by a municipal wastewater treatment plant had a population density of 1.9 capita/acre (roughly equivalent to that of the state of New Jersey; U.S. Census Bureau, 2010), the estimated municipal point source annual TN yield equates to 8.9 pounds/acre (Equation 1). Additional industrial load, not serviced by the WWTP could be included as a yield if the total population of concern were known. It is important that the user carefully evaluate the scale of the sewered population that one wishes to represent.

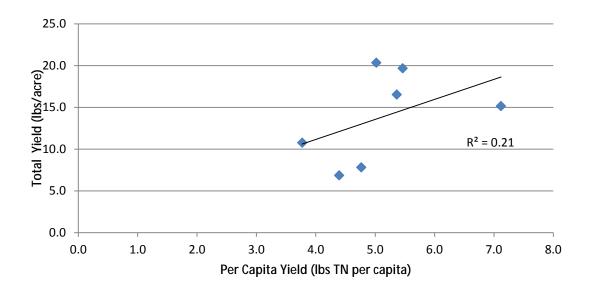


Figure 7. Sewershed point source TN per capita yield versus total area based yield. The total yield includes estimates of both municipal and industrial point source yields calculated from estimated discharges.

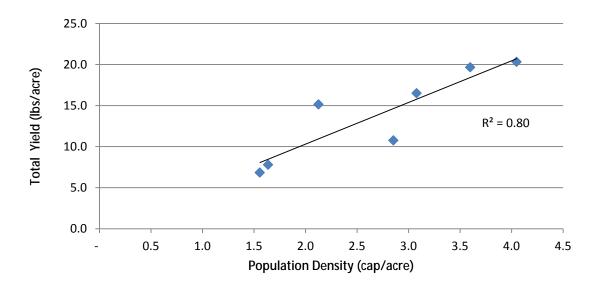


Figure 8. Sewershed population density (cap/acre) versus point source TN area based yield. Total yield includes values from individually permitted municipal and industrial point sources.

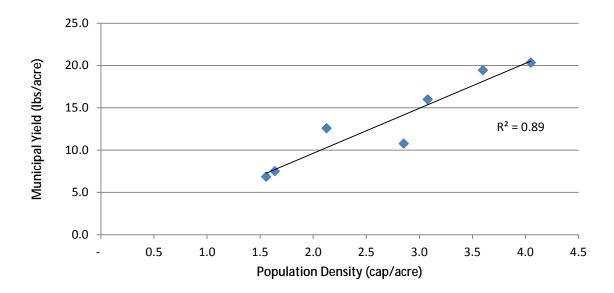


Figure 9. Sewershed population density (cap/acre) versus municipal point source TN area based yield. Municipal yield does not contain values from individually permitted industrial point sources.

## Seasonal patterns

Pollutant loading from wastewater point sources is typically assumed to be constant as compared to nonpoint sources. In this section, seasonal patterns of point source TN loading within the Minnesota River Basin (MRB) are examined in greater detail. Although the MRB has a large number of small individual facilities, the mix of facility type and size makes these patterns suitable to be applied to other basins.

In total there are 236 active point sources within the MRB. This equates to 26% of all active dischargers statewide. Together, they discharge an average annual TN load of 4,717,144 pounds/year. Within the MRB 66% (155) of point sources are domestic and 34% (81) are industrial; primarily cooling water discharges. Furthermore, 37% (87) of all active point sources are municipal stabilization ponds. Ponds are often used by smaller communities. Unlike other treatment systems, ponds do not discharge continuously, but rather, store wastewater for extended periods of time and discharge for a few days to weeks within a regulated time slot. In southern Minnesota, including all of the MRB, the acceptable discharge period is in the spring from March 1 through June 15 and in the fall from September 15<sup>th</sup> to December 31<sup>st</sup>. In the north, acceptable discharge periods are less restrictive and range from March 1 through June 30 in the spring and September 1 through December 31 in the fall.

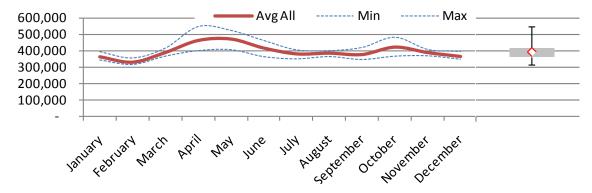


Figure 10. Monthly average point source TN effluent load (lbs) in the Minnesota River Basin (2005-2009). The adjacent box and whisker plot shows the distribution of all monthly values. The grey box indicates the 25th and 75th percentile range. The red diamond represents the mean value; whiskers represent minimum and maximum values.

Five years of monthly average TN data from all active point sources demonstrates a slight seasonal swell in mean loading and an increase in variability (Figures 10 and 11). The median monthly load is 382,265 pounds with a 12% coefficient of variation (Figure 10). The discernible rise in spring (April, May) and fall (October, November) loading coincides with annual precipitation patterns and the pond discharge window. Despite the fact that 37% of point source permits in the MRB are ponds, they only account for 3% of the annual load (Figure 11).

The overall flow volume from these facilities tends to be small. Limited effluent data suggests that the extended detention time in ponds facilitates denitrification. At peak, ponds are estimated to account for 8% (35,529 pounds/month) of monthly load in May and 7% (27,933 pounds/month) in October. This contribution drops to zero from January through March and July through August. In lieu of actual effluent concentration data, ponds are assumed to discharge 6 mg/L TN as compared to larger mechanical facilities which are assumed to discharge between 17 and 19 mg/L. When pond loading is removed from the total, a seasonal load swell is still observed due to increased flow and load from continuous facilities. Therefore, pond effluent only explains a fraction of the seasonal variation; the remainder can be attributed to seasonal precipitation patterns (Figure 11).

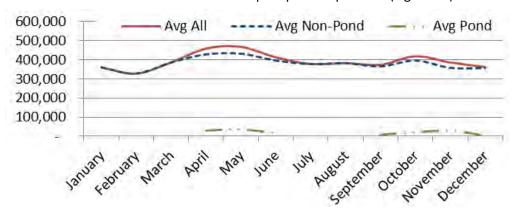


Figure 11. Monthly average point source TN effluent load (lbs) in the Minnesota River Basin (2005-2009). Municipal stabilization pond loads (green dashed), and non-pond loads (blue dashed) are disaggregated from the total monthly load (red solid).

Inflow and infiltration (I/I) of groundwater into municipal collection systems typically increases during storm events and wet seasons. Although many municipal treatment systems were built in the mid twentieth century, the collection systems often date back to the early twentieth century (MPCA 1991). Given the cost and inconvenience associated with maintenance, many of these systems are in need of repair. The remainder of the seasonal load swell, after pond loading is removed, is likely to be due to an increase in I/I. Despite the seasonal change in flow, I/I is generally assumed to have a low TN concentration, thereby resulting in a relatively constant seasonal loading rate. A review of five years of NOx data from over 350 Ohio WWTPs shows an average monthly NOx concentration change of only 3.6 mg/L (Figure 12). In spring, concentrations from all facilities averaged about 9 mg/L NOx, whereas in fall this increased to 12 mg/L. Overall, these data suggest that NOx concentrations remains relatively constant throughout the year. The Ohio data, generally, validate the constant load assumptions made for these load estimates. Effluent data currently being collected by Minnesota dischargers will better inform future analysis.

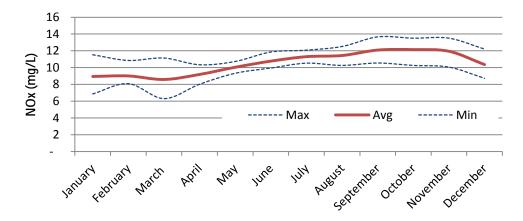


Figure 12. Monthly average NOx from over 350 Ohio WWTPs (2005-2009). Variability is greatest during spring and fall months. The average concentration rises from roughly 9 mg/L in spring to 12mg/L in fall.

# Assumptions and methods

#### Overview

Load estimates were based on five years of discharge monitoring report (DMR) data from 2005 through 2009. At the time of analysis, only a partial year of 2010 data were available, and therefore, these data were not included. Wastewater point source N effluent data in Minnesota are somewhat sparse and coincide with the historical implementation of numeric standards. Ammonia effluent data are, by far, the most abundant. Limits and reporting requirements became more prevalent in the early 1980s. Facilities with ammonia limits generally discharge to low dilution streams or receive waste streams from high protein industries. The direct impact of ammonia from point sources is seasonal and localized. In the summer the combination of ammonia and biological oxygen demand (BOD) can cause a dissolved oxygen (DO) sag that typically occurs 2 to 5 miles downstream of a discharger in an affected stream. In winter, the DO sag typically occurs from between 20 and 30 miles downstream, at which point ammonia and BOD levels return to headwater conditions (MPCA scientist G. Rott, personal correspondence, 6/24/11).

Facilities that report TN, or NO<sub>x</sub> either discharge upstream of a biotic life impairment, in which a form of N has been identified as a stressor, or they were found to contribute to a violation of the nitrate drinking

water standard (10 mg/L NO $_3$ ). Biannual effluent monitoring for TN or NO $_x$  is now being required for all municipal major facilities, which includes municipal point sources with average wet weather design flows (AWWDFs) greater than 1.0 million gallons per day (mgd). Future load monitoring data can be used to refine load estimates and will provide a better understanding of the variability of treatment. It is anticipated that more frequent TN and NO $_x$  monitoring will be required if nitrate toxicity standards are developed for surface waters in Minnesota.

It would have been impractical to estimate facility loads one at a time given the large number of point sources, a five year time frame (2005-2009), and the wealth of flow, and to a lesser extent, concentration data. As such, a database system was designed to select appropriate flow and concentration records based on predetermined conditions and to calculate monthly loads (Figure 13). All DMR records for flow and the four N parameters of concern (TN, NOx, NHx, and TKN) were downloaded from the Delta database, an MCPA repository for regulatory data. No single facility is required to monitor for all four pollutant parameters of interest, so it was necessary to splice in other concentration estimates for each flow record of concern when DMR concentration data were unavailable. Concentration assumptions were either applied to specific facilities identified by permit number, or they could have been applied to a larger category of similar facilities. The success of such a system is based on two factors including: 1) database architecture, and 2) the accuracy of the concentration assumptions and actual data. Additional WWTP effluent data supplied by the Metropolitan Council Environmental Services (MCES) made it possible to test both factors.

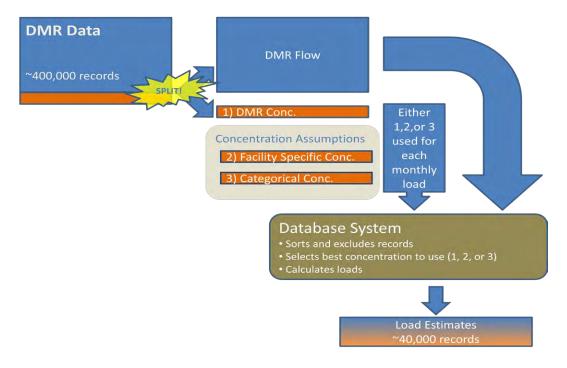


Figure 13. Overview of point source N load estimation process.

#### Database architecture validation

Database architecture refers to the sequence of conditional statements programmed into the database system used to select desired records and calculate loads. In total, there were nearly 400,000 flow and concentration records statewide. From this larger data dump, only approximately 40,000 records (10%) were used in this study. The remaining records were typically duplications and had undesired units,

periods of records, or limit types (i.e. maximum, minimum etc.). Mistakes associated with faulty database architecture often result in undesired records selected, and more often, multiple loads calculated for the same time period. When errors of this sort occur, results are often distorted by a factor of two or more.

The MCES Metro facility is currently required to submit monthly average NOx concentration data as part of their DMRs which were, in turn, used to calculate loads within the database system, hereafter referred to as MPCA loads. In order to generate monthly average values, MCES collects sub-monthly NOx concentration samples. Sub-monthly values were used independently by MCES to calculate annual NOx loads, hereafter referred to as MCES loads. By comparing MPCA and MCES loads for the same facility, one can verify that the database architecture functions correctly. In this situation, long term annual average MCES and MPCA loads were only 0.1% different. Results demonstrate that the database architecture is capable of calculating loads correctly for the Metro facility, one of the largest and more complex facilities statewide. Therefore, it is reasonable to conclude that the database system is capable of deriving accurate loads for the hundreds of other point sources given the accuracy of the data and assumptions provided.

#### Data and assumption validation

Of the eight MCES facilities that discharged between 2005 and 2009, only Metro was required to submit NOx data. Nonetheless, MCES collected NOx samples from the remaining seven facilities for their own records and provided annual NOx loads to MPCA for this study. Long term average annual MPCA NOx loads, derived by the database from concentration assumptions, were only 5% different than MCES loads. It should be noted that these facilities are among the largest point sources in Minnesota. Results demonstrate that the concentration assumptions used in this study, and the resulting load estimates, are reasonable. In the end, MCPA loads were used in this study because they provided a finer resolution monthly estimate which could be used to analyze seasonal load patterns. In summary, point source loads were derived from actual flow and a combination of actual and assumed concentration values. Based on the comparison between MCPA and MCES loads, it is reasonable to conclude that long term average NOx and TN load estimates are within a confidence interval of 5 to 10%.

Concentration assumptions for TKN and NHx are based on a much larger body of DMR data but cannot be validated in the same manner as TN and NOx because the large majority of facilities required to report also have limits. Those without limits have the capacity to discharge at higher concentrations, the magnitude of which is somewhat difficult to estimate without effluent data.

#### **Concentration assumptions**

Categorical concentration assumptions were used to estimate most point source N loads (Table 2). Concentration assumptions were based on several sources including: limited DMR data from Minnesota and Wisconsin, additional data from MCES, and a larger database from Ohio. Following a review of available data, facilities and individual outfalls were categorized. Concentration assumptions were then used to calculate loads (Table 2). A review of over 350 WWTPs in Ohio demonstrates that seasonal concentration patterns are limited (Figure 12). Therefore, no seasonal adaptations were built into categorical concentration estimates where actual data were unavailable. The Ohio dataset also demonstrates high variability among pollutant parameters (Figure 14). With the information available, individual Ohio facilities could not be classified into categories for direct comparison with Minnesota facilities. Nonetheless, Ohio data provided another line of evidence for the evaluation concentration assumptions.

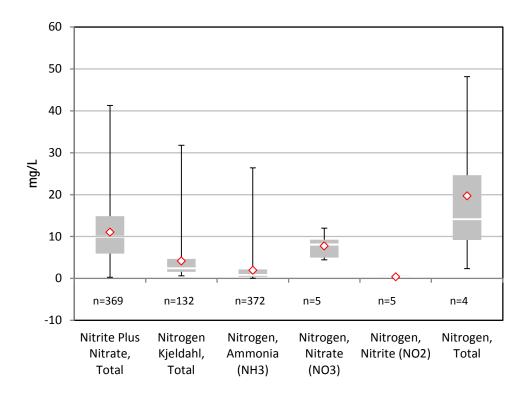


Figure 14.Distribution of effluent concentration data (2005-2009) from over 350 municipal wastewater treatment plants in Ohio. Whiskers represent minimum and maximum values. Boxes represent the interquartile range (25<sup>th</sup> to 75<sup>th</sup> percentile). Red squares and white lines represent median and mean values, respectively. Sample size (n) varies considerably among constituent.

Municipal wastewater treatment facilities were divided into four categories, A through D, which were based primarily upon design capacity and also the treatment components. Constituents like NOx have a discernible pattern among municipal categories (Figure 15). Class A larger facilities generally have higher NOx values. This may reflect a higher incidence of N-rich industrial users or possibly a lower proportion of I/I flow as a result of more recent waste collection system improvements. In contrast, smaller facilities (Class B – D) which serve incrementally smaller communities may have a higher percentage of low concentration I/I flow. In addition, most Class D and some Class C facilities are stabilization ponds which have sufficient retention time to facilitate denitrification. The available data suggests that wastewater effluent from stabilization pond dischargers often has NOx values less than 5 mg/L. Nonetheless, effluent variability from all facility classes appears to be high.

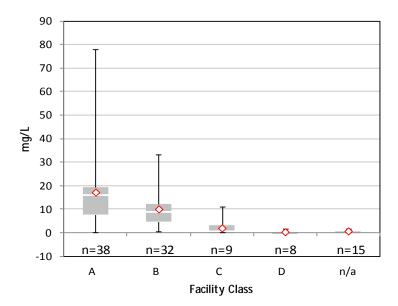


Figure 15. NOx data from municipal wastewater treatement plants in Minnesota (2005-2009). Sample size (n) varies considerably among facility classes.

Categorical concentrations for TKN and NHx were primarily derived from DMR effluent data. In addition, the difference between TN and NOx was also used to estimate TKN categorical concentrations. Class A facilities without DMR data were assumed to have TKN and NHx values of 4 and 3 mg/L, which was based upon existing data from similar classed facilities. For Class B facilities, it appeared that, on average, there was a 7 mg/L difference between TN and NOx, and therefore, it was assumed that TKN was 7 mg/L. Class B NHx was assumed to be 4 mg/L, a bit higher than other groups, due to the wide range of observed effluent data (2-70 mg/L). Class C and D municipals were assumed to have TKN of 3 mg/L and NHx of 1 mg/L. These assumptions were more closely tied to DMR data.

Industrial effluent load estimates were calculated using more facility or industry specific assumptions. As compared to municipal discharges, industrial concentrations were assumed to be moderate to low. In a few cases, two or more categories have identical concentration assumptions. In the event that future data allows for refinements of the assumptions, statewide limits can be quickly recalculated.

Industrial concentration assumptions are generally divided into two categories, high concentration and moderate to low concentration. Four categories of high concentration industrial effluents were identified; paper (P), tile lines (T), peat (PEAT), and other (O). These discharges were assumed to have TN, NOx, TKN, and NHx values of 10, 7, 3, and 2 mg/L, respectively. Paper industry assumptions were based upon data collected at one facility. Pulp rich effluent requires that nutrients, both phosphorus and N, be added to promote bacterial growth and subsequently reduce BOD. Facilities reporting tile line flow are typically draining land on which nutrient rich effluent was spray irrigated. In some cases it may be possible that these tiles are also partially draining adjacent agricultural lands. Assumptions for tile lines to surface water (T) are consistent with United States Geological Survey agricultural research in lowa and southern Minnesota (Kalkhoff, 2000). Similarly, peat mines typically drain wetlands with the potential to be nutrient rich. As such, assumptions for PEAT were equivalent to those of tile. Assumptions for PEAT can be refined in the future when effluent data become available. The "other" category includes contact cooling water effluent with the potential for contact with N rich sources.

Table 2. Categorical concentration assumptions (mg/L)

Category	General Description	TN	NOx	TKN	NHx
Α	Class A municipal - large mechanical	19	15	4	3
В	Class B municipal - medium mechanical	17	10	7	4
С	Class C municipal - small mechanical/pond mix	10	7	3	1
D	Class D municipal - mostly small ponds	6	3	3	1
О	Other - generally very low volume effluent	10	7	3	2
PEAT	Peat mining facility – pump out/drainage from peat	10	7	3	2
Т	Tile Line to Surface Discharge	10	7	3	3
P	Paper industry	10	7	3	2
NCCW	Non contact cooling water	4	1	3	2
POWER	Power Industry	4	1	3	2
WTP	Water treatment plant	4	3	1	1
GRAV	Gravel mining wash water	2	1	1	1
GW	Industrial facilities, primarily private ground water well	0.25	0.25	0	0
MN00xxxx	Other individual facility assumptions based on limited data and applied per NPDES preferred ID number	Na	Na	Na	Na

Industrial categories with moderate effluent concentrations include non-contact cooling water, and the power industry (POWER). Both were assumed to use ammonia based additives, and therefore, were assigned categorical TN and NHx values of 4 and 3 mg/L respectively. There are additional challenges when estimating the load from the power industry. Most of the water used is collected from a lake or river, passed through a cooling system once without additional additives, and discharged back to the receiving water resulting in no net load increase. Most facilities use a small amount of groundwater, to which they apply ammonia-containing additives. In order to not overestimate POWER loading, categorical concentrations were only applied to a fraction of total effluent flow corresponding to the volume of groundwater which receives additives, typically 1% of total effluent flow (J. Bodensteiner at Xcel Energy, personal communication, February 3, 2011).

Industrial categories with low effluent concentrations include mine pump out and gravel mine wash water (GRAV) and industrial facilities that primarily use private well water (GW). A review of private well data determined that 75% of commercial industrial wells contained nitrate concentrations of 0.5 mg/L or lower (Kroening, 2011). Only 10% of these wells contained nitrate N concentrations greater than 2.4 mg/L.

Concentration assumptions for a short list of individual facilities, including four fish hatcheries and one small industrial facility, were based upon short-term data collected and stored outside of the MPCA Delta database. The aforementioned industry manufactures explosives, presumably with ammonium nitrate, resulting in NHx concentrations in excess of 40 mg/L. Mining activities that use explosives containing ammonium nitrate may contribute higher TN loads than what was assumed in this study (Environment Canada, 2003). Unfortunately, N effluent data and more detailed information regarding specific mining activities were not available for this study but may be a consideration for future load estimate refinements.

In summary, there is a high degree of confidence in municipal Class A load estimates. Class A facilities have the largest pool of actual concentration data for direct load calculations and from which to base concentration assumptions. In addition, Class A municipals discharge more water than all other groups

(49%, Figure 16). Loads from other categories, particularly industrials, have a lower degree of confidence. However, these lesser categories also typically discharge lower volumes of water, resulting in somewhat insignificant estimated loads on a statewide basis (Figure 16, 17). As more N concentration data become available, load estimates will be more accurate. However, given that we currently have the highest confidence in the largest point source group, additional data in the near future is not likely to significantly change either the magnitude or degree of confidence in load estimates statewide.

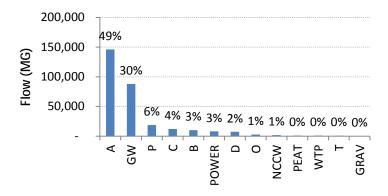


Figure 16. Flow in million gallons (MG) from various groups of point source dischargers statewide.

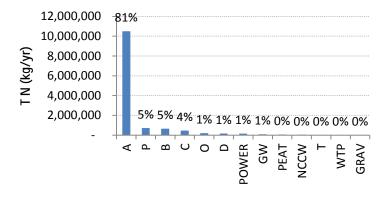


Figure 17. Total nitrogen (TN) loading in kilograms per year (kg/yr) from various groups of point source dischargers statewide.

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# D3. Atmospheric Deposition of Nitrogen in Minnesota Watersheds

Authors: Dave Wall and Thomas E. Pearson, MPCA

# Background

#### **Emission sources**

Atmospheric nitrogen from natural and human sources can fall on to land and waters through both wet weather deposition in rainfall and snow, or through dry weather deposition when particles and vapor are deposited without precipitation. Sources of nitrogen (N) to the atmosphere include, but are not limited to, automobiles, power plants, livestock manure, fertilizers, and lightning.

Providing a national perspective on sources of reactive N to the environment, the U. S. Environmental Protection Agency's (EPA) Science Advisory Board developed N flux estimates from various sources (Table 1). Each area of the country will have different percentages coming from these sources. Cities will have more combustion sources (mostly NOx) and rural areas will often have more livestock and fertilizer sources (mostly NHx).

Table 1. United States N inputs to the atmospheric environmental system in 2002. (EPA, 2011)

Emission inputs	billion lbs N/yr	%
NOX-N emissions*	13.7	61
Fossil fuel combustion – transportation	7.7	
Fossil fuel combustion – utility & industry	4.2	
Other combustion	0.9	
Biogenic from soils	0.7	
Miscellaneous	0.4	
NHx-N emissions*	6.8	31
Agriculture: livestock NH3-N	3.5	
Agriculture: fertilizer NH3-N	2.0	
Agriculture: other NH3-N	0.2	
Fossil fuel combustion – transportation	0.4	
Fossil fuel combustion – utility & industry	0.06	
Other combustion	0.6	
Miscellaneous	0.2	
N2O-N emissions	1.8	8
Agriculture: soil management N2O-N (nitrification and	1.1	
denitrification processes)		
Agriculture: livestock (manure) N2O-N	0.06	
Agriculture: field burning agricultural residues	0.002	
Fossil fuel combustion – transportation	0.2	
Miscellaneous	0.2	

<sup>\*</sup>NOX-N emissions include nitrate (NO3) and nitrite (NO2), but also include NO, N2O5, HONO, HNO3, PAN and other organonitrates. NHx emissions mostly include ammonia (NH3) and ammonium (NH4) (EPA, 2011).

#### **Objective**

Our objective was to estimate typical wet and dry atmospheric inorganic N deposition for each of the 8-digit Hydrologic Unit Code (HUC8) watersheds in Minnesota. Our goal was to develop atmospheric deposition estimates for nitrogen falling directly onto a) land, and b) waters. Our objective was not to determine relative amounts of atmospheric N from specific sources, but rather to estimate the combined N deposition from all sources.

It was beyond the scope of this study to estimate how much of the N deposited in Minnesota originates from Minnesota vs. other states/provinces, nor was it within the scope to estimate how much atmospheric N from Minnesota sources is deposited in other states/provinces. We also did not intend to evaluate all of the environmental effects associated with atmospheric N deposition. A brief summary of environmental concerns related to atmospheric N is included in Chapter A2.

#### Approach

The primary approach was to use results from atmospheric deposition modeling conducted by the EPA, and cross-check these results using wet weather monitoring results from the National Atmospheric Deposition Program.

Modeling results for wet and dry N deposition were provided by EPA (Dennis, 2010). The model used by EPA was the Community Multiscale Air Quality (CMAQ) modeling system, which is described in Byun and Schere (2006). The model includes components for meteorological atmospheric states and motions, emissions from natural and man-made sources, and chemical transformation and fate after being injected into the atmosphere. The CMAQ model uses precipitation monitoring results from the National Atmospheric Deposition Program (NADP), and then adds N source information to improve spatial estimates of wet deposition and to model dry deposition amounts.

The modeled results provided by EPA for this study included wet and dry deposition of both oxidized (mostly nitrate and nitrite, but also include NO, N<sub>2</sub>O<sub>5</sub>, HONO, HNO<sub>3</sub>, PAN and other organo-nitrates) and unoxidized (mostly ammonia and ammonium) forms of N. The N source estimates are from a 2002 base year inventory. The dry deposition is not expected to vary appreciably from year to year, unless major new sources are added or removed, and wet weather deposition can be expected to vary linearly with increases or decreases in precipitation (Dennis, 2011).

# Atmospheric nitrogen deposition (per acre)

#### Statewide and major basin average nitrogen deposition

Basin and statewide averages of modeled dry and wet weather deposition are shown in Table 2. On average across the state, wet weather deposition accounted for 52% of the total atmospheric N deposition, and dry deposition accounted for 48% of the total. The unoxidized fraction represented 62% of the wet plus dry N, with 38% in the oxidized form. The statewide average inorganic N deposition (wet plus dry) is 8.4 pounds/acre/year.

Table 2. Minnesota basin and statewide spatially weighted averages of wet and dry atmospheric N deposition in pounds/acre based on CMAQ model results for the 2002 base year. Low and high precipitation represent 10<sup>th</sup> and 90<sup>th</sup> percentile annual precipitation amounts.

Basin	Oxidized wet	Unoxidized wet	Oxidized dry	Unoxidized dry	Avg. precip. yr total N wet + dry	Low precip. yr Total N wet + dry	High precip. yr total N wet + dry
Lake Superior	1.30	1.97	1.80	0.48	5.55	5.03	6.21
Upper Mississippi River	1.72	2.97	1.71	2.28	8.67	7.92	9.61
Minnesota River	1.86	3.31	1.59	4.38	11.14	10.31	12.17
St. Croix River	2.15	3.45	2.02	1.37	9.00	8.10	10.12
Lower Mississippi River	2.68	4.12	2.15	4.25	13.20	12.12	14.57
Cedar River	2.23	3.51	2.02	4.67	12.44	11.52	13.58
Des Moines River	1.77	3.17	1.57	4.81	11.32	10.53	12.31
Red River of the North	1.09	2.10	1.19	2.06	6.44	5.93	7.08
Rainy River	1.04	1.70	1.43	0.57	4.75	4.31	5.29
Missouri River	1.63	3.04	1.55	5.25	11.47	10.72	12.40
MN - Statewide	1.59	2.72	1.59	2.49	8.40	7.71	9.26

#### Watershed deposition amounts

Because there is substantial spatial variability across the state in atmospheric N deposition, modeled results for each HUC8 watershed were individually calculated based on a spatial average across each watershed (Appendix D3-1 - Table 1). The pattern of deposition shows higher deposition rates in the southern part of the state, where agriculture, urban, and other human sources are more common (Figures 1, 2, and 3). Inorganic N amounts varied from over 14 pounds/acre in the southern part of the state to just over 4 pounds/acre in the northeastern region, during years of average precipitation.

# **Modeled Atmospheric Deposition of Nitrogen (Total)**

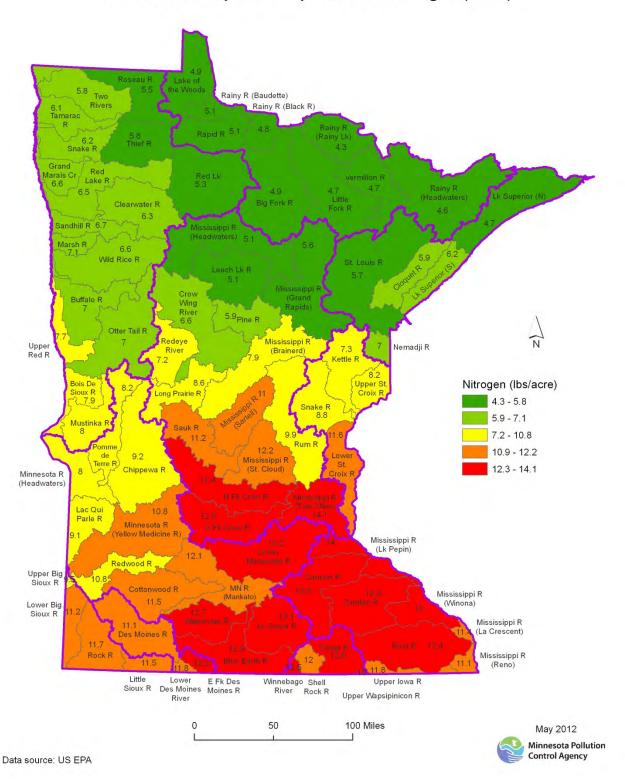


Figure 1. Total annual inorganic N deposition estimated by the CMAQ model, including both wet and dry deposition.

# **Modeled Atmospheric Deposition of Nitrogen (Dry)**

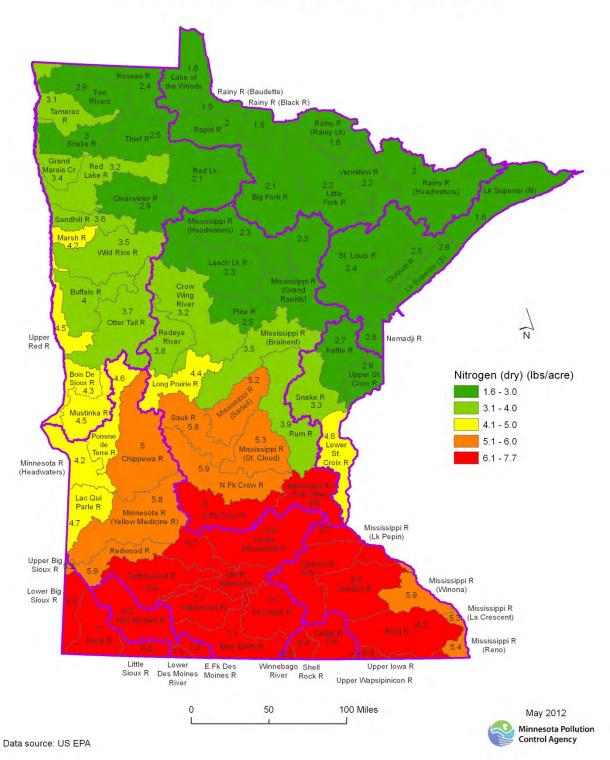


Figure 2. Total annual inorganic N *DRY* deposition estimated by the CMAQ model, and spatially averaged across the HUC8 watersheds.

# Modeled Atmospheric Deposition of Nitrogen (Wet)

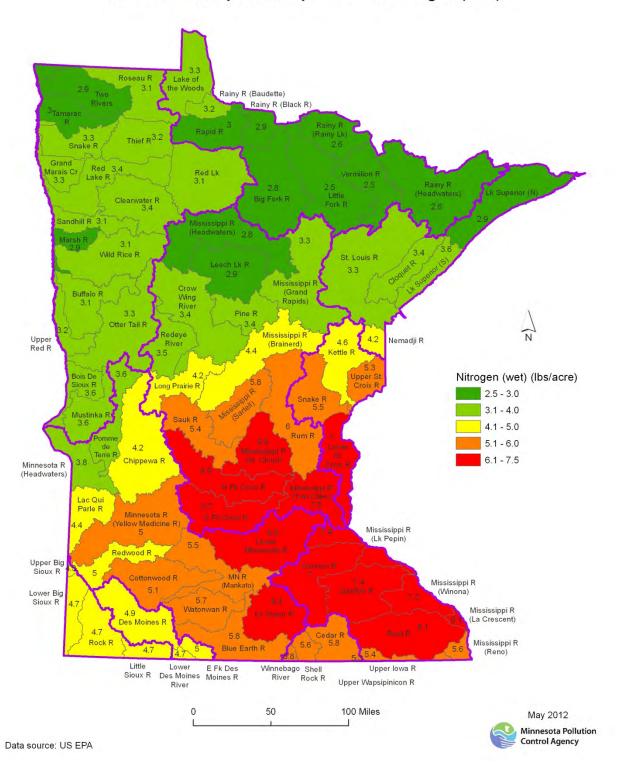


Figure 3. Total annual inorganic N *WET* deposition estimated by the CMAQ model, and spatially averaged across the HUC8 watersheds.

#### Direct deposition into waters

Most of the atmospheric deposition of N falls on land, where it mixes with the soil to be a source of N for vegetation, or in some situations becomes part of the surface runoff nutrient losses. Yet some falls directly into waters. We used spatial data layers and GIS software, along with CMAQ modeled results, to estimate the amount of N which falls during average precipitation years onto a) dry land, b) wetlands and marshes, c) lakes, and d) rivers and streams.

#### Calculation of surface water area

To calculate the surface area for rivers, we used three classes of streams within the high resolution 1:24,000 scale National Hydrography Dataset (NHD) including stream/river, canal/ditch, and connector. We then ran the intersect command in ArcGIS 10 (ESRI, 2010) using the NHD and the Minnesota Department of Natural Resources (DNR) HUC8 watershed data layer. We used the summarize command in ArcGIS to sum the total stream length for each watershed. We then multiplied the total stream length values by the average estimated width value of seven meters to obtain a final estimate of stream surface area.

For lake surface area calculations, we considered using the high resolution NHD but found numerous errors in the dataset, and we felt that the medium resolution 1:100,000 scale NHD would provide a more accurate assessment. We calculated surface area for lakes using two classes of water bodies within the medium resolution NHD including lake/pond and reservoir. We ran the intersect command in ArcGIS using the NHD and the DNR HUC8 watershed data layer. We then used the summarize command in ArcGIS to sum the total lake area for each watershed.

To calculate surface area for wetlands, we considered using the high-resolution NHD, but the primary wetland class, swamp/marsh was not populated for this data layer. We also considered using the National Wetlands Inventory (NWI), however this dataset for Minnesota is dated, it was developed circa 1980, and it is our understanding that the accuracy of wetlands in the medium resolution NHD is better than the NWI. Therefore, we calculated surface area for wetlands using the swamp/marsh class in the medium resolution NHD. We ran the intersect command in ArcGIS using the NHD and the DNR HUC8 watershed data layer. We then used the summarize command in ArcGIS to sum the total wetland area for each watershed.

#### Results - into waters

Based on this assessment, 374 million pounds (82.5%) of inorganic N falls onto land in Minnesota and 79 million pounds (17.5%) falls directly into lakes, marshes, wetlands and rivers. For wet and dry years, these amounts would be expected to average about 10% lower and higher, respectively, across the state. Of the N falling directly into waters, over 97% falls into lakes and marshes, which have a high capacity for assimilating and reducing N levels (see Appendix B5-2). About 2.1 million pounds, or 2.5% of the total falling into waters, falls directly into rivers, streams, and creeks. Specific annual estimated amounts falling directly into waters in different basins and HUC8 watersheds are included in Table 4 and Table 2 in Appendix D3-1.

For the statewide source assessment comparison of N into lakes and streams from major sources (Chapter D1), we used the atmospheric deposition into rivers and lakes and did not include deposition into wetlands and marshes. Wetlands can remove large quantities of nitrogen (see Appendix B5-2), and most atmospheric deposition falling into wetlands is not expected to leave the wetlands and move into streams, rivers or lakes.

# Watershed Atmospheric Deposition of Nitrogen Falling Directly into Rivers and Lakes

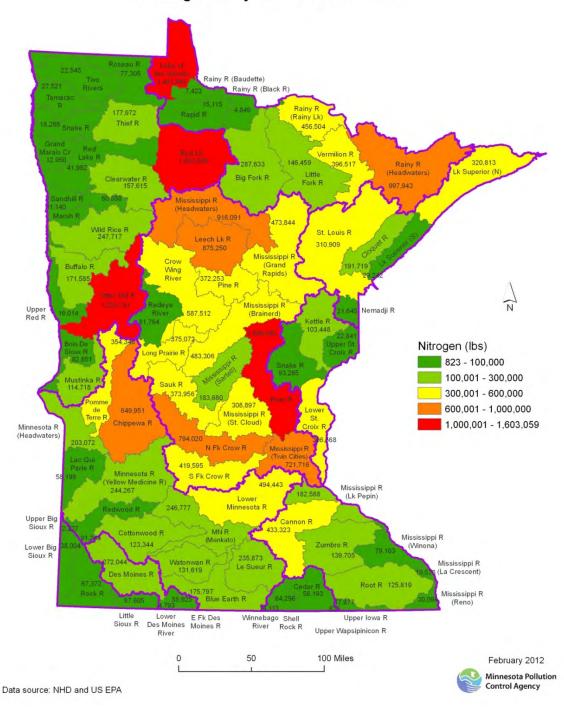


Figure 4. Estimated annual amount of wet plus dry oxidized and unoxidized inorganic N falling directly into rivers and lakes in each HUC8 watershed (note that this does not include wetland deposition).

Table 4. Atmospheric deposition estimates of wet+dry inorganic N falling directly into rivers and streams, marshes/wetlands, lakes, dry-land, and the total onto all land and waters. Results are shown for each of the major basins in the state.

Basin	Rivers	Marsh	Lake	Land	Total
Lake Superior	97,525	4,761,219	812,006	16,166,410	21,837,160
Upper Mississippi River	401,053	12,780,788	8,955,538	89,432,276	111,569,654
Minnesota River	553,936	757,661	2,640,104	102,810,198	106,761,900
St. Croix River	80,860	2,913,266	474,632	16,777,994	20,246,753
Lower Mississippi River	435,344	345,523	576,129	51,859,283	53,216,278
Cedar River	44,561	47,015	94,418	8,091,877	8,277,871
Des Moines River	57,190	36,554	275,639	10,770,989	11,140,371
Red River of the North	328,772	7,720,136	3,974,825	60,896,642	72,920,375
Rainy River	108,812	10,834,347	3,722,212	19,651,106	34,316,476
Missouri River	112,501	7,413	82,828	12,881,475	13,084,217
MN - Statewide	2,220, 553	40,203,921	21,608,332	389,338,250	453,371,055

## Comparing modeled results with wet deposition measurements

Wet weather deposition data from the NADP were compared to CMAQ-modeled results. We accessed the NADP on-line data base <a href="mailto:nadp.sws.uiuc.edu/">nadp.sws.uiuc.edu/</a> to obtain inorganic N (nitrate+nitrite-N plus ammonium-N) deposition information for sites in and near Minnesota. Our search was limited to those sites for which deposition information was available for each year between 1999 and 2009. Eight Minnesota locations met these criteria. We combined the Minnesota results along with information from monitoring locations in lowa, Wisconsin, South Dakota, and North Dakota.

We used data from 24 monitoring sites in Minnesota and neighboring states together with a kriging method in ArcGIS to create an interpolated spatial data layer of mean annual wet weather inorganic N deposition amounts (1999 to 2009). We then used this interpolated data layer together with a zonal statistics method in ArcGIS to calculate the average annual deposition amount, in pounds per acre, for each HUC8 watershed in Minnesota. Results from this process are shown in Figure 5, which shows the average wet weather inorganic N deposition from Minnesota based on the interpolated NADP data.

The pattern of deposition determined from precipitation monitoring is very similar to modeled results using CMAQ (Figure 5), with higher amounts in the southern part of the state and lowest amounts in the north. The CMAQ results estimate slightly higher wet weather deposition in the southeast and central Minnesota and slightly lower deposition in the northeast, as compared to the NADP-based estimates. However, the results are similar enough to provide assurance in the reasonableness of CMAQ results provided by the EPA.

# Wet Weather Atmospheric Deposition of Nitrogen NADP Monitoring (1999-2009)

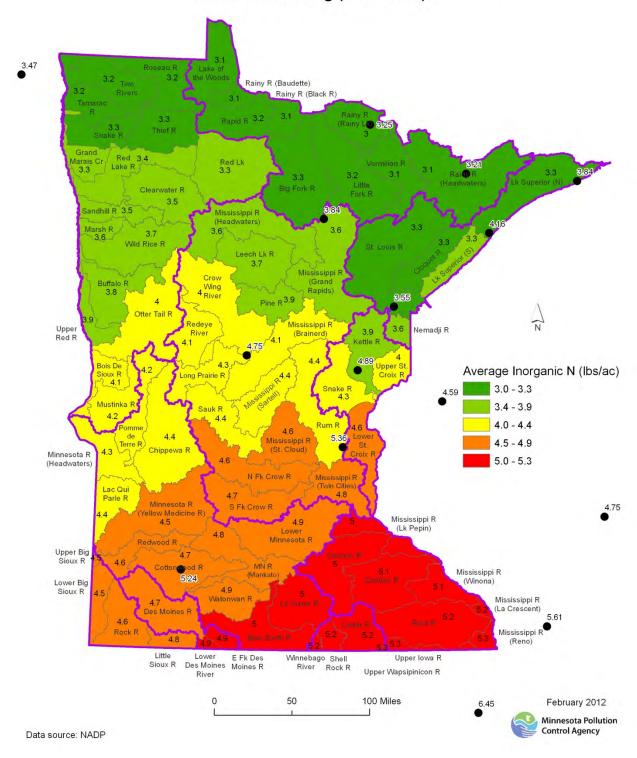


Figure 5. Inorganic N monitored from wet weather deposition (average between 1999 and 2009). Data source NADP. Amounts between monitoring points (triangles) were interpolated.

### Organic nitrogen

Organic N deposition is not included in the CMAQ modeled results. Organic N deposition is likely to contribute to atmospheric deposition total nitrogen inputs, although the magnitude of the deposition rate is highly uncertain. Goolsby et al. (1999) noted that if the fraction of organic N/total N in wet deposition measured in a 1998 study by Scudlark is assumed to be similar to the fraction that occurs in the Mississippi Basin, wet deposition of organic N in the Mississippi Basin can be estimated as 25% of the total wet deposition. The EPA concluded from the literature that organic N can be about 10% as much as the NOx from atmospheric deposition, but could be as much as 30% (EPA, 2011). This would mean that the organic N deposition likely represents an additional 4% to 13% of the total wet and dry inorganic atmospheric deposition.

With limited information and no modeled results, along with the relatively small expected contribution from organic N, we did not include an organic N amount in the predicted atmospheric deposition for this study.

### Summary

Based on the Community Multiscale Air Quality-modeled results provided by the EPA, wet plus dry atmospheric inorganic N deposition contributes between 4 and 14 pounds annually per acre to Minnesota soil and water, averaging 8.4 pounds/acre/year across the state. Atmospheric deposition is highest in the south and southeast parts of the state and lowest in the north and northeast where fewer urban and agricultural sources exist. The annual wet and dry deposition amounts are nearly equal, on average, across the state. The inorganic N in wet plus dry deposition is about 62% unoxidized (NHx – mostly ammonia and ammonium) and 38% oxidized (NOx - nitrite, nitrate, other). Approximately 82.5% of total statewide inorganic N deposition falls onto land (374 million pounds), and 17.5% (79 million pounds) falls directly into lakes, marshes, wetlands, and flowing waters. Of the N falling directly into waters, 97.5% falls into lakes and marshes, and about 2.5% (2.1 million pounds) falls directly into rivers, streams, and creeks.

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# D4. Nonpoint Source Nitrogen Loading, Sources, and Pathways for Minnesota Surface Waters

Authors: David J. Mulla, Jacob Galzki, Karina Fabrizzi, and Ki-In Kim, University of Minnesota, and Dave Wall (MPCA)

### Introduction

Nonpoint source nitrogen (N) loading to Minnesota Surface Waters was estimated for the primary N sources, including cropland, urban/suburban nonpoint sources, forested areas, and feedlots. Pathways for cropland sources were divided into three parts: 1) cropland runoff, 2) tile drainage, and 3) leaching to groundwater which subsequently flows into surface waters. Nitrogen from these sources was estimated for average, wet, and dry precipitation years at the watershed, major basin, and statewide scales.

A cropland soil N balance was also conducted as a separate and distinct element of this study. The cropland balance provided estimates of the N inputs and outputs to the cropland soil. The balance was not used to calculate cropland N sources or delivery to surface waters. Yet certain elements of the N balance, such as fertilizer and manure additions, were also used to estimate N losses to surface waters.

### **Project goals**

- Assess soil N budgets (N additions to soil and losses from soils) for combinations of soils, climates and land uses representative of the most common Minnesota conditions.
- Assess N contributions to Minnesota rivers from each of: a) the primary land use sources (excluding point source municipal and industrial), and b) the primary hydrologic pathways.

### Materials and methods

### Study area

Minnesota has diverse climatic factors, land use, land cover, soil and geologic materials, and landscapes. In addition, the density of permanent streams, drainage ditches, and lakes varies across the state. This diversity affects water quality and water quantity. It also affects the types of crop and animal production systems and their associated suite of management practices. Mean annual precipitation varies from less than 20 inches in the northwestern part of the state to over 34 inches in the southeastern part of the state. Soil parent material and geologic materials at the land surface include alluvial, outwash, peat, glacial moraine, glacial till, and lacustrine materials. The soils and their associated landscapes range from flat to steep in slope, and from poorly drained to well drained. This combination helps determine the potential for runoff, leaching and the likelihood of artificial drainage and losses of nitrate-N to surface waters.

The diverse range in Minnesota climate, soil and landscapes, and land use/land cover can be broadly described using the concept of agroecoregions (Figure 1), which is defined further in Brezonic et al. (1999). Agroecoregions are units having relatively homogeneous climate, soil and landscapes, and land use/land cover. Agroecoregions can be associated with a specific set of soil and water resource concerns, and with a specific set of management practices to minimize the impact of land use activities on soil and water resource quality.

Land use in Minnesota includes urban areas, forest, forested wetlands, wetlands, agriculture, and barren rock. Land use associations include agriculture, forest, agriculture-forest, forest-wetlands-agriculture, forest-wetlands, and urban-agriculture. Agricultural uses include both crop and animal production. Crop production is diverse, major crops considered for the study include corn, soybeans, wheat, hay, potatoes, sugar beets, oats, and barley. The main cropping production systems include corn-soybeans, corn-soybeans-hay, corn-hay, wheat-hay-mixed, wheat-soybeans-mixed, and hay. Animal production systems include cattle-hogs, cattle-hogs-turkeys-chickens, cattle-poultry, and hogs-cattle, and cattle. If not properly managed, N contained in the manure produced by these animals may pollute the atmosphere, or surface and groundwaters.

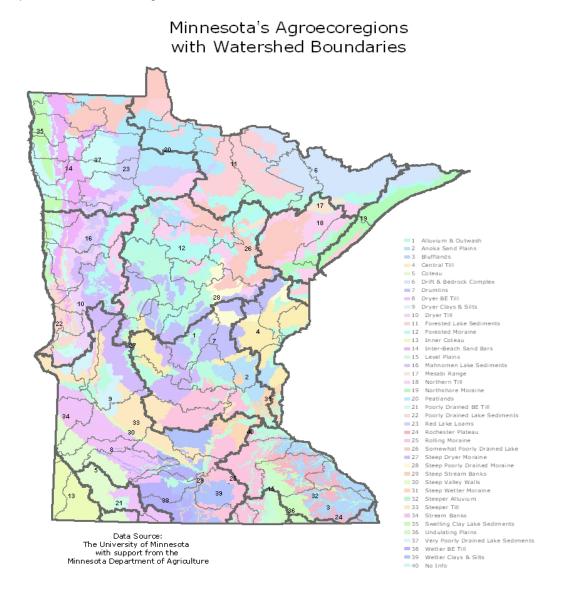


Figure 1. Minnesota's agroecoregions with basin and major watershed boundaries.

#### Methods overview

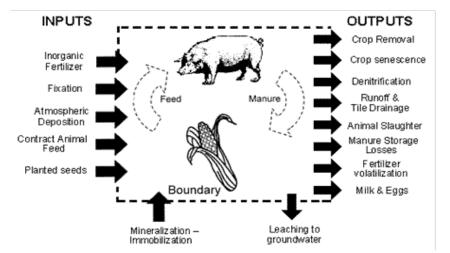
Two separate methods were used for two distinct purposes within the scope of this project. First, a statewide cropland N budget (or balance) was developed so that specific inputs and outputs to the cropping system could be estimated. Since inputs should roughly equal outputs, comparing the sum of the inputs with the sum of the outputs provides one way to check the estimates. One of the N outputs is an estimate of the amount of cropland N inputs which reach surface waters. This output was determined through the second project objective, and then was also used to complete the N balance.

The second objective was to determine the amount of N that reaches surface waters from all nonpoint sources, including cropland, urban/suburban, septic systems, and forest. The goal was to also break down cropland sources to waters into the three major pathways, tile drainage, groundwater and surface runoff. While some of the information from the cropland N budget was used for the nonpoint sources estimates, most of the information came from information sources separate from the N balance study. The specific methods for each of these two project objectives are described below.

### 1: Cropland nitrogen balance methods

The approach used to carry out this mass-balance of the state of Minnesota was to compile the information necessary for each component to the balance individually, and then assemble all of these components in a format that would be both easy to interpret, as well as accessible, for changes in the future when updated information becomes available. The fluxes included were chosen based on their implicit importance within the boundaries of the study area, as well as the availability of sufficient information and methods to confidently include them.

An N balance was estimated for the cultivated cropland component of this study. Forest, urban/suburban and septic system inputs and outputs were not considered in the N balance, but N export to surface waters for these sources was considered separately. Ideally, N inputs and outputs should be equal in the N balance. The inputs represented in this balance include mineralization minus immobilization (net mineralization), symbiotic and non-symbiotic fixation, inorganic fertilizer, atmospheric deposition, animal feed, and planted seeds. The outputs include tile drainage and runoff, denitrification, leaching to groundwater, crop senescence, fertilizer volatilization, crop removal, milk,



eggs, and animal slaughter. The two fluxes considered internal to this balance are a portion of the harvested crops that are fed to livestock and the livestock manure that is returned to the fields (Figure 2).

Figure 2. Nitrogen balance used to evaluate the N use efficiency in the state of Minnesota (extracted from Stuewe, 2006).

Area in various land uses (forest, urban) and major crops were determined for each agroecoregion based on 2006 National Land Cover Database land use coverages. (NLCD, 2006).

Harvested crop area for each agroecoregion was determined using a five year average (2005-2009) of data from the National Agricultural Statistics Service (USDA-NASS, 2011) for the following crops: corn, soybeans, spring wheat, barley, oats, sugarbeet, potatoes, alfalfa. For corn silage and other hay, a weighted average was reported (USDA-NASS-CDL, 2009). Total cultivated area was the sum of all harvested crop area.

### Nitrogen inputs

The estimated N balance and specific inputs and outputs were not used to estimate nitrogen loads to surface waters, except that fertilizer and manure inputs were used for certain elements of the cropland source pathway estimates. The balance provides a framework for understanding the cropland soil N sources and processes, but is not used to attribute N contributions to surface waters.

#### Planted seeds

Corn and soybean growers in the Midwest annually purchased seeds from seed dealers. This annual purchase represents an input of N into the system that needs to be estimated and included in the N balance. It was assumed that 0.34 kg N ha<sup>-1</sup> and 4.5 kg N ha<sup>-1</sup> (0.3 lb N ac<sup>-1</sup> and 4.0 lb N ac<sup>-1</sup>) are contained in the seeds planted for corn and soybeans, respectively (Meisinger and Randall, 1991). For barley, oats, spring wheat and potatoes, planted N seed (lb) was calculated as following:

N seeds (lbs N/ac) = seeding rate/ac \* N content (%) in the seed

Planted seeding rates were 80, 80 and 133 lb ac<sup>-1</sup> for barley, oat and spring wheat (MAES, 2006). Nitrogen content was 1.86%, 3.5% and 2.6% for barley, oat, and spring wheat (Sims et al. 2002, Pan and Hopkins, 1991, Hofstetter, 1988). Thus, the estimated planted N seed was 2, 2.3 and 3.9 pounds ac<sup>-1</sup> for barley, oat, and spring wheat respectively. Nitrogen content in the potatoes was estimated at 23.4 pounds N ac<sup>-1</sup>, using N content of 1.608% and 1.648% for tubers and vines (Rosen et al. 1999). Estimates of the N contained in alfalfa seeds, other hay and sugar beets were not included. Total planted N seed was calculated as:

Planted N seed (lb) =  $\Sigma$ (harvested crop area (ac) \* N seeds (lb ac<sup>-1</sup>)

### Atmospheric deposition

Atmospheric N deposition comprises both wet and dry depositional processes, and includes all oxidized and reduced forms of N, including  $NO_3$  and  $NH_4$ . Total atmospheric deposition rate was area-weighted for each agroecoregion (EPA, 2011; Byun and Schere, 2006), as described in more detail in MPCA, 2012. Atmospheric deposition represents an average over many climatic years.

#### Symbiotic nitrogen fixation

Symbiotic and non-symbiotic fixations were included in this balance. In symbiotic fixation, specialized root-nodule bacteria attached to leguminous plants and converts N<sub>2</sub>-N from the atmosphere into N compounds that are taken up by the plant (Graham, 1998). Non-symbiotic fixation is essentially the same process, but the soil bacteria carrying out the process are free living and unattached to a leguminous host plant (Meisinger and Randall, 1991).

The symbiotic fixation rates used in this balance are reported in Table 1. The total land area over which these fixation rates were applied includes the harvested acres of soybean, alfalfa, and grass/legume crops (USDA-NASS, 2011, USDA-NASS-CDL, 2009).

The non-symbiotic N fixation estimates made for this balance are based on Meisinger and Randall (1991) and a rate of 2.2 kg N ha<sup>-1</sup> (2 lb N ac<sup>-1</sup>) was applied to all of the harvested cropland area.

Table 1. Symbiotic fixation rates estimated for soybean, alfalfa and grass/legume.

Crop	Symbiotic fixation rates		
Soybean <sup>‡</sup>	60.5 kg N ha <sup>-1</sup> yr <sup>-1</sup>	50 lb N ac <sup>-1</sup> yr <sup>-1</sup>	
_ Alfalfa <sup>†</sup>	22.86 kg N ton <sup>-1</sup>	50.4 lb N ton <sup>-1</sup> yr <sup>-1</sup>	
Grass/legume <sup>†</sup>	19.7 kg N ton <sup>-1</sup>	43.5 lb N ton <sup>-1</sup> yr <sup>-1</sup>	

†Source: Plants Database, USDA (http://npk.nrcs.usda.gov) reported by MDA, 2005: Reports, publications and fact sheets. ‡Russelle, M (pers. comm.)

#### Mineralization

Mineralizable N was estimated using the same approach presented by Burkart and James (1999a), and reported by Stuewe (2006), with a small modification in the soil elemental N content (from 3.0% to 3.2%). The following equation was used:

Nm = 1000 Db\* Om/100 \* Vs\* Ne \* Np

where:

Nm = Mineralizable nitrogen (lb ac<sup>-1</sup>)

Db = Bulk density of specific soil (Mg/m<sup>3</sup>) (constant=1.471 Mg m<sup>-3</sup>)

Om = Organic matter content of soil (%)

Vs = Volume of 30 cm thick soil in one hectare (constant = 3,000 m<sup>3</sup> ha<sup>-1</sup>)

Ne = Elemental nitrogen fraction of soil organic matter (constant = 3.2%)

Np = Annual mineralizable portion of soil organic nitrogen (constant = 2%)

The percent organic matter used in these calculations is from SSURGO mapping unit values (USDA NRCS, 1995). Percent organic matter was estimated only in cultivated lands (NLCD, 2006). High anomalous values were removed to maintain data integrity (eg. Anoka Sand Plain average went from 8.4% with anomalous values to 2.02%, a much more appropriate value based on Delin et al. 1994). The bulk density assumed across the entire study area is the commonly used estimate of 1.471 Mg m-3 (2,000,000 pounds ac-1-6 inches deep). The volume of soils considered was the top 30 cm (11.8 inches) of soil, equivalent to 3,000 m3 ha-1 (Burkart and James, 1999a). The annual mineralizable portion of the soil organic N used was 2% (Schepers and Mosier, 1991).

#### **Immobilization**

The amount of immobilized N (converted from inorganic N to organic N by micro-organisms or plants) was estimated after all volatilization losses were accounted for both the inorganic fertilizer and the manure applied in the study area. This amount of N immobilized should not be considered a complete loss from the system, and should be viewed as N held in the soil organic matter pool, unavailable for immediate plant uptake during the first year of application, but possibly available in subsequent years (Burkart and James, 1999b).

The immobilization rate for all forms of inorganic fertilizer was assumed to be 40% (Burkart and James, 1999a). The immobilization rates for each type of livestock manure are presented in Table 2 (Burkart and James, 1999b, adapted from Elliot and Swanson, 1976; Schepers and Mosier, 1991; reported by Stuewe, 2006).

Table 2. The N immobilization rates assumed for each type of livestock manure applied to cropland (reported by Stuewe, 2006).

Animal type	% N immobilized
Beef Cows	70%
Milk Cows	60%
Hogs	10%
Chickens (broilers)	25%
Turkeys	25%

### **Inorganic** fertilizer

The total amount of inorganic N fertilizer considered in this balance was calculated based on the N fertilizer rate and the cultivated area of each crop.

For crops other than corn, a constant rate was used for all agroecoregions (Table 3). Soybean fertilizer rates were adjusted from 20 to 3 pounds ac<sup>-1</sup> since only 15% of soybeans fields are fertilized (NASS, 2002-2004-2006-2008).

Fertilizer N rates for corn in each agroecoregion were determined based on county-level farmer surveys (Figure 3) (Bierman et al., 2011). Nitrogen rates for corn were based on non-manure fields; however rates were adjusted according to manure credit calculations. The Minnesota Pollution Control Agency (MPCA) feedlot registration database was used to determine animal units of different species. These registration numbers are often reported on the high-end of an operation's potential animal capacity so as to not limit the operation. Since actual animal numbers are often less than reported in this database, animal numbers were corrected downward based on surveyed values from the Minnesota Department of Agriculture (MDA). National Agricultural Statistics Service (NASS) animal statistics were used to cross check this method, and confirm that it accurately represented animal numbers.

Using these adjusted feedlot numbers, available N from manure was calculated using two different methods (Midwest Plan Service MWPS-18 2004; University of Minnesota Extension Service 2001). It was assumed that 50% to 70% of calculated first year N credits would be taken, with no second year credits considered in this calculation, and also 59% of poultry manure would be burned.

Total amounts of N fertilizer were initially estimated as the product of fertilizer N rate times area of each crop planted based on remote sensing data collected for the 2009 CDL. This amount was compared with statewide estimates of N fertilizer sales, excluding sales in urban areas, and found to be slightly low. Initial estimates of corn acres planted were then adjusted upwards based on improved estimates of corn acreage using statistical survey data from NASS. The improved corn acres planted estimate was then multiplied by the surveyed N rates applied to corn (Bierman et al., 2011) and credits for land applied manure were then subtracted to obtain the total amounts of N fertilizer applied to corn.

Table 3. Nitrogen fertilizer rates for each crop

Crop	Fertilizer N rate
	lbs ac <sup>-1</sup>
Soybeans	3
Spring wheat	107 <sup>1</sup>
Barley	66 <sup>2</sup>
Oats	48 <sup>3</sup>
Sugarbeet	83 <sup>4</sup>
Potatoes	195 <sup>5</sup>
Alfalfa	10 <sup>6</sup>
Other Hay	10 <sup>6</sup>

<sup>1</sup>MDA

### Nitrogen outputs

### Crop harvest (grain nitrogen removal)

The total amount of N removed with harvested crops was calculated based on 5- year average yield data and N content in the grain. Average yield data (2005-2009) for the following crops: corn, soybeans, spring wheat, barley, oats, and sugar beets were obtained from USDA-NASS (2011). Potato yield data

were provided by Carl Rosen (pers. comm. March 2011). Weighted yield average was used for corn silage and other hay to estimate grain N removal (USDA-NASS-CDL, 2009). The percentage of N in grain and stover for each crop is presented in Table 4.

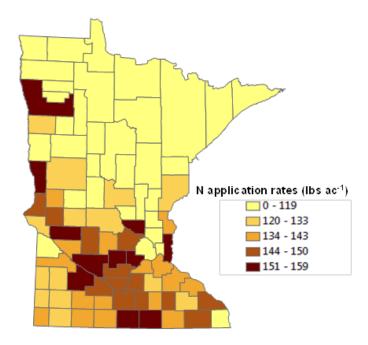


Figure 3. County N application rates for corn obtained from farmer surveys (Bierman et al. 2011).

<sup>&</sup>lt;sup>2</sup> NASS, 2003

<sup>&</sup>lt;sup>3</sup> NASS, 2005

<sup>&</sup>lt;sup>4</sup> NASS, 2001 and U of MN recommendations

<sup>&</sup>lt;sup>5</sup> Weighted average based on U of MN recommendations for irrigated and non-irrigated potatoes

<sup>&</sup>lt;sup>6</sup> U of MN recommendations

Table 4. Percentage of N in grain and stover for each crop used to estimate the grain and stover N removal.

Crop	N grain	N stover
		%
Corn <sup>1</sup>	1.2 1	0.70 <sup>1</sup>
Corn silage <sup>2</sup>		1.18 <sup>2</sup>
Soybeans	6.34 <sup>3</sup>	1.21 <sup>3</sup>
Spring wheat	2.62 <sup>5</sup>	0.55 <sup>4</sup>
Barley	1.86 <sup>6</sup>	0.36 <sup>6</sup>
Oats	3.5	0.36 6
Sugarbeet	0.58	2.28
Potatoes	1.619	1.65 <sup>9</sup>
Alfalfa		3.1 <sup>10</sup>
Other Hay		2.34 <sup>11</sup>

<sup>&</sup>lt;sup>1</sup>Randall and Vetsch (2005)

The total amount of grain and N removal was calculated as follows:

Total amount of grain N removal (lb)= N removal rate (lb ac-1)\* Number of acres for each crop Total amount of stover removal (lb)= N removal rate (lb ac-1)\* Number of acres for corn silage Alfalfa and other hay

A proportion of the N in harvested crops is subsequently fed to livestock within the study area; the remainder is in grain that is sold for human consumption. Livestock feed N from harvested crops (estimated using methods described below) was subtracted from the total amount of harvested crop N, this remainder is a N output in the mass balance. It was assumed that all of the independently grown livestock in the study area are fed crops grown in Minnesota.

#### Crop senescence

During senescence, plants will volatilize N into the atmosphere, primarily as NH<sub>3</sub>, from the maturing vegetation (Wetselaar and Farquhar, 1980). The rates of N senescence for corn, soybean, alfalfa, and small grains used in this balance are presented in Table 5.

<sup>&</sup>lt;sup>2</sup> Sheaffer et al. (2011)

<sup>&</sup>lt;sup>3</sup> Salvagotti et al (2008)

<sup>&</sup>lt;sup>4</sup> Mullen and Lentz (2007)

<sup>&</sup>lt;sup>5</sup> Sims et al. 2002

<sup>&</sup>lt;sup>6</sup> Pan and Hopkins (1991)

<sup>&</sup>lt;sup>7</sup> Hoftstetter, 1988,

<sup>&</sup>lt;sup>8</sup> Kumar et al. 2009a

<sup>&</sup>lt;sup>9</sup>Rosen et al. 1999

<sup>&</sup>lt;sup>10</sup> Rosen et al. 1995

<sup>&</sup>lt;sup>11</sup> Roger (2003)

Table 5. Crop N senescence rates estimated for major crops grown within the study area (Burkart and James, 1999a, reported by Stuewe, 2006).

Crop	Senescence rate	
	kg N ha <sup>-1</sup> yr <sup>-1</sup>	lb N ac <sup>-1</sup> yr <sup>-1</sup>
Corn	50	44.6
Soybeans	45	40.1
Alfalfa	22	19.63
Small grains†	35	31.2

<sup>†</sup> Small grains include spring wheat, barley and oats (Burkart and James, 1999a).

#### Volatilization of stored manure

Volatilization of stored manure decreases the amount of N subsequently available for land application. Manure N volatilization rates during storage for each animal species estimated for this study are presented in Table 6 (Purdue, 2001).

Table 6. Manure N volatilization rates during storage used in this balance.

Fertilizer type	% N loss
Beef	35%
Dairy	20%
Swine	20%
Chickens	25%
Turkeys	25%

### Volatilization of land applied fertilizer and manure

Volatilization losses of N from organic and inorganic fertilizers primarily occur as NH3 during application (Burkart and James, 1999a; Mosier et al., 1998). In this balance, different volatilization rates were assumed to each type of inorganic fertilizer and animal manure applied.

Nitrogen volatilization losses during the application of synthetic fertilizers are based on the estimates described by Stuewe (2006) (Table 7).

Table 7. Percentage of total sales and N volatilization rates for each inorganic fertilizer applied in the study area.

Fertilizer type	% of total sold†	% N loss‡
Anhydrous Ammonia (82-0-0)	45.9%	2%
Urea (46-0-0)	44.8%	5%
UAN (28-0-0 & 32-0-0)	4.9%	5%
Custom Blends (all other blends)	4.4%	4%

†Bierman et al. 2011. ‡ Stuewe (2006)

Volatilized N losses during the application of livestock manure were estimated for each type of animal manure (Table 8). The manure N considered available for volatilization losses during application is the amount remaining after all storage and burned losses were accounted.

Table 8. Nitrogen volatilization rates during manure application to cropland in the study area used in this balance (Reported by Stuewe, 2006).

Fertilizer type	% N loss	Source
Beef	21%	Schmitt, 1999
Dairy	10%	Written comm. w/ Dr. Gyles Randal & verbal confirmation by Dr. David Mulla (2005)
Swine	10%	Written comm. w/ Dr. Gyles Randal & verbal confirmation by Dr. David Mulla (2005)
Chickens	18%	Schmitt, 1999
Turkeys	18%	Schmitt, 1999

#### Denitrification

Soil denitrification rates were assigned according to soil drainage and other soil characteristics in each agroecoregion. Denitrification rates for each agroecoregion with the described soil characteristics are presented in Table 9. Most tile drained lands were assumed to have half the rate of denitrification of untiled lands in each agroecoregion (Table 9).

Table 9. Denitrification percentages estimated for applied and in situ forms of soil N used in the N balance.

	No-Tile	Tile
	% of inorganic	N denitrified
Excessive to well drained (sandy, loam, muck) <sup>1</sup>	3	1
Somewhat poorly drained (loam) <sup>2</sup>	20	10
Poorly and very poorly drained <sup>2</sup>	30	15

Percentage estimated from Venterea (2011)

#### Total denitrification

Denitrification rates were calculated separately for the amount of N in land applied livestock manure and inorganic fertilizer, in N deposition and in the mineralizable N from soil organic matter. The amount of N in applied manure and inorganic fertilizer available for denitrification is the amount remaining after all volatilization and immobilization losses have been considered. The calculations carried out for each of these sources were combined to come up with an overall estimate of the N escaping from the study area through denitrification. For the N balance, denitrification occurs only at the field scale. To estimate N loadings from groundwater discharge, an additional denitrification factor was applied as discussed below in the section 2 "Methods: Nonpoint Source Nitrogen Loadings to Surface Waters".

### Cropland nitrogen leaching losses

A literature review was conducted to determine the N leaching rate for each agroecoregion. Details of estimated N leaching rates are presented in Section 2. Total nitrogen leaching as an output in the agricultural N balance does not account for denitrification losses that occur beyond the edge of field as groundwater travels towards and is discharged to streams.

<sup>&</sup>lt;sup>2</sup> Percentage estimated from Meisinger and Randall (1991), reported by Stuewe (2006)

### Cropland nitrogen losses in tile drainage

Total N losses in tile drainage were calculated for dry, average and wet conditions based on growing season precipitation data and N rate applied. Details of tile drainage calculations are presented in Section 2.

### Cropland nitrogen losses in surface runoff

Nitrogen losses in surface runoff were calculated as a function of runoff volume and N concentration for each agroecoregion. Details of calculations are presented in Section 2.

### Nitrogen exported in milk

Nitrogen exported in milk is based on an assumed average crude protein content of 3.1% and the assumption that 16% of crude protein is N (Ferguson, 2001, reported by Stuewe, 2006). Considering these assumptions, the N content in the milk used in this balance was 0.496%. The quantity of milk considered in these applications is the total amount of milk reported to have been produced within each of agroecoregion (USDA-NASS, 2011, NASS county data weighted average 2005-2009).

### Nitrogen exported in eggs

The N content assumed for each egg is 1.00 gram, based on information from the Human Nutrition Information Service (USDA, 1989). The amount of eggs produced in each agroecoregion was estimated assuming 230 eggs per year per layer (NASS, 2010). For this balance, it was assumed that all eggs produced within the study areas (agroecoregions) are sold to customers outside of this area.

### Nitrogen exported in meat

The percentage of livestock slaughtered for each agroecoregion was estimated based on the total slaughter counts for the state of Minnesota (Table 10). Total slaughter counts were determined based on the MPCA feedlot registration data developed from 2006 to 2010, which represents the maximum livestock numbers in the feedlot during that time period. Data were adjusted for over-reporting feedlot data using a correction factor of 90% for dairy and swine, 70% for beef, 80% for turkey and 85% for chicken (Wayne Cords, personal communication with D. Wall, MPCA).

The slaughter-weights were estimated for each type of livestock based on the percentage of slaughter count for each agroecoregion and the total slaughter weight for the state of Minnesota (Table 11) (NASS, 2011a, b). Estimates of the live weight percentage of N in each animal type sent to be slaughtered are presented in Table 1.10 (Powers and Van Horn, 2001, reported by Stuewe, 2006). The amount of N contained in livestock sent to be slaughtered is calculated based on the live weight percentage of N and the slaughter-weights for each type of animal.

Table 10. The total slaughter-weights and counts used to estimate the total amount of N removed from the state of Minnesota within slaughtered animals.

Animal Type	State-Total Slaughter Count	State-Total Slaughter Weight
	#	lb
Cattle <sup>1</sup> (average of dairy & beef)	2530243.4	1270655000
Hogs <sup>1</sup>	938839.9	2691772000
Chicken <sup>2</sup> (typical 9wk broiler)	13010263.2	248966000
Turkey <sup>2</sup> (2002 12 month average)	21177624.8	1127139000

For total slaughter count: MPCA Feedlot registration data (2006-2010) with corrections for over-reporting of feedlot data For total slaughter weight: NASS, 2011a. Livestock slaughter 2010 Summary.

Table 11. Whole body live weight percent N content used to estimate the N in livestock sent to be slaughtered (Powers and Van Horn, 2001; reported by Stuewe, 2006).

Animal Type	Whole Body % N	
Cattle (average of dairy & beef)	1.40%	
Hogs	2.32%	
Chicken (average of hens & broilers)	2.40%	
Turkey	2.10%	

### Nitrogen cycling between crop and animal agriculture

### **Animal manure**

The manure N production rates applied in this balance are shown in Table 12. The amount of manure produced for each animal category was calculated using:

Livestock manure production (lb yr<sup>-1</sup>) = # of slaughter livestock \* manure N rate production (lb day<sup>-1</sup>) \*  $365 \text{ days year}^{-1}$ 

Approximately 59% of chicken and turkey manure is assumed to be burned each year based on MPCA and Fibrominn records (personal communication with J. Jones, 2010), and only 41% will be available for land application.

Manure N volatilization rates during storage for each animal species were reported in Table 6. Volatilized N losses during the application of livestock manure were presented in Table 8. The manure N considered available for volatilization losses during application is the amount remaining after all storage and incineration losses were accounted for.

The available N in manure after land application is affected by soil processes, such us immobilization by soil microorganisms. For this balance, it was assumed that 50% (for beef, chicken and turkey), 55% (dairy), and 70% (hogs) of N will be available in the first year, and 25% in the second year after the initial manure application.

<sup>&</sup>lt;sup>2</sup> For total slaughter count: MPCA Feedlot registration data (2006-2010) with corrections for over-reporting of feedlot data For total slaughter weight: NASS, 2011b. Poultry slaughter 2010 Summary.

Table 12. Livestock manure N production rates and animal counts for each animal category used to estimate the manure N produced by the livestock in this balance

	State total ‡	NI water.
A	Animal counts	N rates±
Animal Type	#	lb N day <sup>-1</sup>
Beef		
Bull	1213657	0.350
Cow	787172	0.350
Calf finish	225953	0.270
Calf	414801	0.270
Dairy		
Cow-lactating	1084383	0.720
Cow-dry		0.300
Calf	343690	0.060
Heifer/steer	468707	0.230
Hog		
Hogboar	156883	0.04
Sow-farrow finish	1246290	0.09
Farrow feed	417560	0.02
Chicken		
Broiler big	6035232	0.002
Broiler little	17036814	0.0011†
Layer big	343039	0.003
Layer little	25839825	0.0013†
Turkey		
Big	23073859	0.009
Little	13754302	0.0047

†Data not available. These values are half of the big broiler and big layer N production rates.

### Harvested crop used for animal feed

Corn and soybean grain are used for animal feed in beef, cattle, swine, and poultry production. Also, corn silage, alfalfa and other hay are fed mainly to beef and dairy cows. Coefficients for harvested corn and soybean use in Minnesota were obtained from the Department of Agriculture (Ye, 2010; Ye, 2009a; Ye, 2009b; MDA, 2010) and are reported in Table 13.

<sup>‡</sup>MPCA Feedlot registration data with corrections for over-reporting of feedlot data.

<sup>±</sup> MWPS (1993).

Table 13. Percentage of corn and soybean uses in Minnesota.

Crop	Use
	%
Corn	
Export	42
Ethanol use	34
Feed use	17
Residual use	7
Soybean	
Export	40
Crush for feed	56
Seed and Residual	4

In summary, 17% and 56% of the harvested corn and soybean are being used for feeding animals in Minnesota, respectively. Approximately 25% of the soybean meal from crush is used for feed (75% is exported). The percentages used for each animal are presented in Table 14.

Ethanol production comprised 34% of the harvested corn (Table 13). During ethanol production, starch is extracted from corn grain, and the remaining nutrients are converted to by-products that can be used for animal feed, including Dried Distiller Grains (DDGs). For the N balance, it was assumed that 14.5 pounds of DDGs were produced for each bushel of corn used in the ethanol process with a crude protein (CP) content of 30% and 16% N in CP. Also, 50% of DDGs were exported out of state.

Table 14. Percentage of feed use from corn and soybean for different animal categories in Minnesota.

	Feed use
	%
Corn	
Beef	15
Hogs	46
Dairy	21
Poultry	17
Others	1
Soybean	
Beef cattle	9
Hogs and pigs	41
Dairy (milk cows)	15
Poultry	35
Others	0.4

#### Livestock feed

Feed N intake for each category of livestock was determined based on recommended nutrient requirements for each livestock species. All the assumptions used to estimate N consumption rate for each animal species are presented in detail in Stuewe (2006). Feed N intake was summed over all species and categories of animals in order to determine whether or not enough harvested crop used for animal feed was available to meet livestock nutritional requirements. The result of this analysis was that harvested crop used for animal feed was sufficient, and consequently, no additional nutritional supplements were added to the overall N balance.

The animal population numbers used for these estimates were obtained from the MPCA.

#### Swine feed

The population estimates used for swine in these calculations were reported in two categories, "hogs" and "nursery hogs. The consumption rates and crude protein requirements used for both the "hogs" and "nursery hogs" are presented in Table 15 (NAS, 1998, reported by Stuewe, 2006). The N consumption rate was calculated as follows:

N consumption (lbs  $yr^{-1}$ ) = (N° Hogs + N° nursery hogs)\* N consumption rate\*365

Table 15. Feed consumption rates and crude protein requirements for "hogs" and "nursery hogs" used to estimate the feed N consumed annually by these animals (NAS, 1998, cited by Stuewe, 2006).

Livestock	Feed Consumption Rate	Crude Protein (CP)	Nitrogen in CP	N Consumption Rate	N Consumption Rate
	(kg feed day <sup>-1</sup> )	%	%	(kg N day <sup>-1</sup> )	(lb N day <sup>-1</sup> )
"Hogs"	2.502	15.6%	16%	0.063	0.139
"Nursery Hogs"	0.750	22.3%	16%	0.027	0.060

#### **Beef cattle**

The population estimates acquired for beef cattle within the study area were reported in four categories, including "beef heifers", "feedlot beef", "calf finish", and "beef calves". The consumption rates and crude protein requirements used for each category are presented in Table 16 (NAS, 1998, NAS, 2000; reported by Stuewe, 2006).

Table 16. Feed consumption rates and metabolizable protein requirements for "beef heifers", "feedlot beef", "calf finish", and "beef calves" used to estimate the feed N consumed annually by these animals (NAS, 1998, cited by Stuewe, 2006).

Livestock	MP Consumption Rate	Conversion Factor to CP	Nitrogen in CP	N Consumption Rate	N Consumption Rate
	kg MP day <sup>-1</sup>		%	kg N day <sup>-1</sup>	Ibs N day <sup>-1</sup>
"Beef Heifers"	0.624	divided by 0.67	16%	0.149	0.328
"Feedlot Beef"	0.665	divided by 0.67	16%	0.159	0.351
"Calf finish"				0.159	0.351
"Beef Calves"				0.027	0.060

#### **Dairy cattle**

The population estimates obtained for dairy cattle within the study area were reported in four categories including "lactating dairy", "dry dairy", "young dairy steers", and "dairy calves". The consumption rates and crude protein requirements used for each category are presented in Table 17 (Linn, 2004; MWPS, 2003; NAS, 2001; reported by Stuewe, 2006).

Table 17. Feed consumption rates and crude protein requirements for "lactating dairy", "dry dairy", "young dairy steers", and "dairy calves" used to estimate the feed N consumed annually by these animals (Linn, 2004; MWPS, 2003; NAS, 2001, cited by Stuewe, 2006).

Livestock	Feed Consumption Rate	CP in Feed	Nitrogen in CP	N Consumption Rate	N Consumption Rate
	kg day <sup>-1</sup>	%	%	kg N day <sup>-1</sup>	lbs N day <sup>-1</sup>
"Lactating Dairy"	20.4	16%	16%	0.523	1.153
"Dry Dairy"	13.6	13%	16%	0.283	0.624
"Young Dairy Steers"	8.8	14.2%	16%	0.200	0.441
"Dairy Calves"	4.2	16.9%	16%	0.114	0.251

#### **Poultry**

The population estimates for turkeys within the study area are reported in only one category, "turkeys". The population estimates reported for chickens within the study area are reported in two categories: "broilers" and "layers". Nitrogen consumption rate for turkeys and chickens are presented in Table 18 (NAS, 1994; reported by Stuewe, 2006).

Table 18. Feed consumption rates and crude protein requirements for "turkeys" and "chickens" used to estimate the feed N consumed annually by this poultry (NAS, 1994, cited by Stuewe).

Livestock	Feed Consumption Rate	Crude Protein (CP)	N in CP	N Consumption Rate	N Consumption Rate
	kg feed day <sup>-1</sup>	%	%	kg N day <sup>-1</sup>	lbs N day <sup>-1</sup>
"Turkeys"	0.300	22.3%	16%	0.011	0.024
"Chickens Broiler"	0.117	20.3%	16%	0.004	0.008
"Layer Chickens"				0.002	0.004

### 2: Methods: nonpoint source nitrogen loadings to surface waters

### Cropland losses of nitrogen via groundwater discharge to surface waters

### N leaching losses

"N leaching" here refers only to that N which leaches to shallow groundwater, where it will over time either be denitrified in the groundwater, or discharge into surface waters. Discharge into well waters was not considered. N leaching into tile drainage waters is a separate study component, and is not considered in the category of "N leaching losses." However, N leaching that moves vertically on tile-drained land and does not move into tile lines is considered in the "N leaching losses" component.

Total cropland N leaching was determined based on the amount of leaching on undrained soils in: 1) fertilized crops (corn, corn silage, wheat, barley, oats, sugarbeet, potato, 2) non-fertilized crops (soybean and alfalfa), and 3) leaching losses from all crops on drained soils.

Cropland area in each agroecoregion was classified as either drained or un-drained according to soil hydrologic class for soils with slope steepness between 0-3% (SSURGO classification, USDA- NRCS, 2006b).

A literature review was conducted to determine the N leaching rate for each agroecoregion. Most of the research related to N leaching in Minnesota has been conducted in the Sand Plains area (Venterea et al., 2011, Wilson et al., 2010, Wilson et al., 2008, Errebhi et al., 1998, Sexton et al., 1996, Delin et al., 1995, Rosen et al., 2010, Rosen, pers. comm.).

Using existing data for Minnesota, statistical algorithms were developed for N leaching losses based on the applied N rate in dry and wet years. For average climatic years, the N leaching algorithm was based on a mean of the algorithms in dry and wet years. Dry years occurred when precipitation was lower than the average using a 30-year climatic record for each Minnesota location in a particular research study. Wet years occurred when precipitation was greater than the average using a 30-year climatic record for each Minnesota location studied.

Algorithms for N leaching losses to groundwater with fertilized crops in undrained areas of Region 4 (Figure 4) were, thus, a function of the N application rate (N fertilizer +N manure):

N losses= N rate \* 0.0602 + 22.245,  $R^2 = 0.0871$  for dry conditions

N losses= N rate \* 0.2945 + 37.6,  $R^2 = 0.459$  for wet conditions

Leaching is greatly reduced during dry conditions, regardless of the fertilizer rate, and thus the relationship between rate of application and nitrogen leaching during dry years was rather weak and the slope was low compared to the wet years. The poor statistical relationship during the dry years is expected. This relationship does not have much influence on the leaching loss estimates, given the narrow range of average fertilizer rates which are applied in different agroecoregions and the low leaching rates during dry years. Even if the dry years slope in figure 4 was zero, the N leaching load estimates would remain largely unaffected.

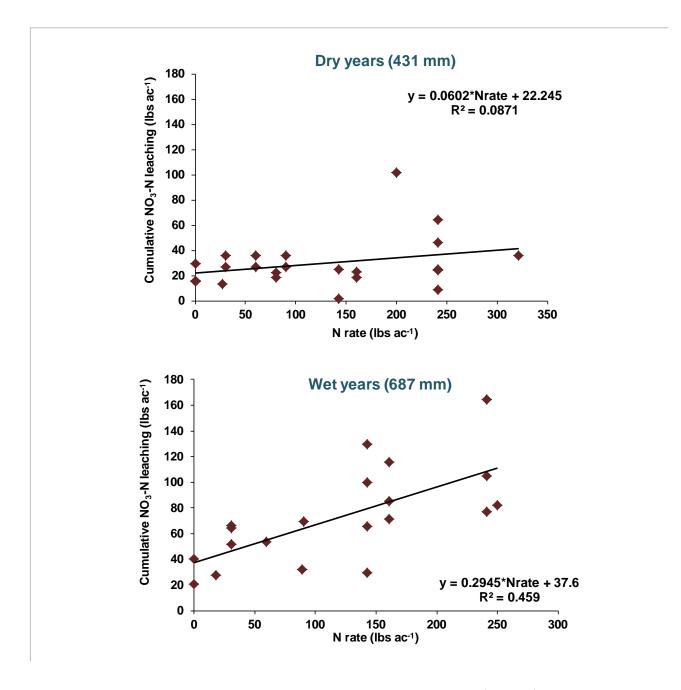


Figure 4. Cumulative NO<sub>3</sub>-N leaching as a function of N rate for the Sand Plain area (Region 4) in Minnesota.

Each agroecoregion was assigned to one of four groundwater leaching regions according to groundwater contamination susceptibility in Minnesota. Assignment into each region was based on the

measured occurrence of nitrate-N in drinking water wells from a database of 40,000 wells monitored by MDH, MPCA, USGS, and MDA. Regions were also based on results from the DRASTIC model (Depth, Recharge, Aquifer, Soil, Topography, Impact, and Conductivity).

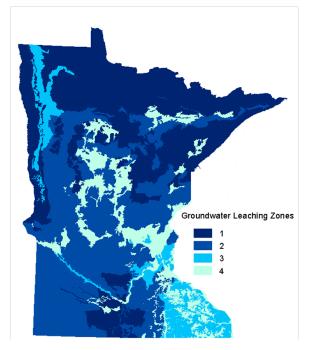


Figure 5. Nitrogen groundwater contamination vulnerability regions in Minnesota.

Table 19. Groundwater contamination vulnerability regions, and associated agroecoregions and coefficients to adjust the N leaching rate in undrained fertilized cropland for each region.

Region	Agroecoregion	Coefficient
1	Drift & Bedrock Complex, Forested Lake Sediments, Mahnomen Lake Sediments, Northern Till, Northshore Moraine, Peatlands, Poorly Drained Lake Sediments, Red Lake Loams, Somewhat Poorly Drained Lake, Steep Poorly Drained Moraine, Swelling Clay Lake Sediments, Very Poorly Drained Lake Sediments, Wetter BE Till, Wetter Clays & Silts	0.007
2	Central Till, Coteau, Drumlins, Dryer BE Till, Dryer Clays &Silts, Dryer Till, Forested Moraine, Inner Coteau, Mesabi Range, Poorly Drained BE =Till, Rolling Moraine, Steep Dryer Moraine, Steep Stream Banks, Steeper Till, Stream Banks	0.25
3	Bufflands, Inter-Beach Sand Bars, Level Plains, Steep Valley Walls, Steep Wetter Moraine, Steeper Alluvium, Undulating Plains	0.50
4	Alluvium & Outwash, Anoka Sand Plains, Rochester Plateau	1

Leaching coefficients to adjust N leaching rate in Regions 1 and 2 were determined based on SWAT model information, and coefficients for Region 3 were assumed to be halfway between the coefficients for Regions 2 and 4, since no data were available (Table 19). No adjustment was needed in Region 4, because this is where experimental data on N leaching losses were abundant. Even though the geology differs in the Anoka Sand Plains region and Rochester Plateau (karst region) of southeastern Minnesota, it was justifiable to combine them into the same groundwater contamination vulnerability region. Each has roughly the same probability of groundwater contamination.

For non-fertilized soybean on undrained land, N leaching rates were assumed equal to N leaching rates for soybean under tile drainage. These N leaching rates were adjusted using the coefficients in Table 19 for Regions 1 and 2. For alfalfa, N leaching rates were assumed to be 1.56 pounds ac<sup>-1</sup> (Chung et al.2001) for dry, average, and wet years.

Leaching losses on drained cropland were calculated assuming N rate loss of 3 pounds ac<sup>-1</sup> for dry, average, and wet years.

### Denitrification of groundwater

The main form of N in groundwater baseflow is nitrate, which moves with water and ultimately can reach surface waters. However, nitrate can be lost before discharging to surface water through a biological process called denitrification.

Denitrification can occur within the unsaturated soil zone, within saturated soils, in the aquifer, and/or in the riparian zone. Levels of oxygen in groundwater < 0.5 mg L<sup>-1</sup> can promote denitrification, since bacteria will use nitrate to oxidize organic carbon sources, and as a result, nitrate contributions from low-oxygen baseflow will be negligible or minimal. However if these conditions are not present, then all the nitrate that moves through the soil into groundwater will eventually emerge in streams via groundwater baseflow.

The amount of groundwater N discharging to surface waters was calculated by multiplying the N leaching losses by a denitrification factor. The denitrification factor was determined based on a literature review which summarizes possible nitrate losses in the groundwater for different types of soils (Böhlke et al., 2002; Dubrowvsky et al., 2010; Duff et al., 2007; Duff et al., 2008; Gentry et al., 2009; Goolsby et al., 1999; Hill, 1996; Korom, 2010; Korom et al., 2005; Masarik et al., 2007. McCallum et al., 2008; MPCA, 1998; Patch and Padmanabhan, 1994; Puckett, 2004. Puckett and Cowdery, 2002; Puckett et al., 1999; Puckett et al., 2008; Rodvang and Simpkins, 2001; Sauer et al., 2001; Schilling, 2002; Schilling and Helmers, 2008; Schilling and Libra, 2000; SCWRS, 2003; Sogbedji et al., 2000; Spahr et al., 2010; Tesoriero et al., 2009; Triska et al., 2007; and Trojan et al., 2002). The actual losses within groundwater prior to discharge into surface waters is highly variable, and will depend on the subsurface and groundwater chemistry, residence time in aquifers, and the types of sediments it moves through in the riparian zone. Based on the available information, denitrification losses within the groundwater itself were assumed to be 25% for Karst agroecoregions, 40% for Sand Plain and Alluvial agroecoregions, 60% for finer textured soil agroecoregions, and 50% for all other agroecoregions (Table 20).

Considerable lag time can occur between the time of leaching into groundwater and the point of discharge into surface waters. Land management changes that affect leaching losses can take from weeks to centuries before the changes are reflected in surface waters. This lag time was not directly accounted for in this study. Estimates of discharge into surface waters are independent of travel time, except that denitrification coefficients were adjusted based on the hydrologic conditions within the agroecoregion. The estimates of N reaching surface waters through leaching losses will not necessarily be reflected in the stream monitoring for a single year, or even a single decade.

Table 20. Groundwater denitrification factor assigned to different agroecoregions.

Agroecoregion	Denitrification factor
Blufflands, Rochester Plateau	0.25
Anoka Sand Plains, Alluvium and Outwash, Inter-Beach Sand Bars, Steep Valley Walls, Steeper Alluvium.	0.40
Forested Lake Sediments, Mahnomen Lake Sediments, Poorly Drained BE Till, Poorly Drained Lake Sediments, Red Lake Loams, Somewhat Poorly Drained Lake, Swelling Clay Lake Sediments, Very Poorly Drained Lake Sediments	0.60
Other agroecoregions	0.50
Drained soils	0.60

### Cropland nitrogen losses to surface waters in tile drainage discharge

Annual tile drainage N losses are difficult to estimate, since several factors influenced N export through tile drainage. In Minnesota, extensive research has been developed on N losses in tile drainage (Chung et al., 2001, Randall et al., 1997, Huggins et al., 2001, Nangia et al., 2008, Randall and Iragavarapu, 1995, Randall and Vetsch, 2005, Randall et al., 2003, Sands et al., 2008, Randall et al. 2000, Gast et al., 1978).

Total N losses in tile drainage were determined based on the amount of N losses in croplands under: 1) fertilized crops (corn, corn silage, wheat, barley, oats, sugar beet, potato), 2) and non-fertilized crops (soybean and alfalfa).

Based on the available information, two algorithms were developed for corn and soybean crops (Figure 6). Algorithms were a function of growing season precipitation and N rate (N fertilizer + N manure) for fertilized crops, and only growing season precipitation for non-fertilized crop (soybean) in each agroecoregion:

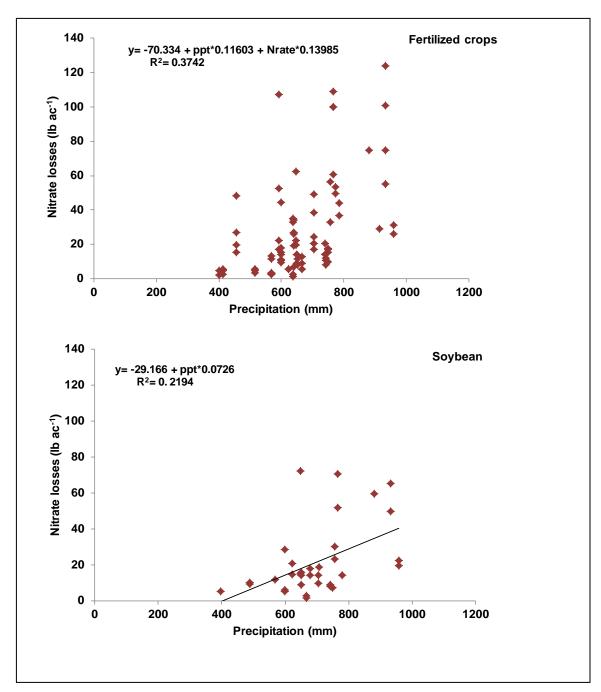


Figure 6. Nitrate losses through tile drainage as a function of precipitation for corn and soybean. The regression equation for corn is based on both precipitation and N rate.

Algorithms for N losses to surface waters through tile drainage took the form:

NO<sub>3</sub>-N losses (fertilized crops) = -70.334 + Precipitation\*0.11603 + N rate \* 0.13985

 $NO_3$ -N losses (soybean) = -29.166 + Precipitation\*0.0726

For alfalfa forage, an N leaching rate of 1.56 lb ac<sup>-1</sup> was estimated based on N leaching research in Minnesota (Chung et al., 2001).

Total N losses were calculated for dry, average, and wet climatic conditions based on growing season precipitation data (MPCA HUC8 precipitation data 1980-2010, MN DNR, 2010).

Tile drainage N losses estimated using the algorithms above were inflated an additional 12% to account for contributions of TKN (organic N forms) based on studies conducted in Minnesota (Dave Wall, personal communication with S. Matteson, Nov. 2011).

### Cropland nitrogen losses in runoff

Nitrogen in surface runoff was calculated as a function of runoff volume and N concentration for each agroecoregion.

Thirty years of precipitation data were analyzed at the basin scale, and wet, average, and dry years were determined based on the statistical 90th, 50th, and 10th percentiles, respectfully. Discharge volume from USGS monitoring was determined using average, low and high flow discharge data for these same years in each agroecoregion.

Runoff as a percent of discharge was determined based on available data from SWAT modeling for the agroecoregions cited in Table 21. For the remaining agroecoregions runoff percentages were calculated based on a water budget approach for each agroecoregion.

Table 21. Runoff (percent of discharge) from SWAT modeling.

Area	Agroecoregion	Runoff (%)
7 Mile Creek	Wetter Clays and Silts	22
Root River	Undulating Plains	16
Karst	Blufflands, Rochester Plateau	24
Red River	Swelling Clay lake sediments, Very poorly drained lake sediments	71
Sunrise	Central till, Anoka Sand Plains, Alluvium and Outwash	6

Similar to the approach used to estimate cropland N losses through leaching and groundwater discharge, each agroecoregion was assigned a runoff category according to their susceptibility to surface runoff in Minnesota (Table 22). For Blufflands and Rochester Plateau, runoff was assigned an N concentration of 10 mg L<sup>-1</sup> based on data reported by Peterson and Vondracek (2006) for the Karst region.

Table 22. Nitrogen concentration in cropland runoff for each Agroecoregion.

Region	Agroecoregion	N concentration (mg L <sup>-1</sup> )
1	Drift & Bedrock Complex, Forested Lake Sediments, Mahnomen Lake Sediments, Northern Till, Northshore Moraine, Peatlands, Poorly Drained Lake Sediments, Red Lake Loams, Somewhat Poorly Drained Lake, Steep Poorly Drained Moraine, Swelling Clay Lake Sediments, Very Poorly Drained Lake Sediments, Wetter BE Till, Wetter Clays & Silts	3.5 <sup>1</sup>
2	Central Till, Coteau, Drumlins, Dryer BE Till, Dryer Clays &Silts, Dryer Till, Forested Moraine, Inner Coteau, Mesabi Range, Poorly Drained BE =Till, Rolling Moraine, Steep Dryer Moraine, Steep Stream Banks, Steeper Till, Stream Banks	1.8 <sup>2</sup>
3	Blufflands, Inter-Beach Sand Bars, Level Plains, Steep Valley Walls, Steep Wetter Moraine, Steeper Alluvium, Undulating Plains	0.7 <sup>3</sup>
4	Alluvium & Outwash, Anoka Sand Plains, Rochester Plateau	0.244

<sup>&</sup>lt;sup>1</sup>Kumar et al. 2009 (East Grand Forks, MN), Ginting et al. 2000 (southern Minnesota River Basin)

### Forest export of nitrogen to surface waters

Total acres of forest (deciduous, coniferous, and mixed forest) were obtained from the National Land Cover Database (NLCD, 2006). Approximately 11 million acres are under forest statewide. Nitrogen export coefficients for dry, average and wet conditions are presented in Table 23. Estimation of these coefficients was based on available information for forested lands in Minnesota, Wisconsin, and eastern Unites States regions (Mulla et al. 1999, Gold et al., 1990, Timmons et al., 1977, Verry and Timmons, 1982, Clark et al., 2000, Clesceri et al., 1986, Boyer et al., 2002, Campbell et al., 2004, Beaulac and Reckhow, 1982, Reckhow et al., 1980, Cooke and Prepas, 1998, Rast and Lee, 1978, Lin, 2004, Loerh et al., 1989, McFarland and Hauck, 2001, Dodd et al., 1992, Groffman et al., 2004).

Table 23. Nitrogen export coefficients for forested lands in Minnesota.

Conditions	N export (lbs N ac <sup>-1</sup> )
Dry	1
Average	2
Wet	3

<sup>&</sup>lt;sup>2</sup> Thoma et al. 2005 (Lamberton, MN)

<sup>&</sup>lt;sup>3</sup> No research data were available for zone 3 (assumed intermediate values)

<sup>&</sup>lt;sup>4</sup>Delin and Landon (2002) (Sand Plain-Princeton)

### Nonpoint source nitrogen export in urban/suburban regions

Based on information from National Land Cover Database (NLCD, 2006), the total acres of developed land use (open space, light, medium, and heavy developed) was approximately 1 million acres statewide.

Nitrogen export coefficients used to calculate total nonpoint source N export in urban/suburban areas of Minnesota are presented in Table 24. Nitrogen export coefficients were estimated based on available information sources (Weiss et al., 2008, Dodd et al., 1992, McFarland and Hauck, 2001, Rast and Lee, 1983, Frink, 1991, Lin, 2004, Reckhow et al., 1980, Peterson and Vondracek, 2006, Brezonik and Stadelmann, 2002, Mulla et al. 1999, Groffman et al., 2004, Horner et al., 1994, Wollheim et al., 2005, Deacon et al., 2006, Lerner, 2000, Trojan et al., 2003, Shields et al., 2008, Evans, 2008, Brian Vlach, (pers. Comm. 2010), Mike Trojan, (pers. Comm. 2011), Mike Perniel, (pers. Comm. 2011.).

Table 24. Nonpoint source N export coefficients for urban/suburban lands in Minnesota.

Conditions	N export (lbs N ac <sup>-1</sup> )
Dry	2
Average	4
Wet	6

### Nitrogen export from septic systems

Nitrogen losses from septic systems were based on county data from MPCA (2011). Losses were estimated for septic systems that are Imminent Public Health Threats (IPHT) and for those that are not IPHT as follows:

Septic N to Groundwater = [(# Septics per county) \*(Persons per household by county)\* ({9.1 pounds N per person}\*{85% for denitrification losses})] \*(% NOT Imminent Public Health Threat (IPHT))

Septic N to Surface Water = [(# Septics per county) \*(Persons per household by county) \*(9.1 pounds N per person)] \* (% Imminent Public Health Threat (IPHT))

Information to determine the number of people per household by county was obtained from U.S. Census (2010). The per capita N coming out of septic systems was assumed to be 9.1 pounds N per person (Information provided by Mark Wespetal, MPCA). Denitrification was assumed to remove 15% of the septic system N within the soil prior to reaching groundwater. Once in the groundwater, the same groundwater denitrification loss coefficients for cropland (Table 20) were assigned to septic system N. All non-metropolitan population data were classified using 2008 ZIP code populations to improve spatial accuracy of county data.

### Feedlot nitrogen losses in runoff

The number of out of compliance feedlots for open runoff was determined from an MPCA survey of counties in 2010 (pers. comm. Don Hauge, MPCA). Some counties had missing information for the number of feedlots out of compliance, and numbers had to be estimated using results from similar counties.

Feedlot N runoff was estimated using the Minnesota Feedlot Annualized Runoff Model (MinnFarm model). MinnFarm model (version 2.3) was run for a 75 AU beef/dairy operation to represent feedlots in the 50-100 AU category, a 150 AU beef/dairy to represent feedlots in the 100-300 AU category, and a 300 AU beef/dairy to represent feedlots in the >300AU category, recognizing that not all animals at the farm typically have access to the noncompliant lots.

The MinnFARM model assumed 200 square feet per animal on the lot and over 100% animal unit density - all soil covered with some manure in the lot. Also the model considered a small buffer downslope of the lot, which reduced the N losses by half. This is equivalent to about a 25 foot length meadow or 75 feet of fair pasture.

These estimates do not account for runoff from non-registered feedlots, feedlots in counties with minimal animal agriculture and small amounts of N from compliant feedlots using vegetation to treat runoff.

## Methods for assessing sensitivity and uncertainty in cropland nitrogen balance

Due to uncertainty in the estimation of the variables that affect the agricultural N balance, a sensitivity analysis was conducted to determine how changing these variables would affect the overall agricultural N balance. In the sensitivity analysis, each source or coefficient was varied in increments of plus or minus 5, 10, 15, 25, or 50% of its baseline value. For each of these changes, we computed the resulting percentage change in the overall agricultural N balance relative to its baseline value.

Also, a sensitivity analysis was conducted for the main N pathways to surface water (runoff, leaching, tile drainage).

# Conversion of agroecoregion based nitrogen loadings to watershed based nitrogen loadings

The majority of N inputs and outputs were calculated based on agroecoregion boundaries because of how inherent similarities in soil type and parent material largely influence the amount of N stored or delivered. To convert these N loadings into data representing major watershed boundaries, they were area-weighted. Agroecoregion data totals were converted to pounds per acre N yield raster data sets. Zonal statistics were then used to calculate an area-weighted average N yield for HUC8 watershed polygons. This average N yield value was converted back to a total delivery in pounds based on watershed areas.

Some rounding errors may introduce small discrepancies between the agroecoregion based and watershed based data, but this is the best representation of the original data. When possible (i.e. urban N deliveries, forest N deliveries), data were calculated for each watershed based on 30 m landuse rasters. In other words, area-weighting was avoided when data resolution could be better represented with direct landuse calculations.

Finally, the area-weighting process introduced a high amount of tile drainage N delivery from the Mississippi Twin Cities major watershed, a watershed having little to no tile drained cropland. For this specific case, the Mississippi Twin Cities watershed was determined to have zero tile drainage, and the amount removed from this watershed was "de-weighted" or assigned back to the watersheds associated with the influencing agroecoregion.

### Results

### Minnesota cropland nitrogen balance

### Physical description of study area

Minnesota has 54,000,000 acres of land in total and nearly 36,000,000 acres of cropland, forest and urban landuses (Figure 7). Cropland accounts for 44% of the total area in Minnesota, while forest accounts for 20%, and urban landuse accounts for 1%. There are another 18 million acres (33% by area) of lakes, rivers, shrub and grasslands, and wetlands not considered in this study. Cropland accounts for

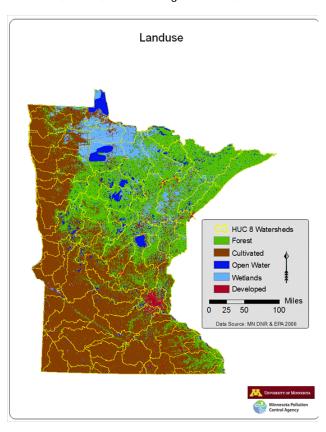


Figure 7. Minnesota landuse categories for this study

67% of the area (36,000,000 acres) represented in this study of nonpoint source N pollution, forest accounts for 31% and urban-suburban land accounts for 2% (Figure 8). Cropland includes land in corn, soybean, small grains, sugar beet, potato, alfalfa and hay. The three largest Basins in Minnesota (Minnesota River, Red River of the North, and Upper Mississippi River) account for nearly 60% of the area in the state. The largest concentration of cropland is in the Minnesota River, Red River of the North, and Upper and Lower Mississippi River Basins (Figure 9). Cropland accounts for 74% of the area in the Minnesota River Basin, 51% of the area in the Red River of the North, and only 21% of the area in the Upper Mississippi River Basin (Figure 10). The Lower Mississippi River Basin has 47% of its area in cropland. The Rainy River and Lake Superior Basins, by contrast, have only 1.2% and 0.2% of their areas in cropland.

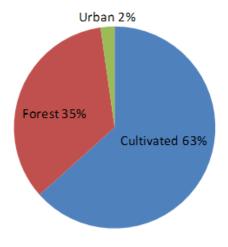


Figure 8. Landuse percentages for this study

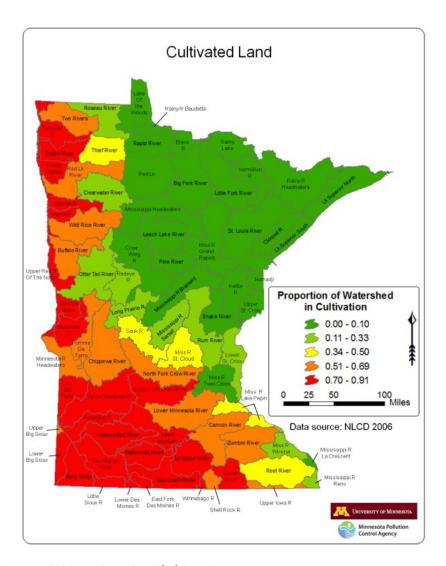


Figure 9. Cultivated cropland (ac) in Minnesota.

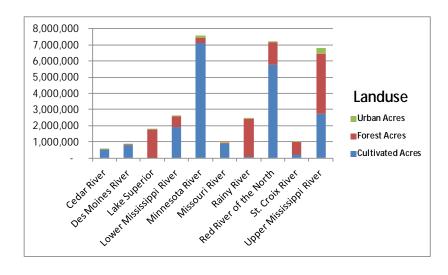
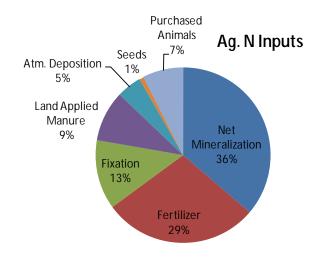


Figure 10. Landuse distributions (ac) by river basin.

### Agricultural nitrogen inputs

Agricultural N inputs to cropland include soil mineralization, N fertilizer; N fixation by legumes, atmospheric deposition, planted seeds, and purchased animals. Land applied animal manure can also be compared with agricultural N inputs, though technically it is an internally recycled nutrient, and should not be explicitly considered. When land applied animal manure is included, agricultural N inputs total about 4.8 billion pounds of N. Mineralization accounts for 36% (1.73 billion pounds) of the N inputs to cropland (Figure 11a, b), while N fertilizer accounts for 29% (1.36 billion pounds). Nitrogen fixation by legumes (0.61 billion pounds) accounts for 13% of the N inputs. Land applied manure (0.45 billion pounds), atmospheric deposition (0.22 billion pounds), and purchased animals (0.36 billion pounds) each account for roughly 5-9% of the N inputs to cropland. Purchased seeds account for less than 1%. Not surprisingly, because of relatively large areas of cropland, the largest agricultural N inputs to cropland (Figure 12) occur in the Minnesota River Basin (1.7 billion pounds), followed by the Red River of the North Basin (1.0 billion pounds) and the Upper Mississippi River Basin (0.71 billion pounds). The Lower Mississippi River Basin receives roughly 0.52 billion pounds of N annually. A majority of the N inputs for these four basins arises from soil mineralization and N fertilizer.



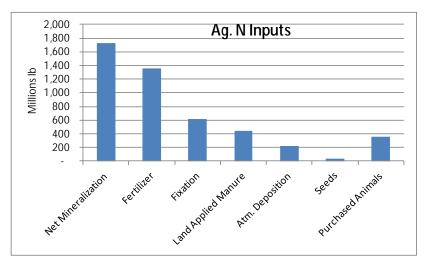


Figure. 11a, b. Agricultural inputs (% or lb) by source to the N balance.

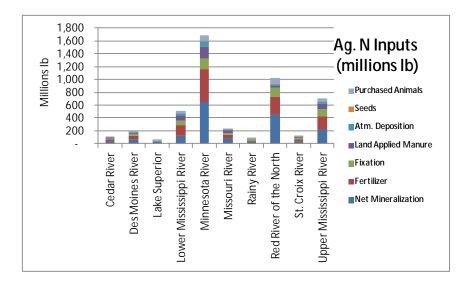


Figure 12: Agricultural N inputs (lb) by source and river basin.

When normalized by total watershed area, the largest N inputs to cropland from a single source occur with soil mineralization (Figure 13) in the Minnesota River, Missouri River, and Des Moines River Basins (54-75 pounds/acre). Mineralization of cropland soils is relatively insignificant (4-5 pounds/acre) in the Rainy River and Lake Superior Basins. The second largest source of N inputs is fertilizer (Figure 14). Fertilizer applications account for 48 to 57 pounds/acre annually in the Minnesota River, Missouri River, and Des Moines River Basins when averaged over the total watershed area (including non-cropland acres). When averaging only for cultivated acres (including unfertilized and fertilized crops, fertilizer application rates in these same basins are approximately 70 pounds/acre. Fertilizer rates range between 2.2 and 2.9 pounds/acre annually in the Rainy River and Lake Superior Basins.

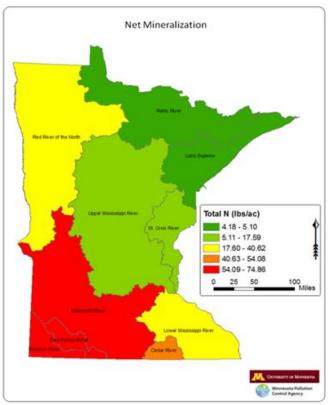


Figure 13. Net mineralization (lb/ac) by basin.

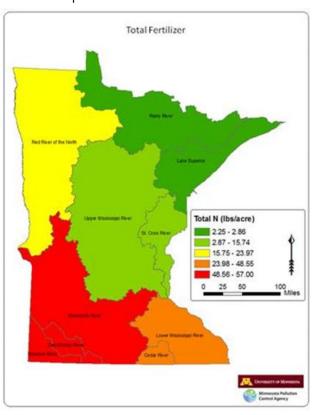


Figure 14. Fertilizer N (lb/ac) by basin

Most of the fertilizer is applied to land used for growing corn, with some also applied to land used for growing other crops, including wheat, potatoes, edible beans, etc. Rates of N fertilizer applied to cropland used for growing corn generally range from 136-152 pounds/acre across a wide area covering the Minnesota River and Lower Mississippi River Basins, as well as the southern portions of the Upper Mississippi River Basin (Figure 15).

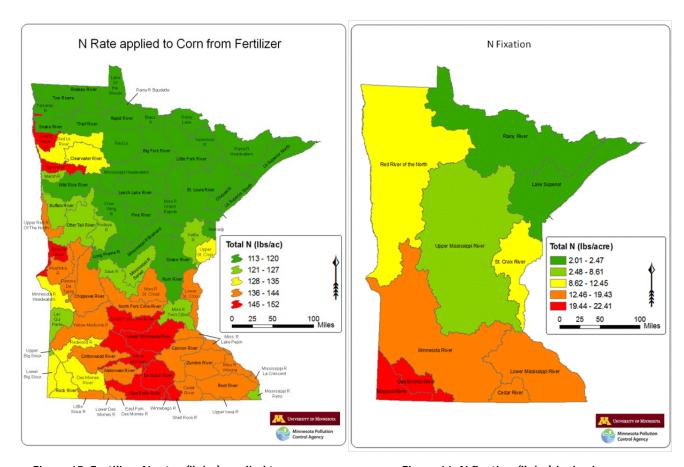


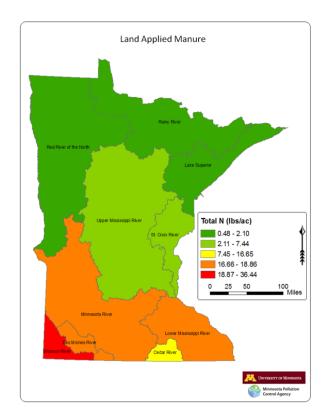
Figure 15. Fertilizer N rates (lb/ac) applied to corn.

Figure 16. N fixation (lb/ac) by basin.

Nitrogen fixation ranges between 12 and 22 pounds/acre annually in the Minnesota River, Missouri River, Des Moines River, and Lower Mississippi River Basins (Figure 11). Land applied manure ranges between 17 and 36 pounds/acre (normalized to total watershed area) in the Lower Mississippi River, Minnesota River, Des Moines River and Missouri River Basins (Figure 17). Not surprisingly, the heaviest concentration of farm animals (Figure 18) occurs in a broad swath covering the Minnesota River and Lower Mississippi River Basins.

Total N inputs (excluding land applied manure) normalized to watershed area are greatest for the Minnesota River, Missouri River, and Des Moines River Basins, ranging from 155-174 pounds/acre annually (Figure 19). Total N inputs range between 11 and 15 pounds/acre in the Rainy River and Lake Superior Basins.

Total N inputs (excluding land applied manure) are greatest for the Minnesota River Basin (1.5 billion pounds annually) and Red River of the North Basin (1.0 billion pounds) (Figure 20). The Upper Mississippi River Basin (0.63 billion pounds) and Lower Mississippi River Basin (0.44 billion pounds) have moderate amounts of total N inputs. Nitrogen inputs are less than 0.07 billion pounds in the Lake Superior Basin.



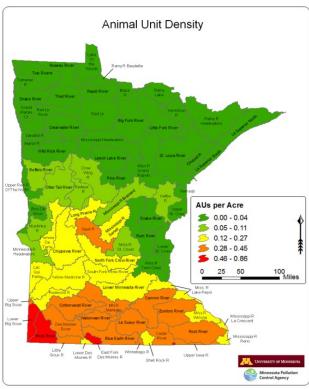


Figure 17. Land applied manure (lb/ac) by basin.

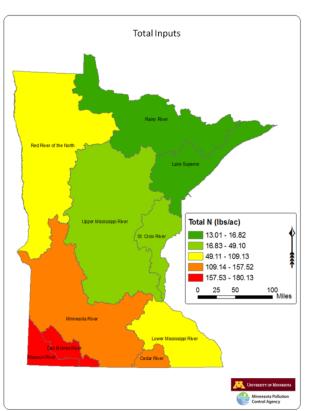


Figure 18. Animal units by major watershed.

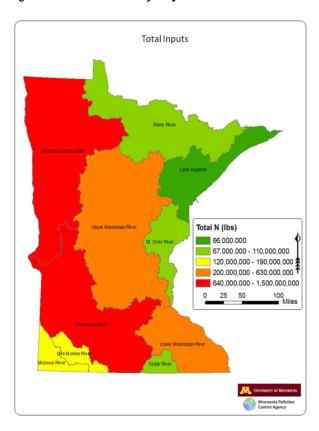


Figure 19. Total inputs of agricultural N (lb/ac) by basin.

Figure 20. Total inputs of ag. N (lb) by basin.

### Agricultural nitrogen outputs

Agricultural N outputs to cropland include crop removal (harvest), senescence, denitrification, animals sold, volatilization of fertilizer and manure, incinerated animal manure, milk and eggs sold, and N losses to the surface and groundwater by drainage, leaching and runoff. Animal feed (harvested crop fed to animals) can be compared with agricultural outputs, though technically it is an internally cycled nutrient, and should not be explicitly considered. Agricultural N outputs (including animal feed) total roughly 5.0 billion pounds annually. Crop removal (harvest) accounts for 45% (2.2 billion pounds) of the total N outputs, by far the largest pathway (Figs. 21-22). Harvested crop used for animal feed accounts for another 15% (0.75 billion pounds). Senescence and denitrification account for 14% (0.72 billion pounds) and 10% (0.48 billion pounds), respectively, of the N outputs. Volatilization of fertilizer and manure together account for 6% (0.27 billion pounds). Sales of meat, milk and eggs also account for about 3% (0.16 billion pounds). Losses to the environment by agricultural drainage, leaching and runoff together account for about 6% (0.29 billion pounds) of the total N outputs.

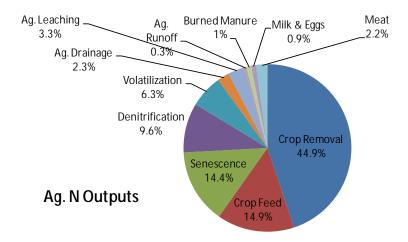


Figure 21. Agricultural N outputs by source (%). Crop removal is crops harvested for sale, export or ethanol production. Animal feed is crops harvested for livestock feeding in Minnesota, plus distiller dry grains from ethanol production that are fed to Minnesota livestock.

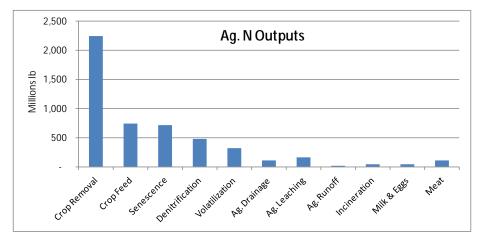


Figure 22. Agricultural N outputs by source (lb). Note that denitrification only refers to soil denitrification, and not subsequent denitrification in the underlying groundwater.

The four basins with the largest agricultural N outputs are the Minnesota River (1.5 billion pounds), Red River of the North (0.85 billion pounds), Upper Mississippi River (0.61 billion pounds), and Lower Mississippi River (0.56 billion pounds) Basins (Figure 23). A majority of the N outputs from each of these Basins arises from crop removal (harvest) and senescence plus denitrification. When normalized by watershed area, crop removal (Figure 24) is largest in the Missouri River and Des Moines River Basins (82-104 pounds/acre). Crop removal averages roughly 75-82 pounds/acre in the Minnesota River and Cedar River Basins. Crop removal accounts for 41-75 pounds/acre in the Lower Mississippi River. Crop removal averages only 3-5 pounds/acre in the Rainy River and Lake Superior Basins. Senescence is largest in the Missouri River and Des Moines River Basins (27-33 pounds/acre). Rates of senescence (Figure 25) average 14-27 pounds/acre in the Lower Mississippi River, Cedar River and Minnesota River Basins. Senescence averages 1-1.5 pounds/acre in the Rainy River and Lake Superior Basins.

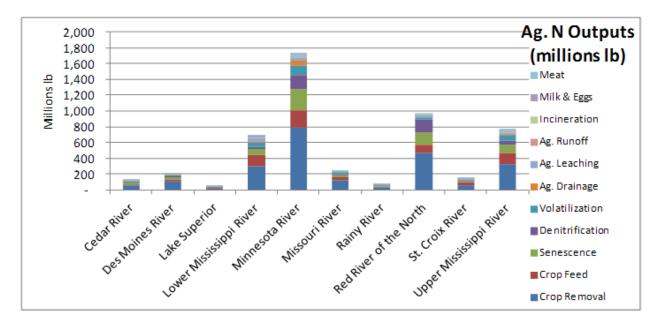
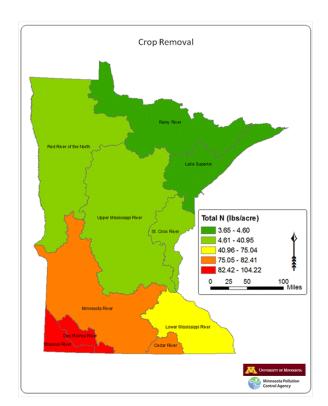


Figure 23. Agricultural N outputs by source (lbs) and river basin.



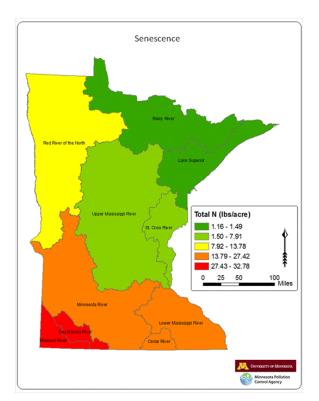
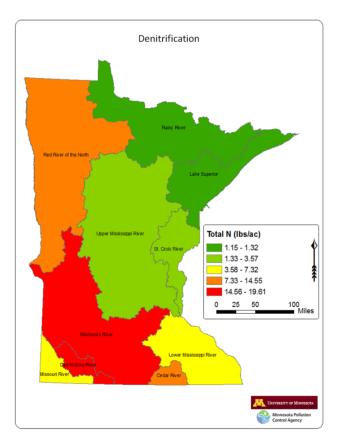


Figure 24. Crop removal (lb/ac, minus animal feed) by basin. Figure 25. Crop senescence (lb/ac) by basin.

Denitrification is largest in the Minnesota River and Des Moines River (14-20 pounds/acre) Basins (Figure 26). It is moderately large in the Red River of the North and Cedar River (7-14 pounds/acre) Basins. Denitrification is elevated in all four of these Basins relative to the other Basins as a result of a large proportion of land that is poorly drained. Much of this cropland, particularly in the Minnesota River Basin, has been improved by installation of artificial drainage to make growing annual crops more economically profitable or feasible (Figure 27).



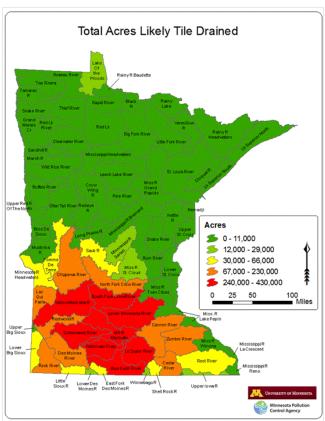
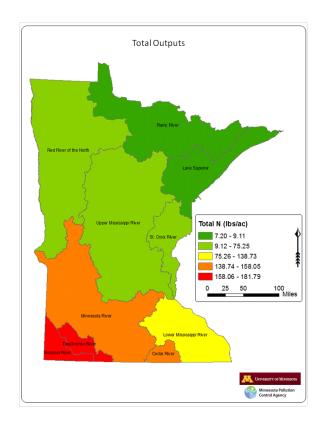


Figure 26. Denitrification (lb/ac) by basin.

Figure 27. Tile drained acres by major watershed.

Total N outputs (excluding crop harvested for animal feed) normalized to watershed area (Figure 28) are greatest for the Missouri River and Des Moines River Basins, ranging from 179-181 pounds/acre annually. Nitrogen outputs are also significant in the Minnesota River and Cedar River Basins (158 pounds/acre) and the Lower Mississippi River Basin (138 pounds/acre). Total N outputs range between 7 and 9 pounds/acre in the Rainy River and Lake Superior Basins.

Total N outputs (excluding crop harvested for animal feed) are greatest (Figure 29) for the Minnesota River Basin (1.5 billion pounds annually). Total N outputs for the Red River of the North Basin are next highest at 0.85 billion pounds. The Upper Mississippi River Basin (0.61 billion pounds) and Lower Mississippi River Basin (0.56 billion pounds) have moderate amounts of total N outputs. N outputs are less than 0.06 billion pounds in both the Rainy River and Lake Superior Basins.



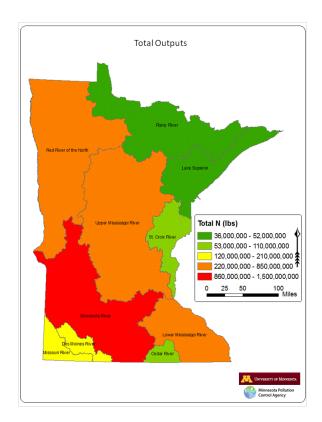
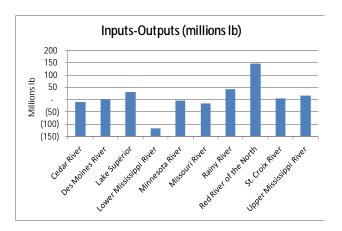


Figure 28. Total ag. N outputs (lb/ac) by basin

Figure 29. Total ag. N outputs (lb) by basin

# Overall nitrogen balance

The overall N balance is obtained by subtracting total N outputs (4.3 billion pounds) from total N inputs (4.2 billion pounds). The inputs and outputs do not include internally recycled N from the harvested crops which are fed to livestock and then later returned to the soil as manure. Results of this give 0.09 billion pounds of N (outputs exceed inputs), about 2.1% of the inputs or outputs. This result shows that the overall N balance is excellent. Individual N balances (Figs. 30a, b) are excellent for the Cedar, Des Moines, Lake Superior, Minnesota, Missouri, Rainy, St. Croix, and Upper Mississippi River Basins (errors less than 1% of total inputs). The errors in the N balance arise primarily from the Lower Mississippi River and Red River of the North Basins. The N balance in the Red River of the North Basin is overestimated by about 3.4% or 0.15 billion pounds (inputs exceed outputs by 13 pounds/acre), while the N balance is underestimated by about 2.8% or 0.12 billion pounds (outputs exceed inputs by 29 pounds/acre) in the Lower Mississippi River Basin (Figs. 31-32).



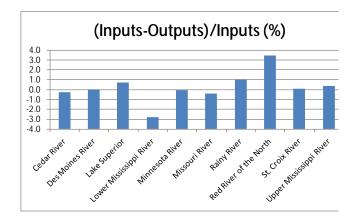
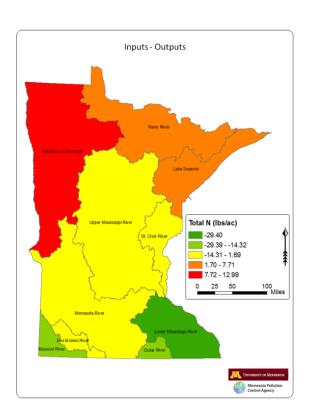


Figure 30a, b. Agricultural N inputs minus outputs (lb or %) by basin.





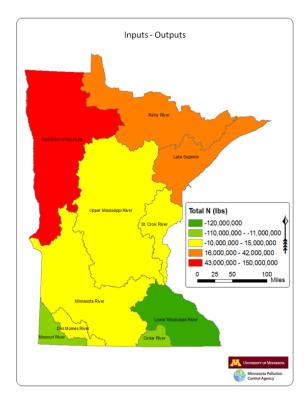


Figure 32. Ag. N inputs minus outputs (lb) by basin.

# Agricultural nitrogen balance sensitivity analysis and uncertainty

The agricultural N balance is dependent on many sources of N, each of which itself depends on various coefficients. Development of the agricultural N balance was based on the principle that each source and coefficient should independently be estimated based on the best available data or scientific research relevant to site-specific conditions in Minnesota. As such, there was little to no calibration of sources or coefficients.

There is a certain level of uncertainty inherent with each source and coefficient used in the agricultural N balance. A sensitivity analysis was conducted to determine how varying certain key sources or coefficients would affect the overall agricultural N balance. In the sensitivity analysis, each source or coefficient was varied in increments of plus or minus 5, 10, 15, 25, or 50% of its baseline value. For each of these changes, we computed the resulting percentage change in the overall agricultural N balance relative to its baseline value.

The agricultural N balance was most sensitive to changes in three factors (Figure 33), namely; crop removal (excluding crop harvested for animal feed), net mineralization and amount of applied N fertilizer. Changing any of these three factors by plus or minus 50% would cause the overall balance to change by plus or minus 17-28%.

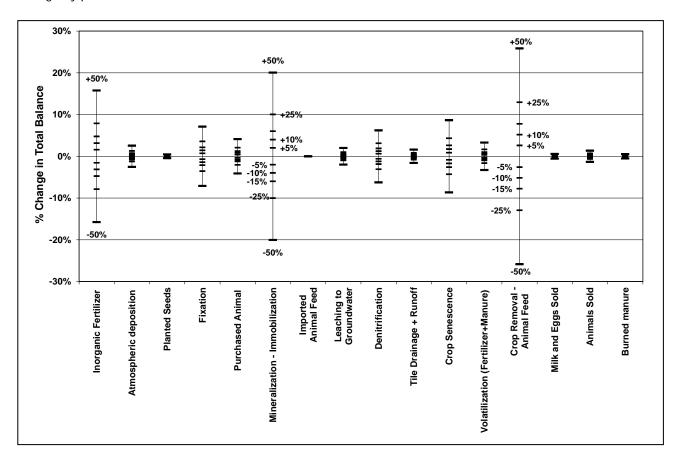


Figure 33. Sensitivity analysis of N input factors on agricultural N balance.

There is a difference, however, between sensitivity and uncertainty. While a change in applied N fertilizer of 50% would cause the N balance to increase by about 17%, the uncertainty in the amount of basin wide N fertilizer application rates is believed to be relatively small. The amount of N

fertilizer applied in Minnesota is accurately known compared to other inputs due to good data collection and survey methods to track fertilizer sales and application rates. Similarly, there is a low uncertainty in the amount of N removal by crops, because the amount harvested is accurately known.

In contrast, the amount of net mineralization is moderately uncertain. Net mineralization fluctuates from year to year and place to place based on variations in soil moisture and temperature. Our estimates of net mineralization are based on state-wide average soil moisture and temperature conditions. It is likely that these estimates of net mineralization have an uncertainty of plus or minus 10-25%. With these levels of uncertainty in net mineralization, the N balance would change by up to plus or minus 10% (equivalent to up to 0.4 billion pounds of N). Future research should address the impacts of variations in soil moisture and temperature on net mineralization.

As stated in the previous section, the N balance in the Red River of the North Basin is overestimated by about 0.15 billion pounds, while the N balance in the Lower Mississippi River Basin is underestimated by about 0.12 billion pounds. These differences could be a result of poor estimates of net mineralization in each Basin. The Red River of the North Basin tends to have soils which are cooler and drier than soils in many of the other Basins. This would cause net mineralization to be reduced relative to rates in other Basins. A decrease in net mineralization of 10% in the Red River Basin would be able to correct for the overestimation of N inputs in that Basin. In contrast, soils in the Lower Mississippi River Basin tend to be warmer and wetter than soils in many of the other Basins. This would cause net mineralization to be increased relative to rates in other basins. An increase in net mineralization of 10% in the Lower Mississippi River Basin would be able to correct for the underestimation of N inputs in that basin.

The agricultural N balance was moderately sensitive to three factors, namely; senescence, denitrification, and N fixation. All three of these factors are known to be rather uncertain as a result of variations in climate and soil type. Yet, changing any one of these three factors by as much as plus or minus 50% would only cause the N balance to change by plus or minus 6-9%. Therefore, while we are uncertain about the values of senescence, denitrification or N fixation, errors in estimating them would not cause large changes in the N balance.

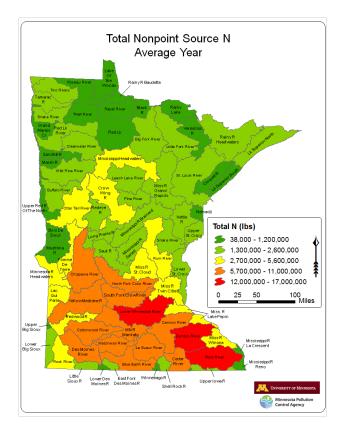
Uncertainty in any of the remaining factors (atmospheric deposition, planted seeds, purchased animals, N losses to groundwater, N losses in runoff or tile drainage, volatilization of fertilizer or manure or sales of milk, eggs or meat) would have only minor impacts on the agricultural N balance. Changing any one of these factors would change the agricultural N balance by at most a few percent.

# Results: Minnesota nonpoint source N loadings to surface waters

Total nonpoint source N loadings to Minnesota surface waters are estimated at 254 million pounds during an average climatic year. Sources of N loadings to surface waters included cropland drainage (114 million pounds in an average year), cropland runoff (16 million pounds) and cropland leaching (93 million pounds); forest export of N (22 million pounds); urban/suburban export of nonpoint source N (3 million pounds); feedlot runoff (0.2 million pounds), and individual septic treatment system losses (5 million pounds).

The spatial distribution of modeled (estimated through this study) total nonpoint source N loadings to Minnesota surface waters during an average climatic year is shown in Figure 34. These modeled results compare well with water quality monitoring data as shown below (Figure 35). Predicted N loadings are highest for the Zumbro and Root Rivers of southeastern Minnesota, where N loadings from groundwater, drainage and runoff are all high. Predicted N loadings are next highest in a cluster of major watersheds centered in the Minnesota River Basin, where N losses in drainage are high, but

groundwater and runoff losses are smaller than in southeastern Minnesota. These 15 major watersheds in southeastern, southern, and west central Minnesota contribute 140.6 million pounds of nonpoint source N loadings to surface waters. This is 55% of estimated N loadings in the entire state of Minnesota. On a per acre basis, the highest loadings occur in 8 watersheds located in southern Minnesota (Figure 34). Loadings per acre are generally highest in the Minnesota River and Lower Mississippi River Basins.



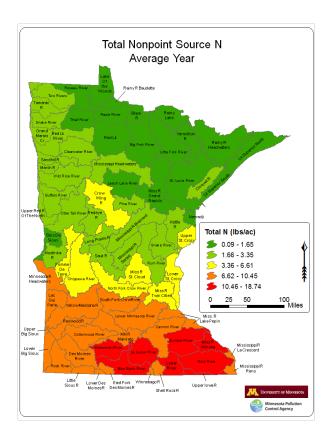


Figure 34. Modeled average N loading to major watersheds, in lb (left) or lb/ac (right).

#### Comparison between modeled and monitored nitrogen loadings

A comparison between the combined-source modeled nonpoint source N loadings to Minnesota surface waters (in an average climatic year) and monitored N loadings (average of two typical years) was conducted for 33 MPCA monitored major watersheds across Minnesota. Monitored N loadings were not used to calibrate the modeled nonpoint source N loadings, as the modeled N loadings were estimated independently, without calibration. Linear regression between modeled and MPCA monitored N loads (Figure 35) was very good (y = 1.33x - 631,920;  $R^2 = 0.69$ ). Modeled N loadings across all monitored watersheds were 10% higher than monitored N loads. It should be noted that modeled nonpoint source loadings are estimated before in-stream and channel losses would take place (these are reflected in observed monitoring results). Thus, it is not surprising that modeled N loads are larger than monitored N loads. Other differences could arise because monitoring results include effects of point sources, whereas modeled results do not.

Further analyses comparing river monitoring results and estimated total N delivered to waters from all sources (point sources, nonpoint sources and atmospheric deposition directly into waters) are described in Chapter E1.

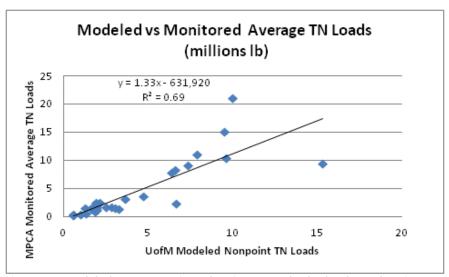


Figure 35. Modeled versus monitored major watershed N loads. Each point represents one HUC8 watershed average TN load obtained between 2007 and 2009.

The Lake Superior Basin consists of 5 major watersheds, 3 of which have one year of water quality monitoring data. Modeled nonpoint N loads in the Cloquet River are comparable in magnitude to average monitored total N loads (Figure 36). Modeled nonpoint N loads are lower than monitored loads in the St. Louis River watershed.

The Rainy River Basin consists of 9 major watersheds, 3 of which each have three years of water quality monitoring data. Modeled nonpoint N loads in the Vermillion, Little Fork, and Big Fork River watersheds are comparable in magnitude to average monitored total N loads (Figure 37). Modeled nonpoint loads are slightly lower than monitored loads in the Little Fork watershed.

The Red River of the North Basin consists of 17 major watersheds. Eleven of these have one to three years of water quality monitoring data. Modeled nonpoint source N loads in the Otter Tail, Buffalo, Marsh, Wild Rice, Sandhill, Thief, Clearwater, Snake, and Tamarac River watersheds are higher than average water quality monitoring results (Figure 38). This is reasonable, given the fact that modeled N loads do not account for in-water denitrification beyond the edge of field. Modeled nonpoint source N loads in the Two Rivers watershed are lower than monitored N loads.

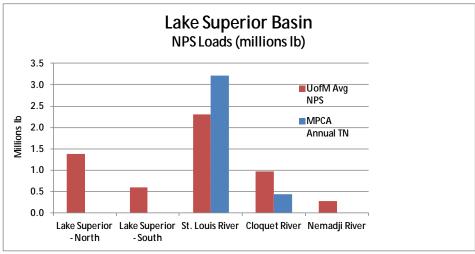


Figure 36. Modeled versus monitored N loads Lake Superior Basin.

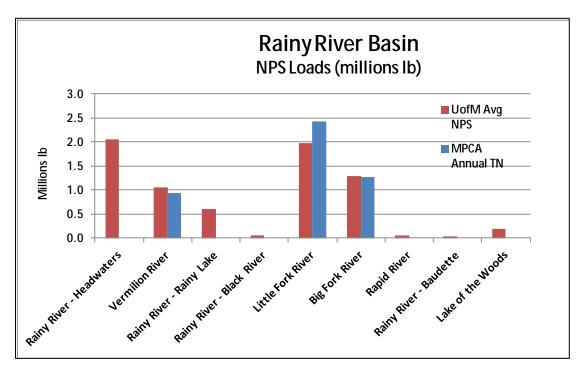


Figure 37. Modeled versus monitored N loads Rainy River Basin.

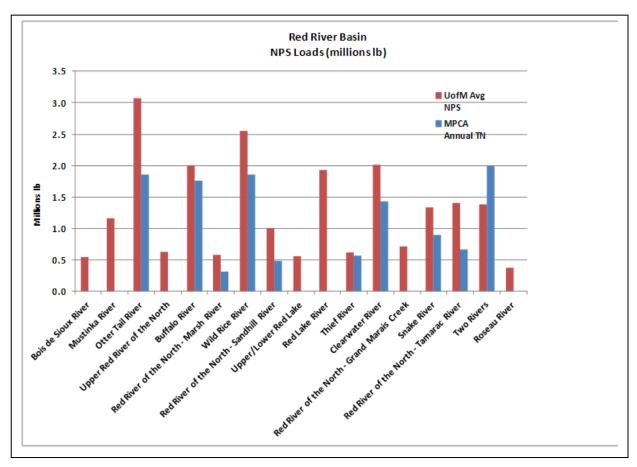


Figure 38. Modeled versus monitored N loads Red River of the North Basin.

There are 15 major watersheds in the Upper Mississippi River Basin. Nine watersheds have from one to three years of water quality monitoring data. Modeled nonpoint source N loads are higher than average water quality monitoring results in the Leech Lake, Pine, Crow Wing, Red Eye, Long Prairie, and Rum River watersheds (Figure 39). This is to be expected, since modeled N loads do not account for denitrification or biological uptake that occurs beyond the edge of field. Modeled N loads are quite a bit higher than measured loads in the North Fork of the Crow River watershed. The South Fork of the Crow River watershed has about 0.5 million pounds of N from point sources that are not included in modeled results. Modeled N loads in the Upper Mississippi River Twin Cities watershed also do not include about 11 million pounds of point sources.

The St. Croix River Basin includes 4 major watersheds, of which 2 have each been monitored for three years of water quality data. Modeled nonpoint source N loads are very comparable to (although somewhat higher than) average monitored water quality data in the Kettle and Snake River watersheds (Figure 40).

The Lower Mississippi River Basin includes 7 major watersheds. The Cannon and Root River watersheds have been monitored for water quality during the last 17 to 18 years. Modeled nonpoint source N loads are slightly larger than average water quality monitoring data in both the Cannon and Root River watersheds (Figure 41). Thus, modeled and monitored N loads agree quite well in the Lower Mississippi River Basin.

The Minnesota River Basin includes 12 major watersheds. Nine of these watersheds have been monitored for one to three years by the MPCA. Modeled nonpoint source N loads are somewhat larger than, or comparable in magnitude to average water quality monitoring data in the Pomme de Terre, Chippewa, Redwood, and Watonwan River watersheds (Figure 42). Modeled N loads are significantly higher than measured loads in the Cottonwood River watershed. Modeled N loads are significantly lower than measured N loads in the Le Sueur and Blue Earth River watersheds.

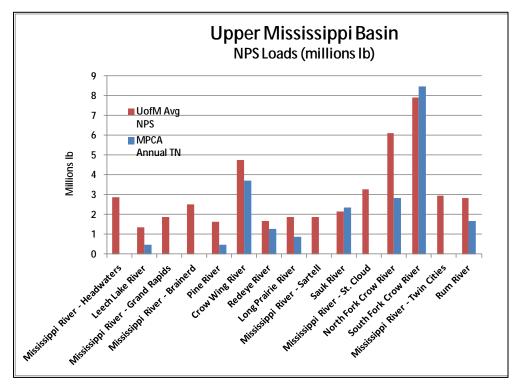


Figure 39. Modeled versus monitored N loads in the Upper Mississippi River Basin

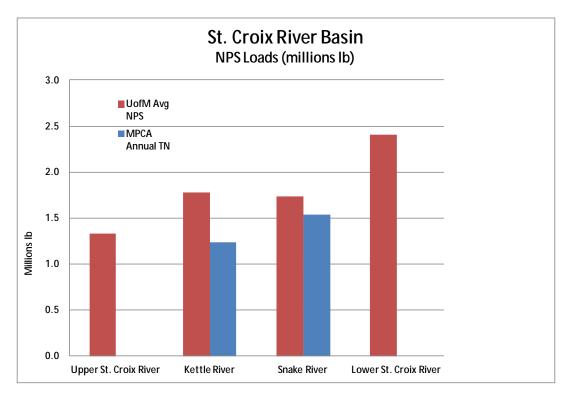


Figure 40. Modeled versus monitored N loads in the St. Croix River Basin.

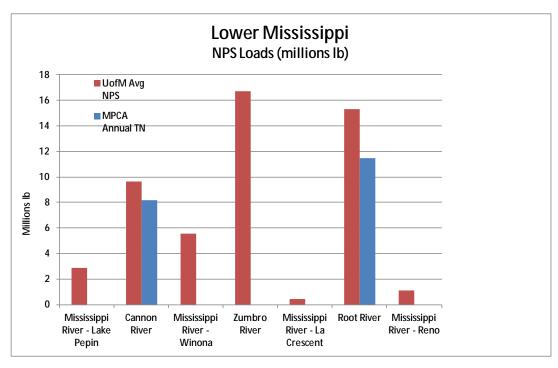


Figure 41. Modeled versus monitored N loads in the Lower Mississippi River Basin.

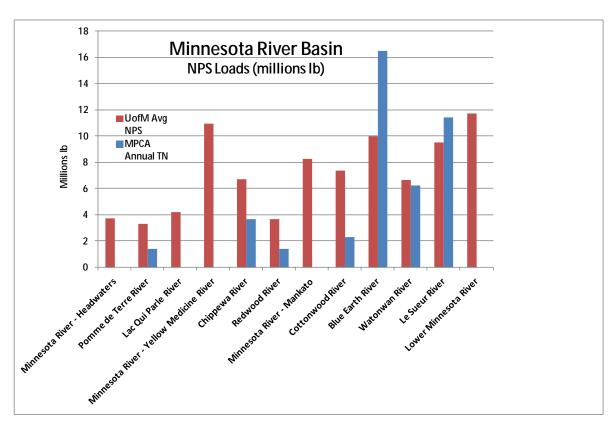


Figure 42. Modeled versus monitored N loads in the Minnesota River Basin.

Several possible reasons could be invoked to explain the difference between modeled and monitored N loads in the Blue Earth and Le Sueur River watersheds. These watersheds have large areas of lacustrine soils and are intensively tile-drained. The modeled tile drainage losses may be underestimated in these watersheds, due to underestimates of tile-drained lands and/or underestimating losses from tile-drained fields. Second, the Blue Earth and Le Sueur River watersheds have some very deeply incised river channels and there is significant seepage along the bluff faces. This seepage of groundwater could be a source of additional N that is not accounted for in the modeled results.

## Uncertainties in nitrogen loadings

The three primary pathways for N loadings in agricultural regions were by drainage, leaching, and runoff. There are uncertainties in the factors and coefficients used to estimate N loadings via each pathway. Losses of N in agricultural drainage are primarily dependent on three factors, namely; the areal extent of tile drainage, growing season precipitation, and the amount of N applied to cropland from fertilizer and manure. A sensitivity analysis was conducted to determine how changes in each of these factors affected the losses of N in agricultural drainage (Figure 43). Nitrogen losses in agricultural drainage were very sensitive to growing season precipitation. Increasing or decreasing growing season precipitation by 50% caused N losses in agricultural drainage to increase or decrease by 150%. This has important implications for comparisons between modeled nonpoint source N losses and monitored N losses in tile drained regions. If the period when water quality monitoring data were collected is wetter or dryer than average, modeled N losses will be smaller than or larger than monitored N losses, respectively. Nitrogen losses in drainage were much less sensitive to changes in tile drained area or applied N rates. Changes in either factor of up to plus or minus 50% would change the modeled N losses in drainage by less than plus or minus 50%. As mentioned previously, there is little relative uncertainty in applied N rates. The areal extent of tile drained lands may be larger than the area estimated for this study if landscapes steeper than 3% slope or soils with hydrologic group B have subsurface tile drainage.

Underestimation of tile drained acreages was limited to less than 10% in the small Beauford Watershed located in the Le Sueur major watershed. If the underestimation of tile drainage is limited to 10% or less, then the resulting uncertainty in drainage N losses would be less than 10%. The extent of tile drainage is likely underestimated in the Minnesota River Basin. Adjusting for this would increase N loadings in tile drained regions of the Minnesota River Basin.

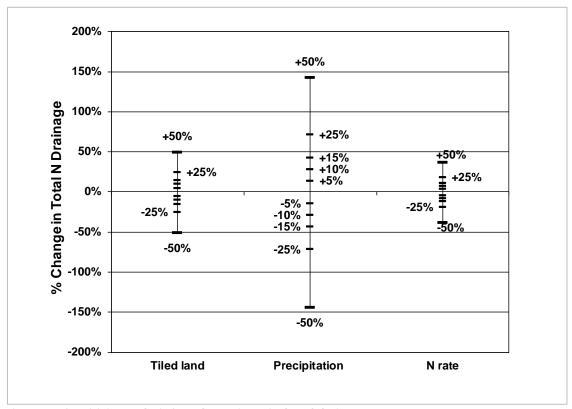
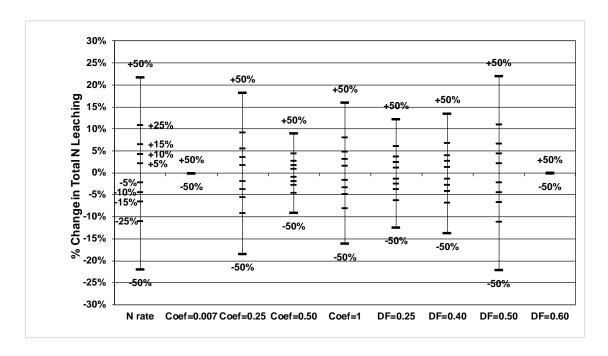


Figure 43. Sensitivity analysis for N losses in agricultural drainage.



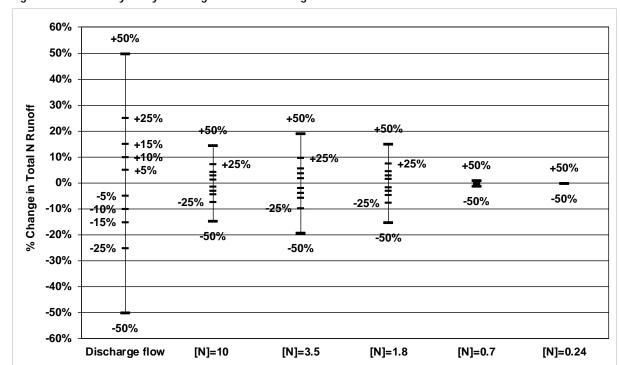


Figure 44. Sensitivity analysis for agricultural leaching contributions to surface water N loads.

Figure 45. Sensitivity analysis for N losses in agricultural runoff.

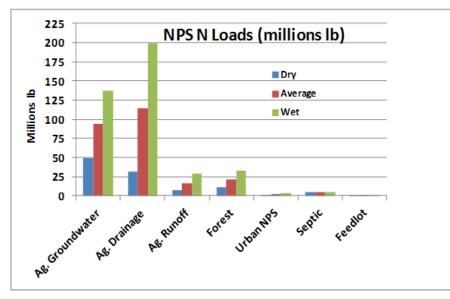
Losses of N in agricultural leaching, with subsequent discharge of groundwater to surface waters, are estimated using algorithms that depend on applied N rate and precipitation. Modeled losses of N for a given precipitation or irrigation regime are primarily affected by four coefficients along with the rate of applied N (Figure 44). As discussed previously, there is little uncertainty in the rate of applied N. The four coefficients determine by how much the leaching algorithm is adjusted for each region of the state. Changing coefficient one would have an insignificant impact on N losses by leaching. Changing any one of coefficients two-four by plus or minus 50% would change the modeled N losses by leaching by plus or minus 9-18%. Because of limited leaching quantification studies, uncertainty exists in the four leaching coefficients, especially coefficients for regions 2 and 3. More important, and more uncertain, are values of groundwater denitrification prior to surface water discharge. Changing the first three denitrification coefficients by plus or minus 50% would increase or decrease groundwater discharge of N to surface water by 17-22%.

Losses of N in agricultural runoff are estimated based on amounts of river discharge contributed by runoff and by concentrations of N in runoff. There are five values used for concentration of N in runoff (ranging from 0.24 to 10 mg/L), which vary region by region across the state. In general, results of the sensitivity analysis showed that as N concentration in runoff increased, the sensitivity of the modeled N losses in runoff also increased (Figure 45). In regions where N concentration in runoff is between 1.8 and 10 mg/L, changing N concentrations in runoff by 50% would change modeled N losses in runoff by up to plus or minus 25%. In regions where N concentration in runoff is between 0.24 and 0.7 mg/L, changing N concentration in runoff by 50% would have little impact on modeled N losses in runoff. Of greater importance is the sensitivity of the model to river discharge, which is sensitive to precipitation. Changing discharge by plus or minus 50% would change modeled N losses in runoff by plus or minus 50%.

Fortunately, river discharges are well known for dry, average and wet climatic conditions for various regions across the state. Hence, there is little uncertainty in river discharge for these three climatic regimes.

## Variation in nitrogen loads for dry, average and wet climatic years

Climate has a significant effect on nonpoint source N loadings to surface waters in Minnesota. Total loadings of N to surface waters modeled for dry, average and wet years are roughly 106, 254, and 409 million pounds, respectively (Figure 46). Nitrogen losses by cropland leaching to groundwater and tile



drainage are particularly sensitive to an increasingly wetter climate.

Figure 46. Statewide nonpoint source N loads (lbs) for various sources in dry, average and wet years.

During a dry year (10<sup>th</sup> percentile precipitation years), the majority (46%) of nonpoint source N losses to surface waters arises from groundwater discharge (Figure 47). Losses from tile drainage (30%) and runoff (7%) on cropland are much smaller in comparison during a dry year. Losses from forested regions account for 10% of the total nonpoint source losses to surface waters. Septic system losses account for 5%. Losses of nonpoint source N from urban areas and feedlots are very small.

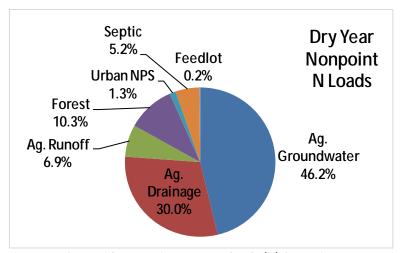


Figure 47. Statewide nonpoint source N loads (%) for various sources in a dry year.

Losses of nonpoint source N during a dry year are largest for the Minnesota River watershed (30 million pounds), followed by the Lower Mississippi River watershed (27 million pounds) and the Upper Mississippi River watershed, with 21 million pounds of losses (Figure 48). Losses in the Red River of the North are about 10 million pounds. The other basins all have very small losses of nonpoint source N during a dry year.

During an average year (Figure 49), the nonpoint source losses from agricultural drainage (45%) increase relative to the losses from agricultural groundwater discharge (37%) in comparison with the losses during a dry year. Forest export of N accounts for 9% of the nonpoint source N losses during an average year, while agricultural runoff accounts for 6%. Septic system and urban losses account for only 2% and 1% of the total nonpoint sources, respectively. Losses from feedlots are insignificant.

During an average year, the Minnesota River Basin (34% or 86 million pounds of total nonpoint source N loadings) contributes more nonpoint source N losses than any other basin (Figs. 50-51). The Lower Mississippi River Basin (21% or 54 million pounds) contributes less than the Minnesota River Basin during an average year, in contrast to their relative contributions in a dry year. Modeled losses of nonpoint source N in the Upper Mississippi River are 18% or 46 million pounds. Losses from the Red River of the North are about 9% or 22 million pounds. The other basins contribute small nonpoint source N losses in comparison to the Minnesota, and Lower and Upper Mississippi River Basins.

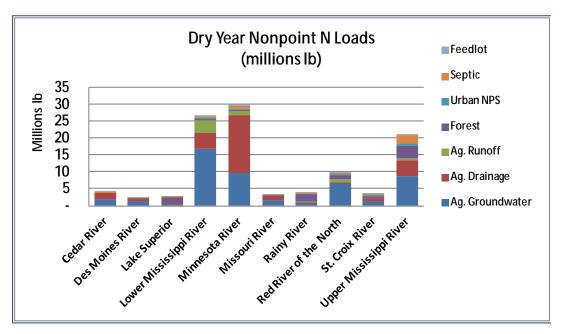


Figure 48. Nonpoint source N loads (lb) for various sources by river basin in a dry year.

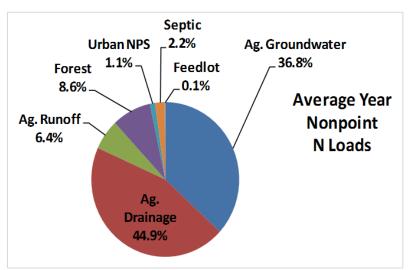


Figure 49. Statewide nonpoint source N loads (%) for various sources in an average year.

During a wet year (90<sup>th</sup> percentile precipitation year), the majority of nonpoint source N losses statewide (Fig. 52) arise from agricultural drainage (49%). Discharge of groundwater from agricultural regions contributes another 34%. Forested regions generate 8%, and agricultural runoff generates 7% of the statewide nonpoint source N losses during a wet year. Other sources are relatively small in comparison.

The largest nonpoint source N losses in a wet year (Figure 53) occur in the Minnesota River Basin (146 million pounds). The Lower and Upper Mississippi River Basins generate 82 and 70 million pounds, respectively, of nonpoint source N during a wet year. The Red River of the North generates 36 million pounds. Other basins generate less than 15 million pounds each of nonpoint source N during a wet year.

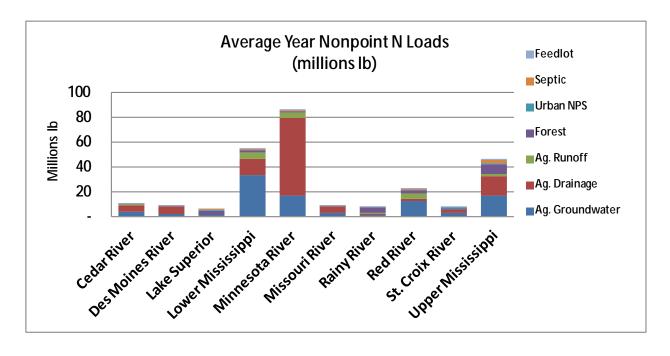


Figure 50. Nonpoint source N loads (lb) for various sources by river basin in an average year.

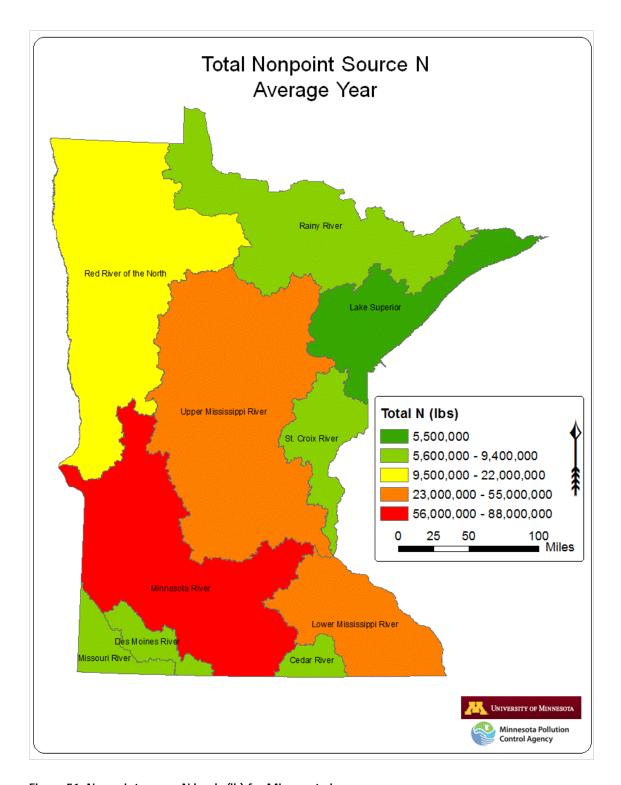


Figure 51. Nonpoint source N loads (lb) for Minnesota in an average year.

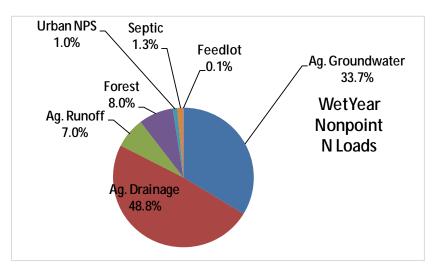


Figure 52. Statewide nonpoint source N loads (%) for various sources in a wet year.

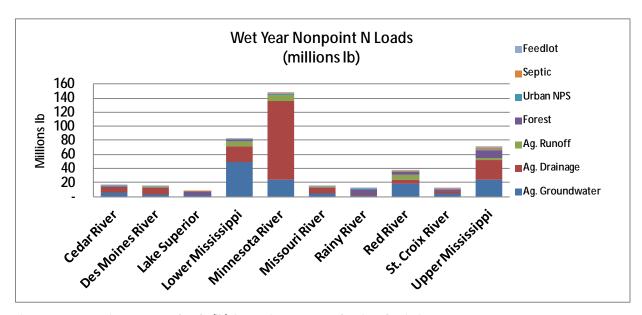


Figure 53. Nonpoint source N loads (lb) for various sources by river basin in a wet year.

#### Comparison between modeled and monitored N loads (including effects of point sources)

Data for point source N loads were provided by MPCA in the Minnesota, Red River of the North, St. Croix, and Upper Mississippi River Basins. These N loads were added to the modeled basin wide nonpoint source N loads described in previous sections. The basin total modeled plus point source N loads were compared with water quality monitoring data in each of the four river basins for dry, average, and wet climatic conditions. The monitoring data only represent the Minnesota contributions to the rivers.

In dry years (Figure 54), there was excellent agreement between monitoring data and modeled plus point source N loads in the Minnesota River Basin (32 million pounds), Red River of the North (10.3 million pounds), and St. Croix River (3.9 million pounds). In the Upper Mississippi River Basin monitored N loads were less than modeled plus point source N loads by about 7.3 million pounds, but this is not unexpected. Watersheds upstream of Sartell in the Upper Mississippi River Basin have from 10-40% of their area covered by wetlands. Nitrogen loads leaving fields and forest and entering these wetlands would be subject to further losses that are not reflected in modeled N loads. This could

partially explain why modeled N loads are larger than monitored N loads in the Upper Mississippi River Basin. Additionally, because of the importance of the groundwater pathway in this region and the slow movement of groundwater, some of the nitrate from past decades has not yet reached the river and therefore would not be included in the monitoring data.

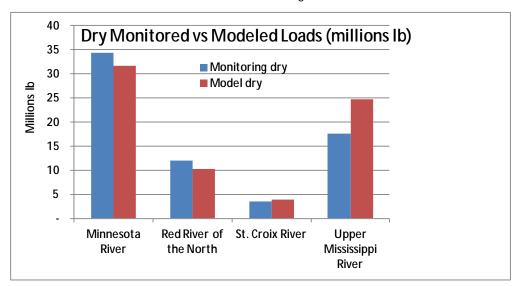


Figure 54. Comparison of modeled + point source N loads with monitored N loads in a dry year.

During average climatic years (Figure 55), there was excellent agreement between monitoring data and modeled plus point source N loads in the Red River of the North (22.5 million pounds), St. Croix River (7.7 million pounds), and Upper Mississippi River (49.5 million pounds) Basins. Modeled loads underestimated monitored loads by about 28 million pounds in the Minnesota River Basin. It appears that there may be other sources of N (such as additional groundwater discharge and/or more tiled land than assumed) in the Minnesota River Basin that are not adequately accounted for in the modeled results.

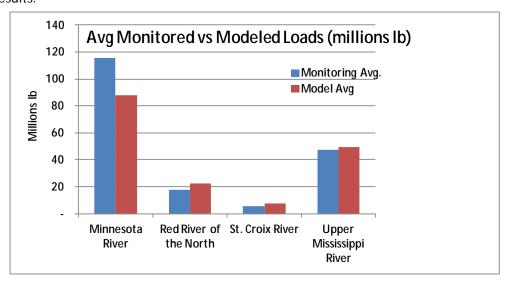


Figure 55. Comparison of modeled + point source N loads with monitored N loads in an average year.

During wet climatic years (Figure 56), there was reasonably good agreement between monitoring data and modeled plus point source N loads in the Minnesota River (148.5 million pounds), Red River of the North (36.7 million pounds), St. Croix River (11.3 million pounds), and Upper Mississippi River (74.2 million pounds) Basins. As with average years, N loadings to the Upper Mississippi River were

overestimated (by 14.6 million pounds), probably because as a result of denitrification losses occurring in wetlands and slow movement of groundwater. Monitored N loads in the Minnesota River Basin were underpredicted by about 34.5 million pounds. This is an underprediction of monitored loads by about 18%. Again, this indicates that there may be underestimated or other sources of N in the Minnesota River Basin not accounted for by modeled results.

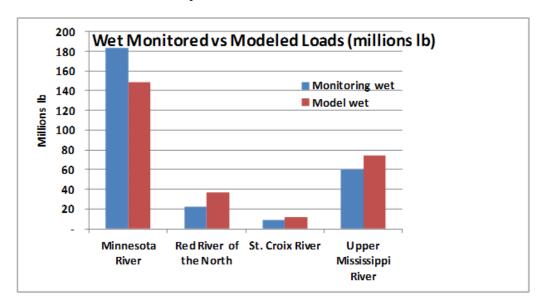


Figure 56. Comparison of modeled + point source N loads with monitored N loads in a wet year.

## Conclusions

An N budget was estimated for Minnesota's agricultural land as a separate and distinct analysis from the efforts to determine sources to surface waters. Inputs included mineralization (1.7 billion pounds), N fertilizer (1.36 billion pounds), N fixation by legumes (0.61 billion pounds), and several other smaller sources. The largest inputs occurred in the Minnesota River Basin. Outputs included crop removal (2.2 billion pounds), senescence (0.72 billion pounds), and denitrification (0.48 billion pounds), and several other smaller sources. The overall statewide N balance (inputs-outputs) was very good, with a difference of only 0.09 billion pounds (or 2.1% of the total inputs). This difference suggests that today's high biomass crops may be mining N from the soil, however, small increases in rates of soil mineralization assumed for the study could easily bring the system into balance.

Total nonpoint source N loadings to Minnesota surface waters were estimated at 254 million pounds during an average climatic year. This is about 6% of the total inputs of N on all Minnesota cropland (including soil mineralization). Sources of N loadings included cropland drainage (114 million pounds), cropland leaching (93 million pounds), forest N export (22 million pounds), cropland runoff (16 million pounds), individual septic treatment systems (5 million pounds), urban/suburban nonpoint source N (3 million pounds), and feedlot runoff (0.2 million pounds). During an average year, the Minnesota River Basin contributes more nonpoint source N loading to surface water (86 million pounds) than any other basin. The Lower Mississippi River Basin contributes (54 million pounds), the Upper Mississippi River Basin contributes 46 million pounds, and the Red River of the North contributes 22 million pounds. At the major watershed scale, modeled nonpoint source N loadings were highest for the Zumbro and Root Rivers of southeastern Minnesota, which are large watersheds where N loadings from groundwater

discharge, drainage and runoff are all significant. N loadings were next highest in a cluster of major watersheds in the Minnesota River Basin, where N losses in drainage are high. These major watersheds include the Lower Minnesota, Blue Earth, and Le Sueur River watersheds.

A comparison between the modeled nonpoint source N loadings to Minnesota surface waters (in an average climatic year) and monitored N loadings (average of two typical years) was conducted for 33 MPCA monitored major watersheds across Minnesota. Monitored N loadings were not used to calibrate the modeled nonpoint source N loadings, as the modeled N loadings were estimated independently, without calibration. Linear regression between modeled and MPCA monitored N loads was very good, with an R² value of 0.69. However, the modeled N loads were lower than monitored loads for several watersheds in south-central Minnesota. Modeled N loadings across all monitored watersheds were 10% higher than monitored N loads, which is not surprising given that additional losses in predicted N loadings may occur as nitrate travels downstream to the mouth of the watershed.

Climate has a significant effect on nonpoint source N loadings to Minnesota surface waters. Total statewide nonpoint source N loadings to surface waters for dry, average and wet years were predicted to be 106, 254, and 409 million pounds, respectively. During a dry year, the majority (46%) of nonpoint source N losses to surface waters arises from groundwater discharge. Losses from tile drainage (30%) and runoff (7%) on cropland are much smaller in comparison during a dry year. Losses from forested regions account for 10% of the total nonpoint source losses to surface waters. During an average year, the nonpoint source losses from agricultural drainage (45%) increase relative to the losses from agricultural groundwater discharge (37%) in comparison with the losses during a dry year. Forest export of N accounts for 9% of the nonpoint source N losses during an average year, while agricultural runoff accounts for 6%. During a wet year, the majority of nonpoint source N losses statewide arise from agricultural drainage (49%). Discharge of groundwater from agricultural regions contributes another 34%. Forested regions generate 8%, and agricultural runoff generates 7% of the statewide nonpoint source N losses during a wet year.

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# E1. Comparing Source Assessment with Monitoring and Modeling Results

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The source assessment of Nitrogen (N) delivery to surface waters, as conducted by the University of Minnesota and the Minnesota Pollution Control Agency (UMN/MPCA) and described in Chapters D1 to D4, have areas of uncertainty. For example, one area of uncertainty is the quantity of N reaching surface waters from the cropland groundwater component. This uncertainty stems largely from: a) limited studies quantifying leaching losses under different soils, climate and management; and b) extreme variability in denitrification losses, which can occur as groundwater slowly flows toward rivers and streams. Another area of uncertainty is the tile drainage acreages, which were estimated based on soils, slopes and crops, and which have been increasing at during the previous few years.

Because of these and other source assessment uncertainties, we compared the N source assessment results with other related findings, using five different ways to check the findings as follows:

- 1) Monitoring results Comparing HUC8 watershed and major basin scale monitoring results with loads estimated by summing the source estimates (Chapter E1).
- 2) SPARROW model comparing modeled estimates of major source categories to source assessment findings (Chapter E1).
- 3) **HSPF model** Comparing Minnesota River Basin HSPF modeled estimates of sources, pathways and effects of precipitation with the source assessment findings (Chapter E1).
- 4) Watershed characteristics analysis Comparing watershed and land use characteristics with river monitoring-based concentrations and yields (Chapter E2).
- 5) **Literature review** Comparing findings of studies in the upper-Midwest related to N sources and pathways with source assessment findings (Chapter E3).

In this chapter, N source estimates reported in Chapters D1 to D4 are compared with the first three approaches noted above, including: 1) monitoring-based load calculations; 2) SPARROW modeling source category results; and 3) HSPF modeling of the Minnesota River Basin. Subsequent chapters include the Watershed Characteristics Analysis (Chapter E2) and Literature Review (Chapter E3).

# Monitoring results comparison with sum of source loads

Monitoring results obtained near major basin outlets (1991-2010) and near HUC8 watershed outlets (2005-09) were compared with the sum of individual source load estimates documented in Chapters D1-D4. The purpose was to see how closely the sum of individual source loads compared to loads calculated from major river and watershed monitoring. With the exception of urban nonpoint source and forest N loss coefficients, which were based on small scale watershed monitoring, the source

estimates were determined from methods that did not involve watershed monitoring. Since the monitoring data used in this comparison was not used to derive any of the source load estimates, it represents an independent check of the source assessments.

It is important to note that there are three important limitations associated with this comparison. First, the source estimates in Chapters D1-D4 do not consider N losses within streams, rivers or reservoirs. The source estimates are expected delivery to the stream; not delivery within the streams. Losses within streams can be minimal to substantial, depending on the hydrologic conditions. For example, reservoirs with a long residence time can result in large decreases of N from algal uptake and subsequent settling to the reservoir bottom, and to denitification. Due to this issue, the sum of the estimated source loads by the UMN/MPCA would be expected to be higher than the monitoring-based loads, if everything else was equal.

Second, the source estimates do not consider the time lag between when nitrate leaches below the root zone in the soil to the time that it moves into and through groundwater and ultimately discharges into the stream. This lag time is particularly important with the groundwater flow pathway below cropland, and could cause monitoring results to be lower than the source assessment results in watersheds which are largely influenced by groundwater transport, such as in karst and sand plain regions.

The third limitation in comparing the source estimates with monitoring results is the challenge of obtaining representative monitoring-based load results. Nitrogen loads can vary tremendously from year to year due to climatic differences. Additionally, load calculations from monitoring information have uncertainty because samples are not collected continuously. The effect of this third limitation was minimized by using long-term average loads for the major basins analysis. For the HUC8 watershed load analysis, we used two-year averages from years without extremely low or high annual flow volumes, and limited the watersheds to those which had two years of monitoring-based load calculations during "normal" flow years between 2005 and 2009, as described in Chapter B3.

While recognizing these anticipated differences between watershed source assessments and watershed monitoring results, the comparison of findings from watershed monitoring with estimated loads from cumulative source estimates can still be useful as an indication of whether the source estimates are generally reflecting actual watershed loading conditions. This validation at larger scale watersheds is important since the source assessment was conducted by using mostly smaller field-scale research/monitoring and expanding the results to larger scales through the use of statewide geographical spatial data.

The source assessment results would need to be questioned if the monitoring results and the sum of the source assessment results were markedly different in watersheds without: a) large reservoirs or other identified N transformation processes; b) extreme climatic conditions during monitoring years; or c) some other scientific explanation. If, on the other hand, the monitoring results and the sum of the source assessment results are reasonably close, then we can have a greater level of confidence in the source assessment results. A reasonably close comparison does not prove the complete validity of the source assessment results, but provides one line of evidence that the source assessment may be providing reasonably accurate estimates.

#### Basin level comparison with monitoring

Monitoring of Minnesota's major rivers is described in Chapter B2. The total nitrogen (TN) loads based on monitoring of major rivers were compared to the sum of N sources to waters in those same basins for average, wet, and dry years (Figures 1 to 3).

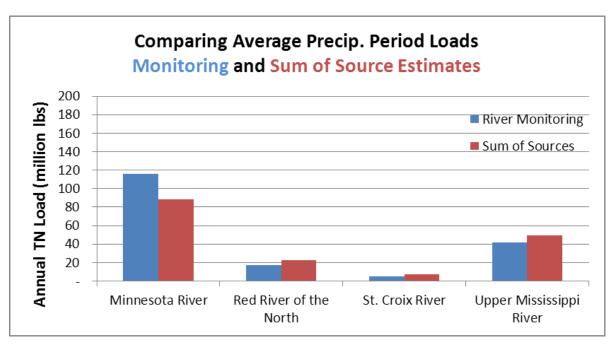


Figure 1. Average TN loads based on monitoring (avg. 1991-2010) of the Minnesota River (Jordan), Red River (Emerson), St. Croix River (Stillwater) and Upper Mississippi River (Anoka), as compared to the sum of estimated N sources to waters for average precipitation conditions.

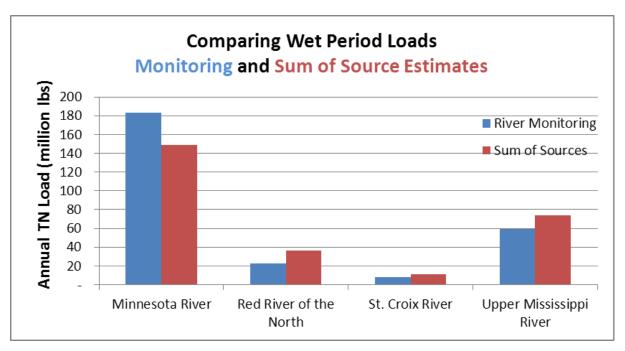


Figure 2. Wet period (90th percentile) TN loads based on monitoring (avg. 1991-2010) of the Minnesota River (Jordan), Red River (Emerson), St. Croix River (Stillwater) and Upper Mississippi River (Anoka), as compared to the sum of estimated N sources to waters for wet period conditions.

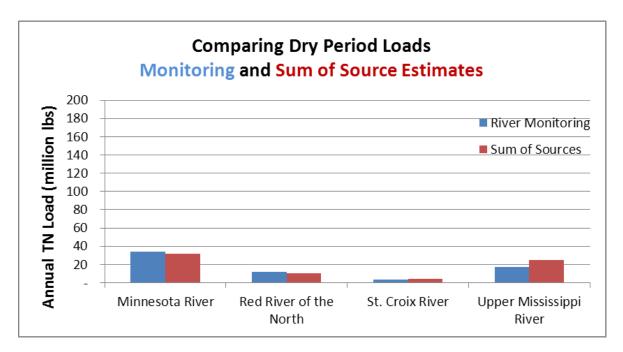


Figure 3. Dry period (10th percentile) TN loads based on monitoring (avg. 1991-2010) of the Minnesota River (Jordan), Red River (Emerson), St. Croix River (Stillwater) and Upper Mississippi River (Anoka), as compared to the sum of estimated N sources to waters for dry period conditions.

Even with the limitations of this type of comparison, the source assessment based loads at the major basin scale were reasonably similar to the monitoring-based results. The relatively close comparison is particularly remarkable when considering that river/stream monitoring results were not used to develop the nonpoint source and point source load assessments, nor were they used to calibrate the source-based load estimates.

In the Minnesota River Basin, the 20-year average monitoring-based results were slightly higher than source-based estimates for the Minnesota River Basin (Jordan). Monitoring-based loads were 31%, 23%, and 8% higher than source-based estimates during average, wet and dry periods, respectfully. As previously noted, we would expect the monitoring results to be less than the sum of sources in areas that are not dominated by groundwater nitrogen inputs to streams. This is because in-stream nitrogen losses are not accounted for in the source assessment, but they are inherently reflected in the monitoring results. Therefore, it is likely that in this basin, which has nitrate levels controlled more by tile drainage than groundwater inputs, the source assessment is under-predicting the sources.

In the other basins, the monitoring-based loads were lower than the source-based estimates. In the Red River Basin (Emerson, Manitoba) monitoring-based loads were 78%, 61%, and 115% of source-based estimates during average, wet, and dry periods, respectfully.

The St. Croix River loads are considerably lower than the other three major rivers during all three precipitation conditions. In the St. Croix River (Stillwater), monitoring-based loads were 69%, 74%, and 89% of source-based estimates during average, wet, and dry periods, respectfully.

In the Upper Mississippi Basin (Anoka), monitoring-based loads were 84%, 80%, and 71% of source-based estimates during average, dry, and wet periods, respectfully.

The relatively close comparison indicates that at the basin scale, the monitoring results alone do not provide a reason to suggest that the source estimates are unreasonable.

### **HUC8** level comparison with monitoring

Chapter D4 presented a comparison of HUC8 level monitoring results with the nonpoint source (NPS) load estimates in corresponding watersheds. Two analyses were presented: 1) bar graphs showing NPS load estimates with monitoring-based load averages obtained from one to multiple years of monitoring in each watershed; and 2) an X-Y plot showing correlation between NPS load estimates and monitoring-based loads obtained by averaging monitoring results. A discussion of these comparisons is included in Chapter D-4.

In this section of the report, monitoring-based results from average loads during normal flow conditions are compared with the sum of the estimated nonpoint source loads, point source loads, and atmospheric deposition falling directly into rivers and streams.

The 28 watersheds and associated monitoring-based data used for this comparison are described in Chapter B3 under the section "Independent HUC8 Watershed Loads (mid-range flow averages)." The monitoring results are only from those watersheds which are independent HUC8 watersheds (not influenced by upstream main stem rivers) and which had two-year average load results obtained during years with mid-range river flows (between 2005 and 2009). Therefore, the monitoring results are a) recent; b) do not depend on a single year of monitoring; c) do not include extreme dry or wet years; and d) are not influenced by water flowing into the watershed from upstream main stem rivers.

Source load estimates were derived by adding point source contributions from Chapter D2, NPS contributions Chapter D4, and atmospheric contributions directly into rivers and streams from Chapter D3.

The comparison shows that most of the HUC8 watershed monitoring results are reasonably similar with the sum of source loads (Figure 4), especially when considering that the source load estimates were mostly derived from small-plot and field scale research rather than watershed scale monitoring, and that the sum of sources does not include in-stream N losses. Yet there are also some notable differences in certain watersheds.

Monitoring results in the Blue Earth and LeSueur watersheds show substantially higher loads than the sum of the sources. Since the point source contributions in these watersheds are rather small in comparison to nonpoint sources, the lower estimates from the source assessment could be due to an underestimate in the nonpoint source load estimates in these watersheds. Some possible reasons for these differences are discussed by Mulla et al. in Chapter D-3. One watershed that had sum of source estimates considerably higher than the monitoring results was the Chippewa River, indicating that sources may have been overestimated for this watershed or that large in-stream N losses are occurring in this watershed.

The results at the HUC8 level monitoring and basin levels both indicate that source estimates may be reasonable for both scales, but that they are better suited for large scale use, such as the basin level.

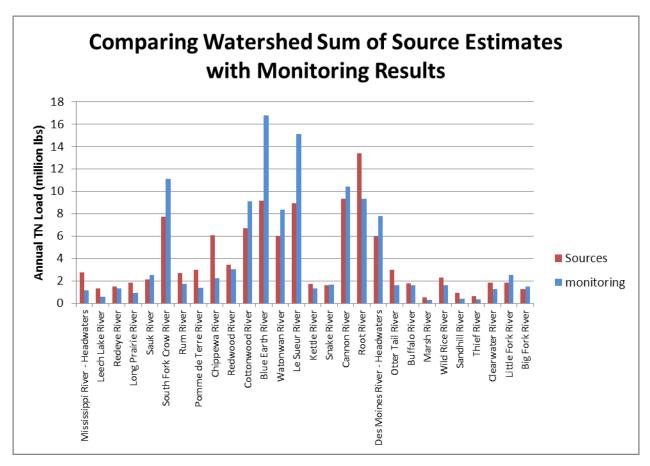


Figure 4. Two-year normal flow average TN loads based on monitoring within the 2005 to 2009 timeframe for independent HUC8 watersheds, as compared to the sum of estimated N sources to waters for average precipitation conditions.

# SPARROW nitrogen delivery to receiving waters by source category

The SPARROW model was used to estimate the delivery of nitrogen to receiving waters by major source categories of: agriculture, wastewater point source, and non-agricultural nonpoint sources to waters. The SPARROW modeling effort for this study is described in more detail in Chapter B4. Background information about the SPARROW model is included in Appendix B4-1. The SPARROW model results were compared with the UMN/MPCA source estimates to waters from Chapters D1-D4. While the source categories from the SPARROW modeling in Chapter B4 and the UMN/MPCA source estimates from Chapters D1-D4 were originally categorized differently, we were able to lump the source assessment findings into like categories for comparison purposes, as follows:

"Agriculture" sources include the cropland tile drainage, cropland groundwater and cropland runoff from the UMN/MPCA source assessment.

"Non-agricultural Nonpoint Sources" include all other sources which are not included in the agriculture or point source categories. SPARROW outputs label this as atmospheric deposition, and it includes atmospheric deposition and other non-agricultural nonpoint sources which are carried to waters by precipitation.

The SPARROW modeling approach is very different than the approach used by UMN/MPCA to estimate N source loads. The SPARROW model leans heavily on statistics and monitoring-based load calculations.

The UMN/MPCA source estimates were developed mostly from small scale research, multiplied to larger scales through the use of GIS data layers.

The results of the comparison between SPARROW load estimates and the UMN/MPCA load estimates by source are quite similar for the broad source categorizations evaluated (Figures 5 and 6). SPARROW estimates of the percent of load coming from point sources was slightly lower than UMN/MPCA estimates (7% vs. 9%). Estimated agricultural contributions for the state are nearly the same with these two approaches (72% with the UMN/MPCA source assessment approach and 70% with the SPARROW model).

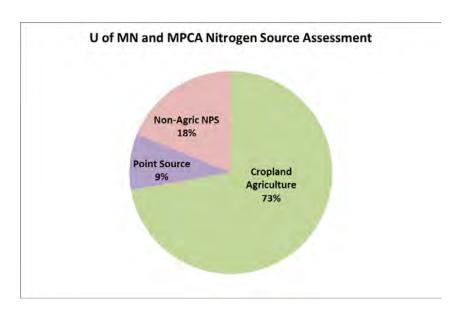


Figure 5. Minnesota statewide nitrogen sources to surface waters developed by the University of Minnesota and MPCA, (from Chapters D1-D4).

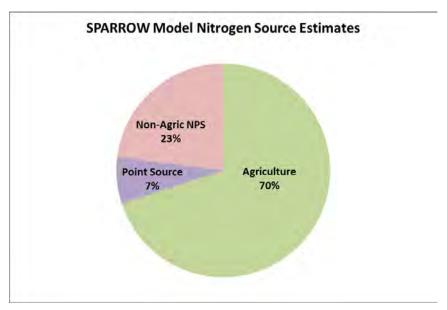


Figure 6. Minnesota statewide nitrogen source estimates for nitrogen delivery to surface waters based on the SPARROW model, as described in Chapter B4.

The close comparison of the SPARROW model source estimates provides another indication that the UMN/MPCA source assessment is reasonably accurate, at least within the broad categories of this comparison.

# HSPF modeling - Minnesota River Basin

The Hydrological Simulation Program - FORTRAN (HSPF) model, as applied to the Minnesota River Basin, was used to evaluate NPS inorganic N: a) transport pathways to surface waters; b) sources to streams; and c) effects of wet and dry years on loads. The Minnesota River Basin has the highest N loads in Minnesota, contributing nearly half of all N which leaves the state in the Mississippi River. Since HSPF modeling for other basins was not completed at the time of this study, we were only able to compare Minnesota River Basin HSPF results to the UMN/MPCA source assessment results.

HSPF modeling results for all years between 1993 and 2006 were used to assess source and pathway findings. These results were then compared to the UMN/MPCA estimates presented in Chapters D1 to D4. HSPF uses a very different modeling approach than either the SPARROW model or the UMN/MPCA source assessment methods in sections D1-D4, allowing another rather independent check of source assessment results.

Only inorganic N loading was assessed with the HSPF model for this analysis. Long term monitoring results presented in Chapter B2 showed that inorganic N represents 85% of the TN load in the Minnesota River Basin (at Jordan). Point source discharges, which represent an estimated 4% of the TN long-term average load in the Minnesota River Basin, were not included in this HSPF modeling assessment.

#### HSPF model background

The HSPF model is a comprehensive model for simulating watershed hydrology and water quality for both conventional pollutants such as nutrients, and toxic organic pollutants. HSPF incorporates the watershed-scale Agricultural Runoff Model (ARM) and NPS models into a basin-scale analysis framework that includes fate and transport in one dimensional stream channels. HSPF allows the integrated simulation of land and soil contaminant runoff processes with in-stream hydraulic and sediment-chemical interactions. The result of this simulation is a time history of the runoff flow rate, sediment load, and nutrient and pesticide concentrations, along with a time history of water quantity and quality at the outlet of any subwatershed.

The quantity of water discharged in surface streams is characterized in the HSPF model by surface runoff, interflow and baseflow. Surface runoff is the water flow that occurs after the soil is infiltrated to full capacity, and excess water from rain, meltwater or other sources flows over the land. Surface runoff is observed in river hydrographs soon after the runoff event. In addition to direct overland runoff, this component of flow can also include runoff which enters waters quickly through open tile intakes and side inlets to ditches. Interflow is water that first infiltrates into the soil surface and then travels fairly quickly in the subsurface to stream channels, reaching streams after surface runoff, but ahead of baseflow. A large component of interflow is tile drainage waters. Yet interflow also can include groundwater that quickly discharges into streams after precipitation events, such as in karst springs or alluvial sands along stream channels. Baseflow results from precipitation that infiltrates into the soil and, over a longer period of time, moves through the soil and groundwater to the stream channel. Baseflow includes most of the groundwater component, but can also include tile drain waters which continue to flow long after storms and melting events.

The HSPF model was calibrated by adjusting model parameters to provide a match to observed conditions. Although these models are formulated from mass balance principles, most of the kinetic descriptions in the models are empirically derived. These empirical derivations contain a number of coefficients which were calibrated to data collected in the Minnesota River Basin. Once calibrated, the model was validated using data independent from that used in calibration. The monitoring data used for both HSPF calibration and validation was different from that used earlier in this chapter to compare monitoring results with the UMN/MPCA source assessment approach in Chapters D1 to D4.

#### Flow pathways comparison

The HSPF modeling of inorganic N hydrologic pathways to the Minnesota River shows that the subsurface pathways of interflow and baseflow are the dominant pathways. Combined, these pathways account for 89% of the inorganic N transport (Figure 7). Interflow represents the highest contribution (54.7%) and baseflow represents the next highest (34.3%). Tile drainage is a major contributor to the interflow pathway, but also can also represent a fraction of the HSPF model surface runoff and baseflow pathways.

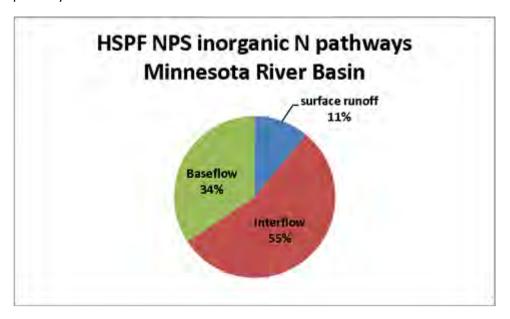


Figure 7. HSPF model estimates of the proportion of nonpoint source inorganic N which enters surface water through the three model flow pathways in the Minnesota River Basin during a typical precipitation year within the timeframe 1993-2006.

The UMN/MPCA estimates of the three major pathways (Figure 8) were determined by assuming the following:

- "Surface Runoff" includes all cropland N runoff, 80% of the N from urban/suburban NPS, 50% of the forested land N, and all feedlot runoff.
- "Groundwater" includes all cropland groundwater, all septic system N, 20% of the urban/suburban NPS component, and 50% of the forested land N.
- "Agricultural Drainage" includes all cropland tile drainage N estimates.

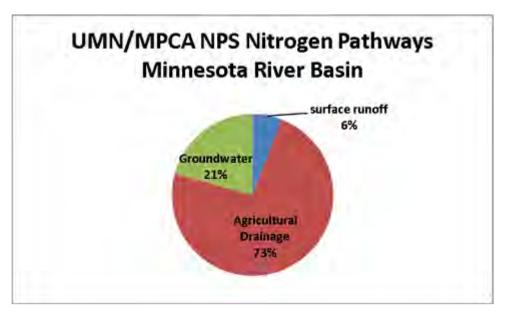


Figure 8. UMN/MPCA N source estimates of the proportion of TN which enters surface water through three major pathways in the Minnesota River Basin during average precipitation conditions (1981 to 2010).

Similar to the HSPF modeling, the UMN/MPCA source estimates show that the dominant pathway of TN in the Minnesota River Basin is subsurface flow, with 94% of N coming from the combined pathways of groundwater and tile drainage. This compares to 89% predicted by the HSPF model for the subsurface pathways. The UMN/MPCA source assessment shows that agricultural drainage is the pathway contributing the most N, representing 73% of the TN into rivers in the Minnesota River Basin. The HSPF model shows interflow to be the largest pathway, accounting for 55% of the inorganic N into the Minnesota River Basin surface waters. In the HSPF model, interflow is mostly affected by tile drainage waters, with a small fraction coming from groundwater adjacent to streams and ditches.

The reason that the HSPF estimated interflow TN fraction is lower than the UMN/MPCA tile drainage estimated TN fraction can be explained by the fact that some of the actual tile drainage waters is represented in HSPF outputs as "baseflow." When tiles continue to flow into streams long after rain or snowmelt events occur, this tile drainage will be considered as "baseflow" in the HSPF model. This hydrograph "baseflow" component of tile drainage is also supported by Schilling (2008), who found in heavily tiled lowa watersheds that the "baseflow" component of the hydrograph increased by 40% in the March to July timeframe, the period of time when tiles are flowing. Yet Schilling found no differences in baseflow between drained and undrained lands during the fall to winter months (September to February). This showed that tile drainage waters likely have a substantial effect on the nitrate contributions from the baseflow part of the hydrograph. If 40% of the HSPF modeled baseflow is actually from tile drainage, then the UMN and HSPF estimates of the relative contribution from tile drainage would be nearly the same.

We only compared the HSPF and UMN/MPCA source assessment pathways for the entire basin. Yet, it is noteworthy that the fraction of HSPF estimated nitrate from these three pathways varies among HUC8 watersheds within the Minnesota River Basin (Figure 9). For example, the less-tiled Chippewa River watershed has an estimated 22% of its nitrate coming from interflow and 57% from baseflow, whereas the heavily tiled LeSueur watershed has an estimated 69% of its nitrate from interflow and only 15% from baseflow.

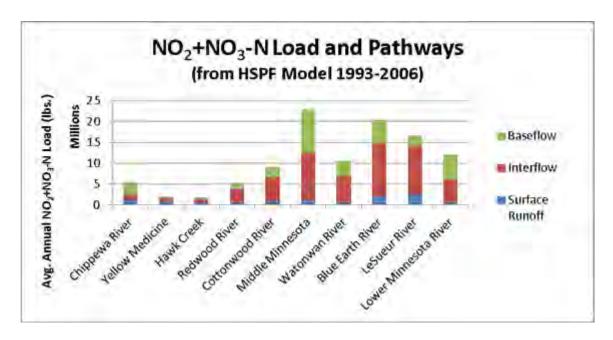


Figure 9. Nitrite+Nitrate-N pathways for HUC8 watersheds in the Minnesota River Basin, as estimated by the HSPF model.

#### NPS land use contributions in the Minnesota River Basin

The HSPF model results indicate that the dominant contributor of nonpoint source inorganic N to the Minnesota River is cropland, with an estimated contribution of 96.6% (Table 1). The UMN/MPCA estimates for cropland contributions in this same basin are very similar at 97.6%. All other sources are relatively small using both approaches. Note that these results did not include point source contributions, which are approximately 4% of the TN load in the Minnesota River Basin. Also note that the HSPF analysis for this chapter only included inorganic N and the UMN/MPCA assessment was for TN. Given that 85% of the Minnesota River TN is in the inorganic form of nitrate-N, this difference in N forms between the two approaches is not expected to greatly affect the relative source contributions of nonpoint source pollutants.

Table 1. Estimated NPS land use contributions of inorganic N (HSPF) and TN (UMN/MPCA) to surface waters during a typical precipitation year in the Minnesota River Basin.

Land use	HSPF estimated percent of total inorganic nitrogen from nonpoint sources	UMN/MPCA estimated percent of total nitrogen from nonpoint sources	
Cropland	96.6%	97.6%	
Urban stormwater	2.1%	0.7%	
Feedlot facilities (note: manure application is included with "cropland")	0.19%	0.06%	
Forest	0.14%	0.7%	
Other	0.97%	0.94	
Total	100%	100%	

#### **Precipitation effects**

The TN load from nonpoint sources was highly influenced by precipitation according to the UMN source assessment results (Chapter D4 – Mulla et al.). Nitrogen loads from the HSPF modeling for wet, normal, and dry years were compared with the loads from the UMN approach for similar climatic situations (Table 2). The increased loads predicted by HSPF for wet years are very similar to those predicted by the UMN source assessment (179% vs. 170% of the median precipitation year loads). Both approaches show substantially lower loads for the dry years (65% and 35% of median year loads). The UMN approach shows a more substantial drop in loads during the dry years. Part of the reason for the larger decrease in dry years from the UMN approach can be explained by the differences in the climatic period of record used for each approach. The HSPF results are based on the three driest years between 1993 and 2006. This period of time was relatively wet compared to the 30-year precipitation record used for developing the UMN/MPCA estimated effects of climate. The dry years between 1993 and 2006 were not as dry as the dry years between 1981 and 2010. The UMN/MPCA approach, using the 1981 to 2010 period of record, included more droughty years, such as the droughts during the late 1980s. Therefore, it is reasonable to expect that the UMN/MPCA approach would show lower loads for the dry years, if all other things are considered equal.

Table 2. Nitrogen loads for the Minnesota River Basin during dry and wet years shown as a percentage of the loads during the median (normal) precipitation. Dry and wet years for the HSPF results analysis considered the average of the 3 driest years (dry) and 3 wettest years (wet) during the period 1993-2006. The UMN/MPCA analysis considered the 10<sup>th</sup> percentile precipitation (dry) and the 90<sup>th</sup> percentile precipitation (wet) during the period 1981 to 2010.

Precipitation	HSPF inorganic N load estimates	UMN/MPCA total N load estimates	
	(percent of normal year load)	(percent of normal year load)	
Dry years	65%	35%	
Average years	100%	100%	
Wet years	179%	170%	

# Summary

The basin and watershed monitoring results overall compared reasonably close to the sum of the sources estimated by the UMN/MPCA source assessment. The monitoring results were not expected to be the same as the sum of sources since the sum of sources do not consider in-stream N losses or lag times in groundwater N transport. Yet the fairly close agreement in the monitoring results, with the source assessment results developed independently from the watershed and basin scale monitoring, provides a greater level of confidence that the source estimates may be realistic. The monitoring results alone do not provide a reason to suggest that the source estimates are unreasonable.

The greatest differences between sum of sources and monitored loads were in the Minnesota River Basin and a few of the high N loading HUC8 watersheds within that basin. In this basin, TN monitoring results were higher than the sum of sources estimates. Monitoring results for the Minnesota River were 131%, 108%, and 123% of the sum of sources estimates for average, wet, and dry periods, respectively. Monitoring results for other basins were lower than the sum of sources.

The SPARROW and HSPF model source estimates both were consistent with the UMN/MPCA source assessment, indicating that cropland sources are the dominant N sources to Minnesota rivers (SPARROW) and surface waters within the Minnesota River Basin (HSPF). The two models use markedly different approaches to arrive at source and pathway estimates, and both models are also very different from the UMN/MPCA source assessment approach. The SPARROW model estimated that cropland sources represent 70% of the statewide TN load (2002), as compared to 73% by the UMN/MPCA source assessment. The HSPF model results estimated that NPS from cropland in the Minnesota River Basin represent 96.6% of the inorganic N to surface waters, as compared to a 97.6% estimated from the UMN/MPCA TN source assessment.

The HSPF model results of N pathways in the Minnesota River Basin were also generally consistent with the UMN/MPCA assessment. The HSPF model estimated that 89% of the Minnesota River Basin inorganic N transport to surface waters is via subsurface pathways of interflow and baseflow. Similarly, the UMN/MPCA N source assessment estimated that 94% of TN reaches waters by subsurface pathways of tile drainage and groundwater.

The effects of high and low precipitation years on N loading to surface waters was also found to be reasonably similar with the HSPF model and UMN/MPCA approach. Wet weather loads were 179% of normal weather loads according to the HSPF modeling, as compared to 170% of normal loads in the UMN/MPCA source assessment. Both approaches estimated substantial load reductions for dry weather periods, but the UMN/MPCA approach showed a much greater reduction, explained in part by the different dry weather climate situations in the timeframes used for the two approaches.

# References

Schilling, Kieth E. and Matthew Helmers. 2008. Effects of subsurface drainage tiles on streamflow in Iowa agricultural watersheds: exploratory hydrograph analysis. Hydrol. Processs. Vol. 22 (4497-4506).

# E2. Comparing River Nitrogen with Watershed Characteristics

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#### Introduction

In-stream nitrogen (N) levels were compared against land use, climate, soils, and other watershed characteristics to determine whether this analysis showed any inconsistencies with the University of Minnesota and the Minnesota Pollution Control Agency (UMN/MPCA) source assessment findings described in Chapters D1 to D4. This analysis was conducted to determine if the relationship between watershed characteristics and stream N levels support or contradict conclusions of the N source assessment, which were derived mostly without the use of statistics or stream monitoring information.

Based on the UMN/MPCA source assessment in chapters D1 through D4, we expected to see the following types of relationships between watershed characteristics and watershed N levels:

- watersheds dominated by forests should have low river N
- watersheds with large percentages of fertilized cropland should have high river N, especially if the land is tiled or is in areas with high groundwater recharge
- river nitrogen loads should be generally independent of human population differences when evaluating rural watersheds

The evaluated watersheds included only those independent 8-digit Hydrologic Unit Code (HUC8) watersheds which: a) were not influenced by upstream main-stem rivers; and b) had two years of N yield and concentration data, obtained during years with mid-range river flows within the 2005-2009 timeframe (see Chapter B3 for more information on the selection of the watersheds meeting minimum criteria).

We analyzed the watershed characteristics and N levels in two different ways: 1) a non-statistical approach to observe the differences in land characteristics between watersheds with low, medium, high, and very high stream N levels; and 2) a statistical multiple regression analysis to identify key watershed characteristics influencing the variability in stream N levels.

This approach follows a central theme in landscape ecology, investigating relationships between spatial patterns in the landscape and ecological processes (Turner et al., 2001), and more specifically, the relationships between land use patterns in watersheds and the conditions of the streams that run through them (Allen 2004). The purpose of the watershed characteristics assessment was to gain a better understanding of similarities and differences among the watersheds with various levels of N pollution. The causes of high and low nitrate levels cannot be isolated as single variables, but are rather due to several confounding factors which involve: the presence or addition of a N source, the amount of water available to drive the N through the soil, an absence of an effective way of removing soil N (such as high density of plant roots), and a transport pathway which circumvents denitrification losses.

This analysis did not include watersheds with large metropolitan areas. This was the case because large metropolitan area watersheds water quality results were influenced by upstream main stem rivers, or we did not have two years of N yield and concentration data for these watersheds, obtained during years with mid-range river flows within the 2005-2009 timeframe.

#### Watershed characteristics

#### Methods of extracting land characteristic data

Watershed areas were delineated upstream from 79 water quality monitoring stations across Minnesota. We used ArcHydro in ArcGIS (ESRI 2012) to complete the delineations. Our ArcHydro implementation was developed using a 30-meter hydrologically conditioned digital elevation model (DEM) together with watershed walls enforced using the Minnesota Department of Natural Resources (MDNR) 16-digit catchments, and burned-in streams using the MDNR synthetic flow lines. We selected 28 watersheds that were not influenced by upstream main stem rivers and which also had two years of N yield and concentration data obtained during years with mid-range flows between 2005 and 2009. We used these 28 watersheds to extract data from a series of data layers listed in Table 1. For categorical raster layers such as the National Land Cover Data (NLCD) we calculated the area covered by specific land cover classes. For continuous raster layers such as percent soil organic material, we calculated the average percent of the material for each watershed. For vector layers such as the 2010 Census, we used a spatial overlay apportionment method and summarized the results by watershed to determine density values for each watershed. We used additional spatial overlays and raster analysis tools to determine areas where land cover characteristics overlapped, for example where row crops and shallow depth to bedrock were both present.

Table 1. List of land characteristic data layers and the associated data sources.

Forest and shrub	NLCD 2006 classes 41, 42, 43, 52		
Pasture, grass and hay	NLCD 2006 classes 71, 81		
Human population density (persons per acre)	U.S. Census 2010 blocks		
Livestock and poultry density	MPCA Delta database for feedlots		
Shallow depth to bedrock (<= 50 feet)	Preliminary Bedrock Geologic Map of Minnesota, April 2010, Minnesota Geological Survey		
Sandy soil areas (>=85%)	USDA NRCS SSURGO soils data		
Row crops	USDA Crop Data Layer 2009 including corn, sweet corn, soybeans, dry beans, potatoes, peas, sunflowers, sugarbeets		
Small grains	USDA Crop Data Layer 2009		
Wetlands	NLCD 2006 classes 90, 95		
Precipitation	Minnesota State Climatology Office		
Irrigation	Permitted acres from the Minnesota Department of Natural Resources		
Soil organic material	USDA NRCS SSURGO soils data		
Estimated area tile drained	USDA Crop Data Layer 2009, USDA NRCS SSURGO soils, USGS National Elevation Dataset 30-meter DEM		
Derived data layers			
RCD	Row crops over shallow depth to bedrock		
RCS	Row crops over sandy soils		
RCDS	Row crops over shallow depth to bedrock or sandy soils		
RCDST	Row crops over shallow depth to bedrock or sandy soils or tile drain		
RCnDST	Row crops not over shallow depth to bedrock, sandy soils, or tile drain		

Acronyms	
DEM	Digital elevation model
NLCD	National Land Cover Database
NRCS	Natural Resources Conservation Service
SSURGO	Soil Survey Geographic Database

Our analysis included a data layer to estimate land area with tile drainage. This layer was developed by the authors using information from scientific publications (Sugg 2007, David 2010) and interviews with technical experts working in various rural areas in the state. Our criteria included the presence of row crop agriculture from the 2009 USDA Crop Data Layer, relatively flat slopes of 3% or less from the United States Geological Survey (USGS) National Elevation Dataset 30-meter DEM, and soils that were poorly drained or very poorly drained based on Soil Survey Geographic Database (SSURGO) soils data developed by the U.S. Department of Agriculture, Natural Resources Conservation Service.

We used the data layers listed at the top of Table 1 to create additional spatial data layers to serve as explanatory variables in our analysis. These data layers are listed in Table 1 in the section titled 'Derived Data Layers.' These include row crop over shallow depth to bedrock (RCD), row crop over sandy soils (RCS), row crop over shallow depth to bedrock or sandy soils (RCDS), row crop over shallow depth to bedrock, or sandy soils, or tile drain (RCDST), and finally, row crop with no shallow depth to bedrock, no sandy soils, and no tile drain (RCDST). The RCD, RCS, and RCDS are considered to be naturally 'leaky' agricultural systems, while the tile drain layer (TD) is considered to be an anthropogenic 'leaky' agricultural system. The RCDST is a combination of these leaky systems, and the RCnDST is a non-leaky system where nutrients are less likely to have rapid pathways to surface waters.

Data coverage for each data layer listed in Table 1 was complete for the full extent of the study area, except for the SSURGO soils layer which was not finished for all areas of Minnesota at the time of this work. However, all 28 watersheds had at least partial SSURGO data coverage, with 17 having 100% coverage; 4 having 80% to 99% coverage; 6 with 50% to 79% coverage; and 1 with less than 50% coverage. For watersheds with incomplete SSURGO data, we assumed that areas with missing data were similar to areas with data present, and we used a proportioning coefficient to reflect that assumption. SSURGO serves as source data for the sandy soil layer and the tile drainage layer, and layers derived from these two. SSURGO was also used to estimate soil organic matter content.

The only watershed with less than 50% SSURGO data coverage was the Little Fork River watershed, which had only 14% coverage. However, we do not believe the minimal SSURGO coverage in the Little Fork River watershed significantly affects the analysis. This watershed has essentially no row crop agriculture, and the only explanatory variables that are based on SSURGO are also based on the presence of row crops (RCS, RCDS, RCDST, RCnDST and TD). So with no row crop agriculture, all these variables have zero values in the Little Fork watershed regardless of the SSURGO soil patterns.

Table 2. List of watersheds with partial SSURGO data coverage

Watersheds with partial SSURGO coverage	Fraction of watershed area covered by SURGO
Otter Tail River	0.99
Crow Wing, Redeye, Long Prairie River	0.96
Wild Rice River	0.87
Snake River	0.81
Rum River	0.73
Big Fork River	0.67
Thief River	0.63
Clearwater River	0.61
Mississippi R Headwaters	0.59
Kettle River	0.54
Little Fork River	0.14

# Non-statistical view of watershed characteristics compared to river nitrogen levels

The non-statistical approach we used to compare watershed characteristics with N concentrations was to categorize each watershed as a low, medium, high or very high N watershed, based on the stream N monitoring results. We then assessed the range and mean of numerous watershed characteristics for each of the four N level category watersheds.

# Categorizing watersheds into low, medium, high and very high nitrogen levels

Twenty-eight independent watersheds with available normal flow conditions fit into one of four distinct categories based on total nitrogen (TN) and nitrite+nitrate-N (NOx) yields and concentrations. The watersheds fitting the low, medium, high, and very high categories of water N levels are shown in Table 3.

Table 3. Watershed groupings based on stream Nitrite+Nitrate-N and Total N yields and concentrations. Watersheds which did not meet selection criteria are not included in this table.

Category	Low N watersheds	Medium N watersheds	High N watersheds	Very high N watersheds
Major	Otter Tail River	Chippewa River	Root River	Blue Earth River
Watersheds	Rum River	Wild Rice River	Cannon River	Cottonwood River
	Snake River	Clearwater River	Des Moines -	South Fork Crow
			Headwaters	
	Leech Lake River	Buffalo River	Yellow	LeSueur River
			Medicine	
	Kettle River	Pomme de Terre	Redwood River	Watonwan River
	Mississippi R.	Sauk River		
	Headwaters			
	Little Fork River	Sandhill River		
	Big Fork River	Marsh River		
	Thief River			
	Crow Wing +			
	Redeye + Long			
	Prairie Rivers			
		Nitrogen ranges	S	
NOx FWMC (mg/l)	0.05-0.5	0.6-1.9	4.8-7.1	7.9-9.5
TN FWMC (mg/l)	0.7-1.4	1.8-3.4	5.6-8.6	9.8-11.1
NOx Yield	0.07-0.53	0.37-2	3.6-8.9	9.3-18.3
(lbs/ac/yr)				
TN Yield	0.51-2.7	1.4-3.9	7.6-12.1	10.9-21.3
(lbs/ac/yr)				

Maps of watershed nitrate and TN concentrations and yields are shown in Figures 1, 3, 5 and 7. The range and average nitrate and TN concentrations and yields for each of the four watershed categorizations in Table 3 are shown in Figures 2, 4, 6 and 8. The same watersheds remain in each of the Table 3 categories throughout all figures in this section. For example, the very high N watersheds are always represented by the Blue Earth, Cottonwood, South Fork Crow, LeSueur, and Watonwan Rivers.

As shown in Figures 1 to 8, the nitrite+nitrate-N (NOx) flow weighted mean concentrations (FWMC) and yields show four distinct ranges and means. For example, the NOx FWMC range in watersheds classified in Table 3 as having high N levels do not overlap at all with the NOx FWMC range of watersheds classified in Table 3 as having medium N levels (Figure 2). The range of TN FWMCs in the four categories of watersheds are also distinct, with no overlapping concentrations among the four categories (Figure 6). NOx yields show the same pattern of a very low range of yields to a very high range of yields in the four categories, although there is a slight overlap in ranges in a couple of the categories (Figure 4). The TN yield ranges are less distinct compared to the NOx yields, since TN includes organic N which is influenced by natural sources as well as human-induced sources (Figure 8).

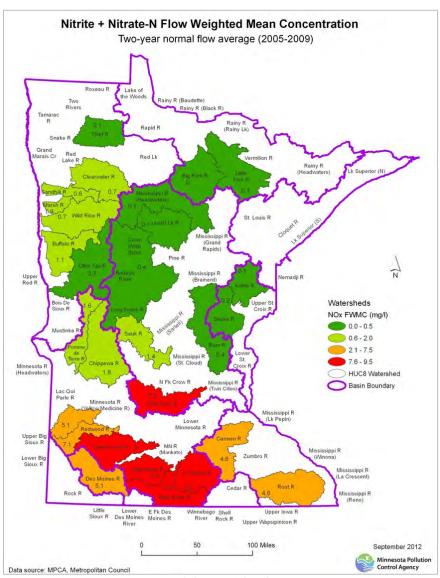


Figure 1. Nitrite+nitrate-N annual flow weighted mean concentration averages from the 28 study watersheds. Monitoring and load calculations were conducted by the MPCA and Metropolitan Council.

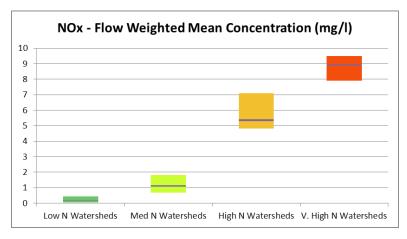


Figure 2. The range (colored bars) and mean (dark line) nitrite+nitrate-N annual flow weighted mean concentration for watersheds in each of the four river N level groupings listed in Table 3.

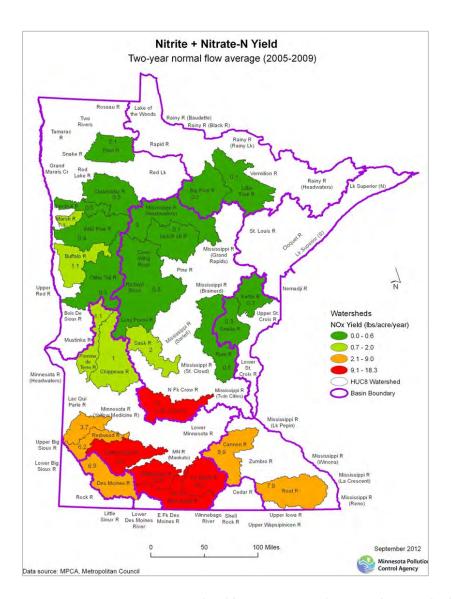


Figure 3. Nitrite+nitrate-N annual yield averages from the 28 study watersheds. Monitoring and yield calculations were conducted by the MPCA and Metropolitan Council.

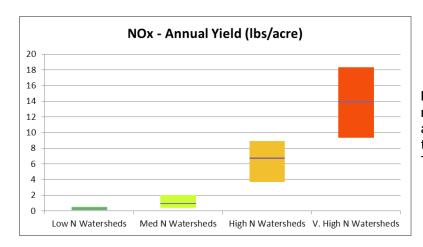


Figure 4. The range (colored bars) and mean (dark line) nitrite+nitrate-N annual yield for watersheds in each of the four river N level groupings listed in Table 3.

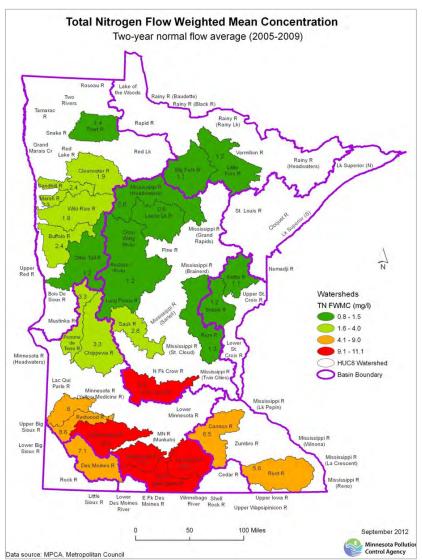


Figure 5. Total nitrogen annual flow weighted mean concentration averages from the 28 study watersheds. Monitoring and load calculations conducted by the MPCA and Metropolitan Council.

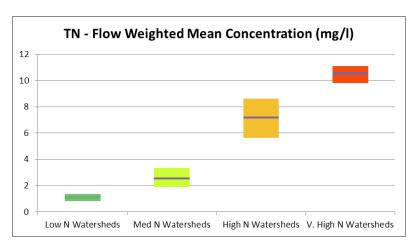


Figure 6. The range (colored bars) and mean (dark line) TN annual flow weighted mean concentration for watersheds in each of the four river N level groupings listed in Table 3.

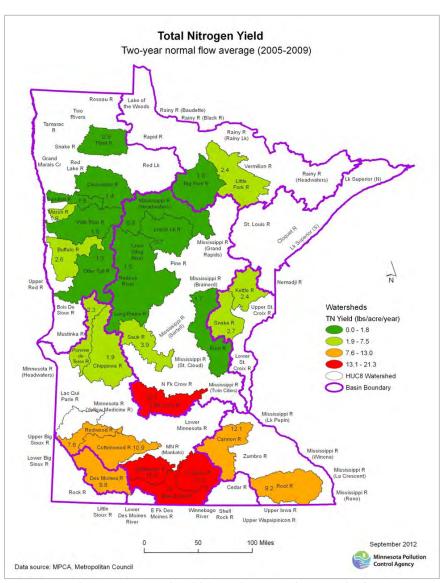


Figure 7. Total nitrogen annual yield from the 28 study watersheds. Monitoring and yield calculations conducted by the MPCA and Metropolitan Council.

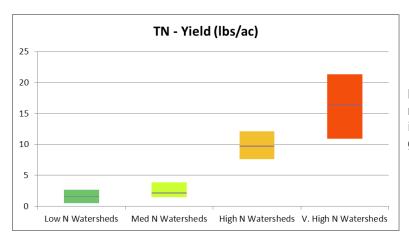


Figure 8. The range (colored bars) and mean (dark line) TN yield for watersheds in each of the four river N level groupings listed in Table 3.

#### Graphical depictions of watershed land characteristics with nitrogen levels

The range of watershed characteristics for each of the four stream N level categorizations (as listed in Table 3) are shown in Figures 9 to 21. Each bar in these figures represents the range in land use for watersheds assigned to that stream N level category, and the dark line in the middle of the colored bars represents the average of watersheds grouped in each category.

**Note:** The following results were not used in any way for estimating N source contributions in Section D of this report. The N source assessment uses a completely different approach which does not include statistical relationships between land characteristics and monitoring results.

#### Forest and grasses

The average percent of watershed land area in forest and grasses is inversely related to the watershed N level, yet there is overlap in the ranges of land percentages in forest and grass among the four categories (Figure 9). The low N watersheds have between 15% and 71% of land in forest and grassland, with a mean of 53%. In contrast, the very high N watersheds have 3% to 15% of their land in forest and grasses, with a mean of 7%.

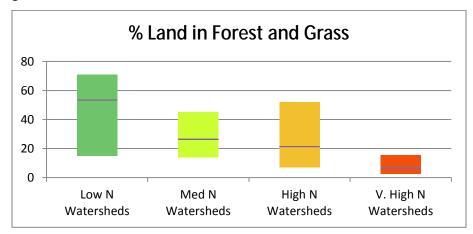


Figure 9. The range (colored bars) and mean (dark line) percent of land in forest and grasses for watersheds classified under each of the four river N level groupings (as listed in Table 3).

#### **Human population**

The range in human population densities among the four categories of N level watersheds does not show any definitive patterns (Figure 10), suggesting that differences in human population among the studied watersheds is not a major factor influencing water N ranges in the studied watersheds. Note, however, that the watersheds with major urban centers, such as the Twin Cities, Rochester, or Duluth, did not meet the watershed selection criteria and are not included among the watersheds assessed within this chapter. It is possible that if the evaluated watersheds had included larger urban areas that an effect from high human population centers would be observed.

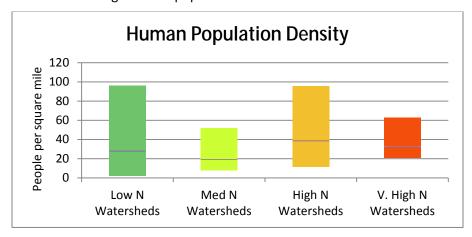


Figure 10. The range (colored bars) and mean (dark line) human population density for watersheds classified in each of the four river N level groupings (as listed in Table 3).

#### Irrigated agriculture

Differences in stream N levels did not appear to be closely associated with low or high percentages of the watershed under irrigation. The highest average percentage of land under irrigation was in the medium N watershed category (Figure 11). While irrigated fields could contribute N to localized surface waters, the total amount of irrigated acreage was less than 9% in all watersheds and was, therefore, not a dominant land use in any of the studied watersheds. Irrigation does not appear to be an important factor affecting the very high N level watersheds, as these five watersheds each had less than 1% of the land in irrigated agriculture.

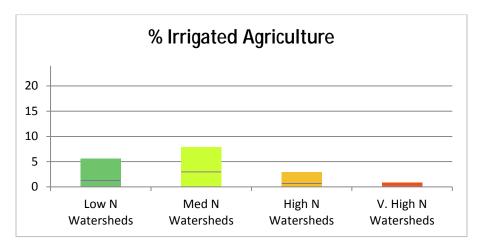


Figure 11. The range (colored bars) and mean (dark line) percent of land under irrigated agricultural production for watersheds in each of the four river N level groupings (as listed in Table 3).

#### Soil organic matter

Soil organic matter ranges and means were highest in the watersheds with the lowest surface water N levels, followed by the medium N watersheds (Figure 12). The high soil organic matter in the low N watersheds is likely attributable to the abundance of wetland and peat soils common in the northern part of the state where river N levels are low. The high and very high N watersheds had the lowest percent soil organic matter. Soil organic matter is one source of N to waters, but is transported to waters most readily when converted to mobile N forms through a mineralization process affected by temperature, soil moisture, and soil oxygen.

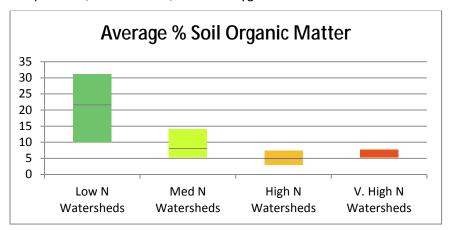


Figure 12. The range (colored bars) and mean (dark line) of the spatial average soil organic matter (%), in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### Wetlands

The average percent of watershed land in wetlands is inversely related to river N levels (Figure 13). The high and very high river N watersheds have an average of about 3% of the watershed area in wetlands. The mean percent of land with wetlands increases to 8% and 29% in the medium and low N watershed categories, respectively. Wetlands remove considerable amounts of nitrate. However, the low N in watersheds with more wetlands is not necessarily attributable to the wetlands, since these same watersheds also have different land use, soils, and land cover as compared to the higher N loading watersheds.

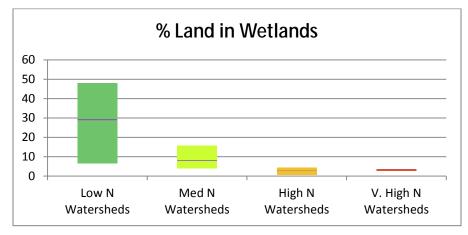


Figure 13. The range (colored bars) and mean (dark line) of the percentage of land with wetlands, in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### **Small grains**

The watersheds with the most land in small grain production had low to medium N levels (Figure 14). The small grains are often grown in areas where soils and climate are less suitable for row crop production and, therefore, we cannot directly attribute small grains as a cause of high or low nitrate. Rather, we can only note that our high N watersheds are those with relatively low percentages of land planted to small grains.

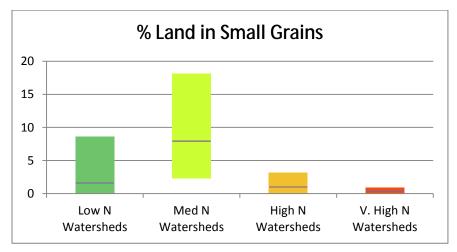


Figure 14. The range (colored bars) and mean (dark line) of the percentage of land in small grain production in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### **Precipitation**

Average annual precipitation was slightly lower in the low and medium N category watersheds as compared to the high and very high N watersheds (Figure 15). However, there is considerable overlap in precipitation levels among the four N categories.

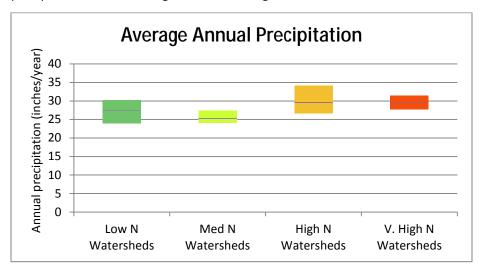


Figure 15. The range (colored bars) and mean (dark line) of the 30 year annual precipitation in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### Land in row crops over sandy soils

The medium, high, and very high N watersheds each had similar percentages of land in row crop over sandy soils (Figure 16). The "low" river N watersheds had a lower fraction of land in row crop in general, and similarly had a lower percentage of row crops over sands as compared to the other watershed categories.

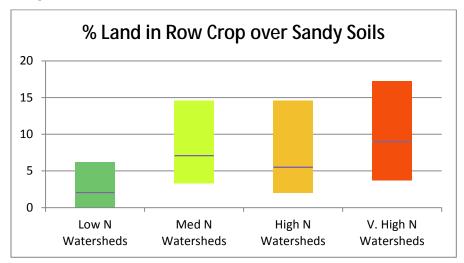


Figure 16. The range (colored bars) and mean (dark line) of the percentage of land in row crops over sandy subsoils, in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### Land in row crops over shallow bedrock soils

The high and very high river N watersheds each had a couple of watersheds in regions with over 5% of the land having shallow depth to bedrock combined with row crop production. The low and medium N level categories did not have appreciable land with row crop over shallow depth to bedrock (Figure 17).

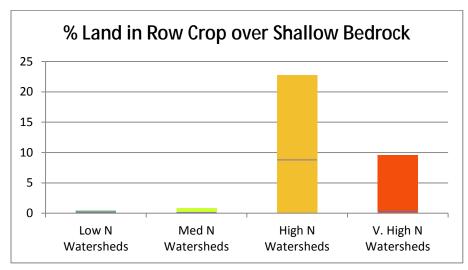


Figure 17. The range (colored bars) and mean (dark line) of the percentage of land in row crops over shallow depth to bedrock soils, in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### **Animal density**

The mean watershed livestock density increases from 20 animal units (AU) per square mile in low N watersheds to 225 AUs per square mile in very high N watersheds (Figure 18). An AU is a measure used in feedlot regulations to approximate manure from a 1,000 pound beef cow. One AU represents 56 turkeys, or 0.7 dairy cows, or 3.3 finishing swine. The pattern in Figure 14 does not necessarily mean that livestock is a significant source of N in surface waters since livestock are concentrated in areas where other N sources, such as fertilizer, are also added to soil.

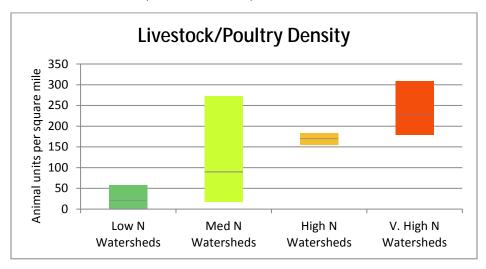


Figure 18. The range (colored bars) and mean (dark line) livestock and poultry AU density in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### **Row crops**

The mean percent of watersheds in row crop production increases from about 5% in low N watersheds, to 39% in medium N watersheds, to 60% in high N watersheds, and 76% in very high N watersheds. Row crops are often located in areas that also have tile drainage and animal agriculture production. Therefore, we cannot conclude from this assessment that row crops are the key explanatory variable for stream N levels; rather it appears that row crops directly correlate with N levels in the watersheds used for this analysis.

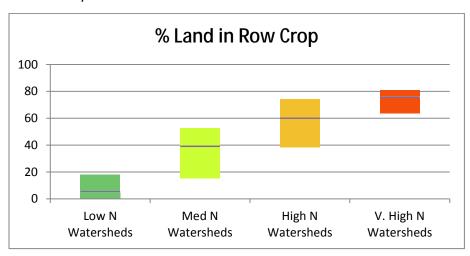


Figure 19. The range (colored bars) and mean (dark line) percent of land in row crop production for watersheds classified under each of the four river N level groupings (as listed in Table 3).

#### Tile drainage estimates

The relationship between watershed N level categories and percent of estimated tile-drained land (Figure 20) has a similar pattern as percent under row crop production. The mean percent of watershed with estimated tile-drained land is 0.2% in low N watersheds, 5% in medium N watersheds, 22% in high N watersheds, and 42% in very high N watersheds. The similarity between the row crop and tile drain variables is not unexpected because the criteria used to estimate tiled lands includes row crop production together with certain slope and soil conditions; thus, these variables are not independent of each other.

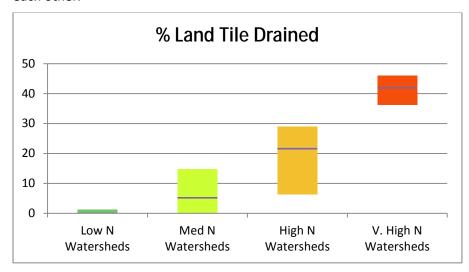


Figure 20. The range (colored bars) and mean (dark line) percent of land estimated to be tile-drained in watersheds classified under each of four river N level groupings (as listed in Table 3).

#### Row crops over leaky soils

The most distinct pattern observed between watershed N levels and land characteristics was with percent of row crop land in the watershed over leaky soils. "Leaky soils" included estimated tile-drained lands, sandy soils/subsoils, and shallow depth to bedrock (Figure 21). The four watershed N level categories each had a distinct and narrow range of percent row crop over leaky soils.

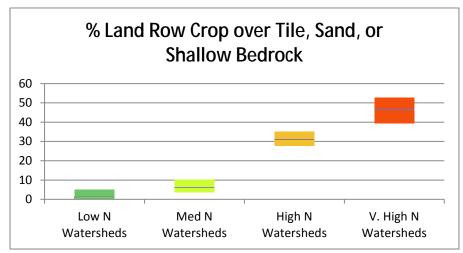


Figure 21. The range (colored bars) and mean (dark line) percent of land in row crops underlain by either tilelines, shallow bedrock or sandy subsoils, in watersheds classified under each of four river N level groupings as listed in Table 3.

#### Patterns from graphs

The patterns of watershed characteristics associated with the low to very high river N levels do not show any inconsistencies with the UMN/MPCA source assessment described in chapters D1 to D4, and instead show several relationships which are generally consistent with the findings of the UMN/MPCA source assessment. A statistical analysis using this information is presented in the following section.

The Low N watersheds are characterized by having relatively high wetlands, high soil organic matter, high forest and grass-lands, and low row crop, low tile drainage, and low animal density. The very high N watersheds are characterized by having relatively low wetlands, low forest and grass, low small grain crops, and high row crop, high tile drainage, and high animal density.

# Statistical assessment of watershed characteristics and river nitrogen

#### Methods

We used ordinary least squares (OLS) multiple linear regression analysis to examine relationships between four dependent variables and a set of 18 explanatory variables. Our four dependent variables were nitrite+nitrate (nitrate) flow weighted mean concentration (NOx FWMC), TN FWMC, nitrate yield (NOx Yield) and TN yield (TN Yield). Our 18 explanatory variables and their data sources are listed in Table 1. We considered many combinations of explanatory variables in an attempt to find the strongest regression models for each dependent variable. Scatter plots were examined using all combinations of dependent and explanatory variables. In cases where we found linear relationships (e.g., row crops and NOx FWMC), the explanatory variables were included in preliminary regression models. Where relationships were non-linear, we used logarithmic and exponential transformations with the explanatory variables, and included the transformed variables in the preliminary models (e.g., forest/ shrub and NOx FWMC). Explanatory variables that had strong correlations with dependent variables were considered to be the best candidates for the preliminary regression models. We used tests of statistical significance for explanatory variables, statistical significance of overall models, distribution of model residuals, variable inflation scores (VIF) that measure variable collinearity, Akaike's Information Criterion (AIC) scores that measure overall model fit, and R-squared values to evaluate the strength of each preliminary regression model (Quinn and Keough 2002).

A number of the explanatory variables that we initially considered to be good candidates for inclusion in the final models were not statistically significant in the regression analysis. These included percent of watershed with forest and shrub; pasture, grass and hay; wetlands; human population density; livestock and poultry density; small grain cultivation; irrigated agriculture; and soil organic matter. Other explanatory variables were statistically significant in the analysis but were highly correlated with other explanatory variables, as indicated by high VIF scores. These included row crops, row crops over shallow depth to bedrock (RCD), row crops over sandy soils (RCS), row crops over shallow depth to bedrock or sandy soils or tile drains (RCDST), row crops not over shallow depth to bedrock, sandy soils or tile drain (RCnDST), and tile drained areas. After completing this exploratory analysis we selected the strongest statistically significant models for each dependent variable.

#### Results

Equations for the final models are listed in Table 4 and results from the statistical tests are included in Table 5. The final models for each of the four dependent variables were statistically significant at the p < 0.01 level. All explanatory variables were statistically significant at the p < 0.01 level. All four models had high R-squared values, each over 0.9. And each model had a comparatively low AIC score; a lower AIC score indicates a stronger model fit. VIF for each model were below an acceptable threshold of 7.5 indicating that collinearity among explanatory variables was not significant. Jarque-Bera tests indicated that model residuals were normally distributed for all four models (ESRI 2012). This result suggests that the models are unbiased and that they capture the critical explanatory variables. Koenker tests for each model indicated that the model relationships exhibited stationarity or consistency across geographic space. Global Moran's Index tests confirmed a random spatial distribution of model residual for the NOx and TN FWMC models; however, the Global Moran's Index tests for the NOx and TN yield models showed statistically significant spatial autocorrelation in the residuals. This result is in contrast to the results from the Jarque-Bera and Koenker tests cited above. Spatial autocorrelation in model residuals indicates spatial clustering of high and low values, and suggests that the model is predicting well in some parts of the study area and not as well in others; this is usually caused by important explanatory variables being absent from the model, or non-stationarity in the model (ESRI 2012). We felt that the models did include the important explanatory variables, so we used geographically weighted regression (GWR), a method that specifically addresses non-stationarity, to determine whether non-stationarity was the cause of the spatial autocorrelation.

Geographically weighted regression calculates explanatory variable coefficients for each feature in the model, based on a set of neighboring features within a specified search radius, rather than the full dataset as in OLS, and thus allows model relationships to vary across space. We used a fixed distance search radius calculated by ArcGIS to be the optimal distance for model development based on model AIC scores (ESRI 2012). The calculated search distance was 91.18 miles. We ran GWR with the NOx and TN yield models, and then ran Global Moran's Index tests on the GWR results. The Moran's Index for these models showed random spatial distribution of residuals, results that suggest non-stationarity was the issue with our original OLS models and the issue was resolved by using GWR. These results also indicate that the GWR models predict well across the study area and that the models are well specified and include the important explanatory variables. The GWR also gave lower AIC scores and higher R-squared when compared with the OLS models, suggesting a better fit with GWR for the NOx yield and TN yield models. We also tested the GWR with the NOx FWMC and TN FWMC but in both cases our AIC scores increased and R-squared values decreased compared to our original OLS results, suggesting that for the FWMC models, the GWR does not represent an improvement over the OLS method.

Table 4. Multiple regression equations for nitrite+nitrate-N flow weighted mean concentrations in mg/I (NOx FWMC); nitrite+nitrate-N yield in lbs/acre (NOx Yield); TN flow weighted mean concentration in mg/I (TN FWMC); and TN yield in lbs/acre (TN Yield). Explanatory variables include estimated percent of land with tile drain in the watershed (TD), percent row crop with shallow depth to bedrock or sandy soils (RCDS), and 30-year average precipitation. Explanatory variables were scaled to have a mean of 0 and standard deviation of 1 (method: ((value - mean) / standard deviation) and, therefore, these equations cannot be used for prediction with data not included in the original dataset.

Regression equations	Model	
(0.13) (0.14) (0.14)	Standard Errors	
NOx FWMC = 2.98 + 2.98 TD + 0.66 RCDS	OLS	
(0.29) (0.33) (0.29)	Standard Errors (mean values)	
NOx Yield = 2.41 + 3.93 TD + 1.42 Precipitation 30 year average	GWR (mean values)	
(0.13) (0.14) (0.14)	Standard Errors	
TN FWMC = 4.33 + 3.24 TD + 0.66 RCDS	OLS	
(0.39) (0.44) (0.39)	Standard Errors (mean values)	
TN Yield = 4.08 + 4.22 TD + 1.76 Precipitation 30 year average	GWR (mean values)	
Acronyms		
Tile Drainage	TD	
Row crops over shallow depth to bedrock or sandy soils	RCDS	
Ordinary Least Squares Regression	OLS	
Geographically Weighted Regression	GWR	

Table 5. Model parameters and test results

	NOx FWMC	NOx yield	TN FWMC	TN yield
Sample size	28	28	28	27
Adjusted R-squared	0.96	0.98	0.97	0.98
AIC	63.48	73.12	65.15	85.44
Model p-value	< 0.01	< 0.01	< 0.01	< 0.01
VIF	1.22	1.26	1.22	1.29
Model	OLS	GWR	OLS	GWR
Moran's Index score	0.12	0.18	0.06	0.12
Moran's Index z-score	1.15	1.56	0.70	1.20
Moran's Index p-value	0.25	0.12	0.49	0.23
GWR Search Radius	NA	91.18 miles	NA	91.18 miles

#### Discussion

The N concentration models (NOx FWMC and TN FWMC) suggest that row crop practices using tile drainage and row crop practices on naturally sensitive lands with high groundwater recharge explain much of the nitrate concentration variability in the 28 Minnesota rivers. Sensitive lands in this context are defined as areas that have a depth to bedrock of less than 50 feet, or sand content in the subsoil greater than 85%, or both. The N yield models (NOx Yield and TN Yield) suggest that N yields in the 28 watersheds are influenced largely by row crop practices using tile drainage and by precipitation. That

precipitation is a significant explanatory variable in the yield models is not surprising since yield (pounds/acre/year) for any chemical parameter is affected by river flow, which, in turn, is largely influenced by precipitation.

We scaled the explanatory variable data to have a mean of zero and a standard deviation of one, so that a comparison of the relative strength of the variable coefficients in influencing N level variability would be possible. As shown in the concentration equations in Table 4, the influence of the estimated tile drain variable on nitrate has four and half times the magnitude of the influence of the RCDS variable, and for TN tile drainage has almost five times the magnitude of influence as RCDS. In the yield equation for nitrate, the estimated tile drain variable has nearly three times the influence of the precipitation variable, and for TN yield it has more than two times the influence. These coefficient values suggest that the amount of watershed land in tile drainage is the leading predictor of river nitrate and TN concentrations and yields.

In addition, the GWR analysis for the N yield models showed specific spatial trends in the model relationships, as indicated by the variance in the explanatory variable coefficients. Specifically, the model coefficients for estimated percent of watershed with tile drainage, and mean annual precipitation are higher in southern Minnesota than in the northern half of the state (Figures 1-4). This result suggests that with higher amounts of tile drainage and precipitation in the study watersheds, these explanatory variables have increased influence on levels of nitrate and TN yield in corresponding rivers.

Maps showing the spatial pattern of explanatory variables in the regression models are included in Appendix E2-1. Maps showing the GWR coefficients for explanatory variables in the NOx and TN yield models are included in Appendix E2-2. And scatter plots showing relationships between dependent variables and the explanatory variables in the regression models are included in Appendix E2-3.

# Summary

The strong correlation between estimated tile drained lands and high nitrate and TN yields and FWMCs is generally consistent with the UMN/MPCA source assessment findings (Chapters D1-D4) showing tile drained cropland as the largest contributor to N loads in the state. The source assessment showed that cropland groundwater was the second highest N source/pathway. This is somewhat consistent with the statistical modeling results showing that cropland over potentially high groundwater recharge lands (shallow bedrock and sandy soils) was another important variable correlated with nitrate and TN FWMCs. The cropland over shallow bedrock and sands variable was not, however, found to be a key explanatory variable affecting nitrate or TN yield in the best statistical models.

The UMN/MPCA N source assessment also showed that loads/yields are highly dependent on precipitation. This is generally consistent with the best statistical models for N yield, which showed that average annual precipitation in the watershed was the second most important variable after tile drainage affecting variability in watershed nitrate and TN yields. Future analyses should assess whether groundwater recharge, integrating precipitation and geologic sensitivity, over cropland is correlated with nitrate and TN yield.

As noted earlier, the statistical analyses do not show causes, but relationships. The multiple regression analyses, along with the single variable graphs and scatter plots, did not show results that are inconsistent with the source assessment findings, and there were several relationships which supported the source assessment findings.

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# E3. Other Studies of Nitrogen Sources and Pathways

A review of published literature related to nitrogen (N) sources was conducted to see how other study results compared with the N source assessment findings reported in Chapters D1-D4 (UMN/MPCA Source Assessment). This chapter discusses the findings of the other studies, which is the fifth way we compared the UMN/MPCA source assessment findings with other information (the other four approaches are discussed in Chapters E1 and E2). For this review, we focused mostly on watershed or larger scale studies in Minnesota and the upper Midwest, but also included conclusions from a national study by the U.S. Geological Survey (USGS) to provide broader context.

# A national U.S. Geological Survey assessment

In its recently published summary of water quality in 51 hydrologic systems across the nation, the U.S. Geological Survey (USGS) concluded that human impacts are the primary reason for elevated N in United States surface waters (Dubrovsky, et al., 2010). The study also found:

- 1. Low N levels where land use is dominated by non-urban and non-agricultural land uses
  - Background concentrations were 0.24 mg/l for nitrate-N, 0.025 mg/l for ammonia+ammonium-N and 0.58 mg/l for total nitrogen (TN). These numbers were determined from 110 stream sites across the country which had less than 5% urban and less than 25% agricultural land. The 75<sup>th</sup> percentile of the flow weighted mean concentrations was determined to represent the background concentration.
  - "Nutrient concentrations in streams and groundwater in basins with significant agricultural or urban development are substantially greater than naturally occurring or "background" levels."
- 2. Nitrogen levels are elevated in agricultural and/or urban dominated watersheds
  - Concentrations of nitrate, ammonia, and TN exceeded background levels at more than 90% of 190 streams draining agricultural and urban watersheds.
  - Concentrations of TN were higher in agricultural streams than in streams draining urban, mixed land use, or undeveloped areas. Yet the amounts of N lost from watersheds to streams (expressed as mass per unit area) increased with increasing nutrient inputs regardless of land use.
  - Elevated concentrations of nitrate mostly occurred in streams that drain agricultural watersheds where the use of fertilizers and/or manure is relatively high.
  - Nitrate-N concentrations exceeded the Maximum Contaminant Level (MCL) of 10 mg/l at 7.3% of stream samples draining urban land, 28.1% of streams draining agricultural land uses and 5.3% of streams draining mixed land-use settings; whereas none of the samples from streams draining undeveloped land exceeded the MCL.
  - Most surface-water samples with nitrate concentrations exceeding the MCL were collected from small streams in the corn belt region.

# A Minnesota U.S. Geological survey study

Using data collected between 1984 and 1993, the USGS conducted an in-depth study of stream nutrients in large parts of Minnesota, including the southern half of the Mississippi River Basin; the Cannon and Vermillion River watersheds, and the St. Croix River Basin in Minnesota and Wisconsin (Kroening and Andrews, 1997).

The percentages of N added to the land (and water for wastewater additions) in the study area from different sources was estimated to be as follows:

- Fertilizer 49%
- Manure 23%
- Nitrogen fixation 15%
- Atmospheric deposition 11%
- Municipal wastewater treatment plants 2%

Nitrate-N concentrations in the tributaries to the Mississippi River were found to be significantly greater in streams draining agricultural lands, as compared to streams draining forested or mixed forest and agriculture areas. Median concentrations in agricultural areas ranged from 2.0 to 5.3 mg/l, and were 0.2 to 0.6 mg/l in mixed forest and agriculture, and 0.05 to 0.1 mg/l in forested areas.

Nearly 11% of the added N was found to be exported to streams. Note that soil mineralization was not included as an added source in the Kroening and Andrews study. If soil mineralization is added to the list of N sources, the percent of inputs lost to waters in this USGS study would be reduced.

# Iowa nitrogen budget

While lowa land uses and characteristics are somewhat different than Minnesota's, there are also many similarities, including population density (66 and 54 people per square mile in Minnesota and Iowa, respectively); cropland acreages (22 and 26 million acres in Minnesota and Iowa, respectively); same average farm size (331 acres); and both states with a large fraction of the corn, soybean, and livestock production in the United States. Therefore, we would expect to see somewhat similar fractions of N inputs and outputs from the various sources and exports in the two states.

Inputs and outputs of N were estimated for Iowa by Libra et al. (2004). Iowa N budget data represent an average year between the period of 1997-2002. Stream load estimates were based on monthly monitoring between 2000-2002 at 68 major watersheds that covered 80% of the state.

Inputs of N to the state total about four million tons per year or about 216 pounds per acre. Estimated annual average N inputs to individual watersheds ranged from 143 to 347 pounds per acre. The inputs in lowa, expressed as a percent of total inputs, compared similarly to Minnesota estimates (Table 1). Point sources account for about 8% of the stream N loads statewide in lowa, varying from 1% to 15% for individual watersheds. In Minnesota, point sources were estimated to account for 9% of the N inputs during an average precipitation year. In both states, soil N mineralization and N fertilizer were the two highest N inputs.

The outputs in Iowa were also similar to Minnesota outputs (Table 2). Iowa streams discharged about 200,000 tons of N during the relatively dry 2000-2002 period, an amount equivalent to 11 pounds per acre annually. This represents about 5% to 7% of the inputs. For Minnesota, the amount of N inputs estimated to reach streams was similar to Iowa, with about 6% of N reaching waters during average precipitation conditions. Crop harvest accounted for more than half of the N outputs in both states.

Table 1. Nitrogen inputs to land in Iowa compared to the relative inputs to land in Minnesota. Iowa estimates are from Libra et al. (2004). Minnesota estimates are from Chapters D1 to D4 of this report.

Input source	Inputs (tons of N Iowa)	lowa Percent of total inputs	Minnesota Percent of total inputs	
Fertilizer	984,000	25%	30%	
Legumes	762,000	20%	14%	
Wet Deposition	363,000	9%	4%	
Soil N	1,014,000	26%	38%	
Manure	493,000	13%	10%	
Human	16,000	<1%	<1%	
Dry Deposition	254,000	7%	4%	
Industry	2800	<1%	<1%	
Total	3,888,000			

Table 2. Nitrogen outputs for Iowa compared to the outputs in Minnesota. UMN/MPCA outputs did not include soil N storage, and therefore to allow direct comparisons the relative output percentages for Iowa were recalculated without soil N storage included. Iowa estimates are from Libra et al. (2004). Minnesota estimates are from Chapters D1 to D4 of this report.

Output categories	Outputs (tons of N)	lowa percent of total outputs	lowa percent of total if soil N storage not included	Minnesota percent of total outputs
Harvest	1,565,000	40%	53%	
Grazing	172,000	4%	6%	63%
Crop Volatilization	353,000	9%	12%	15%
Soil N (storage)	1,014,000	26%	-	-
Manure Volatilization	249,000	6%	8%	
Fertilizer Volatilization	17,000	<1%	1%	6%
Denitrification	413,000	10%	14%	10%
Waters	198,000	5%	7%	6%
Total	3,981,000			

# Assessing nitrogen sources in Iowa watersheds

Similar to the Minnesota source estimate conclusions, several studies of large Iowa watersheds concluded that agricultural nonpoint sources accounted for the majority of nitrate reaching streams. Modeling of the Raccoon River in Iowa using the Soil and Water Assessment Tool (SWAT model) indicated that 92% of the nitrate loading was from agricultural nonpoint sources (Jha et al., 2010).

The Des Moines River Basin covers 6,245 square miles and has nitrate concentrations near Des Moines, lowa, ranging from 0.5 to 14.5 mg/l, exceeding the 10 mg/l maximum contaminant level (MCL) 16.4% of the time between 1995 and 2005. Nitrate yield from the subbasins ranged from 3.2 to nearly 54 pounds/acre, averaging 13.9 pounds/acre. Nearly 40% of the subbasins had nitrate losses greater

than 13.3 pounds/acre. Modeling of the Des Moines River Basin in Iowa (and part of southern Minnesota) using the SWAT model indicated that nitrate loading to streams was dominated by agricultural non-point source pollution, affecting 95% of the loading (Schilling and Wolter, 2010). The authors concluded that the greatest influence on nitrate concentrations in this intensively agricultural landscape was fertilizer application. Animal and human waste contributed about 7% and 5% of the nitrate export in streams, respectively. By completely eliminating manure sources, modeled nitrate concentrations in waters were reduced by 7.3%. Elimination of human waste resulted in an estimated 4.8% nitrate reduction.

# Row crops – correlation to stream nitrate

Schilling and Libra (2000) found a direct linear correlation (p<0.0003) between the percent of row crops in lowa watersheds and average stream nitrate concentrations. By comparing stream nitrate levels with row crop production acreage in 25 lowa watersheds, the authors concluded that mean annual stream nitrate-N concentrations in lowa watersheds can be approximated by multiplying the percentage of land in row crops by a factor of 0.11.

In eastern Iowa (Cedar, Iowa, Skunk, and Wapsipinicon River Basins), Weldon and Hornbuckle (2006) found that in addition to row crop density, feedlot animal unit density was correlated to stream nitrate concentrations.

Watkins et al. (2011) examined stream N concentrations in 100 southeastern Minnesota sampling sites (Figure 1) to see if there was a similar relationship as found in Iowa between percent of land in row crops and stream nitrate levels during periods expected to represent baseflow conditions. Most samples were taken during a minimum of four years at each site, however some sites in the Root River Watershed had less than four years of sampling. In the study area, where relatively few human or urban waste sources exist, the investigators observed a linear relationship between watershed row crops and nitrate levels (Figure 2). The slope of the regression line would suggest that stream baseflow nitrate-N concentrations in non-urban parts of southeastern Minnesota can be approximated by multiplying the percentage of land in row crops by 0.17. The regression analysis indicated that when about 60% or more of the watershed is in row-crop production that the baseflow nitrate-N concentration would be expected to exceed 10 mg/l. The study suggested that nitrate concentrations are essentially zero when there are no row crops in the subwatersheds of this part of Minnesota. Regression analysis studies can show correlation, but not necessarily cause and effect. The investigation showed that other factors besides row crop acreages can affect nitrate concentrations. One stream monitoring point impacted by municipal wastewater discharges showed higher nitrate concentrations (14 mg/l) compared to other sites with similar row crop acreages, and was therefore an outlier in Figure 2.

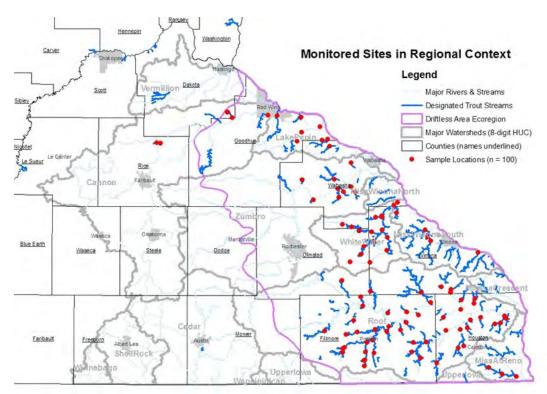


Figure 1. Stream site locations in southeastern Minnesota where samples were taken and analyzed for nitrate-N. From Watkins et al. (2011).

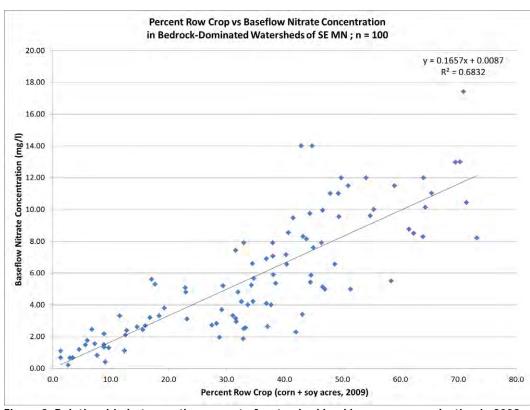


Figure 2. Relationship between the percent of watershed land in row crop production in 2009 and the nitrate-N concentrations of southeastern Minnesota streams during periods of time when stream flow is all or mostly groundwater baseflow (from Watkins et al., 2011).

# Tile drainage impacts

David et al (2010) found that N fertilizer and artificial drainage explained most of the variation in stream N loadings, while examining relationships between stream N loads (winter-spring) and land uses in 153 watersheds across the Upper Mississippi River Basin. The greatest N yields to rivers corresponded to the highly productive tile-drained corn belt from southwest Minnesota across lowa, Illinois, Indiana, and Ohio. Human waste explained 7% of the variability and animal manure was not a significant explanatory variable affecting stream N loads in this large scale study.

Kronholm and Capel (2013) examined nitrate in 16 watersheds located in seven states, including three midwestern states. They found that the highest nitrate yielding watersheds were those which had a dominant flow pathway of subsurface tile drainage. Watersheds dominated by groundwater or surface runoff flow pathways had much lower nitrate levels.

While it is widely acknowledged that artificial tile drainage exerts a large influence on river nitrate loading in the Midwest, Nangia et al. (2010) concluded that the amount of N leaving each field in a given year varies with climate. Substantial year to year nitrate loading variability was found in a heavily drained Minnesota watershed which received varying precipitation amounts.

#### Groundwater contributions to stream nitrate

Similar to the findings of the UMN/MCPA Minnesota N source assessment, other studies have shown that groundwater baseflow is an important pathway for N entering surface waters, particularly in areas with minimal agricultural tile drainage.

Groundwater baseflow is generally considered to be the portion of stream flow that represents longer term groundwater discharge from underground watershed storages, which typically moves slowly and continuously into streams, even during periods of reduced precipitation. Some use the term "baseflow" to refer to all portions of the streamflow that are not partitioned or separated from surface runoff and quick-flow groundwater in the stream hydrograph (Spahr 2010). Under this second definition, a portion of tile drainage flows can show up in the "baseflow" part of the stream hydrograph, due to the lag time between the storm event and when infiltrating waters reach tile lines and surface waters.

In a study of stream nutrients from around the United States, baseflow was found to contribute a substantial amount of nitrate to many streams (Dubrovsky et al., 2010). In two-thirds of the 148 studied streams, baseflow contributed more than a third of the total annual nitrate load. These findings are based on data from streams that drain watersheds less than 500 square miles. The researchers found less baseflow influence in areas of the Midwest that are heavily tile-drained, similar to the source/pathway assessment findings by the UMN/MPCA in Chapters D1 and D4 of this report.

Tesoriero et al. (2009) examined nitrate flow pathways in five aquifer and stream environments across the United States., including one Minnesota stream (Valley Creek). As the proportion of stream flow derived from baseflow increased, nitrate concentrations also increased. They concluded that the major source of nitrate in baseflow dominated streams was groundwater; and rapid flow pathways (i.e. tile lines) were the major source of N in streams not dominated by baseflow. Another finding of the study was that baseflow does not enter the stream uniformly, but rather through preferential flow paths in high conductivity stream-bed sediments (i.e. sands) or as bankside seeps or springs.

In eastern Washington County, Minnesota, two studied creeks had over 90% of the nitrate load delivered during non-storm event periods (SCWRS, 2003). Groundwater was determined to be the major source of N to the creeks, and the difference in N yields between the two creeks was attributed to differing groundwater nitrate concentrations.

While groundwater baseflow often contributes a substantial part of N loads to streams, not all of the nitrate entering groundwater ends up in streams. Recharge rates of nitrate to groundwater beneath the land are commonly greater than discharge rates of nitrate in nearby streams (Böhlke et al., 2002). Part of the reason is that it can take months to years before the nitrate that leaches to groundwater is transported into streams; and therefore groundwater can continue to contribute nitrate to streams long after all nitrate sources are removed (Goolsby, Battaglin et al. 1999; Tesoriero et al. 2013). Additionally, nitrate can be reduced through denitrification as it flows within groundwater toward streams.

Dubrovsky et al. (2010) concluded that the amount of N in baseflow depends, in part, on how much of the baseflow is coming from deep aquifers and how much is coming from shallow ground waters. Deep aquifers usually contain water with lower concentrations of N than shallow aquifers because of several reasons: (1) it takes a long time—decades or more, in most cases—for water to move from the land surface to deep aquifers (resulting in long residence times for groundwater and any solutes, like nitrate, it may contain); (2) long travel distances increase the likelihood that nutrients will be lost through denitrification; (3) protective low-permeability deposits (which inhibit flow and transport) may be present between the land surface and deep aquifers; and (4) mixing of water from complex flow paths over long distances and time periods tends to result in a mixture of land-use influences on the chemical character of deep groundwater, including contributions of nutrients from areas of undeveloped lands where concentrations are generally lower than those from developed lands.

Groundwater baseflow was found to be an important contributing pathway in several additional studies, especially in areas not dominated by tile line flow. Using data collected between 1984 and 1993, the USGS conducted an in-depth study of stream nutrients in large parts of Minnesota, including the southern half of the Mississippi River Basin; the Canon and Vermillion River watersheds, and the St. Croix River Basin in Minnesota and Wisconsin (Kroening and Andrews, 1997). Nitrate concentrations in the Minnesota River near Jordan, and the Straight and Cannon Rivers in southeastern Minnesota, were found to be greatest in the spring and summer months, when precipitation, runoff, and tile-line flows are typically highest. However, for much of the rest of the study area, nitrate concentrations were greatest in the winter months when stream flow is dominated by groundwater baseflow.

Burkhart (2001) found an association between base flow contributions of nitrate to streams and the permeability of soils and underlying bedrock. The USGS report stated "nitrate loads from base flow were significantly lower (contributing about 27% of total stream nitrate load) in streams draining landscapes with less permeable soils and bedrock than in those draining landscapes with permeable soils and (or) bedrock (contributing 44% to 47% of the total stream nitrate load)."

Other studies have also shown that soil and bedrock permeability affects nitrate levels in water. In a small Wisconsin karst landscape watershed largely under row crop land uses, 80% of nitrate loadings to streams came from groundwater baseflow (Masarik, 2007). Nitrate-N ranged from 4.7 to 23.5 mg/l in the Fever River watershed. In this highly permeable setting of loess soils over fractured carbonate bedrock, baseflow was found to be the dominant pathway of N to surface waters.

The nitrate loading due to baseflow into two south-central lowa streams in a non-karst watershed with relatively shallow soils were also found to be high, and accounted for 61% to 68% of nitrate loads in Walnut Creek and Squaw Creek watersheds, respectively (Schilling, 2002). Bedrock in the Iowa study is overlain by 20 to 100 feet of soil, in a rolling naturally well-drained landscape.

Schilling et al. (2000) also found that karst watersheds showed higher nitrate than would be expected based on land use influences only. They postulated that this was due to less surface runoff, and alternatively more water going down through the soils into groundwater and coming out as baseflow and springs. Baseflow typically has higher nitrate concentrations than the surface runoff. Sauer (2001) noted that low soil and bedrock permeabilities do not necessarily translate to low nitrate in streams, particularly in areas where tile drainage occurs. In tiled lands, nitrate concentrations in streams are typically elevated, even though the natural permeability of the soil is low.

#### Conclusions

Other studies of N sources and pathways to surface waters found:

- Agricultural lands, and to a lesser degree urban lands, are the dominant contributors to N in waters, especially where N inputs are high (i.e. fertilizers or manure applied to row crops).
- Tile drainage is the major pathway where agricultural lands have subsurface drainage.
- Groundwater baseflow is a major pathway in non-tiled cropland, and its effects are particularly important in areas with more highly permeable soils such as karst geology and sandy soils.
- · Surface runoff is a relatively minor pathway for N in watersheds with high N loads.

These findings are consistent with the conclusions reached in the Minnesota N source assessment (Chapters D1-D4).

lowa's N source assessment provides a similar breakdown of N source contributions and outputs, as compared to estimates of N contributions to soils in Minnesota.

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# F1. Reducing Cropland Nitrogen Losses to Surface Waters

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Minnesota is one of a dozen states in the Mississippi River Basin developing a state-level action strategy to achieve and track measureable progress for reducing point and nonpoint nutrient losses. The strategy is driven by a need to reduce Minnesota's contribution of nitrogen (N) and phosphorus pollution to downstream waters such as the Gulf of Mexico and Lake Winnipeg, as well as in-state nutrient reduction needs to protect and improve Minnesota waters from excess nutrients. The strategy, when complete, is expected to identify how far we are progressing with current programs and efforts, and identify ways to reach milestone goals and targets. Scientific assessments are being used to develop priorities, targets, monitoring strategies, and ways to use existing and new programs to continue making long-term progress in reducing nutrient losses.

The strategy development effort is designed to align goals, identify the most promising strategies, and ensure that collective activities around the state are working to achieve our goals. The strategy will be used by agencies and organizations to focus and adjust state-level and regional programs, and will be considered by watershed managers and local water planners to translate ideas and priorities into effective local best management practice (BMP) implementation. In support of the Nutrient Reduction Strategy development, Minnesota is examining recently completed reports and tools estimating N load reductions from BMP adoption. Findings from these efforts are described for cropland sources in this chapter and for wastewater point sources in Chapter F2. The primary purposes of these two chapters are to consider the level of N reduction that can be achieved by individual BMPs and combinations of BMPs adopted on lands suitable for the practices.

This chapter is organized in the following sequence:

- Nitrogen reduction from individual BMPs and conservation practices adopted on treated acreages (i.e. percent reductions on a single field with the applied BMP).
- Statewide adoption scenarios for single practices if adopted everywhere suitable for the practice in the entire state.
- Nitrogen reduction expected from adopting multiple practices on land suitable for each BMP. More specifically, the following are evaluated:
  - BMP adoption levels needed to achieve a 30% and 45% reduction from cropland sources statewide.
  - BMP adoption levels needed to achieve 15% and 25% reductions from cropland sources in representative HUC8 watersheds located in different regions of southern Minnesota.

Where possible, we compared Minnesota results with results developed by Iowa State University, which used a different analytical approach than the Minnesota work.

# Best management practices for nitrogen reduction

Best management practices and conservation practices are collectively referred to in this chapter as either "BMPs" or "Practices." Four documents developed in 2012-13 summarize the effects of agricultural BMPs for reducing N to waters: 1) Minnesota BMP Handbook; 2) Nitrogen Fertilizer Management Plan; 3) University of Minnesota literature review; and 4) lowa State University literature review.

#### Minnesota best management practice handbook

Miller et al. (2012) completed a Minnesota Agricultural Best Management Practice (BMP) handbook, which describes different BMPs and associated research findings concerning the effect that individual (BMPs) can be expected to have on reducing pollutants to surface waters, including N loads. The BMP Handbook can be found at:

www.eorinc.com/documents/AG-BMPHandbookforMN\_09\_2012.pdf

#### Nitrogen fertilizer management plan

The Minnesota Nitrogen Fertilizer Management Plan (NFMP) was written by the Minnesota Department of Agriculture. The NFMP describes and references Minnesota's cropland N BMPs for groundwater protection, as required and defined in Minn. Stat. 103H.151. Fertilizer management BMPs for groundwater protection are also important for protecting surface waters, since a large fraction of surface water N comes from groundwater and saturated soils below cropland (see Chapters D1 and D4). While the NFMP focusses on groundwater protection, widespread adoption of the BMPs in the plan would be expected to result in considerable reductions of N into surface waters. The NFMP, which was still in draft at the time of this writing, can be found at

www.mda.state.mn.us/chemicals/fertilizers/nutrient-mgmt/nitrogenplan.aspx

#### Literature review by Fabrizzi and Mulla (2012)

Several BMPs can be used either individually or in combination with other BMPs to reduce N entering waters from cropland sources. Two recent efforts were specifically aimed at estimating effects of N BMPs on surface water protection from field studies and literature reviews. Each is described, starting with a Minnesota analysis, which is then followed by an lowa review.

Fabrizzi and Mulla (2012) conducted a literature review of the primary BMPs which can be used for reducing N from cropland (see Appendix F1-1). These BMPs were classified by the authors into three broad categories of BMPs: 1) Hydrologic, 2) Nutrient Management, and 3) Landscape Diversification (Figure 1).

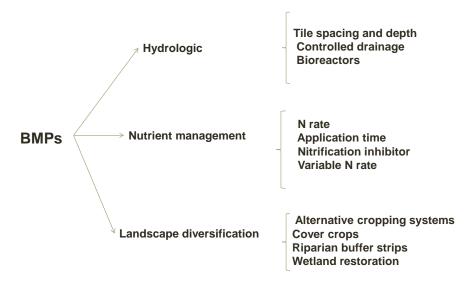


Figure 1. Categories of agricultural BMPs to reduce N loads as defined by Fabrizzi and Mulla (2012).

Table 1 shows the wide range in N reduction effectiveness from different BMPs. The results depend on many variables, such as climate, soils, research design, BMP design, baseline practices and conditions, etc. The wide range in N reductions shown in Table 1 is attributable to the fact that these results include findings from others states and from extreme climatic situations, and are not meant to represent average or typical removals. Lazarus et al. (2012) identified typical N removal percentages for these BMPs when implemented in Minnesota fields suitable for the individual BMP adoption. These results are shown in Table 1 as "N removal default in the NBMP spreadsheet." More information is provided on the NBMP spreadsheet later in this report, including background, assumptions, and how it can be downloaded from the Web.

Table 1. N reductions to waters in the tested/treated area as reported in a literature review by Fabrizzi and Mulla (2012) and compared with typical reduction rates used by Lazarus, Mulla et al., (2012) in the NBMP spreadsheet.

	Range in N reductions from literature review	N removal default in MN NBMP spreadsheet for treated areas	Notes for numbers with *
Tile depth and spacing	15-59%	NA	
Controlled drainage	14-96%	40%	
Bioreactors	10-99%	*13%	*Assumes 44% removal when fully treated, but only 30% of annual flow is treated
Reduced rates of application	11-70%	Varies by watershed and climate	
N application timing and inhibitors	10-58%	Varies by watershed and climate	
Wetlands	19-90%	50%	
Alternative cropping systems	5-98%	*95%	*Perennials replacing marginal land row crops
Riparian buffers	17-99%	*95%	*Perennials replacing row crops near waters
Cover crops	11-60%	*10%	*50% N leaching reduction when successfully established and 10% runoff N reduction. 20% establishment success rate assumed for MN average.

Other BMPs not included in Table 1 are continually being developed and improved. For example, saturated buffers established at field edges to treat tile drainage waters in the subsurface are currently being researched. Additionally, crop genetics research has improved the N use efficiency of crops, allowing farmers to harvest more crops for the same or less N fertilizer use (MDA, 2013). Enhanced fertilizers and other BMP improvements will likely continue to be developed.

#### Iowa literature review

lowa recently completed an extensive review of Upper Midwest studies on the effectiveness of N removal when using various individual and collective BMPs. Their report, which was developed by a team of scientists from Iowa Universities led by Iowa State, can be found at <a href="https://www.nutrientstrategy.iastate.edu">www.nutrientstrategy.iastate.edu</a>. Using a slightly different categorization scheme as Fabrizzi and Mulla (2012), Iowa evaluated three types of practices: 1) Nutrient Management, 2) Land Use, and 3) Edge of Field. Anticipated yield reductions or gains and BMP costs were evaluated in the Iowa study and are included in Iowa State University (2012).

The percent of nitrate reduction from each type of practice expected on fields potentially suitable for those practices in Iowa is summarized in Table 2. Similar to the Minnesota review, Iowa also found considerable variability in N reduction efficiency for individual types of practices described in the research literature. Energy crops, perennials, and buffer practices (e.g. changing from corn/soybeans to grasses or other perennials) had reasonably consistent nitrate reductions from study to study and field to field. However, most other practices had high standard deviations and coefficients of variation. All baseline assumptions and findings are reported in Iowa State University (2012).

Table 2. Iowa findings of BMP average nitrate reduction based on a review of research in the Upper Midwest (numbers extracted from Iowa State University, 2012). Reductions represent nitrate concentration reductions, except where noted as "load reduction."

Practice category	Practice	% Nitrate reduction from treated cropland
Change fertilizer	From fall to spring pre-plant	6
timing	From fall to spring pre-plant/sidedress 40-60 split	5
	From pre-plant application to sidedress	7
	From pre-plant to sidedress – soil test based	4
Change source from	From spring applied fertilizer to liquid swine manure	4
fertilizer to manure	From spring applied fertilizer to solid poultry litter	-3
Nitrogen application rate	From existing rates down to rates providing the maximum return to nitrogen value (133 lb/acre cornsoybean and 190 lb/acre on corn-corn)	10
Nitrification inhibitor	From fall applied without inhibitor to fall applied with Nitrapyrin	9
Cover crops	Rye cover crop on corn/soybean or corn/corn acres	31
	Oat cover crop on corn/soybean or corn/corn acres	28
Perennials	From spring applied fertilizer onto corn to perennial energy crops	72
	From spring-applied fertilizer onto corn to land in retirement (CRP)	85
Extended rotations	From continuous row crops to at least 2 years of alfalfa in a 4 or 5 year rotation (stateside estimates assume a doubling of current extended rotations)	42

Practice category	Practice	% Nitrate reduction from treated cropland
Tile drainage waters	Drainage water management – controlled drainage (nitrate load reduction)	33 (load reduction)
	Shallow drainage (nitrate load reduction)	32
	Wetland treatment (statewide estimate assumes 45% of row crops would drain to wetlands)	52
	Bioreactors (statewide estimate assumes bioreactors installed on all tile-drained acres)	43
	Buffers treating water that interacts with active zone below the buffer – load reductions depend on water amounts treated	91

# Statewide adoption of individual best management practices

Nitrogen load reduction to waters estimates were made by Minnesota and Iowa for their respective states, while using different methods and assumptions. Iowa is similar enough to southern Minnesota that N reduction estimates from Iowa are included in this discussion for comparison purposes, although it should be noted that differences exist between Iowa and Minnesota climate, land uses, and amount of lands suitable for various BMPs. The climate, soils and landscape in the Red River Valley area are particularly different from Iowa.

Most of the practices can only be used under certain conditions, restricting suitable acreages across the state for each practice. Some examples of limitations include:

- Wetlands are best suited in areas of low slopes and high flow accumulation that were likely historic wetlands on the landscape.
- Controlled drainage is largely limited to tile-drained land with nearly flat slopes (i.e. less than 1% slopes).
- Bioreactors can only effectively treat limited quantities of water at a given time, and during high spring flows are less effective in removing nitrate.
- · Climate can be a limiting factor for cover crops in certain areas.
- Changing timing of application from fall to spring is only applicable where fertilizer is currently being applied in the fall.

Because the BMPs for reducing N in waters only work in certain areas and situations, when we assess reductions across large watersheds, the capability of practices to reduce the percent of N loading to waters is not as high as for small areas where the BMP was used on all the land. For example, if a practice achieves a 50% N loss reduction to waters on the area where the BMP is applied, that practice adopted on suitable land throughout a watershed will result in less than a 50% N reduction in that watershed. In this section, we evaluate the adoption of individual BMPs if adopted on land assumed to be suitable for the BMP.

Uncertainties exist in the findings below for several reasons:

1. The literature review points to a wide range of BMP N reduction capabilities. The analyses below use average or representative values for N reduction to waters.

- 2. The results depend on the assumptions about which land is suitable for the BMPs. These assumptions can greatly affect the number of acres where the BMP can be adopted, and both lowa and Minnesota use different assumptions about suitable acreages.
- 3. The N reduction estimates for certain BMPs, such as rate and timing of application, are dependent on the accuracy of the baseline assessments. Uncertainties exist concerning current fertilizer rates, particularly related to N crediting following manure applications.
- 4. The cost information is not static. Fertilizer costs, application costs, crop prices, and other factors vary from year to year.
- 5. There is uncertainty regarding the average nutrient reductions to groundwater which take place when adopting fertilizer rate reduction BMPs. Since groundwater can be a significant pathway of transporting nitrate to surface waters, uncertainty regarding leaching to groundwater can also affect the uncertainty of N reductions to surface water estimates.

Fortunately, we have research and survey information in Minnesota which narrows many of these uncertainties so that the final results are believed to provide an approximate estimate of large scale N reduction potential and associated costs. Each finding should be viewed as a rough estimate of the actual achievable reduction and the cost to achieve such reductions.

# Iowa statewide adoption of individual best management practices

To support Iowa's Nutrient Reduction Strategy, scientists from Iowa universities estimated the likely nitrate load reductions to state waters which could be achieved through adoption of individual BMPs across the state on all land suitable for the particular BMPs (Table 3). The results show a wide range in estimated effects, from a 28% reduction for cover crops, down to a 0.1% reduction by changing fertilizer timing from fall to spring. The methods and assumptions are described in a report by Iowa State University (2012).

Table 3. Iowa findings of BMP N removal based on a review of research in the upper Midwest (numbers extracted from Iowa State University, 2012) and applied to land suited for those BMPs in Iowa. Negative costs represent a net dollar savings.

		% Nitrate reduction in treated area	lowa statewide % nitrate reduction*	Cost \$ per pound of N reduced
Change fertilizer	From fall to spring pre-plant	6	0.1	*
timing	From pre-plant application to sidedress	7	4	0.00
Nitrogen application rate	From existing rates down to rates providing the maximum return to nitrogen value (133 lb/acre cornsoybean and 190 lb/acre on corn-corn)	10	9	-0.58
Nitrification inhibitor	From fall applied without inhibitor to fall applied with nitrapyrin	9	1	-1.53
Cover crops	Rye cover crop on CS or CC acres	31	28	5.96
	Oat cover crop on CS or CC acres	28		
Perennials	From spring applied fertilizer onto corn to perennial energy crops (statewide estimate assumes 1987 levels of pasture/hay converted to Energy Crops)	72	18	21.46

		% Nitrate reduction in treated area	lowa statewide % nitrate reduction*	Cost \$ per pound of N reduced
Extended rotations	From continuous row crops to at least 2 years of alfalfa in a 4 or 5 year rotation (statewide estimates assume a doubling of current extended rotations)	42	3	2.70
Tile drainage waters	Drainage Water Management – controlled drainage	33	2	1.29
	Wetland treatment (statewide estimate assumes 45% of row crops would drain to wetlands)	52	22	1.38
	Bioreactors (statewide estimate assumes bioreactors installed on all tiledrained acres )	43	18	0.92
Buffers	Buffers treating water that interacts with active zone below the buffer	91	7	1.91

<sup>\*</sup>Statewide percent reductions are lower than reductions at the place of adoption since statewide adoption estimates assume that the BMP cannot be used on all lands, but only on lands suitable for the BMP.

lowa concluded that no single practice would achieve the hypoxia nutrient reduction goals (unless major land use changes occurred), but that a combination of practices would be needed to meet long term goals.

In lowa, the N management practices which seem to be the most promising for nitrate reductions to waters are reduced N application rate and planting cover crops. Iowa estimated average N application to a corn following soybeans to be 151 pounds/acre, which compares to 133 pounds BMP rate (maximum return to N assuming\$5.00/bushel corn and \$0.50/pound N). Average N application rate to corn following corn was 201 pounds/acre, which compares to a 190 pound BMP rate. A 9% nitrate reduction to waters was estimated for the entire state of Iowa if fertilizer rate reductions were to occur on all corn ground. If rye cover crops were planted on all corn and soybean acres, an estimated 28% statewide nitrate reduction is estimated from this practice alone. Other BMPs also showed promise in reducing nitrate, including wetland treatment (22% reduction statewide), bioreactors (18% reduction statewide), and side-dressing N rather than spring pre-plant N (4% reduction statewide).

The researchers at Iowa State University concluded that there is limited potential for nitrate reduction with several other BMPs. Controlled drainage adoption is limited by the land area suitable for this practice (slopes less than 1%). Switching all fall applied fertilizer to spring (without a corresponding decrease in rate) showed little potential for nitrate reduction in the Iowa study.

Changes to perennial vegetation can result in dramatic reductions where adopted, but the level of reduction is dependent on the overall amount of land converted to perennial based systems. The cost per pound of nitrate reduced was found to be particularly high for land converting from row crops to perennial energy crops under the current market and subsidy framework, but was considerably lower for extended rotations.

# Minnesota statewide adoption of individual best management practices

To evaluate the expected N reductions to Minnesota waters from individual practices adopted on all land statewide where the practice is suitable for adoption, we used the Nitrogen Best Management Practice watershed planning tool (NBMP or NBMP.xlsm). The NBMP spreadsheet was developed by the University of Minnesota (William Lazarus, David Mulla, et al.) to enable water resource planners

developing either state-level or watershed-level N reduction strategies to gauge the potential for reducing N loads to surface waters from cropland, and to assess the potential costs of achieving various reduction goals. The tool merges information on N reduction with landscape adoption limitations and economics. The tool allows water resource managers and planners to approximate the percent reduction of N entering surface waters when either a single BMP or a suite of BMPs is adopted at specified levels across the watershed. The tool also enables the user to identify which BMPs will be most cost-effective for achieving N reductions.

#### NBMP spreadsheet background

NBMP compares the effectiveness and cost of BMPs that could be implemented to reduce N load entering surface waters from cropland in a watershed. The spreadsheet was not designed for individual land owner decisions, but rather for larger scale watershed or state level assessments. The NBMP.xlsm spreadsheet can be downloaded <a href="mailto:z.umn.edu/nbmp">z.umn.edu/nbmp</a> and more information about the development and use of the spreadsheet is found at <a href="mailto:faculty.apec.umn.edu/wlazarus/documents/nbmp">faculty.apec.umn.edu/wlazarus/documents/nbmp</a> overview.pdf.

The spreadsheet contains data for 17 individual watersheds and for Minnesota as a whole. The watersheds that can be assessed individually with the tool at this time include 15 HUC8 watersheds which have high N loading, plus two HUC10 watersheds - Elm Creek and Rush River. The fifteen HUC8 watersheds include the: Lower Minnesota River, Minnesota River – Mankato, Blue Earth River, Le Sueur River, Minnesota River - Yellow Medicine River, Cannon River, Root River, Zumbro River, South Fork Crow River, Cedar River, Cottonwood River, Watonwan River, Des Moines River, Chippewa River, and North Fork Crow River.

The soil, crop, N loading data, and corn fertilizer response functions were provided by David Mulla as developed for work described in Chapter D4 of this report. Assumptions underlying the calculations, including land deemed suitable for each BMP are described in Table 4.

Table 4. Key assumptions in the NBMP spreadsheet for each N reduction practice (based on Lazarus et al. 2012 and personal communication with Lazarus 2013).

#### Nitrogen fertilizer rates and application timing

Current N rates based on 2010 statewide fertilizer use survey by University of Minnesota (Bierman et al., 2011) as compared to BMP rates based on current U of MN recommendations

U of MN recommendations vary by previous crop.

Corn acres include corn for grain and silage grown during a single year. Because soybeans are typically rotated with corn, the corn acreage during any one year is about half of the total corn/soybean acreage.

N fertilizer product prices vary. Farmer survey information was used to estimate the use of different types of fertilizer.

N fertilizer products change with the timing of application.

Solves for a point estimate of the profit-maximizing N rate based on the corn price and the N price (varies by application timing).

The point estimate of the profit-maximizing rate is increased for fall-application and reduced for spring preplant or sidedressing. Fall application rates were assumed to be 30 pound/acre higher than spring application rates.

The survey of current practices covered only non-manured land.

- Current N rates were adjusted assuming that farm operators are now taking credit for part of the
  estimated crop available N on manured land as follows:85% for swine, 75% for dairy, and 70% for
  poultry and beef.
- The manure N is credited in the BMP N rates.

The percent N load reduction to waters varies depending on current N application rate spatial averages for the agroecoregion.

#### Fall to spring preplant or prepland/sidedress

Switching from fall to spring/sidedressing reduces tile line N loading, but increases the N fertilizer price/pound and adds an extra fertilizer application cost.

This BMP only applies to corn grain and silage acres currently fertilized in the fall (based on farmer surveys as reported by Bierman et al. (2011)). "Sidedressing" here is actually a split application of spring preplant and sidedressing, with a default of 30% preplant and 70% sidedressed.

This BMP Only considers corn acreages for a single year, instead of using all land where corn is grown in the rotation.

The percent tile N load reduction varies between an average year, a wet year, and a dry year because the water volume in the tile line varies. The spreadsheet does not adjust N loading to waters from the surface runoff and groundwater pathways due to this timing BMP.

In a wet year, a percentage of the fertilizer N is lost and not available to the crop. Default is 10% less N available to the crop during the wet year.

Nitrification inhibitors are not a BMP option included with the version of the NBMP spreadsheet used for this analysis.

#### Riparian buffers

This data layer represents a 100 ft. buffer on either side of every stream on DNR's 1:24,000 scale maps. It does not account for land that is already in a buffer condition; and therefore represents the maximum available land for buffering, not how much can be added to current buffers.

The annual cost per acre is based on an enterprise budget for a 10-year stand of switchgrass, not harvested.

Acres of buffers are assumed to come out of acres of corn and soybeans.

The N load from the buffer acres is assumed to be 5% of N loads from corn/soybeans.

#### Wetland restoration

Lands suitable for wetlands were assessed by first using a logistic regression model that utilizes the Compound Topographic Index (CTI) and hydric soil data to isolate areas of low slopes and high flow accumulation that were likely historic wetlands on the landscape. Once these areas are identified, the layer is further refined by intersecting likely historic wetlands with likely tile drained lands. These lands are isolated by finding Crop Data Layer 2009 crops that are likely drained (corn, beans, wheat, sugar beets) and intersecting them with poorly drained SSURGO soils and slopes of 0-3%.

Suitable acres are poorly drained soils with slopes 0-3% and crops that are likely to be drained.

Three types of land are involved: 1) Wetland pool (always flooded); 2) Grassed buffer around the pool that is sometimes flooded so is not available for crop production; and 3) Cropland that is treated by having its water flow into the wetland (assumes approximately 10:1 ratio of cropland to wetland/buffer area (9.87:1))

Costs considered include: 1) Establishment cost, related to the wetland pool and buffer acres annualized over the useful life of the wetland; 2) Annual maintenance cost related to the pool and buffer acres, and 3) Opportunity cost of the crop returns lost on the pool and buffer acres.

A default 50% reduction in N loading is assumed on treated acres. The N loads on acres shifted to the wetland pool and grassed buffer are assumed to be zero.

#### Controlled drainage and bioreactors

This layer uses the likely tile drained land layer (poorly drained soils, 0-3% slope, and 2009 CDL corn, soybeans, wheat, or sugar beets). This layer is further refined with slopes using a 30 meter slope grid. The default is slopes less than 1%, on average. Suitable acres for controlled drainage can be adjusted to include an upper slope limit of 0.5% slope, 1% slope, or 2% slope [default is 1%].

Costs considered include an establishment cost, annualized over the useful life, and an annual maintenance cost, per treated acre.

For controlled drainage, a default 40% reduction is assumed in the tile line N load, with no change in leaching to groundwater and runoff N load. The tile line N load reduction can be changed by the user.

For tile line bioreactors, the tile line N load reduction in the treated flow varies based on loading density (treated acres/footprint), with a default of 44%. Only 30% of the drainage system water is assumed to be treated, however, due to factors such as spring overflow, so the default reduction is 13% of the overall tile line N load (44% times 30%).

#### Cover crops

Suitable acres include total of corn grain, corn silage, and soybean acres in the watershed.

Cover crops of cereal rye are seeded in September into standing corn and soybean crops, by air.

Only a percentage of the seeded acres achieve a successful stand. The default success rate is 20%.

A cost for a contact herbicide and custom application is included for the successfully-seeded acres.

The N loads in tile lines, leaching, and runoff are all reduced, but the runoff reduction is much less than the reductions in tile line and leaching N. On successfully-seeded acres, the tile line and leaching N loads are reduced by a default 50%, with a 10% reduction in the runoff N load. Considering the 20% success rate, the overall reductions/seeded acre are 10% for tile line and leaching N, with a 2% reduction in runoff N.

The corn yield is reduced by default on cover-cropped acres in a wet year, but not in an average year or a dry year.

#### Perennial energy crops

The default is "marginal land." This is from a data layer that isolates National Land Cover Database (NLCD) 2006 cultivated land with Crop Productivity Index values of less than 60 to identify marginal cropland that be converted to perennial crops.

The annual net return/acre is based on an enterprise budget for a 10-year stand of switchgrass, with a user-specified crop price/ton. Default switchgrass price is \$0.

Revenue losses from the previous crop are based on average crop yields for the agroecoregion – actual revenue loss is expected to be less than on average lands, where perennials are replacing other crops only on marginal cropland.

- If the grass price is high enough to cover the harvest cost, it is harvested and the net returns are based on the crop value minus an annualized establishment cost, annual maintenance cost, and harvesting cost.
- Otherwise, it is not harvested and the only costs are the annualized establishment cost and annual maintenance cost.

The N load from the perennial crop acres is assumed to be zero.

If the adoption rates entered for buffers, wetland treated acres, and perennial crops exceed total corn and soybean acres, the rates are reduced to equal that total, with the difference coming out of wetland or perennial crop acres, whichever is most costly.

The NBMP spreadsheet was designed so that effects of BMPs cannot be double counted. Since some of the BMPs affect the same acreage in a similar way when adoption rates are high, the spreadsheet only includes the most cost-effective practice(s) on the overlapping acreage.

The NBMP tool can be revised and assumptions changed as new information becomes available. We used a March 25, 2013, version of the spreadsheet to obtain most of the estimates described below, using the default assumptions, unless otherwise noted. Best management practice costs and other results are dependent on several variables which can and do change significantly over time (i.e. fertilizer prices, price of corn, price of equipment, etc.). Therefore, the reported cost estimates should not be viewed as a static number, but rather a number which will fluctuate over time. The results represent our best estimates at this point in time.

Additional BMPs exist for N reductions other than what are provided in the NBMP tool (i.e. tile spacing and depth, nitrification inhibitors, saturated buffers, etc.). The developers of the NBMP spreadsheet only included the BMPs which were believed to represent the combination of the most research-proven and effective BMPs for Minnesota waters at this time.

One BMP which can greatly reduce tile line nitrogen loads is installing tile drains at a shallower depth (i.e. 2.5 feet instead of 3.5 to 4.0 feet). This practice is not expected to reduce nitrate concentrations, but it can reduce the flow and thus reduce the load. The focus of this study was reducing nitrogen loads to surface waters from existing conditions. However, installation of shallower drain tiles should be considered for mitigating nitrogen losses to waters where new tile drains are installed.

#### Minnesota statewide estimates of nitrogen load reduction– from individual BMPs

We used the NBMP tool to estimate statewide N reductions for individual practices, if they were to be adopted on 100% of the suitable acreage in the state during an average precipitation year (Table 5). The most cost-effective BMPs include: optimal N rates, changing from fall to spring/preplant fertilizer timing, controlled drainage and wetland treatment. Since the acreages used for these BMPs would overlap in many cases, the cumulative potential reductions for the state cannot be determined by adding the individual BMPs in Table 5.

Table 5. Nitrogen reduction to waters estimated with the NBMP spreadsheet for individual BMPs, assuming adoption of the individual BMP on all suitable areas for the BMP in Minnesota and average precipitation conditions. A negative cost indicates a net savings.

N reduction BMP	N reduction to waters if adopted statewide (MN) on 100% of suitable acres	Cost - \$ per pound of N reduced in water	Percent of land acres suitable for the BMP in a given year
Optimal N rates	9.8%	\$-4.03	26.2%
Fall to spring N with lower rates	6.4%	\$-0.67	10.5%
Fall to preplant/side-dressing with lower rates	6.7%	\$1.41	10.5%
Wetland treatment	5.2%	\$6.22	5.3%
Bioreactors	0.8%	\$14.09	4.5%
Controlled drainage	2.3%	\$2.35	4.5%
Riparian buffers – converting row crop to perennials	7.2%	\$42.22	5.7%
Perennials – converting marginal row crops to perennials	11.1%	\$38.24	8.3%
Cover crops	7.3%	\$49.92	50.1%

The default for the NBMP spreadsheet for cover crops is a 20% successful establishment rate. If we were able to achieve a better average success rate, the potential to remove N would increase substantially. The NBMP tool shows that under a scenario of a 50% cover crop establishment success, the N reduction would increase from 7.3% to 18.3%. And if the cover crop establishment success were to increase to 75%, then the N reduction to waters statewide would increase to 27.4%.

The numbers change when using the BMPs during a wet or dry year (Table 6). For example, if fertilizer and manure N is lost due to a wet spring, the cost per pound of N reduced in waters increases for the wet year. The cost for wetland treatment per pound of N reduced decreases from \$6 to \$4 during a wet year. The cost for cover crops decreases during a wet year, from \$49 to \$30 per pound of N reduced.

Table 6. Comparison of wet (90<sup>th</sup> percentile annual precipitation), average and dry (10<sup>th</sup> percentile annual precipitation) year estimates of N reduction to waters if adopted on 100% of suitable acres in Minnesota, and the cost (\$) per pound of N reduced in waters (rounded to nearest dollar). Wet year calculations assume a 10 percent loss of manure and fertilizer N due to additional denitrification and leaching.

N reduction BMP	Dry year N reduction (million lbs/year)	Average year N reduction (million lbs/year)	Wet year - N reduction (million lbs/year)	Dry year \$ per pound of N reduced	Average year \$ per pound of N reduced	Wet year - \$ per pound of N reduced
Optimal N rates	11	21	27	-7.9	-3.9	-2.7
Fall to spring N with lower rates	8	14	17	-1	-0.5	-0.2
Fall to preplant/side- dressing with lower rates	8	15	18	3	1.6	1.7
Wetland treatment	4	12	21	19	6	4
Bioreactors	0.4	2	3	59	14	8
Controlled drainage	1	5	9	10	2	1
Riparian buffers – converting row crop to perennials	6	17	28	120	42	25
Perennials – converting marginal row crops to perennials	10	26	42	97	38	24
Cover crops	6	17	28	149	49	30

#### Comparing Iowa and Minnesota best management practice effects

Iowa and Minnesota have several similarities and differences regarding the N reduction and cost from individual BMPs applied to a given treated area or at the statewide scale (Table 7, Figures 2 and 3). Some of the differences are due to:

- Minnesota used GIS-based information to estimate land areas suitable for BMPs, whereas Iowa
  used a larger scale Major Land Resource Area approach;
- Several assumptions concerning the effectiveness of BMPs throughout the year were different between the states, based on differences in climate and other considerations; and
- lowa focused on the subsurface pathways of N loss, whereas Minnesota also considered surface runoff pathways. This difference is relatively minor, since most N losses to surface waters occur through the subsurface.

Additionally, Minnesota and Iowa assumptions about the total number of acres that could be used for each individual BMP differed greatly. These differences were due to differences in assumptions and approaches used to determine suitable lands for each BMP, and due to real differences in land, landscape, and climate between the two states. The differences in statewide N reduction estimates in Table 7 can largely be explained by the above stated factors.

Table 7. Minnesota and lowa estimates of percent N reduction in treated areas and collectively across the state on all lands deemed suitable for the BMPs (average precipitation years).

	N removal range in test area Fabrizi Mulla, 2012	MN NBMP reduction in BMP treated area (average precip yr)	lowa average removal in BMP treated area	MN reduction statewide w/NBMP (average precip yr)	lowa reduction statewide ISU, 2012	MN cost per lb N reduced in water (average precip yr)	lowa cost per lb N reduced in water
	%	%	%	%	%	\$/lb N	\$/lb N
Tile line water							
Controlled drainage	14-96	44	33	2.3	2	2.30	1.29
Bioreactors	10-99	13*	43	0.8	18	14.09	0.92
Wetlands	19-90	50	52	5.3	22	6.09	1.38
N rates							
Reduced rates of application to MRTN	11-70	16	10	9.8	9	-3.92	-0.58
Timing of application							
Timing of application (general)	10-58						-
Preplant to sidedress			7		4		-
Fall to spring preplant			6		0.1		-
Fall to spring preplant with reduced rate		26		6.4		-0.53	
Fall to preplant / sidedress with reduced rates		29		6.7		1.60	
Fall with nitrification inhibitor	18		9		1		-1.53
Vegetation change							
Extended rotations			42		3		2.70
Alternative cropping systems	5-98						
Riparian buffers	17-99	95	91	7.2	7	42.22	1.91
Cover crops (rye)	11-60	10**	31	7.3	28	49.92	5.96
Perennials		95	72	11.1	18	38.24	21.46

<sup>\*</sup>MN estimates assume that only 30 percent of the drainage into bioreactors is treated on an annual basis, reducing treatment from 44 to 13%.

<sup>\*\*</sup>MN estimates assume that tile line and leached N is reduced by 50 percent in tile drained systems with cover crops, but that the establishment rate averages 20%, reducing the N removal rates to 10%.

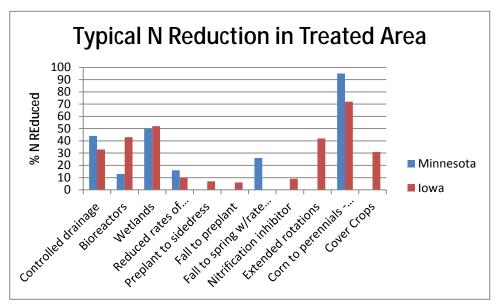


Figure 2. Minnesota and Iowa estimates of the average percent N load reduction in areas treated with the BMPs.

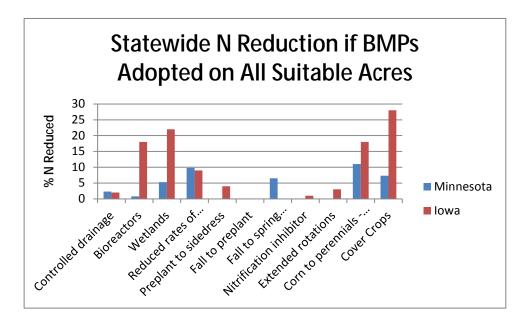


Figure 3. Minnesota and Iowa estimates of the average percent N load reduction statewide if the individual BMPs are adopted on all lands considered suitable for the BMP.

Both states consider that cover crops will reduce large quantities of N when successfully established. lowa costs are much lower and N removal is much higher for cover crops. The higher Minnesota cost of cover crops compared to the lowa estimates is largely due to the low assumed success rate (20%) in establishing cover crops in Minnesota. Climate is a factor, and additionally cover crops were assumed to be seeded by air in Minnesota while the lowa costs assume seeding with a no-till drill after harvest. Aerial seeding requires a greater seeding rate and a higher seeding cost than the lowa estimates assume. With increasing study of cover crops in Minnesota to develop better ways of more consistently establishing cover crops, the cost per pound of N reduced may potentially decrease. If Minnesota could successfully establish cover crops 75% of the time, the statewide N reduction to waters would be about the same as the lowa estimates (28%).

Both states estimate a comparable level of treatment expected from controlled drainage BMPs, although Minnesota's estimates with this practice is slightly higher than lowa. Both states estimate wetland treatment N removals near 50%, but lowa assumes a higher ratio of cropland to wetland/buffer areas and lowa determined that this BMP could be adopted in a larger fraction of the state than Minnesota estimates. Therefore the statewide N reduction estimates for wetlands are considerably lower in Minnesota.

lowa estimates of N reduction from bioreactors is considerably higher than Minnesota estimates. Both states consider a similar average rate of reduction when bioreactors are treating tile waters (40-44% in Minnesota vs. 43% in lowa), but Minnesota assumes that only 30% of the annual tile waters draining to bioreactors will be treated in a given year due to bioreactor limitations during high-flow seasons.

Both states indicate a similar level of statewide N reductions which can be achieved by reducing fertilizer rates to economically optimal rates. Minnesota estimates of cost savings per pound of N reduced to waters are considerably higher than lowa estimates. Evaluation of this practice is highly dependent upon assumptions of: baseline conditions, price of corn, price of fertilizer, and climate.

Effects of changing fertilizer timing to closer to when crops need the nutrients are more pronounced in Minnesota estimates, especially in the fall to spring preplant scenario. Minnesota assumes a corresponding 30 pound N rate reduction in association with the change in timing, whereas lowa did not assume a rate reduction with the change in fertilizer timing.

lowa included an analysis of nitrification inhibitors, whereas the Minnesota NBMP analysis did not. Iowa assumes an average 9% nitrate reduction to waters on acres treated with inhibitors, but that overall statewide reductions to waters from inhibitors would only be 1%. Nitrification inhibitor use in Minnesota has been increasing during recent years. The Minnesota Department of Agriculture estimates use of inhibitors on over 1.2 million cropland acres in 2012, up from about 0.5 million acres in 2010 (Bruce Montgomery, personal communication).

Both states show reasonably similar N reduction expectations for riparian buffers and perennials. Minnesota's cost estimates are much higher for riparian buffers per pound of N reduced compared to lowa, largely due to difference in the type of buffers being considered. Iowa focused on buffers which intercept shallow subsurface waters flowing toward the buffers, and therefore the treatment area for lowa's buffers are larger than Minnesota estimates.

# Statewide best management practices combinations needed for a 45% nitrogen reduction

Goals to reduce the Gulf of Mexico Hypoxic zone down to a 5,000 square kilometer area would require an estimated 45% reduction in N and phosphorus loads to the Gulf (see Chapter A2). Iowa and Minnesota used different methods and assumptions to arrive at estimates of BMP adoption levels (and associated costs) required to achieve a 45% N load reduction in surface waters.

Iowa State University (2012) developed several possible scenarios for Iowa to achieve 45% reductions from cropland (Table 8), equating to an overall 41% reduction of N loads from all sources. The scenarios have different up-front and annual costs for the BMPs. The scenarios represent hypothetical combinations of BMPs and do not necessarily represent the most optimal or achievable scenarios.

Table 8. Three Iowa BMP adoption scenarios predicted to achieve an estimated 45% nitrate-N loading reduction to Iowa surface waters from the cropland sources (adapted from Iowa State University, 2012).

		Initial cost (billion \$)	Annual cost (billion \$)
Scenari	io 1	3.2	0.76
•	100% agric. land with optimal N rate (maximum return to nitrogen)		
	27% of agric. land draining into wetland treatment		
	60% of tile drained land with bioreactor		
Scenari	io 2	1.2	1.2
	100% agric. land with optimal N rate (maximum return to N)		
•	95% of row crops with cover crops		
	34% of agric. land in best-suited regions with wetlands		
	5% of agric. land (additional) retired to perennial vegetation		
Scenari	io 3	4.0	0.08
	100% agric. land with optimal N rate (Maximum return to N)		
	100% of fall N with nitrification inhibitor		
	100% of spring N side-dressed		
	70% of tiled land treated with bioreactor		
	70% of suitable land with controlled drainage		
	31.5% of agric. land draining into wetland treatment		
	70% of agricultural streams with buffers		

For Minnesota conditions, we used the NBMP tool previously described to estimate BMP adoption scenarios to achieve 30%, 35%, and 45% reductions for an average precipitation year (Table 9).

Both states show a very high level of BMP adoption needed to achieve a 45% load reduction. Minnesota estimates indicate that the 45% level of reduction is not achievable with current practices included in the NBMP spreadsheet, but could theoretically be achieved with future BMP improvements. Both lowa and Minnesota show the cost range in billions of dollars to achieve N reductions at or approaching the 45% goal (Tables 8 and 9). The costs in Table 9 incorporate fertilizer savings, where savings are potentially achievable. Costs do not include government and private industry personnel costs to promote BMPs and assist with BMP implementation.

Table 9. Minnesota statewide BMP adoption levels estimated to achieve 30%, 35%, and 45% reductions of N into surface waters. Estimates were developed by using the Minnesota NBMP tool (Lazarus et al., 2012). Percentages of BMP adoption represent percentages of land well-suited for each BMP (i.e. 90% adoption – is 90% of land suitable for the BMP).

	% N reduction	Annual net cost billion \$
30% reduction scenario	30%	1.4
• 90% corn land with optimal N rate (maximum return to N)		
45% fall N switched to spring; 45% fall N switched to		
preplant/sidedress		
<ul> <li>70% of streams with riparian buffers growing perennial grasses</li> </ul>		
100 ft wide on each side of stream 80% (1.36 million acres)		
tiled land draining into wetland treatment and 10% into		
bioreactors		
<ul> <li>70% of corn/soybean land with rye cover crop</li> </ul>		
<ul> <li>90% of suitable land with controlled drainage</li> </ul>		
<ul> <li>44% of all marginal cropland retired to perennial vegetation (all</li> </ul>		
other marginal land was used for other lower cost BMPs)		
35% reduction scenario	35%	1.9
<ul> <li>100% corn land with optimal N rate (maximum return to N)</li> </ul>		
<ul> <li>50% fall N switched to spring; other 50% fall N switched to</li> </ul>		
preplant/sidedress		
<ul> <li>100% of streams with riparian buffers growing 100 ft wide</li> </ul>		
perennial grasses (1.7 mill. acres)		
<ul> <li>80% (1.36 million acres) suitable tiled land draining into</li> </ul>		
wetland treatment and 20% into bioreactors		
<ul> <li>100% of corn/soybean land with rye cover crop (11.7 mill.</li> </ul>		
acres)		
<ul> <li>100% of suitable land with controlled drainage (1.34 mill. acres)</li> </ul>		
<ul> <li>All marginal cropland retired to perennial vegetation (1.35 mill.</li> </ul>		
acres)		
45% reduction scenario	45%	*1.6
More development of BMPs is needed to achieve a 45% reduction. We		
cannot show a 45% statewide N reduction with the NBMP tool using the		
current assumptions and default values. We estimate that we can		
achieve a 45% reduction if we use the above 35% reduction scenario		
BMP adoption rates and additionally we modify the NBMP tool to		
assume: a) that we can find ways to improve establishment of cover		
crops, increasing from a 20% success rate to 60% success rate, and b)		
application rates to corn are reduced from 100% of optimal to 80% of		
optimal (80% of maximum return to N rate. With the better success of		
the cover crop establishment, the overall cost is reduced as compared		
to the 35% reduction scenario.		

<sup>\*</sup>this cost assumes that cover crop establishment success increases from 20% (current) to 60% (hypothetical)

To achieve the 35% reduction scenario, the N reduction BMPs would need to be applied to all cropland in the state that is suitable for the BMPs. Similar to lowa's approach, the scenarios in Table 9 were not evaluated or considered for achievability, and we anticipate that the economic and social constraints would make these scenarios unrealistic at this time.

A 30% statewide N reduction to waters from cropland is theoretically achievable based the NBMP model results, but would require a very high adoption rate of optimal fertilizer management, tile drainage treatment and vegetation change BMPs. According to NBMP tool results, it appears that the first 13% N

reduction to waters from cropland sources can potentially be made if optimal fertilizer/manure rate and timing BMPs are adopted on most (over 90%) of the state cropland (Figure 4). NBMP tool estimates indicate that this can be accomplished with a net cost savings (approximately \$77 million) to producers during an average precipitation year, and a reduced savings during a wet year. The second tier of BMPs is tile drainage BMPs. An additional 5% N reduction to waters can be accomplished with a \$73 million dollar annualized cost to install and maintain wetlands (80% of suitable acres), bioreactors (10% of suitable acres) and controlled drainage (90% of suitable acres). By changing or adding vegetation through another \$1.4 billion annual investment, an additional 12% N reduction to waters can be accomplished. The vegetation changes to achieve the added 12% reduction include a rye cover crop on 70% of row crops; change existing crop to grasses on about 100 feet each side of 70% of the streams in the state; and change 44% of the other marginal croplands from corn to grasses. The costs of the vegetation changes are particularly sensitive to changing crop and fertilizer prices.

The N reduction potential and associated costs vary by watershed, and therefore the statewide numbers shown in Table 9 and Figure 4 are not applicable to individual watersheds.

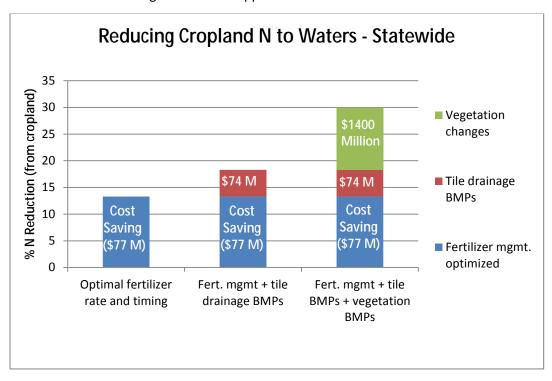


Figure 4. NBMP estimated Minnesota statewide N reductions to surface waters from cropland during an average precipitation year, using fertilizer management BMPs alone (left), fertilizer management with tile drainage BMPs (middle), and fertilizer management with both tile drainage and vegetation change BMPs (right). Cost estimates are incremental in millions of dollars annually calculated for conditions at the time of report writing and will change with fluctuating markets.

# Watershed best management practice combinations to achieve 15% and 25% nitrogen load reductions

Since some BMPs are better suited for one region of the state over another, the N reduction potential and associated costs vary considerably across Minnesota. BMP adoption scenarios were developed separately for four watersheds using the NBMP tool, with the goal of showing potential scenarios for reducing watershed N load by approximately a) 15%, b) 25% and c) maximum reduction % under the

adoption of BMPs as described in Tables 10-14. Numerous combinations of BMP adoption scenarios can be used to achieve the 15% and 25% reductions. The scenarios chosen below are weighted toward higher adoption of the more cost-effective BMPs at each site, but they are not completely cost-optimized. Each scenario includes a variety of BMPs, recognizing that different farmers will not all choose the same BMPs, and assuming that 100% adoption of any single BMP across a watershed is unrealistic. Nitrogen reduction BMP adoption scenarios for achieving 15% and 22% N load reductions in the Root River Watershed are shown in Table 10. The 25% reduction scenario could not be achieved in the Root River Watershed with 100% adoption of the listed BMPs.

Nitrogen reduction BMP adoption scenarios for achieving 15%, 25% and 38-39% N load reductions in the LeSueur River Watershed in south central Minnesota, Cottonwood Watershed in southwestern Minnesota, and North Fork Crow River Watershed in central Minnesota are shown in Tables 11, 12, and 13. To achieve the higher N load reductions, BMP adoption rates were greatly increased.

Table 10. Nitrogen reduction BMP adoption scenarios for achieving 15% and 22% N reductions in the Root River Watershed during an average precipitation year. All BMPs in the table combined must be adopted at the listed acreage amounts in order to achieve the 15 and 22% reductions.

Root River Watershed		22% Maximum* N-reduction	25%	15%
	Area of watershed suitable for BMP in a single year (% of watershed)	Acres treated with BMP during a given year to get 22% reduction	Acres treated with BMP during a given year to get 25% reduction	Acres treated with BMP during a given year to get a 15% reduction
Corn N rate reduced to optimal (from current avg. down to U of MN rec. avg. for a given year)	38.3	307,400	NA	261,300
Switch fall application to spring application and reduce rate 30 lb/acre (only on corn)	4.8	38,700	NA	31,000
Wetlands installed to treat tile line water (land draining into)	2.4	18,900	NA	5700
Bioreactors (land draining into)	1.4	11,200	NA	1100
Controlled drainage	1.4	11,200	NA	3900
Rye cover crop installed – (assumes 25% success rate for establishing cover crop)	58.6	391,800	NA	233,600
Marginal cropland planted to perennials	5.0	40,000	NA	2000
Avg. N reduced per watershed (milli	on lbs/year)	3.1		2.1
Avg. cost per lb N reduced		7.4		5.0
Avg. annual net cost per watershed (million \$/year)		22		10.4
Savings from fertilizer BMPs (million \$/year)		+4		
Cost of tile drainage BMPs (million \$	/year)	0.6		
Cost of perennials and cover crops (	million \$/year)	26		

<sup>\*</sup>Maximum reduction in NBMP tool with 100% adoption of the BMPs listed in this table.

Table 11. Nitrogen reduction BMP adoption scenarios for achieving 15%, 25% and 39% N reductions to surface waters in the LeSueur Watershed. All BMPs combined in the table must be adopted at the listed acreage amounts in order to achieve the 15%, 25% and 39% reductions.

LeSueur River Watershed		39% *Maximum N-reduction	25%	15%
	Area of watershed suitable for BMP in a single year (% of watershed)	Acres treated with BMP during a given year to achieve a 39% reduction	Acres treated with BMP during a given year to achieve a 25% reduction	Acres treated with BMP during a given year to achieve a 15% reduction
Corn N rate reduced to optimal (from current avg. down to U of MN rec. avg. for a given year)	49.3	274,300	225,000	205,800
Switch fall application to spring application and reduce rate 30 lb/acre (only on corn)	32.2	178,800	143,000	17,900
Wetlands installed to treat tile line water (acres draining into)	17.9	99,400	29,800	19,900
Bioreactors (acres draining into)	18.1	50,500	10,000	
Controlled drainage	18.1	50,500	30,300	
Rye cover crop installed – (assumes 25% success rate for establishing cover crop)	87.7	478,200	193,500	97,100
Marginal cropland planted to perennials	3.3	O Marginal land used for other BMPs	900	
Avg. N reduced per watershed (millio	on lbs/year)	3.3	2.1	1.3
Avg. cost per lb N reduced	\$9.00	4.95	2.83	
Avg. annual net cost per watershed (million \$/year)		30	10.5	3.6
Savings from fertilizer BMPs (million	+4			
Cost of Tile drainage BMPs (million \$	/year)	6		
Cost of perennials and cover crops (	million \$/year)	27		

<sup>\*</sup>Maximum reduction in NBMP tool with 100% adoption of the BMPs listed in this table.

Table 12. Nitrogen reduction BMP adoption scenarios for achieving 15%, 25% and 38% reductions to surface waters in the Cottonwood River Watershed All BMPs combined in the table must be adopted at the listed acreage amounts in order to achieve the 15%, 25% and 38% reductions.

Cottonwood River Watershed			25%	15%
	Area of watershed suitable for BMP in a single year (% of watershed)	Acres treated with BMP during a given year to get 38% reduction	Acres treated with BMP during a given year to get 25% reduction	Acres treated with BMP during a given year to get a 15% reduction
Corn N rate reduced to optimal (from current avg. down to U of MN rec. avg. for a given year)	49.8	337,100	286,500	252,800
Switch fall application to spring application and reduce rate 30 lb/acre (only on corn)	27.6	186,700	140,000	26,100
Wetlands installed to treat tile line water (acres draining into)			32,600	16,300
Bioreactors (acres draining into)	11.5	38,900	7,800	
Controlled drainage 11.5		38,900	31,100	
Rye cover crop installed – (assumes 25% success rate for establishing cover crop)	assumes 25% success rate for		247,800	124,500
Marginal cropland planted to perennials	3.7	25,300	1,300	
Avg. N reduced per watershed (million lbs/year)		2.6	1.7	1.0
Avg. cost per lb N reduced		\$18.5	8.4	5.4
Avg. annual net cost per watershed (million \$/year)		47	14.0	5.4
Savings from fertilizer BMPs (million \$/year)		+3		
Cost of Tile drainage BMPs (million \$/year)		6		
Cost of perennials and cover crops (million \$/year)		44		

<sup>\*</sup>Maximum reduction in NBMP tool with 100% adoption of the BMPs listed in this table.

Table 13. Nitrogen reduction BMP adoption scenarios for achieving 15%, 25% and 38% reductions to surface waters in the North Fork Crow River Watershed. All BMPs combined in the table must be adopted at the listed acreage amounts in order to achieve the 15%, 25% and 38% reductions.

North Fork Crow River Watershed		38% *Maximum N-reduction	25%	15%
	Area of watershed suitable for BMP in a single year (% of watershed)	Acres treated with BMP during a given year to get 38% reduction	Acres treated with BMP during a given year to get 25% reduction	Acres treated with BMP during a given year to get a 15% reduction
Corn N rate reduced to optimal (from current avg. down to U of MN rec. avg. for a given year)	33.6	196,900	177,200	161,500
Switch fall application to spring application and reduce rate 30 lb/acre (only on corn)	13.1	76,700	61,400	46,000
Wetlands installed to treat tile line water (acres draining into)	7.8	36,100	29,700	7,300
Bioreactors (acres draining into)	eactors (acres draining into) 5.1		3000	
Controlled drainage	5.1	14,900	19,400	4500
Rye cover crop installed – (assumes 25% success rate for establishing cover crop)	assumes 25% success rate for		210,200	50,600
Marginal cropland planted to perennials	13.4	78,400	15,700	3900
Avg. N reduced per watershed (million lbs/year)		25	1.3	0.8
Avg. cost per lb N reduced		23.4	13.7	3.51
Avg. annual net cost per watershed (million \$/year)		47	18	2.8
Savings from fertilizer BMPs (million \$/year)		+3		
Cost of Tile drainage BMPs (million \$/year)		1		
Cost of perennials and cover crops (million \$/year)		49		

<sup>\*</sup>Maximum reduction in NBMP tool with 100% adoption of the BMPs listed in this table.

The costs per pound of N reduced increase significantly when achieving higher and higher N reductions (Figure 5). The first 10-20% reductions can largely be achieved with lower cost BMPs and cost-saving optimal fertilizer management BMPs. Further reductions can be achieved by increasing adoption of the more costly tile-drainage management and treatment BMPs. The last 7-20% reductions can be achieved by the most costly BMPs, which involve replacing row crops with perennial vegetation (on marginally productive soils) and establishing cover crops.

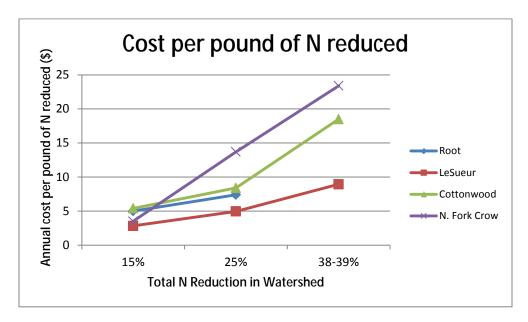


Figure 5. Average estimated net costs per pound of N reduced to waters from four watersheds when achieving N reduction goals of 15%, 25% and 38 to 39% (derived from NBMP tool as presented in Tables 10-13). The 25% reduction scenario for the Root River is actually a 22% reduction, since the 25% reduction could not be achieved with the selected BMPs.

The LeSueur and Cottonwood River Watersheds can achieve a higher estimated N reduction as compared to the Root River Watershed, according to NBMP tool results (Figure 6). This is partly due to a couple of key differences among the watersheds. The Root River Watershed has much less tile-drainage as compared to the other two watersheds, and therefore the BMPs to manage or treat tile-drainage cannot be implemented as much in the Root River Watershed. Additionally, there is little opportunity to switch from fall to spring fertilizer applications in the Root River Watershed, since most farmers in this region are currently applying fertilizer in the spring months. Farmers in the south-central and southwestern watersheds generally have more fall application.

Nitrification inhibitors are being used more frequently with fall applications in these areas to reduce N leaching losses in the fall and early spring months, and sales of these products more than doubled between 2010 and 2012 (personal communication with Bruce Montgomery, MDA). Nitrification inhibitors are not yet included as a BMP in the NBMP tool.

The North Fork of the Crow River can achieve N reduction percentages comparable to the LeSueur and Cottonwood Watersheds (Figure 6). But in order to achieve a 38% reduction in the North Fork of the Crow, a relatively large amount of marginal cropland (13% of the watershed) would need to be converted to perennial vegetation. More marginal cropland is available in this watershed as compared to the LeSueur and Cottonwood Watersheds.

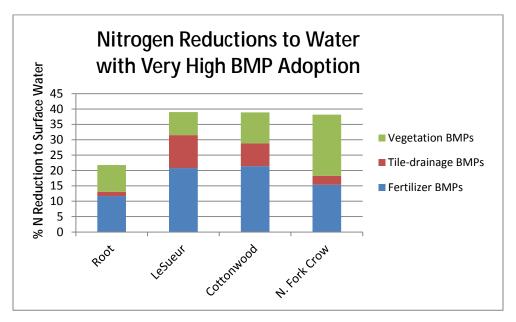


Figure 6. Nitrogen reductions to surface waters (%) in four watersheds which may be achieved by adopting BMPs on 100% of the suitable lands as shown in tables 10-13. The total percentage reduction and reductions from each of the three major BMP categories were estimated with the NBMP tool.

### SPARROW model nitrogen reduction scenarios

The SPARROW modeling conducted for this study, as described in Chapter B4, was used to predict expected statewide delivered total nitrogen (TN) load reductions with different source reduction scenarios (Table 13). Based on these results, 30% reductions to both point source and fertilizers applied to land would result in an estimated 11.2% TN load reduction at the state borders. The agricultural fertilizer category does not include manure sources or any other agricultural N sources except for commercial fertilizer. Similar to results obtained from the NBMP spreadsheet, the SPARROW model scenarios suggest that statewide total N reductions in excess of 10 to 15% will be very difficult to achieve by only reducing N additions to soils.

Table 13. Estimated effects of statewide total N load reductions in streams with source reductions in agricultural fertilizer and urban point sources by 10%, 20% and 30% as estimated with the MRB SPARROW model.

	10% source reduction	20% source reduction	30% source reduction
Point source	-0.7% TN	-1.2% TN	-2.0% TN
Agricultural fertilizer	-3.1% TN	-6.1% TN	-9.2% TN
Total	-3.8% TN	-7.3% TN	-11.2% TN

# Social constraints to cropland best management practice adoption

Based on farmer interview research conducted by Davenport and Olson (2012) in two highly agricultural and heavily tile-drained watersheds (Rush River and Elm Creek), certain BMPs have a greater acceptance by farmers than other BMPs (see report at <u>Nitrogen Use and Determinants of Best Management Practices: A Study of Rush River and Elm Creek Agricultural Producers</u>). While the Davenport and Olson study of farmer and resource manager viewpoints about N reduction BMPs was limited to two watersheds and a limited numbers of farmers, the results identified social constraints which may also exist in other areas. For example, planting perennial crops for energy or forage shows great promise for

reducing nitrate losses, but is not popular due to economic constraints (i.e. current poor market for these crops). Planting riparian buffers along waters is a more accepted practice by farmers, but research shows that it takes large acreages to have a significant effect on reducing N loads. Economic considerations of BMP implementation were the most influential constraints to adoption, including considerations such as cost of the BMP, any associated loss of crop production, land values, and crop prices. Yet, agricultural producer decisions about their farms and BMP adoption are also affected by farm culture, knowledge (education), influence of agricultural professionals, and values such as stewardship, civic responsibility, and human health. Davenport and Olson concluded that the BMPs considered by the interviewed farmers to have the greatest likelihood of adoption at this time are buffer strips along waters, optimal rates as defined by the University of Minnesota, and cover crops.

More information about farmer nutrient management practices and considerations are described in Minnesota Department of Agriculture's Farm Nutrient Management Assessment Program reports found at www.mda.state.mn.us/protecting/soilprotection/fanmap.aspx

# Discussion/conclusions

Information on cropland BMPs presented in this chapter can be considered for larger geographic scale planning purposes (i.e. HUC8 watersheds and larger), but is not intended for small scale strategy development. The potential reductions from BMPs and the costs to achieve those reductions are dependent on: a) the accuracy of baseline assumptions about N fertilizer rates/timing; b) accuracy of infield N leaching and runoff estimates; c) accuracy of assumptions about land suitable for the BMPs; d) annual and regional climate variability; e) ability and willingness of farmers to manage and maintain the BMPs; and f) many other factors. Therefore all N reduction estimates and costs should be viewed as rough approximations for program planning purposes.

#### Scale of reductions

Based on Chapters B2 to B4, large portions of southern Minnesota contribute high N loads to surface waters (yields exceeding 10 pounds/acre), especially south-central Minnesota, but also portions of southeast and southwest Minnesota. A 45% reduction in the highest single HUC8 watershed in the state will only result in about a 3% loading reduction to state rivers. Little cumulative state-level progress will be made unless multiple watersheds (i.e. the top 10 to 20 N loading watersheds) all work to reduce N levels. Meaningful N reductions to surface waters at regional scales cannot be achieved by solely targeting small "hot spots" based on geologically sensitive areas or by targeting "bad actors."

#### **Priority areas**

At the state level, Minnesota will not make meaningful progress in reducing large-scale N loads unless BMPs are adopted on acreages where there is a combination of: high N sources to the land; a seasonally inefficient plant root system which allows considerable vertical movement of the source N; and a way of readily transporting the leached N to surface waters. This pertains mostly to row crops planted on tile-drained lands, but also includes row crops in the karst region and sandy soils.

#### Magnitude and cost of reductions

Based on the statewide results from the NBMP tool, up to an estimated 13% reduction in river N loads can potentially be achieved through widespread implementation of optimal fertilizer rate and timing practices. These results are similar to lowa's estimated reductions from optimal fertilizer rates and timing BMPs. To achieve a 25% N load reduction statewide, a suite of more costly BMPs would also be needed (in addition to the optimal fertilizer rate/timing BMPs). The NBMP spreadsheet indicated that a

25% N loading reduction in Minnesota surface waters is theoretically achievable statewide under very high BMP adoption rates of a variety of field and off-field practices. The cost per pound of N reduced in waters varies from one part of the state to the other, and increases significantly in all watersheds when achieving 25% reductions as compared to 15% reductions. A 30 to 35% statewide reduction of cropland N losses to waters was projected to cost between 1 and 2 billion dollars per year with current crop prices and without further improvements in N reduction BMPs.

#### **Reduction strategy considerations**

- Optimal in-field N management N reduction strategies should start by optimizing in-field
  nutrient management, including: fertilizer and manure rates, fertilizer types, timing of
  application or use of nitrification inhibitors, plant genetic improvements, etc. These types of
  practices can reduce N transport to waters significantly and typically have the least cost,
  potentially saving money in reduced fertilizer costs and/or increased crop yields. Many farmers
  are already using these BMPs, including use of nitrification inhibitors. Yet farmer survey results
  incorporated into the NBMP tool indicate that further reductions are potentially achievable, on
  average.
- Multiple purpose BMPs While this study largely isolates N and N removal BMPs, we recognize that many BMPs provide other benefits apart from reducing N. Any evaluation of recommended practices to reduce N should consider the complete costs and benefits of the BMP. For example, BMPs such as constructed wetlands and controlled drainage could potentially help reduce peak river flows through temporary storage of water. Wetlands and riparian buffers have a potential to create wildlife habitat. Cover crops have added benefits of reducing wind and water erosion and potentially improving soil health. Nitrification inhibitors and spring/sidedress fertilizer applications can improve N use efficiency.
- BMP combinations No single type of BMP is expected to achieve large scale measurable reductions in Minnesota River N levels. Instead, we will need to consider a sequential combination of BMPs which includes in-field nutrient management, tile drainage water treatment and management, and vegetation/landscape diversification. We have enough information to make progress in reducing N in waters with existing BMPs. With continued research and development, further N reductions may be more feasible in the future.
- In-field alternative vegetation Several types of in-field vegetation can achieve large N reductions, including extended rotations involving perennials, cover crops, and perennial energy crops or grasses on marginal lands. It is particularly difficult to achieve N reductions of more than 10 to 15% in minimally-tiled watersheds unless in-field alternative vegetation BMPs are used.
  - Cover crops deserve further study in Minnesota due to the potential desirable effects of significantly reducing nitrate leaching, reducing phosphorus and sediment in runoff, reducing pesticides, and improving soil health. Yet the NBMP tool indicated that cover crops are a costly practice per pound of N reduced, and more work is needed to determine the best ways of seeding and managing cover crops in Minnesota's northern climate. If Minnesota can become more successful at establishing and managing cover crops (e.g. 50-75% success rate) this practice, if widely adopted, could reduce N in rivers by as much as 17-27%.

- Perennial vegetation provides considerable N reductions to underlying groundwater and tile drainage waters. However, the crop revenue losses when converting row crops to perennials, especially during times of high grain prices, makes this practice less likely to be accepted on a widespread scale at this time. If more profitable markets open up for perennial energy crops or forage crops on marginally productive cropland, then this practice will be a more feasible part of N reduction strategies.
- Converting riparian cropland to perennial buffers will not achieve substantial N
  reductions by filtering surface runoff, but this can be an effective practice to reduce N
  leaching on the land where the vegetation change occurs.
- Tile drainage treatment and management Tile line water treatment BMPs are also part of the sequential combination of BMPs needed in many areas to achieve measurable N reductions to waters. Constructed wetlands should be considered in riparian and marginal lands, especially where multiple purpose benefits can be achieved through their use. Bioreactors were found to be more expensive (per pound of N reduced) than wetlands in the Minnesota evaluation, but could be more effective if improvements can be made to treat waters during high-flow times of the year. Bioreactors may be more acceptable in certain areas, such as upland areas where wetland treatment is less feasible. Care must be taken to ensure that BMPs relying on denitrification for N removal do not cause unintended consequences, such as release of metals in waters or greenhouse gasses to the atmosphere.

One BMP which can greatly reduce tile line nitrogen loads is installing tile drains at a shallower depth. This BMP is not generally considered a BMP for reducing N loads from existing conditions, but it can be a preventative measure to reduce the increase of N loads to surface waters in areas where new tile drainage is installed.

# Recommendations for further study

- Develop a cost/benefit planning tool which considers benefits of multiple purpose BMPs, so that planning decisions can be based on a more holistic approach to improving environmental and farm quality, rather than focusing on a single contaminant.
- Research and demonstrate ways to successfully and profitably establish and grow cover crops in Minnesota.
- Research and demonstrate ways to successfully and profitably grow perennial forage and energy crops which have low N losses to waters.
- Further our understanding of how to avoid unintended consequences of adopting BMPs.
- Continue efforts to understanding barriers to adoption of all types of BMPs by discussing with farmers and crop consultants. Refine the existing NBMP tool in the following ways:
  - Verify BMP installation and maintenance cost estimates where developed on limited information.
  - Update with new N fertilizer use surveys and land application of manure data, including how well manure is credited when determining fertilizer rates and current practices related to timing of application.
  - Add nitrification inhibitors as an added BMP option.
  - Continue to add BMP options to the spreadsheet when research demonstrates promising technologies.
  - o Annually update default numbers to the latest fertilizer and crop prices.

- Continue researching improved ways of reducing N loads to surface waters. Saturated buffers show some promise but may need further research and demonstration.
- Continue to evaluate BMPs relying on denitrification processes (i.e. bioreactors and wetlands) to ensure prevention of unintended consequences.
- Evaluate the costs of the BMPs compared to the environmental costs without improvements. Consider full cost accounting studies.
- · Conduct further analysis using the NBMP tool, testing its use at the watershed scale.

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# F2. Reducing Wastewater Point Source Nitrogen Losses to Surface Waters

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Municipal and industrial wastewater treatment facilities remove nitrogen (N) based on their treatment facilities technology and influent N levels. This chapter focuses on potential wastewater N reductions based on additional treatment technologies that could be installed at some treatment facilities.

As mentioned in Chapter D2 of this report, Minnesota currently has over 900 point sources that actively discharge to surface waters. Of these point sources, approximately 64% are domestic wastewater treatment plants (WWTPs) and approximately 36% are industrial facilities. In total, it is estimated that wastewater point sources discharge an average annual total nitrogen (TN) load of approximately 28,131,772 pounds statewide. Most of this load is from municipal dischargers (24,316,038 pounds/year TN, 86%); the remainder is from industrial facilities (3,815,734 pounds/year TN, 14%).

# Nitrogen removal processes

Nitrogen removal from wastewater relies on a number of factors. Two key elements are time and temperature. There must be adequate treatment time for the desired biological activity to occur and the wastewater must be warm enough to insure that the biological activity can occur.

Raw domestic wastewater typically ranges from 20 to 70 mg/L of TN with a typical strength of around 40 mg/L (Water Environment Federation, 2006), consisting of approximately 60% ammonia and 40% organic N. Bacteria take in (assimilate) N from wastewater in a process known as assimilation. In the aerobic treatment process, most of the organic N is changed to ammonia in a process known as ammonification. Then all the ammonia is available to the nitrifying organisms. Biological N removal is a two-step process that involves nitrification and denitrification. Nitrification is an oxidizing process that occurs in the presence of oxygen under aerobic conditions using bacteria to oxidize ammonia to nitrite (NO<sub>2</sub>), and then using another type of bacteria to oxidize the nitrite to nitrate (NO<sub>3</sub>). The treatment process requires both a long solids retention time and hydraulic retention time. Denitrification is a reducing process that occurs in the absence of oxygen under anoxic conditions using bacteria to reduce nitrate to nitric oxide, nitrous oxide and N gas, with the N gas released to the atmosphere from the treatment tank wastewater surface. Nonbiodegradable organic N that is in particulate form is not removed through these processes, but rather through the physical process of solids separation (sedimentation or filtration). For details on estimated TN effluent data from different types of wastewater treatment plants, see the Assumptions and Methods portion of Chapter D2 and Table 2 of that chapter. Table 2 of Chapter D2 shows typical TN effluent values ranging from 6 mg/L at a small pond system up to 19 mg/L at a large class A-type of mechanical plant.

For optimum nitrification, a solids retention time (SRT) long enough to allow a stable population of nitrifiers to be maintained in the process is necessary. The target SRT will vary with temperature, dissolved oxygen, pH, and ammonia concentration. Temperature must be greater than about 45° F to provide a stable population of nitrifiers. A hydraulic retention time (HRT) long enough to allow biomass enough time to react with the ammonia is also necessary. Systems with longer HRTs are less likely to see ammonia break-through due to temperature changes, or variations in flows and loadings.

For optimum denitrification, an anoxic zone that is mixed well and has dissolved oxygen levels less than 0.1 mg/L is necessary. Denitrifying bacteria are facultative and prefer to use oxygen to metabolize Carbonaceous Biochemical Oxygen Demand (CBOD). Any oxygen in the zone will be used before the bacteria start to reduce the nitrate. Sufficient readily degradable CBOD in the anoxic zone is also necessary. Carbon augmentation may be necessary with low CBOD to N ratios and nearly all separate stage denitrification.

Treatment time at a typical mechanical plant, such as an activated sludge plant or trickling filter with contact stabilization, is accomplished through the use of tanks. Tanks can be laid out in a variety of configurations, depending on the type of treatment units.

For aerated wastewater pond systems, N removal may be possible with additional treatment processes. Nitrification can be achieved by either adding an additional treatment unit after the ponds, such as some kind of fixed-film aeration tank/reactor or by modifying the aerated pond system by installing dividing baffling in the pond(s) along with the possible addition of media. A treatment unit for denitrification would also need to be added. This could also include the need for additional clarification. As with mechanical plants, adequate detention time to support the desired biological activity and proper dissolved oxygen concentrations is a key part of the treatment.

Wastewater temperature is the other key element. Raw wastewater temperature varies seasonally and is important because of the significant effect temperature has on the biological process. Heat loss also varies from plant to plant, depending on the treatment units being used. Wastewater temperatures must be greater than about 45° F to provide a stable population of nitrifiers. When wastewater temperatures fall to around 40° F, the nitrification/denitrification process becomes prohibitively slow.

For mechanical plants, wastewater temperatures usually do not fall below this level. Wastewater usually moves through a plant quick enough so that the temperature does not have a chance to drop below 45° F. Also, many mechanical plants have covers on many portions of the plant, especially the head works (grit removal and screening) and the primary clarifiers. For systems with septic tanks, wastewater temperatures in the winter can easily fall below the needed level for N removal. Most septic tanks are buried but they are buried without any insulation and the wastewater can remain in the tank for enough time for the water to cool. This is similar in aerated ponds. Aerated ponds are exposed to the elements and the wastewater easily cools while going from pond to pond prior to discharge. This also applies to stabilization ponds.

The above information regarding temperature was used to estimate N reduction potential at wastewater plants throughout the state. It was estimated that N removal could be implemented at mechanical wastewater treatment plants all year long. While N removal may be possible at aerated ponds during some of the warmer months, it would not be an easy process. Because of this, the analysis below assumes that N removal would not be achieved at aerated ponds. It was also estimated that N removal could not be implemented at stabilization ponds and septic tank-based systems. Of course, this is a general estimation. In reality, each plant would need to be individually evaluated to determine if and/or how N removal could and/or would be implemented. It should also be noted that the operation of a wastewater treatment plant can be a delicate process, easily upset by changes in influent flow and/or loading. This can cause problems in the nitrification process and especially in the denitrification process. In some cases an additional carbon source, such as some type of syrup product, is added to the wastewater.

# Nitrogen removal levels from two technologies

The two primary methods of N removal from wastewater evaluated in this study are Biological Nutrient Removal (BNR) and Enhanced Nutrient Removal (ENR). A third tier of nutrient removal, called Limit of Technology (LOT), is sometimes considered (Section 3 of the Iowa Nutrient Reduction Strategy, Iowa Department of Natural Resources [2012].

Biological Nutrient Removal is most commonly associated with sequenced combinations of aerobic, anoxic and anaerobic processes which facilitate biological denitrification via conversion of nitrate to N gas. Effluent limits achievable using BNR at WWTPs that treat primary domestic wastewater are approximately 10 mg/L TN (Iowa Department of Natural Resources, 2012). For a mechanical WWTP the typical type of treatment would be activated sludge, which could be in the form of an oxidation ditch, sequencing batch reactor or "regular" aeration tanks. Another common option is a trickling filter followed by contact stabilization. Contact stabilization is achieved using tanks similar to aeration tanks. Adequate detention time is a key factor in achieving BNR and N removal.

Enhanced Nutrient Removal typically uses BNR along with filtration to achieve lower effluent N levels. This may also involve chemical addition. Effluent limits achievable using ENR at WWTPs are approximately 6 mg/L TN (Iowa Department of Natural Resources, 2012). For a mechanical WWTP the typical type of treatment would be similar to those listed above in the BNR description with the addition of some type of denitrification filter. As mentioned above, adequate detention time is a key factor.

Limit of Technology is generally associated with the lowest effluent concentrations that can be achieved using any treatment technology or combination of technologies. Potential technologies may include tertiary chemical addition with filtration, advanced effluent membrane filtration and ion exchange. It appears that there may not be consensus establishing specific treatment requirements for LOT or what effluent values could be achieved. The effluent values would be something less than the 6 mg/L TN value associated with ENR. Due to the lack of consensus surrounding LOT, there is no reduction estimates made based on this technology. Reduction estimates have been made on BNR and ENR.

Utilizing the above information as a guide, TN reductions were estimated at facilities based on BNR and ENR application. BNR and ENR, it was assumed, could be applied to mechanical facilities. It was assumed that BNR and ENR could not be applied to aerated ponds, stabilization ponds and septic tank-based systems.

# Statewide nitrogen reduction from wastewater point sources

Current TN load values are based on actual discharge flow as reported to the MPCA by individual permittees via their discharge monitoring reports. Actual discharge TN concentration data was also used when available, and where not available it was estimated based on the type of treatment facility. Since much of the TN data used to calculate the reductions are estimates and not based on actual discharge TN concentration data, N reduction estimates could change once more actual discharge data become available. For more details on the estimated TN effluent data, see the Assumptions and Methods portion of Chapter D2 and Table 2 of that chapter.

Current estimates of wastewater N loads from Chapter D2, along with N removal efficiencies from BNR and ENR technologies as previously described, were used to estimate statewide N load reductions potentially achievable for wastewater. Reductions due to the implementation of BNR and ENR at all

applicable treatment facilities were calculated. Table 1 below, in addition to the estimated current TN load, includes the estimated TN loads if BNR and ENR was implemented. The table also includes the percent reduction compared to the current load.

Implementing BNR technology statewide will reduce N discharges at municipal wastewater discharge points by an estimated 46%, and by 9% at industrial wastewater points of discharge. Implementing ENR technology statewide will reduce N discharges at municipal wastewater discharge points by an estimated 66%, and by 29% at industrial wastewater points of discharge. Combining municipal and industrial wastewater N reductions, BNR and ENR implemented statewide will reduce wastewater point sources by an estimated 41% and 61%, respectively.

Table 1. TN loading rates for the whole state and potential reductions due to BNR and ENR

Discharge source	Current TN load - lbs/year	BNR - lbs/year & (% reduction from current)	ENR - lbs/year & (% reduction from current)
Municipal	24,929,970	13,211,169 (46% reduction)	8,152,457 (66% reduction)
Industrial	3,741,459	3,461,397 (9% reduction)	2,712,060 (29% reduction)
Total	28,671,429	16,672,566 (41% reduction)	10,864,517 (61% reduction)

# Nitrogen reductions in select major basins

Table 2 below includes current TN loading rates for three major basins in Minnesota; the Minnesota River, the Upper Mississippi River, and the Red River of the North. Also included is the estimated TN load if BNR and ENR were to be implemented in each basin, comparing the percent reduction to the current load. Reductions have been included for these three basins due to the amount of attention that has been focused on these basins recently. Water quality issues in the Gulf of Mexico and Lake Pepin have focused attention on the Minnesota River basin and the Upper Mississippi River basin over the last 10 to 20 years. Water quality issues in the Red River of the North and Lake Winnipeg, where the Red eventually empties, have come to the surface in more recent years.

Percent reductions in the Minnesota River watershed and the Upper Mississippi River watershed are very similar. BNR percent reductions for the Minnesota and Upper Mississippi are 43% and 44%, respectively. For ENR, the N reduction estimates are 64% and 65% for the Minnesota and Upper Mississippi, respectively. Percent reduction values for the Red River of the North are lower but still substantial at 35% for BNR and 51% for ENR.

Table 2. TN loading rates for three watersheds and potential reductions due to BNR & ENR

Watershed	Discharge source	Current TN load- lbs/year	BNR - lbs/year & (% reduction from current)	ENR - lbs/year & (% reduction from current)
Minnesota River	Total	4,676,235	2,650,818 (43% reduction)	1,695,525 (64% reduction)
Upper Mississippi River	Total	14,249,666	7,941,375 (44% reduction)	5,010,724 (65% reduction)
Red River of the North	Total	659,696	429,850 (35% reduction)	326,314 (51% reduction)

As shown in the tables above, implementation of BNR or ENR could have a substantial impact on the TN discharged in Minnesota. It should be noted that these reductions are only estimates. Actual reductions can be influenced by numerous factors including but not limited to the amount of influent N a plant is receiving and the type of technology chosen. A full scale pilot study may be the only way to really determine the best technology for a given plant and the actual reductions that may occur when that technology is utilized. Currently in Minnesota there are two facilities with a TN limit of 10 mg/L. Both facilities use some form of activated sludge for treatment and both facilities have had problems meeting their TN limit. There are no TN limits lower than 10 mg/L.

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# G. Conclusions

## Concerns with nitrogen in waters

Nitrogen (N) affects in-state and downstream waters in three primary ways:

- 1. **Aquatic life toxicity** Aquatic life have been found to be adversely affected by the toxic effects of elevated nitrate. The nitrate levels that harm aquatic life are currently being studied so that standards can be developed to protect Minnesota fish and other aquatic life.
- 2. **Gulf hypoxia** The Gulf of Mexico receives about six percent of its nitrogen from Minnesota watersheds. The cumulative effects of multi-state N contributions is largely the cause of the hypoxic (low oxygen) zone in the Gulf of Mexico. While N can increase eutrophication in coastal waters, N has a less prominent role in affecting lake and stream eutrophication within Minnesota, which is mostly controlled by phosphorus.
- 3. **Nitrate in drinking water** Fifteen streams, mostly in southeastern Minnesota, exceed a 10 mg/l standard established to protect potential drinking water supplies.

## River nitrogen conditions and loads

#### Stream N concentrations

Maximum nitrite+nitrate-N (nitrate) levels in Minnesota rivers and streams (years 2000-2010) exceeded 5 mg/l at 297 of 728 (41%) monitored sites across Minnesota, and exceeded 10 mg/l in 197 (27%) of these sites. A marked contrast exists between nitrate concentrations in the southern and northern parts of the state. In southern Minnesota, most river and stream sites exceed 5 mg/l at least occasionally. Most northeastern Minnesota streams have nitrate concentrations which remain less than 1 mg/l. Streams in northwestern Minnesota have nitrate that is typically less than 3 mg/l, even during peak times.

Total Nitrogen (TN) concentrations exhibit the same spatial pattern across the state as nitrate, but are typically about 0.5 to 3 mg/l higher than nitrate-N, since TN also includes organic N and ammonia+ammonium-N (ammonium). Ammonium concentrations are less than 1 mg/l even during peak times at 99% of rivers and streams in the state, and median concentrations are mostly less than 0.1 mg/l. River ammonium concentrations decreased substantially in the 1980's and 1990's, according to previous studies.

#### Mainstem river loads

Monitoring-based annual TN loads show that most of the state's TN load leaves the state in the Mississippi River. Nearly 211 million pounds of TN leaves Minnesota per year in the Mississippi River at the Minnesota-lowa border, on average, with just over three-fourths originating in Minnesota watersheds, and the rest coming from Wisconsin, lowa and South Dakota. This compares to about 37 million pounds in the Red River at the Minnesota-Canadian border (17 million pounds from Minnesota and the rest mostly from North Dakota). The highest TN loading tributary to the Mississippi River is the Minnesota River. The Minnesota River adds about twice as much TN as the combined loads from the Upper Mississippi and St. Croix Rivers. This is not because the Minnesota River contributes more flow, but because its TN concentrations are so much higher than the other rivers, 4 to 8 times higher than the Upper Mississippi and St. Croix Rivers, respectively.

South of the Twin Cities, tributaries from Wisconsin and Minnesota contribute additional TN to the Mississippi River. Only small amounts of N are lost in the mainstem rivers, unless the water is backed up in quiescent waters. In the river stretch between the Twin Cities and Iowa, some TN is lost when the river flow slows in

Lake Pepin and in river pools behind lock and dams. Monitoring based loads show than an average 9% N loss occurs in Lake Pepin. An additional 3% to 13% of the River N is estimated to be lost in the collective pools along the 168 mile Mississippi River stretch between the Twin Cities and Iowa. The net effect of the TN additions and TN losses in the Lower Mississippi Basin is an average 37 million pound load increase between the Twin Cities and Iowa.

Year-to-year variability in TN loads and river flow can be very high. In the Minnesota River Basin, TN loads during low flow years are sometimes as low as 25% of the loads occurring during high flow years. Total nitrogen loads in the Minnesota, Mississippi, and St. Croix Rivers typically reach monthly maximums in April and May. About two-thirds of the annual TN load in the Mississippi River at the lowa border occurs during the months of March through July. This is due to both river flow and TN concentration increases during these months.

### **Priority watersheds**

Both monitoring and modeling show that the highest N yields occur in south central Minnesota, where TN flow-weighted mean concentrations (FWMCs) typically exceed 10 mg/l and yields range from about 15 to 25 pounds/acre/year. The second highest TN concentrations and yields are found in southeastern and southwestern Minnesota watersheds, which typically have TN FWMCs in the 5 to 9 mg/l range and yields between 8 and 15 pounds/acre/year.

Watersheds in the northern two-thirds of the state have much lower nitrate and TN concentrations, with TN FWMCs in northeastern Minnesota less than 1.5 mg/l and yields from 0.1 to 3 pounds/acre/year. Total N FWMC and yields are higher in the northwestern part of the state as compared to the northeast.

The highest N-yielding watersheds include the Cedar River, Blue Earth River, Le Sueur River, and Minnesota River (Mankato), each yielding over 20 pounds/acre/year during an average year. The highest 15 N loading HUC8 watersheds to the Mississippi River contribute 74% of the Minnesota TN load which ultimately reaches the Mississippi River. The other 30 watersheds contribute the remaining 26% of the load.

#### River nitrate trends

Flow adjusted nitrate concentrations in the Mississippi River increased between about 1976 and 2010 at most regularly monitored sites on the river, with overall increases ranging between 87% and 268% everywhere between Camp Ripley and LaCrosse. During recent years, nitrate concentrations have been increasing everywhere downstream of Clearwater at a rate of 1% to 4% per year, except that no significant trend has been detected at Grey Cloud and Hastings in the Metro region. Another study by the National Parks Service and others showed that nitrate and TN loads also increased in the Mississippi River between 1976 and 2005 (see Chapter C2). Because over one-third of the Mississippi River N loads are influenced by groundwater baseflow, ongoing monitoring reflects a mix of waters having recently entered the soil and water, along with waters which entered the soil years to decades ago and are just now starting to reach surface waters.

Increasing nitrate concentration trends were also found in the Cedar River (113% over a 43-year period) and the St. Louis River in Duluth (47% increase from 1994 to 2010). The Red River showed significant increases before 1995, but no significant trends between 1996 and 2010.

Not all locations in the state, however, are showing increasing trends. The two monitored sites on the downstream portion of the Minnesota River (Jordan and Fort Snelling) showed a slight increase from 1979 to 2005, followed by a decreasing trend between 2005-06 and 2010-11. During recent years, all sites on the Minnesota River and most tributaries to the Minnesota have been either trending downward or have shown no trend. Additionally, some tributaries to the Mississippi Rivers have also shown decreasing nitrate trends in recent years, including the Rum, Straight, and Cannon Rivers.

Other rivers in the state have shown no significant trends since the mid-1970's, including the Rainy River, West Fork Des Moines, and Crow Rivers.

Trend studies published elsewhere showed many similarities to the findings in this study; yet the magnitude of % change was often found to be higher in this study.

#### Nitrogen sources

#### Cropland

The amount of TN (hereinafter referred to as "N") reaching surface waters from cropland varies tremendously, depending on the crops, tile drainage practices, cropland management, soils, climate, geology and other factors. Annual N losses to surface waters are less than 10 pounds/acre/year on some cropland and over 30 pounds/acre/year on other cropland.

According to the N source assessment, during an average precipitation year, cropland sources contribute an estimated 73% of the statewide N load to surface waters and 78% of the N load to the Mississippi River. The statewide estimates are similar to the SPARROW model results, which indicate that 70% of N entering surface waters is from agricultural sources. The relative contribution of N loads to surface waters from cropland sources varies by watershed. Cropland sources account for an estimated 89 to 95% of the N load in the Minnesota portions of the Minnesota River, Missouri River, Cedar River and Lower Mississippi River Basins; whereas cropland N accounts for 49% of the Upper Mississippi River Basin N sources. The statewide fraction of N coming from cropland sources also varies with climate, increasing from 72% of statewide N load during an average precipitation year to 79% during a wet year. During a dry year, cropland sources are still the highest N loading sources, but are reduced to 54% of the estimated statewide source N load.

Inorganic N becomes available to crops from several added sources, including commercial fertilizers (47%), legume fixation (21%), manure (16%), and wet+dry atmospheric deposition (15%). The combination of septic systems, lawn fertilizer, and municipal sludge account for about 1% of all N added to soils statewide. Soil organic matter mineralization also contributes a substantial amount of annual inorganic N to soils, yet the precise amount is more difficult to measure or estimate than other sources. Estimates of net mineralization from this study suggest that statewide mineralization from cropland releases an annual amount of inorganic N that is comparable to N from fertilizer and manure additions combined.

Cropland N reaches surface waters through two dominant pathways: 1) tile-line transport, and 2) leaching to groundwater and subsequent flow to surface waters. Surface runoff from cropland adds relatively little N to waters, contributing 1% to 4% of major basin N loads, except that in the Lower Mississippi River and Red River Basin it cropland runoff contributes 9 and 16% of the N load, respectively.

#### Tile drainage

Tile drainage over row crops represents the highest cropland source pathway and highest overall source in the state. During an average precipitation year, row crop tile drainage contributes 37% of the N load to waters around the state, and contributes 67% of the N load in the heavily tiled Minnesota River Basin. During a wet year, tile drainage contributes an estimated 43% of statewide N loads to waters, and contributes 72% of the N load to the Minnesota River.

The highest N yielding watersheds in the state are those which are intensively tiled. Statistical analyses of Minnesota watershed characteristics indicated that the amount of tile drainage (estimated) explained nitrate and TN variability more than any of the 17 other factors examined. Other Midwest studies also showed a direct correlation between the amount of estimated tiled land and N levels entering waters.

#### Cropland groundwater

Nitrogen leaching down into groundwater below cropped fields, and subsequently moving underground until it reaches streams, contributes an estimated 30% of N to statewide surface waters. Groundwater N can take from hours to decades or longer to reach surface waters, depending on the rate of groundwater flow and the flow path distance. Nitrogen leaching into groundwater is the dominant pathway to surface waters in the karst dominated landscape of the Lower Mississippi River Basin, where groundwater contributes an estimated 58% of all N. Yet in the Minnesota River Basin, dominated by clayey and tile-drained soils, cropland groundwater only contributes 16% of the N to surface waters, on average.

If we include both the cropland and non-cropland groundwater N sources, 36% of the statewide N load to surface waters is estimated to be from groundwater. The groundwater source estimates have more uncertainty than other source estimates, due to limited data and high variability in leaching and groundwater denitrification rates. Yet, the importance of the groundwater pathway to surface waters was also supported by results from other studies in the state, region and nation, as referenced in Chapter E3.

## Wastewater point sources

Wastewater point sources discharge an estimated average annual TN load of 28.7 million pounds statewide. The loads are dominated by municipal wastewater sources, which were found to contribute 87% of the wastewater point source N load discharges, with the remaining 13% from industrial facilities. Nearly half (49%) of the point source N discharges occur within the Twin Cities Metropolitan Area. The 10 largest point source N loading facilities collectively contribute 67% of the point source TN load.

Wastewater point sources contribute an estimated 9% of the statewide N load according to the source assessment. This is similar to, but slightly more than, the 7% point source contribution estimated from SPARROW model results. River monitoring shows that the sum of the long-term average river N coming into the Twin Cities is 6 million pounds less than the N leaving in the Twin Cities near Prescott/Hastings. The 6 million pound average difference is a statistically insignificant 3.5% of the Mississippi River Load at Prescott.

When we divide the wastewater point source N discharge by the size of contributing sewershed areas in the Twin Cities region, we obtain an average of 14 pounds/acre/year from wastewater point sources. In higher density population areas, the N yield increases to 20 pounds/acre/year. SPARROW simulated TN yield in the urban dominated Mississippi River Twin Cities Watershed was 17.4 pounds/acre/year, similar to the yield range identified through the source assessment study. These N yields are comparable to many cropland yields, but are generally lower than intensively tiled row-crop areas. However, the wastewater N delivery to rivers is different than from cropland, as it enters waters at a few specific points as opposed to being dispersed across the watershed.

#### Other sources

Two other source categories, atmospheric deposition and forest, each contribute cumulative total statewide N loads that are comparable to wastewater point source N loads. While the N concentrations from these two other sources are much lower than wastewater, the aerial extent of these two sources is vast, thereby accounting for the comparable loads.

Atmospheric deposition is highest in the south and southeast parts of the state and lowest in the north and northeast where fewer urban and cropland sources exist. Atmospheric deposition falling directly into lakes and streams was considered in the source assessment as a direct source of N into waters, contributing about 9% of the statewide annual load to waters. Correspondingly, the areas of the state with the most lakes and streams had the most atmospheric deposition directly into waters. Yet, relatively few other N sources are found in the northern Minnesota lakes regions, and a large fraction of N entering into most lakes will not leave the lake in

streams. Some N, typically less than 3 pounds/acre/year, is exported out of forested watersheds. Forest N contributions are nearly negligible in localized areas and N levels in heavily forested watersheds are quite low. Yet since such a large fraction of the state is forested, the total cumulative N to waters from forested lands adds up to about 7% of the statewide N load.

Other sources were very small by comparison, including septic systems (2%), urban/suburban nonpoint source N (1%), feedlot runoff (0.2%) and water fowl (<0.2%).

## Sources to the Mississippi River

Just over 81% of the total N load to Minnesota waters is in watersheds which end up flowing into the Mississippi River. If we look only at those Minnesota watersheds which drain into the Mississippi River, N source contributions during an average precipitation year are estimated as follows: cropland sources 78%, wastewater point sources 9%, and non-cropland nonpoint sources 13%. Cropland source contributions increase to 83% for these watersheds during wet (high-flow) years, while wastewater point sources decrease to 6%. During a dry year, cropland sources represent an estimated 62% of N to waters in this region and wastewater point sources contribute 19%.

## Reducing nitrogen in surface waters

Because high N levels are pervasive over much of southern Minnesota, little cumulative large-scale progress in reducing N in surface waters will be made unless numerous watersheds (i.e. the top 10 to 20 N loading watersheds) reduce N levels. Appreciable N reductions to surface waters at regional and state-level scales cannot be achieved by solely targeting reductions on relatively small subwatersheds or mismanaged land tracts.

## Cropland source reduction

Based on the N source assessment and the supporting literature/monitoring/modeling, meaningful regional N reductions to rivers can only be achieved if Best Management Practices (BMPs) are adopted on acreages where there is a combination of a) high N sources to soils, b) seasonal lack of dense plant root systems, and c) rapid transport avenues to surface waters (bypassing denitrification N losses which are common in some ground waters). These conditions mostly apply to row crops planted on tile-drained lands, but also include crops in the karst region and over many sandy soils.

Further refinements in fertilizer rates and application timing can be expected to reduce river N loads and concentrations, yet more costly practices will also be needed to meet downstream N reduction goals.

BMPs for reducing N losses to waters can be grouped into three categories:

- In-field nutrient management (i.e. optimal fertilizer rates; apply fertilizer closer to timing of crop use; nitrification inhibitors; variable fertilizer rates)
- Tile drainage water management and treatment (i.e. tile spacing and depth; controlled drainage; constructed and restored wetlands for treatment purposes; bioreactors; and saturated buffers)
- 3) *Vegetation/landscape diversification* (i.e. cover crops; perennials planted in riparian areas or marginal cropland; extended rotations with perennials; energy crops in addition to corn)

Through this study, a tool was developed by the University of Minnesota to evaluate the expected N reductions to Minnesota waters from individual or collective BMPs adopted on lands well-suited for the practices. The tool, Nitrogen Best Management Practice watershed planning tool (NBMP), enables planners to gauge the potential

for reducing N loads to surface waters from cropland, and to assess the potential costs of achieving various N reduction goals. The tool also enables the user to identify which BMPs will be most cost-effective for achieving N reductions at a HUC8 watershed or statewide scale.

We used the NBMP tool to assess numerous N reduction scenarios in Minnesota statewide and in specific HUC8 watersheds. Results from the NBMP tool were also compared to results from an lowa study which used different methods to assess the potential for using agricultural BMPs to achieve N load reductions to lowa waters. Both the Minnesota and lowa evaluation concluded that no single type of BMP is expected to achieve large-scale reductions sufficient to protect the Gulf of Mexico. However combinations of in-field nutrient management BMPs, tile drainage water management and treatment practices, and vegetation/landscape diversification practices can measurably reduce N loading to surface waters.

River N loads can potentially be reduced by as much as 13% statewide through widespread implementation of optimal in-field nutrient management BMPs, practices which also have the potential to reduce fertilizer costs. To achieve a 25% N load reduction, high adoption rates of a suite of more costly BMPs will need to be added to the in-field N management BMPs. The achievability and costs of N load reductions vary considerably from one region to another.

A 30% to 35% statewide reduction of cropland N losses to waters was projected to cost between 1 and 2 billion dollars per year with current crop prices and without further improvements in N reduction BMPs. The results also showed that 15% to 25% N load reductions can be made at a substantially lower cost.

lowa predicted a 28% statewide nitrate reduction if cover crops were planted on row crops throughout the state. Cover crops deserve further study in Minnesota due to a combination of desirable potential benefits to water quality and agriculture. If Minnesota can become more successful at establishing and managing cover crops, and then achieve widespread adoption of this practice, we could potentially reduce N in Minnesota rivers by as much as 17% to 27% from this practice alone.

Tile-drainage water treatment BMPs are also part of the sequential combination of BMPs which can be employed in many areas to achieve additional N reductions to waters. Constructed wetlands and wetland restoration designed for nitrate treatment purposes remove considerable N loads from tile waters (averaging about 50%) and should be considered in riparian and marginal lands. Bioreactors cost more than wetlands to reduce a given amount of N, but show promise if further improvements can be made to treat waters during high-flow times of the year. Bioreactors may be an option in upland areas where wetland treatment is less feasible. If controlled drainage is used in combination with wetlands and bioreactors on lands well-suited for these BMPs, statewide N loads to streams can be reduced by 5% to 6%, and N loads in heavily-tiled watersheds can be reduced by an estimated 12% to 14%.

Perennial vegetation provides large N reductions to underlying groundwater and tile drainage waters. When grasses, hay, and perennial energy crops replace row crops on marginally productive lands and riparian areas, N losses to surface waters are greatly reduced. However, the crop revenue losses when converting row crops to perennials, especially during times of high grain prices, makes this practice less feasible on a widespread scale as compared to other practices.

#### Wastewater N reduction

Wastewater point source N discharges can be reduced through two primary methods: 1) Biological Nutrient Removal (BNR), and 2) Enhanced Nutrient Removal (ENR) which involves biological treatment with filtration and/or chemical additions.

BNR technologies, if adopted for all wastewater treatment facilities, would result in an estimated 43% to 44% N reduction in wastewater point source discharges to rivers in the Upper Mississippi and Minnesota River Basins, and a 35% reduction in the Red River Basin. These reductions correspond with an estimated overall N reduction to waters from all N sources by 9.3%, 2.2% and 0.8% in the Upper Mississippi, Minnesota, and Red River Basins, respectively.

ENR technologies, if adopted for all wastewater treatment facilities, are estimated to result in a 64% to 65% N reduction in wastewater point source discharges to rivers in the Upper Mississippi and Minnesota River Basins, and a 51% reduction in the Red River Basin. These reductions correspond with an estimated overall N reduction to waters from all N sources by 13.5%, 3.2% and 1.2% in the Upper Mississippi, Minnesota, and Red River Basins, respectively.

## Recommendations for future study

Future research can improve the estimates in this study.

Source estimates to surface waters could be improved by conducting the following studies:

- further quantification of N leaching to groundwater for different soils, crops, N management and regions of the state
- evaluate denitrification losses within groundwater under different hydrogeologic settings (as groundwater moves between source area and stream)
- · verify amount of cropland tile drainage that exists and determine recent rates of installation
- conduct new and expanded fertilizer and manure use surveys and incorporate the new information
- supplement the Point Source N concentration information with additional effluent monitoring data

Strategies for reducing N losses to waters can be better evaluated with:

- a tool which integrates N, phosphorus, and sediment reduction BMPs and associated costs so that the total costs and benefits are considered when planning for multi-purpose BMP adoption strategies
- additional information about BMPs under development, such as saturated buffers, cover crop use in Minnesota, perennial energy crop economics, and water retention strategies
- improved and updated baseline information on current fertilizer rates and timing practices on both land with, and without, manure additions
- costs for reducing wastewater point sources of N
- see further recommendations for future study at the end of Chapter F1

# Appendix B4-1. Overview of the United States Geological Survey SPARROW Watershed Model

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### Introduction

The U.S. Geological Survey (USGS) SPAtially Referenced Regressions on Watershed attributes (SPARROW) watershed computer simulation model integrates water monitoring data with landscape information to predict long—term average constituent loads that are delivered to downstream receiving waters. SPARROW models are designed to provide information that describes the spatial distribution of water quality throughout a regional network of stream reaches. SPARROW utilizes a mass-balance approach with a spatially detailed digital network of streams and reservoirs to track the attenuation of nutrients during their downstream transport from each source. Models are developed by statistically relating measured stream nutrient loads with nutrient input sources and geographic characteristics observed in the watershed [Preston et al., 2011a]. A Geographic Information System (GIS) is used to spatially describe constituent sources and overland, stream, and reservoir transport.

The statistical calibration of SPARROW assists in the identification of nutrient sources and delivery factors that are most strongly associated with long-term mean annual stream constituent loads. The mass-balance framework and spatial referencing of the model provides insight to the relative importance of different constituent sources and delivery factors. The networking and instream processing aspects of SPARROW provide the capability of relating downstream loads to the appropriate upstream sources so that constituent contributions from a variety of distant upstream sources can be systematically and accurately evaluated in relation to the delivery point [Preston et al., 2011a]. SPARROW results can be used to rank subbasins within large watersheds and rank the relative difference of constituent sources among subbasins.

The process for developing a SPARROW model enables the ability to identify the factors affecting water quality and their relative importance through the combined use of a mechanistic model structure and statistical estimation of model coefficients. This is accomplished by

- (1) imposing process constraints such as mass balance, first-order nonconservative transport, and the use of digital topography and hydrologic networks that provide spatially explicit descriptions of water flow paths; and
- (2) using observed data, including long-term measurements of streamflow, water quality, and geospatial data of watershed properties, to inform the complexity of the model so that only statistically significant explanatory variables, which are uncorrelated with one another are selected [Preston et al., 2011a].

The USGS National Water Quality Assessment (NAWQA) program developed 12 SPARROW watershed models for six major river basins in the continental United States (Figure 1). Nutrient estimates for Minnesota were based upon the existing SPARROW Major River Basin 3 (MRB3; Robertson and Saad, 2011) model (Figure 2). The MRB3 model includes 15,000 stream catchments and 848 monitoring stations in North Dakota, Minnesota, Wisconsin, Michigan, Iowa, Illinois, Missouri, Indiana, Ohio, Kentucky, Tennessee, West Virginia, Pennsylvania, and New York.

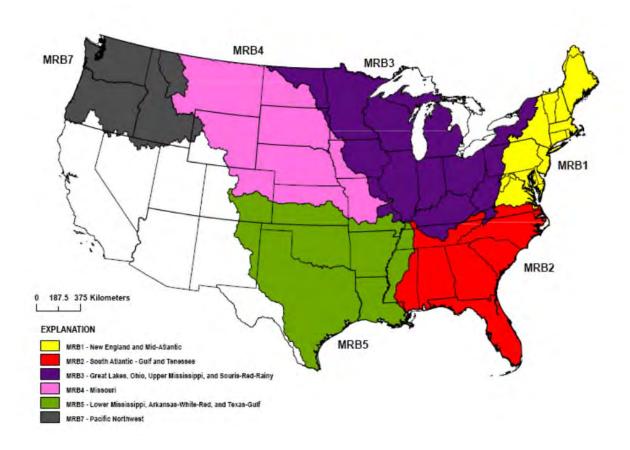


Figure 1. Regions (Major River Basins, or MRBs) selected for the development of SPARROW nutrient models [from Maupin and Ivahnenko, 2011].

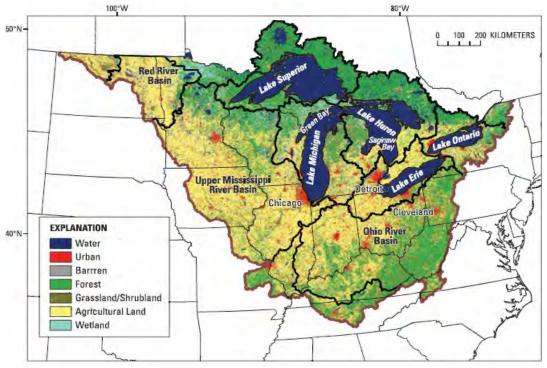


Figure 2. Landuse and land cover of major river basin 3 (U.S. portion) [Robertson and Saad, 2011].

## Methodology

Watershed and water quality simulation models utilize various levels of complexity or process detail to represent the hydrologic and biogeochemical processes present in a watershed. The range of model complexity varies from purely statistical models to detailed mass—balance models (Figure 3). Statistical or empirical models use regression techniques to relate stream monitoring data to watershed sources and landscape properties. As described in Chow et al. (1988): "Statistical methods are based on mathematical principles that describe the random variation of a set of observations of a process, and they focus attention on the observations themselves rather than on the physical processes which produced them. Statistics is a science of description, not causality."

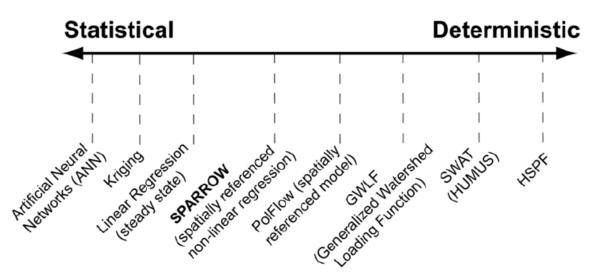


Figure 3. Relationship of SPARROW to the continuum of water quality simulation methods [Schwartz et al., 2006].

At the other end of the scale, deterministic water–quality models have a highly complex mass-balance structure that simulates hydrologic and contaminant transport processes, often according to relatively fine temporal scales. All models reflect some blend of these methods, but most place greater emphasis on one or the other type of model structure and process specification. In comparison to other types of water-quality models, SPARROW may be best characterized as a hybrid process-based and statistical modeling approach. The mechanistic mass transport components of SPARROW include surface-water flow paths (channel time of travel, reservoirs), non-conservative transport processes (first-order instream and reservoir decay), and mass-balance constraints on model inputs (sources), losses (terrestrial and aquatic losses/storage), and outputs (riverine nutrient export). The statistical features of SPARROW include the utilization of nonlinear regression techniques to correlate stream monitoring data to pollutant sources, climate, and watershed hydrography and landuse [Schwartz et al., 2006].

The statistical parameters of SPARROW models are estimated with weighted nonlinear regression techniques by spatially relating water–quality flux estimates at monitoring stations with the geography of point–sources, landscape characteristics, and surface-water properties that affect transport. The calibrated models are then used to predict constituent flux for stream reaches throughout a river network. Total constituent flux and flux by contributing source can be estimated. The constituent load from an individual SPARROW subwatershed can be routed to a selected delivery point in the modeled basin.

A load mass-balance is achieved by linking all measured in-stream loads to identified upstream sources, and by requiring that the accumulation of load across sources and reaches be strictly additive. The contaminant load leaving a reach is the sum of two components: the load generated within upstream reaches and transported to the reach via the stream network plus the load originating within the incremental watershed of the reach and delivered to the stream reach.

The dependent variable in SPARROW MRB3 model is long-term mean annual constituent load normalized to a base year. The base year of 2002 was selected to coincide calculated loads with the most recent geospatial datasets of nutrient sources and environmental characteristics [Saad et al., 2011]. Detrended mean annual loads provide an estimate of conditions normalized to a base year. The use of

detrended mean annual loads in SPARROW helps compensate for differences in the length and amount of monitoring data available among sites and minimizes the inherent noise introduced by year-to-year variations in rainfall – facilitating the identification of environmental factors that affect loading over long periods. The detrended load estimates estimated with Fluxmaster (Schwarz et al., 2006) are based on two statistical models: a water-quality model and a flow model used to remove trends in streamflow.

#### Statistical Analysis System

The SPARROW model code is written in the Base Statistical Analysis System (SAS) Macro Language, with statistical procedures written in the SAS IML. SPARROW model execution requires SAS software components Base SAS, the SAS statistical procedures (SAS/STAT) and SAS/IML. The SAS/GIS software component is optional for producing maps of model output. [Schwarz et al., 2006].

#### Runoff

Runoff is calculated for each streamgage basin by dividing the average daily flow for the water year by the delineated basin area. The runoff for a selected 8-digit hydrologic unit code (HUC8) is determined using an area—weighted method of the streamgage basins. For a HUC8 that is not contained within a streamgage basin, the mean of the HUC8 runoff values within the same HUC4 is used as the runoff value.

#### **SPARROW** algorithms

The mechanistic mass transport components of SPARROW include surface-water flow paths (channel time of travel, reservoirs), non-conservative transport processes (first-order in-stream and reservoir decay), and mass-balance constraints on model inputs (sources), losses (terrestrial and aquatic losses/storage), and outputs (riverine nutrient export). Separate land and water components provide estimates of the rates of constituent delivery from point and nonpoint sources to downstream reaches, reservoirs and estuarine waters. The statistical features of the model involve the use of nonlinear parameter-estimation techniques. Parameters are estimated by spatially correlating stream water-quality records with geographic data on pollutant sources (e.g., atmospheric deposition, fertilizers, human and animal wastes) and climatic and hydrogeologic properties (e.g., precipitation, topography, vegetation, soils, water routing).

#### Flux equation

SPARROW models are developed through a calibration process in which parameter values are estimated to minimize uncertainty in predicting stream constituent loads. Uncertainty is quantified as the residual error in load prediction that cannot be accounted for through parameter adjustment.

The central algorithm of SPARROW is a nonlinear regression equation describing the non-conservative transport of contaminants from point and non-point sources on land to rivers and through the stream and river network. For the MRB3 model, parameter coefficients associated with the sources, land-to-water delivery factors, and in-stream loss and reservoir-loss terms were statistically estimated using weighted nonlinear least squares regression, based on calibrations with long-term mean annual loads normalized to 2002.

SPARROW calculates the load at the downstream end of a stream reach as the sum of monitored and unmonitored contributions to the load at that location from all upstream sources, or

$$L_i = \sum_{n=1}^{N} S_{n,i}$$

where:  $L_i$  is contaminant transport in reach i;

 $S_{n,i}$  is the contaminant load from source n delivered to reach i from all reaches in the subbasin downstream of the upstream monitoring stations.

The land-to-water delivery and in-stream decay terms in the model dictate the fraction of the contaminant mass that completes the terrestrial and aquatic phases of transport within the watershed draining to each stream reach. The land-to-water terms describe the land-surface characteristics that influence both overland and subsurface transport from sources to stream channels. Similarly, the instream decay terms describe the effects of channel characteristics on downstream transport.

## Land-to-water delivery

The source terms Sn,i includes the effects of a two-stage watershed constituent delivery process. The first stage of the process is the delivery of constituent mass from the land surface to reach *j* of the receiving channel network. Watershed characteristics that affect land-to-water delivery of nutrients may include soil permeability, wetland area, land-surface slope, and mean annual climatic factors, such as precipitation and temperature. Land-to-water delivery of TP in MRB3 model was found to be significantly influenced by soil permeability and fraction of the stream catchment with tile drains. For total nitrogen (TN), significant variables include stream drainage density (total stream reach length divided by catchment area), precipitation, air temperature, fraction of stream catchment underlain by tile drains, and clay content of the soil (Robertson and Saad, 2011).

Simulation of the transport of land surface constituents to receiving stream reaches is accomplished with a first-order equation:

nonpoint source<sub>n</sub>:  $= \beta_n e^{(-\alpha' Z_j)}$ point source<sub>n</sub>:  $= \beta_n$ upstream monitored load<sub>n</sub> = 1

where:  $\beta_n$  is a source-specific regression coefficient; and  $\alpha'$  is a vector of regression delivery coefficients associated with a vector of the land-surface characteristics  $Z_i$ .

Point sources and other monitored sources enter reach j directly and therefore lack the exponential decay term, as there is no land-to-stream decay for point source nutrients. The land-to-water delivery regression coefficients ( $\alpha'$ ) are used to determine the statistical significance of different types of land-surface characteristics (Z) for increasing or decreasing the delivery of nutrients from the land surface to the stream reach.

## Stream delivery

The second stage of the delivery process is the delivery of constituents from an upstream reach *j* to a downstream reach *i*. The in-stream loss of constituent mass occurs as a function of three variables: travel time, streamflow (serving as a surrogate for channel depth), and the presence or absence of a reservoir.

Time of travel, based on stream velocity, was the factor used to describe nutrient removal in streams. Travel time is computed as the ratio of reach length over stream velocity, and was estimated from the average annual flow for streamgaging stations during the 1975–2007 monitoring period. Stream flow rates were subdivided into three categories to describe in–stream nutrient loss. The flow rates classifying each category were determined in the SPARROW calibration process for total phosphorus (TP) and TN. For TP, the three stream categories are: small, flow <50 ft $^3$ /s; medium, flow 50–80 ft $^3$ /s; and large, For TN, the three categories of streams were: small, flow <40 ft $^3$ /s; medium, flow  $^4$ 0–70 ft $^3$ /s; and large, >70 ft $^3$ /s.

First order decay of nutrients in streams is simulated as an exponential function of a first-order reaction rate coefficient and the cumulative water travel time as given by:

$$e^{(-\delta'T_{i,j})}$$

where:  $\delta'$  is a vector of first-order decay coefficients associated with the flow path characteristics  $T_{i,i}$ .

#### Denitrification

Analysis of available denitrification rates and mass balance estimates from published studies indicate that N loss rates in streams and lakes generally decline with increases in streamflow, water depth, and hydraulic load (depth/travel time) and decreases in travel time. Stream N loss is simulated using a depth-dependent reaction rate coefficient for each stream size class.

The stream N mass flux at the outlet of a reach i,  $N_i^S$ , is estimated as a function of the upstream N flux entering reach i from reach j ( $N_j^S$ ), the mean water travel time ( $TR_k^S$ ; units of time) in the modeled reach for stream-size class k, and a reaction-rate coefficient dependent upon stream-size ( $\theta_k^S$ ; units time<sup>-1</sup>) [Boyer et al., 2006]:

$$N_i^S = N_i^S e^{\left(-\theta_k^S T R_k^S\right)}$$

Because the SPARROW TN model is based on estimates of the long-term mean-annual flux of TN in rivers, the estimated in-stream loss rates are indicative of permanent or long-term losses of N. Such losses principally include denitrification, but may also include the long-term storage of particulate and organic N in rivers and floodplains.

#### Reservoirs

First order decay of constituents in reservoirs is simulated as the product of the first-order decay term used for stream nutrient decay and a reservoir settling rate loss term:

$$e^{-\delta' T_{i,j}} \left[ \frac{1}{1 + \frac{\theta_i}{h_{load,i}}} \right]$$

where:  $q_i$  is a regression-derived coefficient and  $h_{load,i}$  is the areal hydraulic load of the reservoir (average outflow/reservoir surface area), or

$$h_{load,i} = \frac{Q_{ave}}{A_{res}}$$

Hydraulic loading for each reservoir was calculated as average outflow divided by reservoir surface area based on information from the National Inventory of Dams.

Substitution of the transport equations into the original loading equation produces the following SPARROW loading equation for reach *i*:

$$L_{i} = \left\{ \sum_{n=1}^{N} \sum_{j \in J(i)} s_{n,j} \beta_{n} e^{(-\alpha' Z_{j})} e^{(-\delta' T_{i,j})} \right\} e^{(\varepsilon_{i})}$$

Where:

 $L_i$  = load in reach i

n, N = source index where N is the total number of sources

J(i) = the set of all reaches upstream and including reach i, except those containing or upstream of monitoring stations upstream of reach i

 $\theta_n$  = regression coefficient for source n

 $s_{n,j}$  = point and nonpoint contaminant mass from source n in drainage to reach j

 $\alpha'$  = vector of land-to-water delivery regression parameters

 $Z_i$  = vector of land–surface characteristics association with drainage to reach j

 $\delta'$  = vector of instream—loss regression parameters

 $T_{i,j}$  = vector of channel characteristics between upstream reach j and the outlet of nested basin l, these channel characteristics include time-of-travel and channel size

 $e_i$  = error for reach i

#### Data

The estimation of mean annual stream nutrient load, which represents the dependent variable in the SPARROW nutrient models, requires extended periods of coincident nutrient concentration and flow data. However, an extensively long period can invalidate the estimate of the mean if landuse conditions determining water-quality concentrations undergo significant change. For a predominately statistical

model such as SPARROW, it is important to have a large number of monitoring sites that represent the most extreme combinations of environmental characteristics in the study area to reduce uncertainty in the estimated model coefficients and improve prediction accuracy.

Any constituent source can be potentially included in a SPARROW model, provided the geospatial data are available to describe it and spatial patterns in the source can be successfully correlated with those in the measurements of stream loading of that constituent. Because SPARROW is based on mass balance, sources must be available for all parts of the region to determine their overall importance. Thus, some data sets that provide detailed information for only a fraction of the model area would not be useful in a SPARROW model because the same information would not be available everywhere. For example, detailed estimates of agricultural inputs of N or estimates of a land-to-water delivery variable collected by one state may not be useful for a model covering the entire country if the data is not collected in the other states.

### Water monitoring sites

Daily flow data for each site for the period 1971-2006 were retrieved from the USGS National Water Information System (NWIS) database. Water-quality data for the period 1970-2007 were retrieved primarily from two databases: the U.S. Environmental Protection Agency's STOrage and RETrieval (STORET) database, and USGS's NWIS database. Additional water-quality data was obtained from individual state agencies and local organizations with detailed quality assurance plans. For the 1,371,536 km² MRB3 watershed, 1,688 of the 33,118 water quality monitoring sites met the minimum screening criteria, with 708 sites with long-term detrended loads used in the SPARROW model for TN simulation, and 810 sites used for TP. The record of the water quality data was from October 1, 1970, to September 30, 2007. To be included in the data set, a minimum of 25 samples must be collected, and constituent concentrations must be measured for at least two years, with more than one sample collected during each season (winter: Dec.-Feb.; spring: Mar.-May; summer: June-Aug.; fall: Sept-Nov). The principal reasons that monitoring sites were excluded from consideration for use in SPARROW were an inadequate number of samples or too short of a sampling period.

#### Load computation

The long-term mean annual nutrient loads for each monitored site in the MRB3 watershed were computed with the nonlinear regression methods implemented in the USGS program Fluxmaster. Fluxmaster combines water-quality data at a monitoring station with daily flow values to provide more accurate load estimates than can be obtained by using individual water-quality measurements alone. Total P and TN loads were determined with log-linear water-quality regression models that relate the logarithm of constituent concentration to the logarithm of daily flow, decimal time (to compensate for trends), and season of the year (expressed using trigonometric functions of the fraction of the year). The calculated load and flow rate were detrended (removal of a trend that obscures a relationship of interest, Figure 4) to the 2002 base year. Detrended daily loads were estimated by removing the linear trend in the concentration–discharge relation by using a time value of 2002.5 and using detrended daily flows. Detrended annual loads were then computed by aggregating the daily detrended loads for all years in which a complete record of daily flow was available, and averaged over all such years in the 1971–2006 period to obtain a mean annual detrended load for 2002.

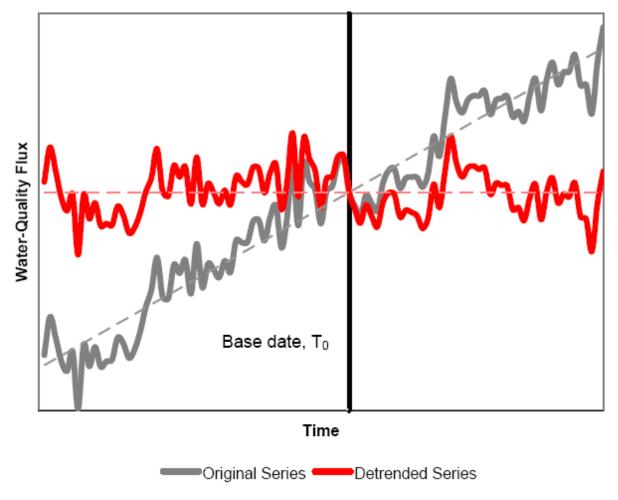


Figure 4. A detrended time series [Schwarz et al., 2006].

The estimates of long-term nutrient loads at monitoring sites used to calibrate the regional model reflect water-quality conditions that should have occurred in 2002, and also incorporate the long-term mean streamflows over the 1971 to 2006 period. The use of the long-term streamflows to estimate the monitoring site loads, rather than the flows during only 2002 ensures that the SPARROW regional model estimates of stream nutrient load, source contribution to streams, and environmental processes that govern the mean rates of nutrient removal and transport in watersheds are representative of long-term hydrologic variability [Preston et al., 2011]. The stream-load values used to calibrate SPARROW models can be interpreted as the mean annual load that would have occurred in a specified base year (2002) if mean annual-flow conditions, based on long-term flow data, had prevailed during that year. Normalizing mean annual nutrient loads to a base year adjusts for differences in monitoring station record lengths and sample sizes, and adjusts for temporal variability related to long-term linear trends (Figure 4), and incorporates the interannual changes in flow.

## Hydrography

The MRB3 watershed was developed using the Enhanced River Reach File 2.0 stream network and 100m digital elevation models. The SPARROW subwatersheds are approximately the same size as HUC12 watersheds. In the future, SPARROW models will be developed using the NHDplus stream network.

#### Atmospheric deposition

Estimates of atmospheric deposition used as input to the SPARROW model are based upon wet inorganic N deposition measurements (nitrate plus ammonia) from National Atmospheric Deposition Program (NADP) sites as a proxy for total (wet plus dry) N deposition [Preston et al., 2011a]

#### Fertilizer

Commercial fertilizer is allocated to major crops (including soybeans). The allocation is not crop specific. Pasture does not receive commercial fertilizer. Estimates of fertilizer use are derived from county–level fertilizer sales and crop distribution databases, and represent the intensity and areal extent of nutrient inputs to agricultural crops. The county data were allocated to each SPARROW stream catchment by the fraction of the catchment's agricultural land. Fertilizer use may serve as a surrogate for other nutrient inputs and the effects of farm practices (e.g., crop rotation, harvesting, and conservation tillage) on nutrient availability and leaching to soils and streams.

#### Landuse

Landuse related inputs include additional agricultural inputs from cultivated agricultural areas, urban inputs from urban and open areas, and natural inputs from forested areas. Landuse information was obtained from the USGS 2001 National Land Cover Data set.

#### Manure

Manure inputs were derived from 2002 county livestock population data from the U.S. Census of Agriculture using species–specific rates. The county–level data was allocated to each SPARROW stream catchment by the fraction of the catchment's agricultural land and grasslands.

## Municipal and industrial point sources

Inputs for point–source facilities in the MRB3 watershed (including sewerage treatment, commercial, and industrial effluent) were estimated from data in the Environmental Protection Agency Permit Compliance System (PCS) database, supplemented with data obtained directly from MPCA staff. Municipal and industrial facilities are designated as major or minor. Major facilities typically discharge more than one million gallons per day (mgd) of effluent, and minor facilities typically discharge less than one mgd of effluent. Annual nutrient loads were calculated only for those facilities with measured effluent flow. For facilities which do not monitor nutrients or have missing values, typical pollutant concentrations for similar types and sizes of facilities were used to develop annual loads [Maupin and Ivahnenko, 2011].

## Sources

The inclusion of a source in a SPARROW model requires a statistically significant correlation of the source with stream loading measurements. Such correlation is dependent upon whether (a) the source is sufficiently large to make an important contribution to the overall mass balance in the stream network, and (b) the spatial variability in that source as described by the geospatial datasets is sufficiently large.

Constituent sources typically include estimates of N mass in atmospheric deposition, nutrients in commercial fertilizer and manure applied to agricultural land, and nutrients in runoff from urban and other land uses. Regression coefficients estimated for each nutrient source represent the amount of TP or TN delivered to streams, and are expressed as fractions for mass variables (e.g., farm fertilizer input)

or absolute quantities (kg/km²/year) for land-use variables (e.g., input from urban and open areas). The values of the source coefficients provide an estimate of land-to-water delivery under the assumption that the spatially variable delivery factors are uniformly distributed throughout the land area being considered under average conditions.

Statistical methods were used to identify specific watershed characteristics important in explaining variability in nutrient delivery to streams and losses in streams and reservoirs. Such methods can have statistical limits to building more highly complex models of similar contaminant sources. The individual statistical coefficients of sources with similar or correlated spatial distributions (e.g., confined and unconfined animal wastes; nitrate and ammonia wet deposition) may be difficult to statistically estimate in a SPARROW model. Difficulties can also arise if individual components of a source (e.g., total fertilizer) contribute relatively small quantities of pollutant mass to streams (e.g., urban fertilizer use). In addition, complications can arise if the monitoring stations are located too far downstream to detect the effects of a sub-component of a major source.

Many environmental characteristics thought to be important in nutrient delivery were examined to determine statistically significant land-to-water delivery factors and in-stream-loss and reservoir-loss factors in the SPARROW models. Sources identified as statistically significant in explaining the distribution in TP and TN loads were retained or, if sources were statistically insignificant, they were combined with other sources in a series of model runs until an acceptable regression was obtained.

Some source variables serve as surrogates for other nutrient sources that are spatially correlated with the variables specified in the model. For example, developed urban land may serve as a surrogate measure of various diffuse urban sources in the model, which may include nutrient runoff from impervious surfaces, inflows from groundwater in urbanized catchments related to fertilizers and septic systems, and N deposition associated with vehicle emissions of nitrous oxides.

An objective in developing SPARROW models is to gain insight and to test hypotheses concerning the role of specific constituent sources and hydrologic processes in supplying and transporting constituents in watersheds. Subsequent to the evaluation of a variety of point sources, it was determined that six sources were statistically significant for TP: point sources, confined manure, unconfined manure, farm fertilizers, urban areas, and a combination of forest and wetland (forested areas). Five sources were found to be statistically significant for TN: point sources, atmospheric deposition, confined manure, farm fertilizers, and additional agricultural inputs from cultivated lands (e.g., crop rotation, harvesting, and conservation tillage).

Inputs from forested and urban areas were found to not be statistically significant for TN. Contributions from these sources would be attributed to other sources in the model. The statistical insignificance of unconfined animal manure for TN may be due to the volatilization of most of the N in the manure deposited by unconfined animals prior to runoff from fields and the redeposition elsewhere as part of atmospheric deposition.

In the MRB3 model, receiving stream reaches received 100% of the point source phosphorus, while only 3% of the farm fertilizer, 9% of the confined manure, and 3% of the unconfined manure was received by the stream reach. For TN, 50% of the atmospheric deposition, 80% of the point source, 10% of the farm fertilizer, and 30% of the confined manure was transported to the stream reach. The high percentage of point source TN may be due to an overestimation of point source TN contributions.

## **Delivery**

Results from the calibrated SPARROW MRB3 model indicated that precipitation, stream drainage density, percentage of the drainage area with tile drains, percent clay, and temperature were landscape characteristics that were statistically significant TN delivery variables, with soil permeability and percentage of the drainage area with tile drains significant for TP [Robertson and Saad, 2011].

#### Stream removal rate

The estimated long-term mean annual rate of nutrient removal in streams is computed in SPARROW as a first-order reaction rate constant. The constant expresses the nutrient removal as the fraction of the nutrient mass that is removed from the water column via denitrification or long-term storage (deposition) per unit of mean travel time in the stream channel. The TN removal rate constants for MRB3 were found to be only statistically significant in streams with depths less than about 1.2 feet, with an exponential decline in magnitude with increasing water depth.

## **Application of results**

Several characteristics of the SPARROW model must be taken into account when applying the model results to management decisions and water-quality assessments. Important among these are that the SPARROW model (1) focuses on spatial rather than temporal detail; (2) integrates long-term discharge and water-quality records to calculate annual stream nutrient loads used for calibration rather than discharges for any specific year; (3) includes only the water-quality factors that are represented in available geospatial data and statistically correlated with stream load; and (4) favors water-quality comparisons across broad regions as opposed to within single catchments.

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# Appendix B5-1. Nitrogen Losses in Groundwater – A Review of Published Studies

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#### Introduction

Groundwater can contribute the majority of nitrate to streams in some watersheds, and yet contribute minimal nitrate in other watersheds. In addition to land use influences, the amount of nitrate entering streams is largely influenced by the types of soil, geologic and hydrologic conditions. These factors not only affect the rate at which water travels, but can also affect groundwater chemistry conditions and the likelihood that nitrate will be removed.

Nitrate is the dominant form of nitrogen (N) in groundwater baseflow. Since nitrate moves freely with water, not sorbing to soil particles or aquifer sediments, it will eventually move to surface waters unless it is first lost through "denitification." As long as dissolved oxygen is present in groundwater above 0.5 mg/l (referred to as oxic conditions) and organic carbon content is low, nitrate is stable and persists in groundwater, sometimes for decades (Dubrovsky 2010). If the dissolved oxygen in groundwater is depleted, nitrate becomes unstable and is converted to N gas through this biologically driven process known as "denitrification." Aquifer sediment types and groundwater chemistry have a significant influence on denitrification and correspondingly on nitrate loads delivered to streams (Tesoriero, Duff et al. 2009).

The denitrification process typically begins after bacteria in groundwater break down organic carbon compounds, thereby reducing dissolved oxygen levels. If dissolved oxygen in groundwater becomes depleted (<0.5 mg/l), the bacteria will use nitrate to oxidize the organic carbon. After nitrate is mostly gone, then bacteria can use organic carbon for other redox reactions such as manganese reduction, iron reduction, sulfate reduction, and reduction of carbon dioxide to methane. As a result of these reactions, nitrate may be removed from the groundwater, only to be replaced by manganese, iron, sulfide, or methane. Often these various processes occur in succession as water moves down and through an aquifer.

Denitrification can occur within the unsaturated soil zone, within saturated soils, in the aquifer, and/or in the riparian zone. Where conditions are suitable for denitrification in the aquifer or riparian zone, nitrate contributions from baseflow will be minimal or negligible. Where conditions are not suitable for denitrification, much of the nitrate which moves through the soil into groundwater will eventually emerge in streams via groundwater baseflow.

## How much denitrification occurs within groundwater?

In a research review of denitrification within aquifers, Rodvang and Simpkins (2001) noted that studies in till and loess have shown that denitrifying bacteria are present at all depths, and that they become active under the appropriate conditions. They also found studies indicating that the organic carbon content in till and loess in central lowa was sufficient to facilitate denitrification of large quantities of nitrate. They concluded that denitrification consistently reduces nitrate to non-detectable levels in unweathered Quaternary aquitards.

Data from a St. Cloud area geoprobe study (MPCA, 1998A) suggest the importance of organic carbon in groundwater as a factor affecting denitrification. The median concentration of carbon at the water table of the underlying surficial sand and gravel aquifer was 2.3 mg/L, but increased to 3.1 and 7.8 mg/L at depths of 7.5 and 15 feet, respectively. Over this same depth range, concentrations of dissolved oxygen and redox potential decreased by 0.028 mg/L/feet and 1.7 mv/feet, respectively. Nitrate over this depth range decreased from a median concentration of 5.6 mg/L at the water table to 0.045 mg/L at 15 feet. These observations pointed to the likelihood of denitrification causing nitrate reductions with depth into the water table.

Patch et al. (1994) used groundwater modeling and N isotope data to study the vertical stratification of nitrate at the water table of the Elk Valley Aquifer in Eastern North Dakota. They noted that dispersion alone could not explain the stratification. Furthermore, nitrate present at the lower depths was enriched in the N isotope N15, relative to nitrate nearer the water table. The researchers concluded that denitrification was the major cause of the vertical nitrate stratification.

The Minnesota Pollution Control Agency (MPCA) sampled wells in different aquifers throughout the state to determine nitrate stability (MPCA, 1998B) (Trojan, Campion et al. 2002). Groundwater with dissolved oxygen concentrations exceeding 0.50 mg/L, redox potential greater than 20 mV, and iron concentrations less than 1.0 mg/L, were considered to represent nitrate-stable conditions where nitrate was less apt to convert to N gas through denitrification. Nitrate concentrations under nitrate-unstable conditions were found to be very low, typically less than 0.10 mg/L. They found that nitrate is absent in aquifers with nitrate unstable conditions. Many groundwaters in the state have conditions which are not stable for nitrate to persist. The fraction of samples from each major aquifer in the state with nitrate stable conditions is listed below. With the exception of the Prairie du Chien aquifer, less than half of the samples in each aquifer had nitrate-stable conditions. In several of the aquifers, less than 20% of samples had nitrate-stable conditions.

#### Percent of well water samples with nitrate-stable chemistry in Minnesota aquifers

Franconia - 33% of 27 samples

Franconia-Ironton-Galesville - 25% of 40 samples

St. Peter - 39% of 23 samples

Prairie du Chien - 53% of 36 samples

Jordan – 42% of 31 samples

St. Peter-Prairie du Chien-Jordan – 46% of 90 samples

Mt. Simon-Hinckley - 19% of 26 samples

Cretaceous – 13% of 39 samples

Galena – 14% of 22 samples

Crystalline Precambrian – 14% of 29 samples

North Shore Volcanics - 35% of 23 samples

Proterozoic Metasedimentary units – 26% of 23 samples

Buried Quaternary artesian aquifers 12% of 386 samples

Unconfined buried Quaternary aquifers – 37% of 104 samples

Buried undifferentiated Quaternary aquifers – 14% of 22 samples

Quaternary water table aquifers – 30% of 119 samples

Cambrian aquifers - 28% of 102 samples

Ordovician aquifers - 38% of 87 samples

Precambrian aquifers – 29% of 80 samples

The same MPCA study reported that waters become more unstable for nitrate as you move further down below the top of the water table and oxygen becomes more depleted. Data from a St. Cloud area geoprobe study (MCPA 1998A) also showed that nitrate concentrations within 7.5 and 15 feet below the top of the underlying sand and gravel aquifer were 0.45 and 0.040 mg/L, respectively, even when concentrations at the water table were well above 1 mg/l. In the St. Cloud area, nitrate concentrations were very low in both deeper wells more than 30 feet below the water table and in buried aquifers (0.030 and < 0.010 mg/L, respectively).

Several researchers have conducted intensive monitoring of groundwater to better define N transformations. Published studies in Minnesota and nearby areas have demonstrated that groundwater denitrification is a common process affecting groundwater and baseflow nitrate levels.

Groundwater was intensively monitored near Princeton, Minnesota as it flowed from under an upland cultivated field to a riparian wetland and stream in a glacial outwash sand aquifer (Böhlke, Wanty et al. 2002). A "plume" of oxic nitrate-rich groundwater present at shallow depths beneath the fields and part of the wetland terminated before reaching the stream or the wetland surface. Groundwater dating and hydraulic measurements indicate travel times in the local flow system of 0 to over 40 years. Zones of active denitrification were found in the aquifer sediments in the recharge area, as well as the discharge area in the more highly organic sediments near the stream. The lower nitrate was therefore due to both older water (recharging decades ago thus predating large nitrate sources) and denitrification. Denitrification was evident in waters moving downward within the surficial sand aquifer, independent of the riparian wetland sediments.

A study in northwestern Minnesota used a mass-balance approach to estimate the amount of N leaching to the Otter Tail outwash aquifer across a 212 km² area (Puckett, Cowdery et al. 1999). Due to the very coarse soils within this region, mineralization was assumed to be negligible and was not accounted for in this balance. They found biological fixation to be the largest single source of N to the system (53.1%), followed by fertilizer (40.9%), atmospheric deposition (4.6%), and commercial feed (1.4%). By their estimates, 56% of the excess N in this balance was discharged to groundwater, while 44% was denitrified in the soil and groundwater below the root zone (Puckett, Cowdery et al. 1999). Denitrification was estimated by adjusting its value so the predicted and measured concentrations of nitrate in groundwater agreed. In support of this assumed denitrification, the authors note that they found 43% of wells in settings which supported denitrification. Wells that had nitrate concentrations agreeing closely with predicted nitrate were well oxygenated, and those wells with nitrate much lower than predicted by the N budget had lower dissolved oxygen, suggesting denitrification.

Korom, Schlag et al. (2005) used large stainless steel chambers designed, constructed, and installed to make in situ mesocosms of aquifer sediments representative of Elk Valley Aquifer in Eastern North Dakota. Denitrification rates were measured in the mesocosms and compared to concentration reductions through dilution. Nitrogen isotopes and other water chemistry information indicated that denitrification was occurring in the aquifer sediments. Sulfur from pyrite was found to be a major electron donor, with sulfate oxidation accounting for 58% of the denitrification. The average measured denitrification rate was 0.22 mg/l per day. This estimated rate was in the middle of a wider range (0.033 to 0.59 mg/l/day) of mesocosm denitrification rates found using sediments from several other eastern North Dakota aquifers (Korom, 2010).

While the above studies show potential for substantial nitrate losses through denitrification in the aquifer, there are some situations where denitrification does not readily occur. In a southern Alberta study, leaching nitrate was not denitrified in the shallow upper aquifer unless deeper groundwater mixed with the shallow groundwater. The amount of denitrification was found to be directly correlated with the amount of deeper groundwater mixing with the shallower groundwater (McCallum, Ryan et al. 2008).

Denitrification can also be rather limited in soils under tile-drained fields. Shallow groundwater denitrification represented 1% of inputs in 2001 and 4% of inputs in 2002 in an east central heavily tiled watershed (Gentry, David et al. 2009).

## Riparian zone denitrification

Riparian zones often have organic rich sediments conducive for denitrification and substantial biological uptake of N. Both have the potential to reduce nitrate concentrations as shallow groundwater enters the riparian zone.

Many studies have shown nitrate depletion in subsurface flow into riparian zones. Yet other studies have shown that riparian flow paths were ineffective in removing nitrate (Triska 2007) (<u>Duff</u> 2007). Denitrification and plant uptake in riparian zones can remove all nitrate in some environmental settings, but they may be relatively ineffective in others (Puckett 2004). Hydrogeologic and biogeochemical processes can limit denitrification; therefore, not all riparian zones are equally efficient at removing nitrate from groundwater before it reaches stream channels (Hill, 1966; Puckett et al., 2002; Puckett, 2004). Interaction of groundwater N with riparian biota depends on subsurface flow paths that intercept the shallow root zone and soils conducive for denitrification. These flow paths occur where a shallow impermeable sediment layer or aquiclude forces the shallow groundwater into biologically active riparian habitats (Duff 2007) (Duff, Tesoriero et al. 2008) .

The removal of nitrate from groundwater near streams is promoted by a combination of hydrogeologic, biological, and biogeochemical processes. Fine-grained sediments result in slow flow rates that allow more time for denitrification to take place. If the surficial sediments are primarily silt and clay, however, the fine-grained sediments can form a confining layer that forces groundwater to flow below the biologically active zone and may result in less nitrate removal. Coarse-grained sediments may force groundwater to flow through the riparian zone faster than the biological processes can remove nitrate. In addition, if surface runoff occurs or if shallow groundwater is routed through tile drains and ditches, riparian zones can be bypassed and nitrate-rich water is discharged directly to streams.

Riparian zones appear to be most effective in settings with thin surficial aquifers, underlain by a shallow confining layer, and with organic-rich soils that extend down to the confining layer. This combination of factors force groundwater to flow through the biologically reactive portions of the aquifer and promotes nitrate removal.

Spahr (2010) compared mean annual base-flow nitrate concentrations to shallow-groundwater nitrate concentrations for 27 sites across the United States. Nitrate concentrations in groundwater tended to be greater than stream base-flow concentrations for this group of sites. Sites where groundwater concentrations were much greater than baseflow concentrations were found in areas of high infiltration and oxic groundwater conditions. The authors noted that the lack of correspondingly high nitrate concentrations in the base flow of the paired surface-water sites may have multiple causes. In some settings, there has not been sufficient time for enough high-nitrate shallow groundwater to migrate to

the nearby stream. In these cases, the stream nitrate concentrations lag behind those in the shallow groundwater, and concentrations may increase in the future as more high-nitrate groundwater reaches the stream. Alternatively, some of these sites may have processes that rapidly remove nitrate as water moves from the aquifer into the stream channel.

Nitrate can be removed from nitrate-rich groundwater as it moves through the riparian zone to the stream, and nitrate can be removed from stream water that flows through sediments in the streambed. Sediments in both of these environments can contain appreciable amounts of organic carbon and other reactants that support bacterial denitrification. In addition, the vegetation in riparian buffer zones can take up nitrate, an important plant nutrient. These processes have been studied in a variety of land-use and hydrologic settings by intensive instrumentation (Puckett (Puckett 2004), (Duff, Tesoriero et al. 2008) (Puckett, Zamora et al. 2008).

Puckett and Cowdery (2002) found that N concentrations in the Ottertail River were very low considering intense agricultural fertilizer inputs. Of the N present in the River, 87% was organic-N (largely dissolved organic N). The riparian buffer zone in this study had only a minor role in preventing nitrate in groundwater from reaching the Ottertail River for two reasons: (1) most nitrate had been removed by denitrification in the upgradient aquifer, and (2) shallow groundwater containing nitrate was able to move along some flow paths below the riparian zone where little nitrate was removed, subsequently moving up into the river along flow paths that did not support denitrification.

## Summary

The amount of nitrate entering streams from baseflow will be dependent on the amount entering the top of the water table; the lag time between groundwater recharge and discharge into the stream; the amount of denitrification occurring within the aquifer; and the amount of denitrification and biological uptake in the subsurface under and adjacent to the stream.

Studies in loess and till have shown that denitrifying bacteria are present at different depths, and that they become active under the appropriate conditions such as a plentiful organic carbon supply. These bacteria can potentially reduce nitrate to non-detectable levels. Several studies of nitrate losses have found high rates of denitrification where oxygen levels are low. Samples of Minnesota aquifer waters have shown that water chemistry was conducive to denitrification in over half of the wells screened into each aquifer, except for the Prairie du Chien. In several aquifers, over 80% of the wells had water chemistry that would support some level of denitrification. Denitrification is more likely to occur as you move deeper into the aquifer, well below the top of the water table.

While it is difficult to quantify the total amount of nitate lost in groundwater by denitrification, some studies have estimated that over 40% of nitrate may be lost due to denitrification. Other studies have estimated rates of denitrification greater than 0.2 mg/l per day.

Additional nitrate can be lost as groundwater moves into organic-rich zones often found in many river and stream valleys. Fewer losses will occur when groundwater discharge to streams occurs through springs and seeps which bypass subsurface organic sediments in the riparian zone.

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# Appendix B5-2. Nitrogen Transport and Transformations in Surface Waters of Minnesota

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#### Overview

Generalizing the movement and transformations of total nitrogen (TN) in surface waters of Minnesota is complicated given the wide range of aquatic systems and nitrogen (N) loads delivered to those systems throughout the state. Nitrogen transport in surface waters is spatially and temporally variable which also makes generalizations difficult. The literature of the past two decades has greatly increased our understanding of N transport in surface waters. Some of this work was directly or indirectly related to the transport of N via rivers to estuaries with particular emphasis on N loads from the Mississippi River Basin delivered to the Gulf of Mexico. Research has focused on transport in small streams up to major rivers such as the Mississippi River. Nitrogen data from field-based monitoring have been incorporated into models to estimate downstream transport of N. We will focus on N transport within Minnesota in this chapter. Information for the Mississippi River downstream of the Minnesota state line is summarized in the recent literature (Robertson et al. 2009, Strauss et al. 2011).

Nitrogen is present in detectable amounts in most surface waters in Minnesota. In surface waters with relatively low N inputs, N is typically present in low concentrations of inorganic forms (often near detection limits) with the majority of N present in organic forms bound in various components of living and dead organisms. As N loading increases to a given surface water beyond its ability to assimilate N inputs, detectable amounts of dissolved inorganic nitrogen (DIN) are measured. In well oxygenated waters, DIN is typically present as nitrate ( $NO_3$ -N) with lesser amounts of nitrite ( $NO_2$ -N) and ammonia/ammonium (combination of both =  $NH_X$ -N). The majority of  $NO_3$ -N and nitrite  $NO_2$ -N (combination of both =  $NO_X$ -N) exists as nitrate in streams and rivers and it is common for some to use  $NO_3$ -N and  $NO_X$ -N interchangeably. This chapter will focus on  $NO_X$ -N ( $NO_3$ -N +  $NO_2$ -N) to be consistent but will specify  $NO_3$ -N when  $NO_2$ -N was not analyzed in a particular monitoring program. Ammonia and Ammonium (combination of both =  $NH_X$ -N) can also make up a portion of DIN in Minnesota waters. It is most common in waters with low dissolved oxygen such as wetlands and the hypolimnion of stratified lakes.  $NH_X$ -N is more common and persistent in oxygenated waters during winter immediately downstream of wastewater treatment plants. Nitrification or uptake of  $NH_X$ -N by organisms typically processes  $NH_X$ -N to other forms of N in oxygenated surface waters during the other seasons.

Many factors influence the transport of N in surface waters of Minnesota. This chapter will discuss factors such as N loading, residence time, temperature, nitrate concentration, discharge, depth, velocity, and land use. Some of these factors are inherently different based on the type of surface water. Wetlands and lakes are common in northeast Minnesota along with relatively low N inputs, all contribute to low N yields. Nitrate concentrations in streams of northeast Minnesota are often near detection limits. Yields of N from watersheds in south-central Minnesota are much higher due to low densities of lakes and wetlands and higher inputs of N (especially NO<sub>X</sub>-N) during seasonally higher stream discharge. The concentration of TN in streams can drop during low flow periods in mid-late summer due to a combination of lower input loads and in-stream processing if inputs are not excessive. In terms of downstream loading, the reduction in mid-late summer TN concentration does not result in substantially reduced annual load since the majority of TN is transported from late-March to mid-July

when stream discharge is typically highest in Minnesota rivers. Streamflow is highest from spring to early summer in all watersheds in Minnesota resulting in the highest loads during this time frame. Seasonal fluctuations of TN concentrations in rivers draining other watersheds in Minnesota represents a gradual transition from south central to northeast Minnesota. Watersheds in southeast Minnesota are unique to the other watersheds in the state due to the large inputs of high  $NO_X$ -N groundwater which maintain elevated TN levels during low flow, and therefore have less seasonal concentration fluctuations of TN than south-central Minnesota.

Residence time is a key factor for N removal across all aquatic ecosystems. Residence time is basically the time it takes to replace the volume of water for a given surface water. Longer residence time allows for more interaction with biota (including bacteria) within a given aquatic resource. Streams typically have much shorter residence times compared to wetlands and lakes. Consequently, streams generally transport more N downstream than lakes and wetlands. The removal efficiency of streams generally decreases with stream size and N loading.

Special consideration was given to the Mississippi River downstream of the Minnesota River due to the unique rapidly flushed impoundments (navigational pools) on this river and availability of models and monitoring data. In this river system and other rivers throughout the state, N loading is typically at its annual peak during spring and early summer when streamflow is seasonally higher. Lake Pepin, a natural riverine lake on the Mississippi River, removed only 6%to 9% of the average annual input load of TN during the past two decades. Lake Pepin has the longest residence time of all the navigational pools on the Minnesota portion of the Mississippi River by a factor of at least 5. Upstream removal and loading reductions of N throughout the tributary watersheds is needed to substantially reduce downstream transport of N by the Mississippi River from Navigational Pools 1 to 8 during spring and early summer. Estimates of the collective impact of all the navigational pools in Minnesota, including Lake Pepin, range from removal of 12% to 22% of average annual input loads.

Outputs from the SPARROW model are useful to illustrate annual downstream delivery of TN loads in Minnesota streams and rivers. The general findings of this review indicate that 80% to 100% of annual TN loads to rivers are delivered to a state border unless a large reservoir with a relatively long residence time is located in the stream/river network downstream of a given headwater stream. Large headwater reservoirs such as Lake Winnibigoshish remove a larger proportion of inputs than riverine lakes such as Lake Pepin which has a much larger contributing watershed. Losses in surface waters upstream of the SPARROW watershed outlets are not included in the SPARROW results presented here, so actual statewide losses in all surface waters exceed those presented here which are more representative of losses in flowing waters and reservoirs included in the SPARROW model. Other approaches described in this chapter based on mass balances estimated from monitored rivers, also showed that the majority of annual TN loads loaded to a given river reach are delivered to downstream reaches.

## Basics of nitrogen cycle (emphasis on streams and rivers)

The longitudinal processing of N in a lotic ecosystem (stream or river) is often referred to as N spiraling which is essentially the phenomenon of N cycling in flowing waters. Nitrogen can exist in several forms in surface waters and can change forms depending on various factors (Table 1, Figure 1). Denitrification is the most important process in the N cycle in freshwater for removing N from the water and returning it to nitrogen gas  $(N_2)$ , which essentially removes it from downstream transport. Nitrogen fixation can return  $N_2$  to a more biologically active form, but this process is generally limited in streams with available DIN. We will discuss most of the components of the N cycle throughout this chapter (Table 2).

Table 1. Most common forms of N in aquatic systems.

Form of nitrogen	Abbreviation	Description	
Nitrogen gas	N <sub>2</sub>	Biologically inert form of nitrogen that is the most common gas in the atmosphere	
Nitrous Oxide	N <sub>2</sub> O	Intermediate in denitrification process, greenhouse gas	
Nitrate	NO <sub>3</sub>	Dissolved form of nitrogen common in systems with excess nitrogen loading, most oxidized state of dissolved nitrogen	
Nitrite	NO <sub>2</sub>	Dissolved form of nitrogen, intermediate in N transformations, uncommon when oxygen is present	
Organic Nitrogen	NH <sub>2</sub>	Generic symbol for various forms of nitrogen in tissue of organisms	
Ammonium	$NH_4^+$	Most common form of ammonia in surface waters	
Ammonia	NH <sub>3</sub>	Dissolved form of nitrogen that is readily assimilated by algae and bacteria, typically present as NH <sub>4</sub> dependent on pH and temperature	

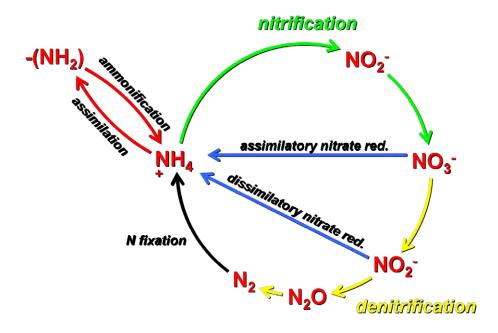


Figure 1. Simplified N cycle for aquatic ecosystems.

Table 2. Generalized transformations and forms of N in aquatic systems.

Process	Inputs	Output	Description
Denitrification	NO <sub>x</sub> -N, organic matter	N <sub>2</sub>	Bacterial mediated process that occurs in anoxic conditions or sediment interface, carbon source is also needed, inhibited by cold temps
Nitrification	NH <sub>x</sub> -N	NO <sub>X</sub> -N	Bacterial mediated process that occurs in oxic conditions or sediment interface, inhibited by cold temps
Ammonification	Organic matter	NO <sub>x</sub> -N	Bacterial decomposition of organic matter to ammonia
Assimilation	NH <sub>x</sub> -N, NO <sub>x</sub> -N	Organic-N	Multiple pathways for dissolved inorganic nitrogen to be incorporated into algae, plants and bacteria
Dissimilatory nitrate reduction to NH <sub>X</sub> -N	NO <sub>x</sub> -N	NH <sub>x</sub> -N	Bacterial mediated process that occurs in anoxic conditions or sediment interface, less common than denitrification in streams (Lansdown et al., 2012)
Excretion	Organic matter	Organic-N, NH <sub>x</sub> -N	Various forms of Organic-N and urea from organisms may be converted to NH <sub>x</sub> -N;
Nitrogen fixation	N <sub>2</sub>	NH <sub>x</sub> -N	Cyanobacteria are capable of converting nitrogen gas to ammonia for assimilation
Anammox	NH <sub>4</sub> <sup>+</sup> , NO <sub>2</sub> <sup>-</sup>	N <sub>2</sub>	Anaerobic ammonium oxidation, important in N cycling in oceans

## Stream and river transport of nitrogen

## Literature/theory

Transport of N in the streams and rivers of Minnesota is influenced by several factors that are temporally and spatially variable throughout the state. Monitoring transport along a stream network is expensive, and existing water-quality monitoring programs are often not designed to specifically estimate fate and transport of N. Thus, available monitoring data is often used to calibrate models to estimate N transport over greater temporal and spatial scales than the original monitoring covered. Even though models are never perfect, they can be useful for estimating the impact of a stream network on the downstream movement of N. The chapter on SPARROW modeling in this report (Chapter B3) summaries the modeled collective impact of streams on downstream transport of N in Minnesota. We will briefly highlight some of the SPARROW results. This chapter will cover some Minnesota examples where adequate data exists and will discuss the key factors that influence downstream transport of TN in streams. Agricultural streams will be discussed in detail since these streams typically receive large N inputs and consequently deliver the largest downstream loads. Forested and urban streams will also be discussed briefly.

A fraction of N transported in streams and rivers is lost to denitrification, some is assimilated and temporarily stored in biota and the rest is transported downstream. The literature has extensive coverage of the loss of  $NO_x$ -N via denitrification since this process results in the true loss of DIN within an aquatic system. Burgin and Hamilton (2007) advocate for a more detailed view of all of the alternate pathways for  $NO_x$ -N removal beyond just denitrification (Figure 2). They outline multiple pathways for  $NO_x$ -N to be assimilated or converted to  $N_2$  beyond the standard denitrification discussed earlier. Recently, Helton et al. (2011) proposed that more complicated models need to be developed over the next decade to address multiple pathways of N transport in river networks (Figure 3). Improved models

will include approaches to terrestrial-aquatic linkages including hydrologic exchanges between the channel, floodplain/riparian complex, and subsurface waters, and interactions between coupled biogeochemical cycles.

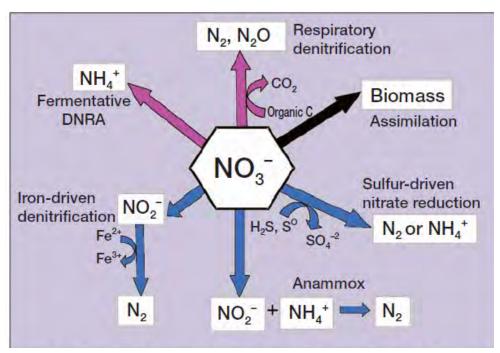


Figure 2. Conceptual diagram of nitrate removal pathways identified by Burgin and Hamilton (2007). Blue arrows denote autotrophic pathways, while purple arrows denote heterotrophic pathways.

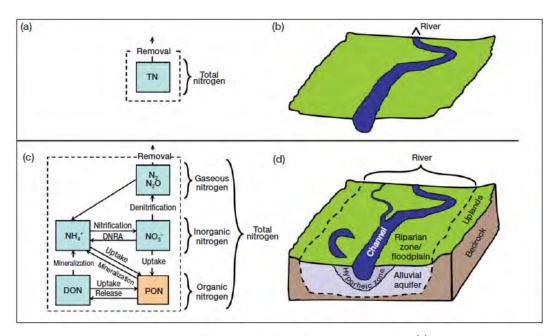


Figure 3. Existing river- network models typically describe one-way TN flux (a) from simple river channels (b). Future models will include more complicated N cycling (c) in both channel and off-channel ecosystem components (d). DON= dissolved organic N, PON = particulate organic N. Reprinted from Helton et al. (2011)

#### Research studies from Minnesota

Studies in Minnesota have demonstrated the importance of riparian zones and other wetted areas beyond the stream channel itself for impacting downstream N transport. We will briefly discuss their results here to illustrate the complexities of N transport in streams and rivers. Triska et al. (2007) did extensive testing of surface and groundwater of the Shingobee River (second order stream) near the origin of the Mississippi River. The Shingobee watershed is a mix of wetlands, lakes, and intermittently grazed pastures. They found that DIN in the hillslope groundwater (ridge to bank side riparian) and alluvial riparian groundwater was reduced before reaching the river itself especially during summer months. In the hyporheic zone and stream itself, DIN removal was controlled by temperature which resulted in more DIN removal during the summer than winter. Triska et al. (2007) found that watershed retention of DIN during summer was effective given the current land use of the watershed and complex aquatic and riparian features that currently exist. They stated that more intensive land use such as row crops in the watershed would result in decreased NO<sub>3</sub>-N retention efficiency and increased loading to surface waters. Most of this chapter will focus on instream transport, but it is important to consider that DIN can be processed before it enters a stream in groundwater and riparian areas. These areas can have a combination of low dissolved oxygen and abundant organic carbon which are ideal for denitrification (See groundwater chapter).

Ditch systems are often relatively simple systems by design and complexity of existing simple models may be adequate to represent these systems. Magner et al. (2004, 2012) found that channels in headwater streams and ditches have been entrenched in the Blue Earth River Basin. They found that highest concentration of  $NO_X$ -N occurred in May and June. They also found that the 1.02-2.0 year peak flows have increased 25% to 206% over the past 25 years which certainly contributes to increased loading during high flows. Tile drainage allows nitrate to enter the streams directly without access to the riparian or hyporheic zone which limits N losses. Once the water is in the entrenched stream, it is isolated from the riparian zone which could remove N (Figure 4). The multitude of factors discussed above help illustrate why watersheds with extensive ditching efficiently transport N downstream during wet periods.

Initial findings from altered ditches are promising for removing TN in ditch networks. Large scale networks of altered ditches are not currently available to monitor in Minnesota to determine the total collective impacts of implementing widespread ditch alterations. Two-stage ditches are designed to have floodplain "benches" within the ditch that could potentially increase N removal in ditch systems (Ward et al., 2004; Magner, et al. 2010; Figure 5). Anderson (2008 as cited in Magner 2012) sampled Judicial Ditch #8 in central Minnesota since it had been widened to protect a downstream bridge. The ditch demonstrated the third highest qualitative habitat evaluation index score and some of the lowest values of N (nitrite + nitrate), total phosphorus, and total suspended solids of all the channelized streams surveyed in 2003 in the Minnesota River Basin by the MPCA.

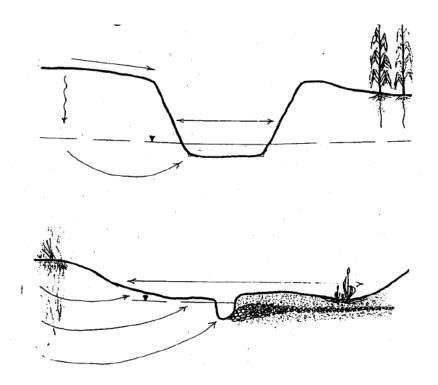


Figure 4. Cross section of trapezoidal ditch (top) and natural stream (bottom). Reprinted from Magner (2001).

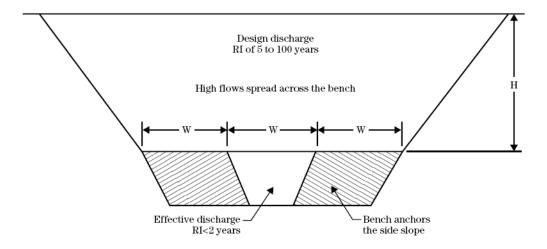


Figure 5. Two-stage ditch geometry illustrating benches not found in typical trapezoidal ditches (Source: USDA NRCS).

Natural headwater streams such as the Shingobee system discussed earlier have greater access to the floodplain and ability to reduce N loading. Magner (2001) found that natural first order streams in the Chippewa River Basin of Minnesota provide both hydrologic and N attenuation compared to trapezoidal ditches. A natural stream maintained a stable bed and bank that was 2-4 times wider than two classic ditch systems that were monitored.  $NO_x$ -N concentrations in the ditches were 2.5 mg/L compared to 0.25 mg/L monitored in the natural stream.

#### Applied modeling of nitrogen transport in streams

The amount of N lost in a given stream reach is influenced by a multitude of factors. Alexander et al. (2009) used a dynamic stream transport model to estimate denitrification based on streamflow, temperature and nitrate concentration. This model was calibrated on monitoring data from 300 measured values from a variety of U.S. streams. The model was then used to develop monthly nitrate budgets for Sugar Creek, an agricultural watershed on the Illinois/Indiana border and the North Nashua River a forested watershed with some urban areas in Massachusetts. Key findings are summarized from a portion of the abstract from the Alexander et al. (2009) paper:

"Results indicate that the removal efficiency of streams, as measured by the percentage of the stream nitrate flux removed via denitrification per unit length of channel, is appreciably reduced during months with high discharge and nitrate flux and increases during months of low-discharge and flux. Biogeochemical factors, including land use, nitrate inputs, and stream concentrations, are a major control on reach-scale denitrification, evidenced by the disproportionately lower nitrate removal efficiency in streams of the highly nitrate-enriched watershed as compared with that in similarly sized streams in the less nitrate-enriched watershed. Sensitivity analyses reveal that these important biogeochemical factors and physical hydrological factors contribute nearly equally to seasonal and stream-size related variations in the percentage of the stream nitrate flux removed in each watershed."

Factors found to influence nitrate transport by Alexander et al. (2009) will be discussed in terms of the spatial and temporal patterns found in Minnesota (Figure 6). They found that the reaction rate constant "k" (per day) for denitrification is negatively correlated with nitrate concentration, streamflow and depth. When all three of these factors are relatively high such as during wet springs in southern Minnesota, little  $NO_X$ -N is lost. Conversely, during late summer when all three of these factors are relatively low, much  $NO_X$ -N is lost or converted to organic N.

Mulholland et al. (2008, 2009, as cited in Alexander 2009) predicted the percentage of stream loads to the outlet of two distinct watersheds during May. Modeled percentage of nitrate delivered from the agricultural watershed Sugar Creek is a minimum of 75% from headwaters and increases with proximity to the watershed outlet (Figure 7). Predicted delivery of nitrate loads from the Nashua River, which is primarily a forested watershed with some urban areas, is considerably lower for streams throughout the watershed than that predicted for Sugar Creek. Alexander et al. (2009) also plotted percentage removal by month for the same rivers (Figure 8). Removal rates peaked from August to October. Modeled removal rates in Sugar Creek were approximately 2% from March through June and approximately 5% in July. Even though these watersheds are not located in Minnesota, they serve as an example for watersheds with similar land use and stream networks in this state.

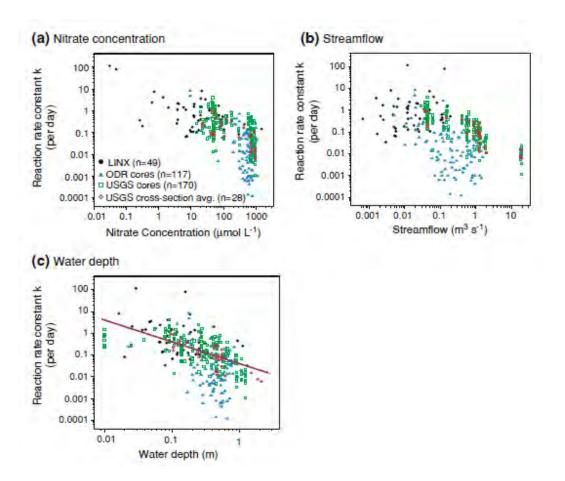


Figure 6. Observed measures of the reaction rate constant k for the separate field data sets, plotted as a function of nitrate concentration(a), streamflow (b), and water depth (c). The field datasets include USGS, LINX, and ODR. The slope of the line in (c) is expected for a constant mass-transfer rate,  $V_f$ . Figure reprinted from Alexander et al. (2009).

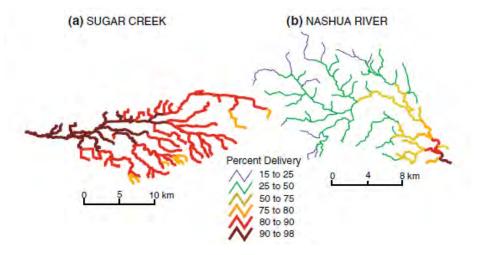


Figure 7. Modeled percentages of nitrate loads delivered to the outlets of Sugar Creek (a) and Nashua River (b) during May. Figure reprinted from Alexander et al. (2009).

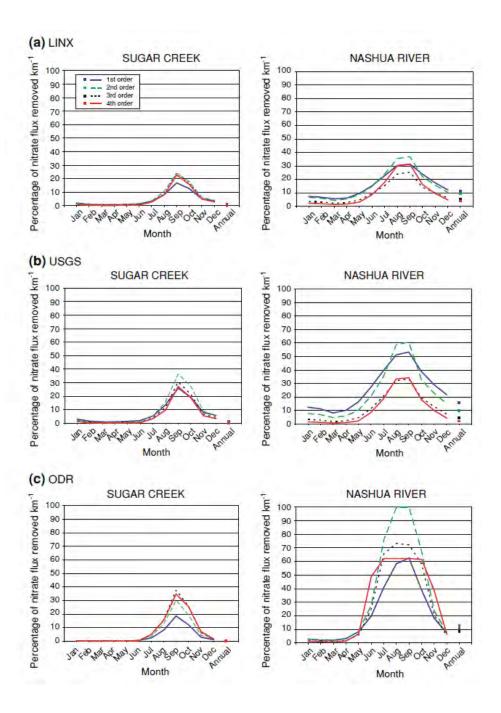


Figure 8. Median percentage of in-stream nitrate flux removed per kilometer of stream channel in streams of the Sugar Creek and Nashua River watersheds by strahler stream order, reported for the reaction rate constant regressions for the field datasets: (a) LINX, (b) USGS, and (c) ODR. Figure reprinted from Alexander et al. (2009).

Further understanding of N transport will be important for targeting approaches that maximize N processing in stream networks to minimize downstream transport of N. Current models may not characterize all N pathways or lateral exchanges but they do help users to determine primary factors that influence downstream movement of N.

#### SPARROW: transport from SPARROW watersheds to state border

This short section will focus on outputs derived from the Spatially Referenced Regressions on Watershed attributes (SPARROW) Decision Support System (<a href="www.cida.usgs.gov/sparrow/">www.cida.usgs.gov/sparrow/</a>). This web based tool provides access to national, regional, and basin-wide SPARROW models. We will focus on the TN model for the Great Lakes, Ohio, Upper Mississippi, and Souris-Red-Rainy Region - 2002 (<a href="www.cida.usgs.gov/sparrow/map.jsp?model=41">www.cida.usgs.gov/sparrow/map.jsp?model=41</a>). Users can view maps of modeled water-quality conditions (loads, yields, concentrations, incremental yields) by stream reach and catchment. Percent transport estimates by watershed to a user specified downstream receiving water such as a reservoir or an estuary are useful outputs from this tool. Finally, the tool can be used to evaluate management source-reduction scenarios by reducing inputs from TN sources as specified by the user.

One of the advantages of SPARROW is its ability to estimate downstream delivery fraction of TN from a large contributing area to a user specified downstream reach. The SPARROW outputs presented later in this section represent the fraction of TN loads from the outlet of SPARROW watersheds that are delivered to a specified downstream reach in a river. These losses are a relatively small percentage of TN losses that occur across the land/water continuum of a given watershed (Figure 9). Additional TN is lost in the surface waters upstream of the SPARROW watershed outlets. Quantifying the precise losses of TN in all surface waters within a SPARROW watershed is not possible since the stream reach file that is the base stream network of the SPARROW model does not include all of the surface waters in Minnesota directly.

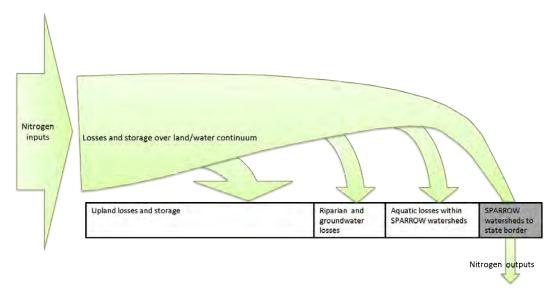


Figure 9. Generalized losses of TN inputs across the land/water continuum of a river basin. Note that the distribution of losses is highly variable depending on a given watershed in Minnesota and the magnitude of individual losses are not drawn to a specified scale here.

The Mississippi River at Minnesota/Iowa (MN/IA) border is the largest river in terms of contributing watershed area, annual TN load and average flow in the state of Minnesota. Based on estimated delivery fractions from SPARROW, the majority of TN loads at the outlets of the SPARROW watersheds in the Mississippi River Basin are delivered to the MN/IA border (Figure 10). The contributing watersheds with the highest delivery fractions are direct tributaries to the Mississippi River downstream of the Twin Cities Metro Area. In most of the remainder of the contributing watershed, greater than 80% of TN loads from the SPARROW watersheds are delivered to the state border. A few SPARROW watersheds have lower delivery fractions due to in-stream lakes/reservoirs [i.e. Cannon River headwaters, Mississippi River headwaters, Minnesota River headwaters, and Chippewa River (Wisconsin) headwaters]. Since the majority of loads loaded to reaches in the Mississippi River Basin are delivered to the MN/IA border, local TN loads to reaches within the SPARROW watersheds in the basin are the most important driver to the total load of the Mississippi River.

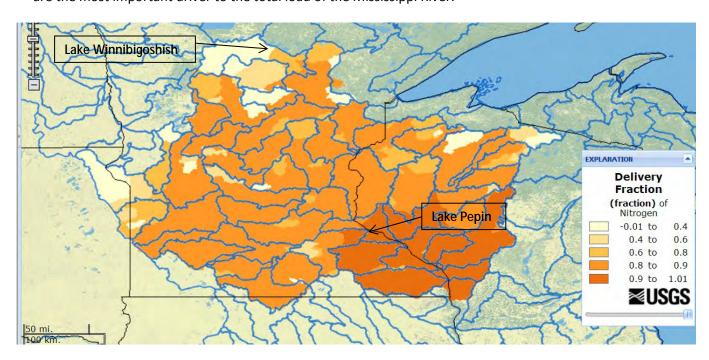


Figure 10. Annual estimated downstream delivery fraction of TN from outlets of SPARROW watersheds to the Mississippi River at the Minnesota/Iowa border.

Estimated delivery of TN from SPARROW watershed outlets in the Red River of the North Basin is quite variable. Model results indicate that 54% of the modeled SPARROW watersheds in the Red River Basin (including North Dakota watersheds) deliver more than 90% of their outlet loads to the Red River of the North at Pembina at the U.S./Canada border (Figure 11). Many of these reaches are direct tributaries or tributaries to direct tributaries to the Red River of the North. There are few to no lakes or reservoirs on these stream reaches. Certain areas of the Red River Basin have lakes or reservoirs downstream of SPARROW watershed outlets. The combination of distance from Pembina and lakes and reservoirs on some reaches results in 25% of the contributing watersheds delivering less than 20% of their TN load to the international border. Reaches near upper and lower Red Lake and the city of Detroit Lakes are examples of reaches that deliver a small fraction of their TN loads to the Red River at Pembina, North Dakota.

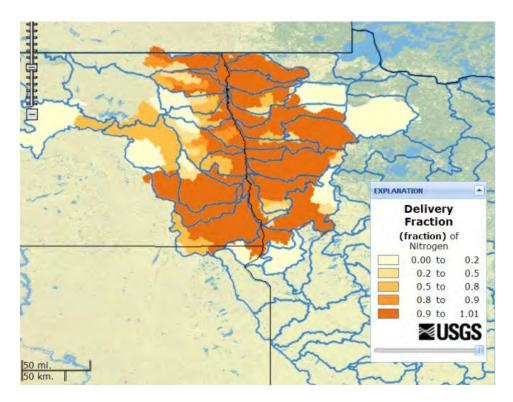


Figure 11. Annual estimated downstream delivery fraction of TN from outlets of SPARROW watersheds to the River of the North at the US/Canada border.

## Monitoring results from Minnesota rivers and streams

Seasonality of N delivery has already been discussed elsewhere in this report and this chapter. The Rush River of central Minnesota is a predominately agricultural watershed with extensive drain tiles to improve production of row crops. Stream samples were collected at road crossings throughout the watershed on June 4, 2003, by Sibley Soil and Water Conservation District (Matteson, S., personal communication). Flow at the outlet of watershed was 161 cfs which was a 79<sup>th</sup> percentile flow (based on monitoring from April through September). Streamflow was at 1,150 cfs two weeks prior to the sampling event. Drain tiles were flowing at low to moderate levels on this date according to field observations, and most stream samples that were greater than 20 mg/L NO<sub>x</sub>-N. The relatively consistent downstream concentration of NO<sub>x</sub>-N implies conservative transport of nitrate during early June of 2003 (Figure 12). The only stations below 10 mg/L were downstream of the lakes in the watershed. Clearly the ability of Rush River watershed to remove high inputs of nitrates was overwhelmed on this date. Without streamflow data at all of the sampling stations and a comprehensive sampling network of sources such as tile outlets and groundwater, a mass balance calculation cannot be completed to estimate percentage of N lost in streams for this watershed for one day or season. The relatively high transport rate of nitrate in the Rush River during late spring is similar to the modeling results for the Sugar River discussed earlier in this chapter [Mulholland et al. (2008, 2009) as cited in Alexander et al. (2009)].

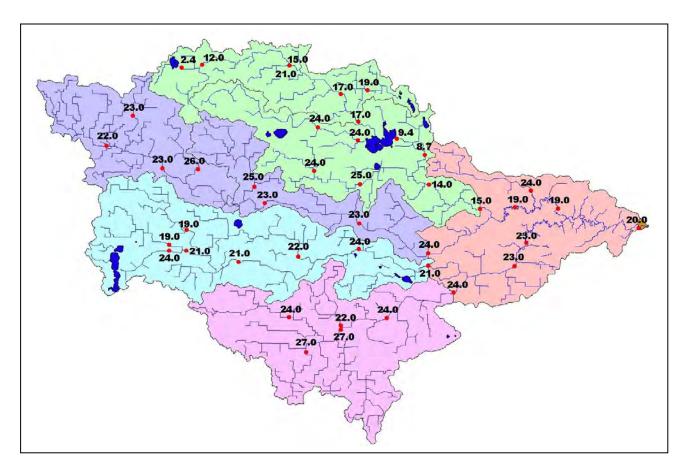


Figure 12. Nitrate ( $NO_X$ -N) concentration in mg N /L of streams throughout the Rush River watershed monitored at bridge crossing on June 4<sup>th</sup> 2003.

Transport of NO<sub>x</sub>-N and TN in the Minnesota River from La Qui Parle (River Mile 284) to St. Peter (river mile 89.7) is relatively conservative based on annual loads calculated from monitoring collected in 2009 (Table 3). This is consistent with previous results from a nitrate budget on a shorter reach of the Minnesota River from 2000-2008 (Matteson, S., Unpublished data, Table 4, Figure 13). Given that the Minnesota River is a relatively large river with seasonally high N loads, it should be expected that losses in the Minnesota River itself are relatively small on an annual basis. To further explain the factors that minimize transport losses, the average annual hydrograph of the Minnesota River needs to be examined. The five months from March to July account for 75% of the average water budget of the Minnesota River at Mankato based U.S. Geological Survey (USGS) monitoring from 1903-2011. NO<sub>x</sub>-N and consequently TN concentrations are also elevated during this time of year so the load is even greater than 75% of the annual budget from March to July. Recent data suggest that May-July flows are increasing in the Minnesota River (Figure 14) which could translate into higher annual loads if concentrations remain stable or increase in these months.

Table 3. Annual TN mass balances for two reaches (A and B) of the Minnesota River for 2009 based on calculated loads for tributary watershed and mainstem stations. Water volume and catchment area are included for water balance and total area of upstream stations respectively.

A) Upstream station and tribs	Mass (kg)	Mass (lbs)	Vol (acre ft)	Catchment (acres)
Minnesota River nr Lac Qui Parle, MN	4,707,520	10,378,305	1,210,000	2,592,000
Yellow Medicine R. Granite Falls, MN	366,483	807,957	68,029	424,960
Chippewa River nr Milan, MN40	1,670,465	3,682,745	416,151	1,203,200
Hawk Creek nr Granite Falls, CR52	1,081,695	2,384,728	89,444	323,082
Redwood R. nr Redwood Falls, MN	630,325	1,389,629	75,237	402,560
Total upstream: Minn. R. at Lac Qui Parle plus tributaries	8,456,488	18,643,364	1,858,861	4,945,802
Downstream, Minnesota River at Morton, MN	8,652,176	19,074,782	1,750,660	5,740,800
B) Upstream station and tribs	Mass (kg)	Mass (lbs)	Vol (acre ft)	Catchment (acres)
Minnesota River at Judson, CSAH42	9,660,620	21,298,021	2,165,170	7,216,237
Le Sueur River nr Rapidan, MN66	2,152,120	4,744,613	203,655	710,400
Blue Earth River nr Rapidan, CSAH34	3,432,217	7,566,743	398,540	987,029
Watonwan R. nr Garden City, CSAH13	930,254	2,050,859	110,565	544,640
Mankato WWTP*	139,434	307,400	6,209	NA
Total upstream: Minn. R. at Judson plus tributaries	16,175,211	35,967,636	2,884,139	9,458,306
	<del> </del>	-		+

<sup>\*</sup> Estimate based on limited monitoring data

Table 4. Average annual nitrate and water balance for Minnesota River from Judson (river mile 120) to St. Peter (river mile 89.7). The Blue Earth River (river mile 12.0) and LeSueur River (river mile 0.3) are the only monitoring inputs or tributaries included in this mass balance. (S. Matteson, unpublished)

2000-2008 Flow (cf) and Constituent Loads (tons)

Parameter	BLU 12.0 + LES 1.3	MIN 120.0	Total	MIN 89.7	% Difference
Acres	2,265,670	7,186,921	9,452,591	9,634,760	98.11%
Flow	415,747,996,215	562,552,030,275	978,300,026,489	1,000,813,294,620	97.75%
TSS	4,155,740	2,390,131	6,545,871	6,889,747	95.01%
NO3-N	136,572	95,125	231,697	232,139	99.81%
TP	5,537	4,901	10,438	10,606	98.41%
PO4	1,563	1,890	3,453	3,275	105.44%



Figure 13. Monitoring locations on Minnesota River and tributaries used to calculate a nitrate mass balance from 2000-2008.

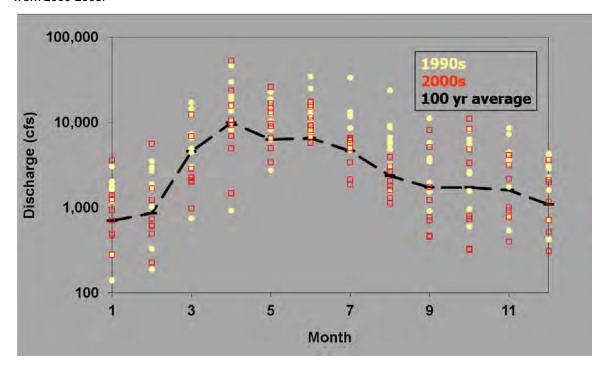


Figure 14. Average monthly discharge of the Minnesota River at Mankato for 1903-2008. Individual symbols represent monthly average for a given year in the past two decades.

The Mississippi River Basin upstream of Anoka has an extensive monitoring network similar to the Minnesota River Basin. Mass balances for TN during 2009 were examined for the Mississippi River to determine transport losses. Approximately 90% of the estimated TN loaded from the Mississippi River at Aitkin and other tributaries was found at the downstream monitoring site near Royalton. Eight percent of the watershed upstream of Royalton was not accounted for in this approach so losses of TN may be greater than 10%. These results are based on calculated loads for tributaries and Mississippi River stations designed for estimating loads. Transport in this reach of the Mississippi River may not be completely conservative, but more monitoring is needed to confirm the transport losses observed in 2009. The flow-weighted mean concentration of NOx-N for the Mississippi River and tributaries ranged from 0.09 to 0.76 mg/L. These concentrations are certainly lower than the Minnesota River where high NO<sub>x</sub>-N concentrations/loads overwhelm removal via denitrification during higher flows when a large portion of the load is transported downstream. Mass balance results from the Mississippi River from Sauk Rapids to Anoka indicate conservative transport (near 100% transport), but missing tributaries such as the Elk River make this evaluation difficult. The flow weighted mean of NO<sub>x</sub>-N increases from 0.31 mg/L at Sauk Rapids to 1.2 mg/L at Anoka primarily due to tributaries like the south fork of the Crow River. This reach of the Mississippi River is simply receiving a large load of TN from tributaries near the end of the reach where there is limited travel time to remove any meaningful amount of TN.

### Mississippi River from the Twin Cities to Minnesota/Iowa border

Nitrogen transport in the Mississippi River downstream of the Minnesota River confluence to the MN/IA border (Lower Miss) has been monitored and studied for N transport in rivers as much as anywhere in the state. Metropolitan Council Environmental Services (MCES) and the Long Term Resources Monitoring Program (LTRMP) of the USGS have maintained monitoring programs for at least 20 years to collect water quality samples on the Lower Miss. Wasley (2000) assembled much of the available N data up to 1997 for the Lower Miss and its tributaries and found that TN was generally conservative, meaning that a relatively small percentage of N was lost during transport down the river. Houser and Richardson (2010) summarized transport, processing and impact of phosphorus, and N on the Lower Miss. This paper adds much detail to what was previously known about the processing of N within the river compared to the original mass balance budgets that were completed prior to their summary work. Questions regarding assimilation, storage and loss of N in the Lower Miss still remain after many years of study, but the original findings that the majority of N is transported downstream have been confirmed. The complex and dynamic biology and hydrology of the Lower Miss greatly influence the transport of N in this system. Bruesewitz et al. 2006 found that zebra mussels may increase denitrification near sediments via coupled nitrification and denitrification of high NH<sub>x</sub>-N mussel wastes. Dynamic levels of phytoplankton and submersed aquatic plants certainly influence N spiraling in the river, but their overall impact on movement of TN downstream has not been fully quantified. Detailed pathways have been monitored on backwater lakes that will be discussed later in this section.

A recent paper from Strauss et al. (2011) utilizes the extensive research on the Mississippi River to estimate N losses from a 2,400 km reach of the Mississippi River from Minneapolis, Minnesota to the Atchafalaya diversion in Louisiana (Figures 15 - 18). The entire length of the Mississippi River downstream of Minneapolis has been classified for habitat type. Denitrification rates monitored in Navigational Pool 8 by habitat were used to estimate TN removal rates throughout the Mississippi River. They estimated that 9.5% of TN load is lost through denitrification from Minneapolis to the Atchafalaya Diversion. Losses and assimilation are higher in upper portions of the river such as Minnesota's reach where impoundments and backwaters elevate TN losses. The percentage of backwaters and impounded

areas drop dramatically after Pool 13 resulting is less processing of TN inputs (Figure 14). Unfortunately, the TN loads to the Mississippi River increase downstream of Pool 13 due to large tributaries: Des Moines River, Illinois River, Missouri River, and Ohio Rivers (Figure 16).

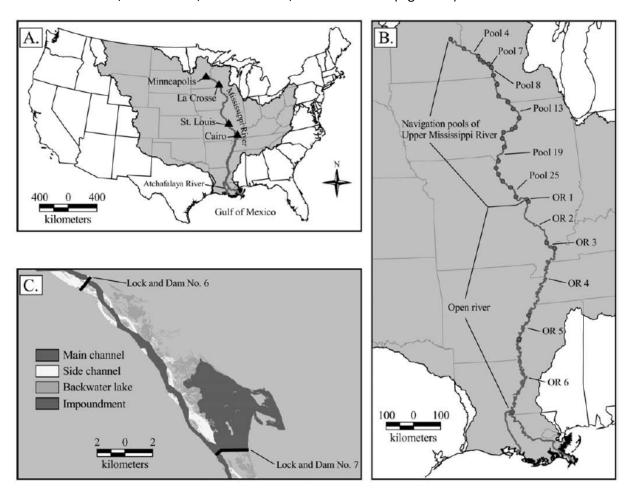


Figure 15. The Mississippi River watershed (A) covers 41% of the conterminous United States (shaded area on map). The two main reaches analyzed in this study (B) were the reach containing the navigation pools (Minneapolis, Minnesota to St. Louis, Missouri) and the open river reach (St. Louis, Missouri to the Atchafalaya River diversion in Louisiana). The circles located on the river are the nodes of the 30 sub-reaches used. Select sub-reaches of the northern reach and all the open river (OR) reaches are labelled. Navigation Pool 7 (C) is a representative example of the aquatic habitat spatial data used to extrapolate N loss in the river. Reprinted from Strauss et al. (2011).

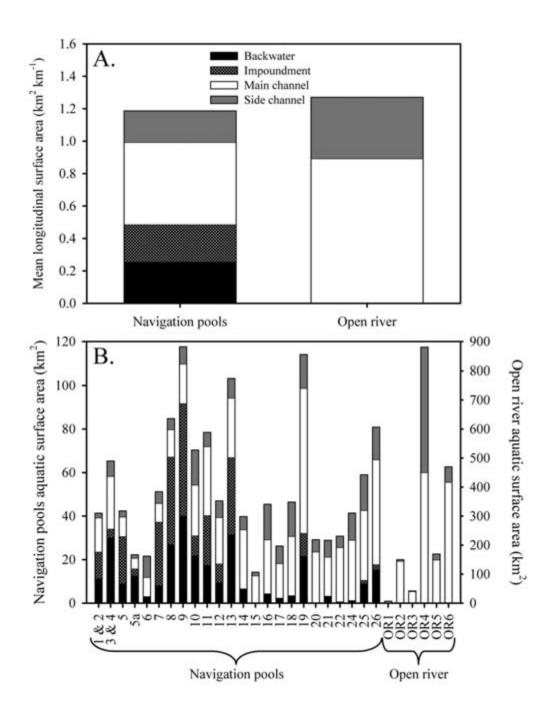


Figure 16. Mean longitudinal surface area (A) of the four aquatic habitats in the two main reaches of the Mississippi River. Total surface area (B) of the aquatic habitats in all of the navigation pool reaches of the Mississippi River north of St. Louis and the open river south of St. Louis to the Atchafalaya River diversion in Louisiana. Reprinted from Strauss et al. (2011).

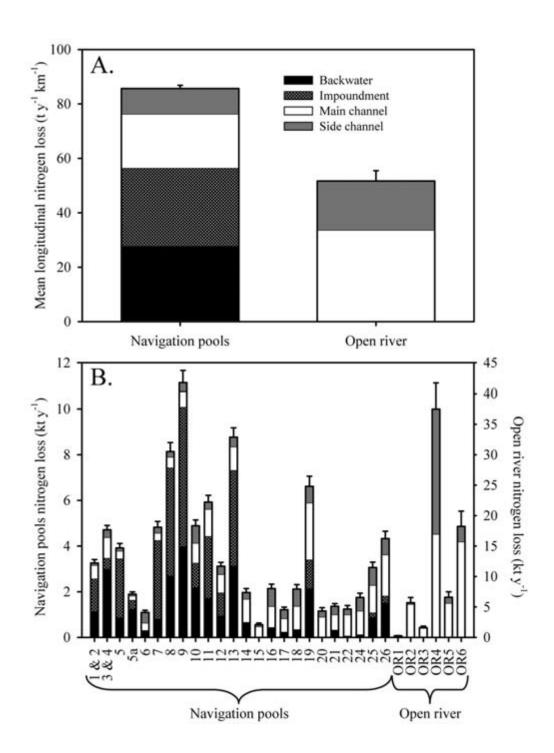


Figure 17. Mean longitudinal N (N) loss (A) within each of the four aquatic habitats in the two main reaches of the Mississippi River. Total N loss (B) in the aquatic habitats of the navigation pool reaches and the open river. Error bars = +1 standard error of total N loss. Reprinted from Strauss et al. (2011).

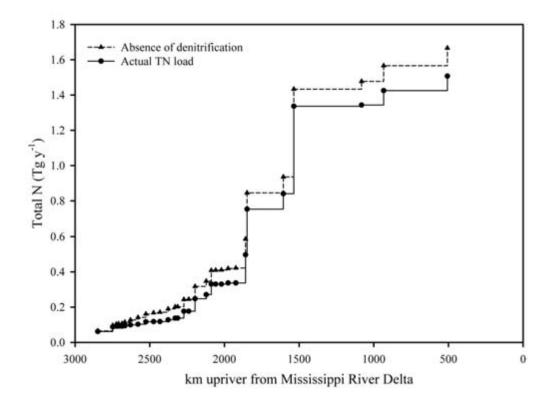


Figure 18. Total nitrogen (N) flux in the Mississippi River in the presence and absence of denitrification. The vertical distance between the two lines depicts the cumulative loss of N from denitrification. The symbols on the lines show the location of the 30 sub-reach nodes used for analysis. Reprinted from Strauss et al. (2011).

### Mississippi River Pools 2-4

Mass balance results and model outputs for shorter segments of the Lower Miss are useful to compare to other approaches such as SPARROW or the extrapolation approach by Strauss et al. (2011). Recent models results and load calculations confirm that the majority of annual TN loads to the Lower Miss are transported downstream. The MPCA and their consultant LimnoTech Inc. (LTI) combined data from MCES, LTRMP and other sources to develop a 3-dimentional model of the Mississippi River from Pool 2 through Pool 4 including Lake Pepin (LTI 2009, Figure 19). Model results from Pools 2 to 4 and a recent mass balance budget of Lake Pepin by the author estimate that over 90% of input N loads to a given pool are transported to subsequent pools or reaches (Table 5, Table 6). Some of the same data was used for these two estimates but they are not the same method. The cumulative impacts of minor losses of N in a given reach of river will be discussed in more detail in the SPAAROW chapter of this report.



Figure 19. Navigational Pools 2 through 4 of the Mississippi River. Pools are located upstream of Lock and Dams (e.g. Pool 2 is located between Lock and Dams 1 and 2).

Table 5. Average annual TN budgets in metric tons for Pools 2-4 based on the UMRLP model from 1985-2006. Note that Lake Pepin is contained within Pool 4.

Reach	Input	Tributaries	WWTP	Total inputs	Output	Transport coefficient
Pool 4	193,004	46,213	-		223,095	0.93
Lake Pepin	210,449	572	-		198,131	0.94
Pool 3	176,417	19,842	126		193,291	0.98
Pool 2	43,207	123,721	12,668		176,437	0.98

Table 6. Average estimated monthly percentage transport of the TN and  $NO_X$ -N through Lake Pepin based on loads calculated from 1993-2009. "percent transport" = output load / input loads

	% tra	nsport
Month	TN	NO <sub>x</sub> -N
1	1.07	1.13
2	1.07	1.13
3	0.89	0.97
4	0.83	0.93
5	0.85	0.92
6	0.86	0.92
7	0.96	1.02
8	1.04	0.78
9	0.96	0.72
10	1.04	0.78
11	1.01	1.10
12	1.05	1.12
Average*	0.91	0.94

<sup>\*</sup>Annual average is based on transport of annual loads. It is not an average of monthly averages.

Closer examination of the N load transported through Lake Pepin is useful for several aspects of river transport since Lake Pepin is fed by three large river basins (i.e. Mississippi, St. Croix, and Minnesota). Annual patterns in streamflow and N loads to Lake Pepin serve as an example for general patterns observed in the streams throughout the state. Average annual discharge (22,000 cfs = long-term average) of the Mississippi River upstream of Lake Pepin peaks in April and gradually falls until August when average flows stabilize until late March (Figure 20). Elevated flows can occur from March to October. From November to February, flows seldom exceed 40,000 cfs.

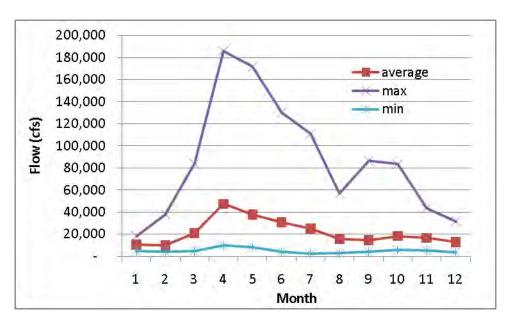


Figure 20. Average, maximum and minimum daily discharge of the Mississippi River at Prescott, Wisconsin by month from 1980-2009.

The different fractions of TN are processed differently by Lake Pepin. Residence time for Lake Pepin during summer is rather short (range 5-50 days) and less than 7 days on average during spring (Figure 21). The majority of TN entering and present in Lake Pepin is DIN which is generally conservative during most months (Table 6, Figure 22).  $NO_X$ -N transport is greater than 92% for all months except August and September when nitrate is likely transformed into organic N during late summer/early fall algal blooms when residence time is greater and  $NO_X$ -N loads are reduced from tributaries compared to spring and early summer. Riverine production of algae is significant upstream of Lake Pepin, and there is generally a peak in algal levels in upper Lake Pepin before levels decline at the deeper downstream portion of the lake. Deposition of organic N is prevalent from April to June when suspended solids loads are greatest. Lake Pepin is a trap for total suspended sediment with only 41% of average inputs exiting the lake on an annual basis (LTI 2009). Algal settling and processing in bottom sediments also complicate the spiraling of N through Lake Pepin. Algal processing is certainly important to the biology of Lake Pepin but it does not have a major impact of N transport in Lake Pepin during average conditions. On average during August, only 5% of the TN pool loaded to Lake Pepin is contained in viable algae and only 3% of the TN pool at the outlet is contained in viable algae (LTI 2009).

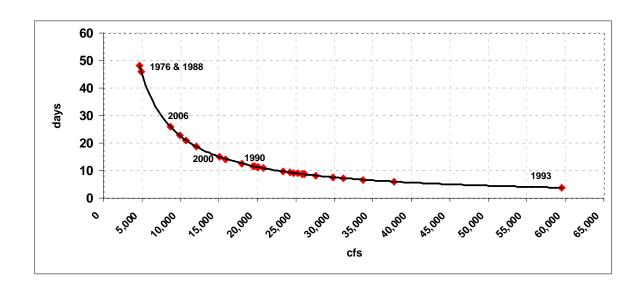


Figure 21. Estimated residence time of Lake Pepin verses mean summer (June- September) discharge of the Mississippi River at Prescott. Individual summers are identified for reference (1976=drought, 1993 = flood).

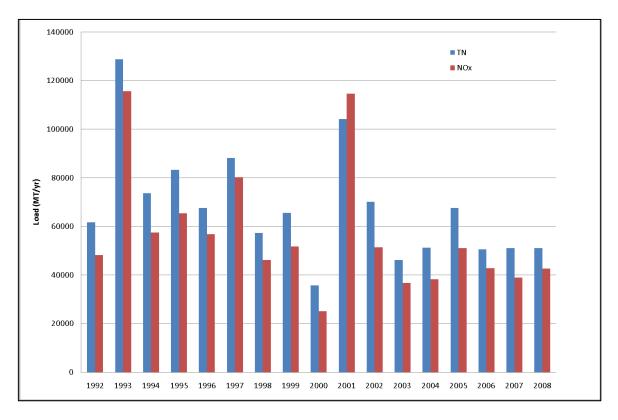


Figure 22. Average monthly load of TN and  $NO_X$ -N of the Mississippi River at the outlet of Lake Pepin from 1993-2009.

A comprehensive set of loads of the Mississippi River and its tributaries from the outlet of Lake Pepin to lower Pool 8 have not been compiled at this time to update results from Wasley (2000) or validate results from Strauss et al. (2011) and SPARROW modeling results. Loads at lower Pool 8 are greater than the outlet of Lake Pepin due to tributary loads and relatively conservative transport in this reach (Figure 23). Large tributaries to this reach include the Black and Chippewa Rivers from Wisconsin and the Zumbro and Root Rivers from Minnesota. Submersed aquatic vegetation is common in impounded areas and backwaters of the Mississippi downstream of the outlet of Lake Pepin. Average residence time of Navigational Pools 5-8 is less than two days on average (Wasley, 2000).

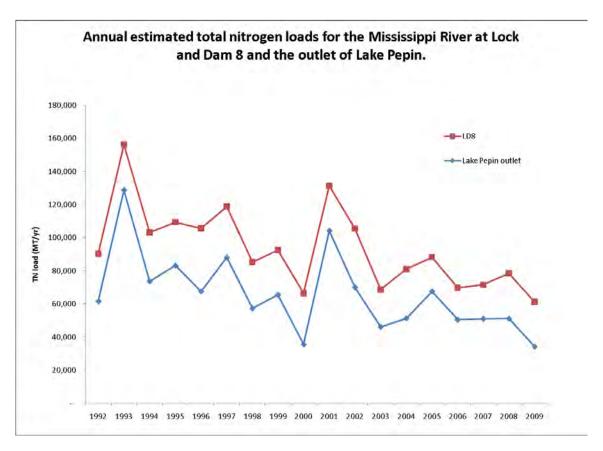


Figure 23. Annual estimated TN loads for the Mississippi River at the outlet of Lake Pepin and Lock and Dam 8.

### Backwaters of the Mississippi River

Nitrogen processing in backwaters of the Mississippi River can alter the N levels, but the overall impact of reductions in backwaters is generally overwhelmed by the large load transported in the main channel of the river. Research on backwaters can be applied to other shallow lakes and deep wetlands where study of N processing in Minnesota has been less thorough. Houser and Richardson (2010) have documented that NOX-N is often lower in backwater areas than the main channel, but quantifying the volume of water exchanged with backwaters is often lacking which prevents an accurate estimate of N lost in any individual or group of backwaters. Forshay and Stanley (2005) found that the floodplain including backwaters of the lower Wisconsin River were responsible for rapid depletion (within days) of nitrate delivered to the floodplain. During April of 2011 as discharge levels fell and connectivity between the river and floodplain was disrupted, nitrate levels in water trapped on the floodplain were reduced from 1.09 mg/L to <0.002 in 8 days. They concluded that enhancing the connection of large rivers to their floodplains may enhance overall retention of TN loads from large rivers.

James (2010) completed extensive N processing analysis of Second Lake from mid-May to October of 2006. Second Lake is a backwater lake in upper Pool 5 with a metered culvert at its inlet so a detailed mass balance could be completed for this backwater (Figure 24, 25). This shallow backwater lake has a surface area of 7.5 ha with mean depth of 0.4m (max depth = 2.4 m). Thirty-one percent and 54% of TN and NO<sub>x</sub>-N inputs to Second Lake were removed respectively during the monitoring period in 2006. Estimated removal via denitrification in Second Lake accounted for 57% of retained NO<sub>X</sub>-N, suggesting assimilation of NO<sub>x</sub>-N by biota for the remainder of NO<sub>x</sub>-N losses. Second Lake had extensive Lemna sp. (duckweed) during June and July when 86% of macrophyte transects were occupied with floating Lemna sp. Submersed macrophytes dominated by Ceratophyllum demersum (Eurasian water milfoil) and Potamogeton crispus (curly leaf pondweed) occupied 46% to 65% of transect stations. C. demersum biomass peaked in August. P. crispus dies back in early June after peaking earlier in the season than most natives. Nymphaea odorata (white water lily) was also present. A large pulse of DON or DIN was not observed as various plants went through senescence in late summer and early fall. James (2010) suggests that N could be trapped in plant tissue which may be lost to sedimentation, processed later via aerobic or anaerobic mineralization of N, or exported as larger fragments of plant tissue that are not sampled via typical water-quality sampling techniques. It is common for backwaters to export Lemna sp. during water level fluctuations on the Mississippi River. The overall significance of N in large particulate matter to the overall N budget of a given pool has not been quantified. Flow through Second Lake was fixed at 4.24 ft<sup>3</sup>/s via the metered culvert, resulting in a theoretical residence time of 3.3 days for the entire study. Flow in the Mississippi River at Winona from mid-May to October 2006 (best gaging station near Pool 5) ranged from 8,430 to 70,600 ft<sup>3</sup>/s with a median and mean of 14,000 and 21,015 ft<sup>3</sup>/s respectively. Even during the lowest flow in the Mississippi River of the study period, the flow through Third Lake only represents 0.05% of the downstream flow of the Mississippi River. Needless to say, the impact of this individual backwater lake on downstream transport of N is very small. Extrapolation of removal rates in backwaters and other habitat types is required to determine the collective impact of all habitat types on the downstream movement of TN (Strauss et al. 2011).

Radio-isotopes have been used with in situ mesocosm experiments to measure nitrate assimilation rates of macrophytes, epiphyton and microbial fauna (Kreiling et al. 2010). This study was completed during June and July of 2005 on Third Lake which is a backwater lake directly west of Second Lake discussed in the previous paragraph. Tracking of  $^{15}N-NO_3-N$  revealed that denitrification accounted for 82% of  $NO_3-N$  losses with the remainder being assimilated by macrophytes and epiphytes (Figure 26). This study also found that denitrification potential and assimilation rates increased with increasing nitrate concentration. Denitrification potential (represents maximum removal rate of sediments) was measured in the laboratory with sediments from Third Lake. Denitrification potential rates plateaued at 5 mg/L suggesting that backwaters can remove up to 3,000 mg  $N \cdot m^{-2} \cdot d^{-1}$  (Figure 27).  $NO_X-N$  loading beyond this rate to a given flow-through backwater will be transported downstream. Backwaters with excessive loading at concentration greater than 5 mg/L are essentially  $NO_X-N$  saturated.

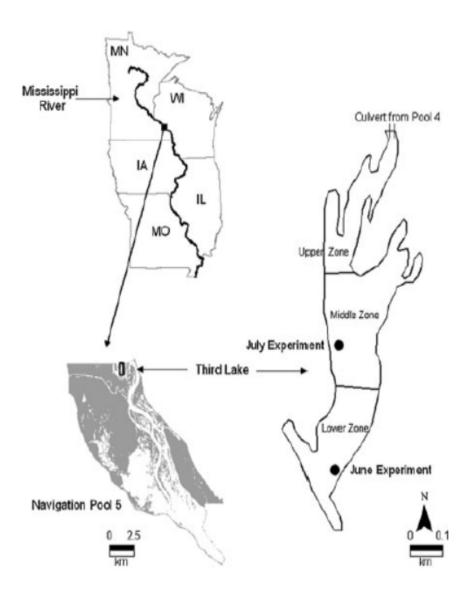


Figure 24. Third Lake is three miles east of Kellogg, Minnesota in the upper portion of Navigational Pool 5 of the Mississippi River. Reprinted from Kreiling et al. (2010).

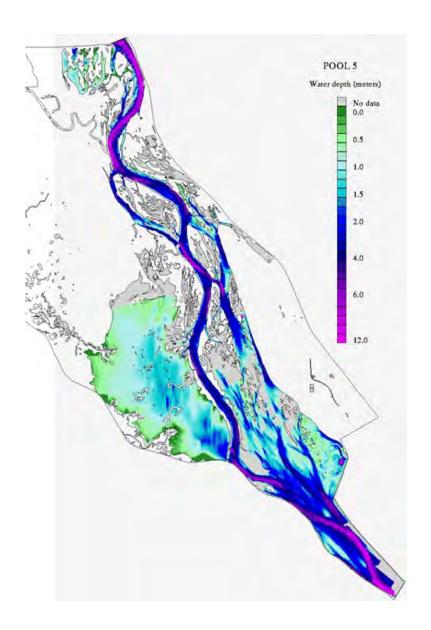


Figure 25. Bathymetric map of Navigational Pool 5 of the Mississippi River. (Solid oval = Third Lake, dashed oval = Second Lake). Source: USGS.

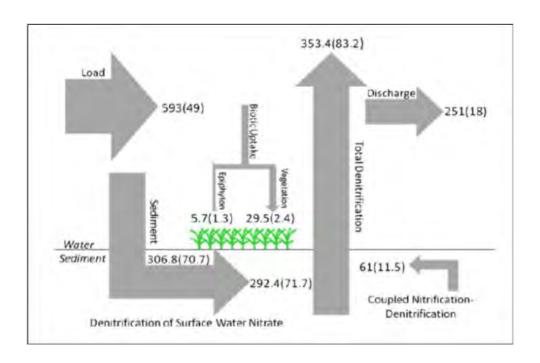


Figure 26. Net  $NO_3$ -N budget (mean (1 SE), (mg m-2 h-1) for Third Lake, Navigation Pool 5 during June and July 2005. n = 3 for discharge and load, n = 8 for coupled nitrification–denitrification and total denitrification, n = 16 for biotic uptake and denitrification of surface water nitrate. Reprinted from Kreiling et al. (2010).

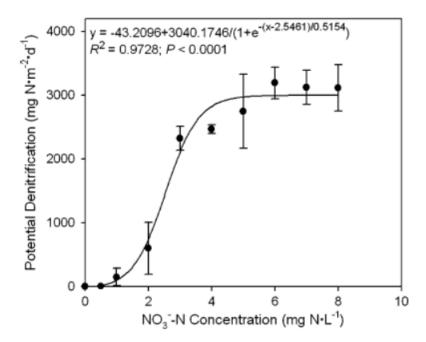


Figure 27. Relationship between  $NO_3$  –N concentration and potential denitrification rates (mean  $\pm$  1 SE, n = 8) for Third Lake, Navigation Pool 5. Sediment was taken from the middle and lower portions of the lake in June and July 2005. Reprinted from Kreiling et al. (2010).

The two backwater studies by James (2010) and Kreiling et al. (2010) examined similar backwaters and found different rates of denitrification by a factor of three (94 mg m $^{-2}$  day $^{-1}$ , 292 mg m $^{-2}$  day $^{-1}$  respectively). The difference in denitrification rates may be expected given the differences in the two studies including spatial, temporal and design differences. The more important finding is that denitrification was the dominant path for NO<sub>X</sub>-N removal in both studies. This suggests that removal of NO<sub>X</sub>-N from the system is more prevalent than assimilation. Thus, the dominant pathway is removal verses assimilation which may result in a delayed transport of N in the system. The applicability of these results to other surface waters may be best suited for shallow vegetated lakes and wetlands.

## Fate of wastewater treatment plant nitrogen loads

The fate of N discharged by wastewater treatment plants (WWTPs) is dynamic and generally similar to the processing of N inputs from other sources. The actual rate of contribution from point sources to aquatic resources is much more constant than that of sources such as atmospheric deposition, overland runoff or tile line flow. Based on the discussion in the previous sections of this chapter, it is assumed that during high flows much of the N from all sources is transported downstream. Transport of DIN from WWTPs during low flows in summer is variable with some assimilation into biota and losses to denitrification depending on the receiving stream. Many WWTPs promote nitrification to comply with  $NH_X$ -N limits. Thus,  $NO_X$ -N is the dominant form of N discharged by many WWTPs. More information regarding the forms of N in wastewater is covered in the WWTP chapter of this report.

#### Literature

Isotopic signatures of NO<sub>3</sub>-N sampled longitudinally throughout the Illinois River indicated the presence of NO<sub>3</sub>-N discharged from the Chicago area WWTPs throughout the river system (Panno et al. 2008). During high flow periods, NO<sub>3</sub>-N in the upper Illinois River, which is dominated by point source loading, was slightly diluted by NO<sub>3</sub>-N derived from tributaries with extensive drainage tiles as it flows to the Mississippi River. Even though concentration decreases in the river during high flows, the load goes up dramatically due to the substantial contributions of the tributaries. NO<sub>3</sub>-N transport during high flows was generally conservative regardless of the source of N. During low flows in August of 2005, NO<sub>3</sub>-N in the Illinois River was predominately from point sources. Dilution from deep groundwater, which showed the highest degree of denitrification in the study, was the primary source of water besides point sources to the river during low flows. Approximately 50% of NO<sub>3</sub>-N (concentration drop of 1.69 to 0.83 mg/L) in the Illinois River was removed in Peoria Lake (impoundment on Illinois River) during low flow. Further investigation would be needed to definitively determine whether NO<sub>3</sub>-N was lost to denitrification or assimilated into algae in Peoria Lake. Assimilated N may still be transported downstream as algae or transported when higher river flows return.

Available N data for WWTPs and receiving waters in Minnesota are not adequate to estimate annual transport losses of WWTP N loads in rivers. Low-flow sampling was completed from the late 1970s through early 1990s to assess the conversion rate of  $NH_X$ -N downstream of WWTPs in headwater streams. Concentration of  $NH_X$ -N typically returns to upstream levels with 2-3 miles downstream of point sources during low flow conditions in summer. Sampling results are inconclusive to discern if the  $NH_X$ -N is converted to  $NO_X$ -N via nitrification, assimilated by biota or lost to  $N_2$  gas via coupled nitrification denitrification. During winter low flows,  $NH_X$ -N from WWTPs is more conservative due to low temperatures which reduce rates of nitrification and assimilation. Downstream sampling beyond the first five miles was not available to determine when or if  $NH_X$ -N is lost downstream of WWTPs in winter.  $NO_X$ -N and TKN were generally conservative downstream WWTPs for the first five miles during summer

and winter. Many factors such as ungaged tributaries, groundwater contributions, and low sample numbers at any given site make it difficult to characterize transport of  $NO_X$ -N and TN downstream of WWTPs. We will discuss transport beyond five miles in the following paragraph.

The following example is based on available data at the time of this report. The city of Marshall, Archer-Daniels-Midland Company, and other smaller point sources, discharge approximately 441 pounds/day (75% DIN) to the Redwood River. During August of 2009, the load of  $NO_x$ -N and TKN of the Redwood River upstream of the Minnesota River confluence was 22 pounds/day and 110 pounds/day respectively indicating that at least 70% of TN was lost in the Redwood River. Continued monitoring of the MPCA's load monitoring sites located at the outlets of HUC 8 watersheds will be useful for quantifying what level of flow would be considered low flow for all the watersheds in the state in the future. Additional point source monitoring will greatly improve our estimates of N losses during low flow periods. The loss of N described here during a low flow in summer is a stark contrast to what happens during spring when a much higher portion of  $NO_x$ -N loaded to rivers is transported downstream.

## Nitrogen transport in lakes and reservoirs

Definitions: 1) Residence time: Time in days or years to replace water in a given lake (Volume of lake / volume of water inputs per unit time= residence time). 2) Areal hydraulic load (m yr-1) = (annual water inputs in  $m^3$  / surface area of lake in  $m^2$ )

Lakes and reservoirs (lentic systems) are important sinks for N throughout the world. Harrison et al. (2009) modeled the amount of N removed by lentic systems on regional and global scales to estimate the cumulative impacts of these resources. They estimated that small lakes (<12,355 acres) were responsible for removal of 47% of N removed by lentic systems. Certainly the majority of Minnesota lakes are smaller than 12,355 acres (50 km²). They also found that although reservoirs only occupy 6% of the total surface area of lentic systems, reservoirs remove 33% of all N removed by lentic systems. Given the relatively short residence of reservoirs compared to lakes this may not seem probable. One major difference in lakes and reservoirs is the load of N delivered to these systems. Reservoirs may or may not be as efficient as lakes for removing N, but the large watersheds of reservoirs' typically deliver much larger loads of N to reservoirs.

Nitrogen removal efficiency of lakes is influenced by external loading and size of the lake relative to that loading. Alexander et al. (2008) calculated areal hydraulic load (see definitions) and compared it to percentage of N and phosphorus removed. They found that percentage of N removal is negatively correlated with areal hydraulic load (Figure 28). They compared modeled results with results from the literature to verify their model. Their findings are consistent with the basic concept that N can be removed from aquatic systems if loading rates are low and residence time is high. The larger the areal hydraulic loading to a given lake the shorter the residence time assuming that depth is the same for all lakes being compared. Greater depth also increases residence time; so large lakes with small watersheds remove most of the input N while small (relative to watershed) lakes tend to remove very little input N.

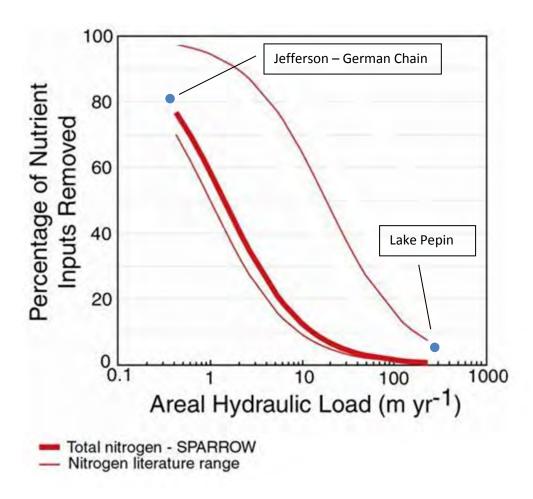


Figure 28. SPARROW predicted removal rates of N for lakes and reservoirs based on areal hydraulic load. Modified and reprinted from Alexander et al. (2008). Lake Pepin and Jefferson-German estimates were added to original figure.

David et al. (2006) found that Lake Shelbyville in central Illinois removed 58% of input  $NO_3$ -N on average from 1981-2003. Average residence time during this time period was 0.36 year with a range of 0.21 – 0.84 yr. The watershed for Lake Shelbyville is > 80% row crops (corn and soybeans) with extensive tile drainage to enhance crop yields. David et al. (2006) found that incorporation of  $NO_3$ -N to organic N (measured as TKN) accounted for approximately 10% of  $NO_3$ -N losses observed in Lake Shelbyville from 2002-2003. They also commented that even though reservoirs can be effective N traps the expense of constructing reservoirs are excessively high. Problems with sedimentation of reservoirs in the Midwest often limit the effective lifespan of reservoirs. Several reservoirs in Minnesota in key locations for N removal that have lost (and/or continue to lose) much of their original volume include: Lake Redwood on Redwood River, Lake Zumbro on Zumbro River, Lake Byllesby on Cannon River, Rapidan Dam on Blue Earth River, and Lake Pepin on Mississippi River.

A recent study found that monitoring nitrogenous gases ( $N_2O$  and  $N_2$ ) is another technique to directly measure N lost to denitrification. Deemer et al. (2011) found that  $N_2O$  and  $N_2$  accumulated in the hypolimnion of Lacamas Lake (small eutrophic reservoir) in Washington State. Their results were comparable to other techniques for estimating denitrification rates. Early in the stratification period  $NO_X$ -N was present and  $N_2$  was the primary gas produced close to the sediment-water interface. Later in

the season as  $NO_X$ -N was depleted,  $N_2O$  production increased and was produced throughout the water-column. This suggested that nitrification was a source of  $N_2O$ . Overall production of  $N_2$  was seven times that of  $N_2O$  produced on average.  $N_2O$  is a potent greenhouse gas so quantifying its production is important.

#### Minnesota lakes and reservoirs

Existing monitoring programs are typically designed to monitor the surface water-quality of lakes at their center or deepest portion. Natural lake outlets often drain water from the epilimnion (upper portion of thermally stratified lake) of the upstream lake. This section will focus on N data collected at the top two meters of lakes since this where the majority of the samples have been collected in Minnesota and is most representative of what is expected to be exported via lake outlets. Most N in Minnesota lakes is present as organic N during summer (June-September) when most lake samples are collected. Summer average TN for lakes ranges from 0.2 to 4.0 mg/L (Figure 29). NO<sub>X</sub>-N is typically near detection limit and is most common in early spring when watershed loads are greatest and possibly due to conversion of NH<sub>X</sub>-N (accumulated during winter) to NO<sub>X</sub>-N. Sampling data is limited during early spring to confirm NO<sub>X</sub>-N concentration when lakes are most likely to discharge water to downstream resources. NH<sub>X</sub>-N is also scarce in lakes except in anoxic hypolimnions of stratified lakes where NH<sub>X</sub>-N at concentrations greater than 1 mg/L are common. This is important at turnover when mixing exposes NH<sub>X</sub>-N to aerobic conditions where it is likely converted to NO<sub>X</sub>-N or assimilated by algae.

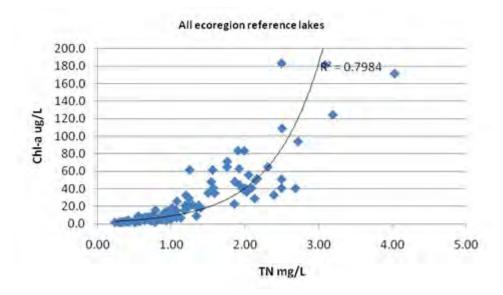
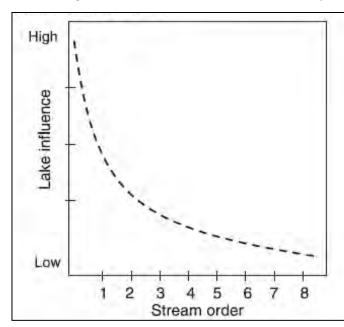


Figure 29. Summer average TN verses chlorophyll-a for reference lakes in Minnesota monitored from 1985-1988.

Minnesota has relatively few reservoirs on rivers with adequate residence time to process high nitrate loads in the southern portion of the state. We will examine actual data from some Minnesota lakes and reservoirs to determine if these systems mimic what has been documented in the literature. We have already discussed Lake Pepin in a previous section. This is one of our best examples of system where relatively little N is removed due to short residence time and high external loading. Nitrogen budgets for other lakes in Minnesota are not nearly as comprehensive as what we have available for Lake Pepin. True N removal is difficult to determine given the relatively scarce amount of TN data for the outlets of lakes throughout a given sampling year. We know that N is loaded to lakes to some degree throughout the state and we know that NO<sub>X</sub>-N is typically below detection limit in most lakes unless nitrate loading

is high and residence time is short.  $NO_x$ -N loaded to lakes is assimilated into biota of the lake which would be measured as TN if it was assimilated by suspended algae. Nitrogen assimilated by plants, epiphyton and other organisms would not be measured in typical surface monitoring techniques. Based on research from reservoirs and backwaters discussed earlier, we know that much of the  $NO_x$ -N is lost via denitrification (David et al. 2006, Kreiling et al. 2010). The practical matter is that the TN exports from lakes and reservoirs are low given adequate residence time. Whether the TN is stored in lake sediments via plant and algae settling and ultimately denitrified or denitrified directly is likely variable depending on a given lake and its watershed.

Many of the lakes in northern Minnesota can be characterized as aquatic systems with long residence times and low to modest N loading. The concentrations of these systems are less than detection level for  $NO_X$ -N and approximately 1 mg/L TN. The combination of low TN loading and TN removal/assimilation in these systems result in low loading to downstream lakes and rivers. Lake "chains" or networks exist in certain areas of the state where a series of lakes are directly connected or connected by streams or rivers. Nitrogen removal rates from these lakes are quite high for several reasons. First, residence time of chain of lakes is typically much longer than that for a single lake. Second, these systems tend to slow the rate of runoff since the outlets to lakes often restrict flow which results in more time to process N during wet periods. Third, streams that connect lake chains can be shallow and slow moving with wetland fringes. All of these factors result in low N exports. Jones (2010) discussed the ecological impact



of lakes on lake/stream networks and found that the location and density of lakes in a watershed influences the ultimate impact of lakes on a stream network. The impact of stream order upstream of a lake network can be used to estimate N removal (Figure 30). Smaller streams have lower water and N loads which allows for greater residence time to remove a relatively smaller N load. Extremely large lakes such as Lake of Woods and Lake Superior would be exceptions to the general pattern discussed here, but the use of stream order upstream of a given lake or lake network is a useful predictor for N removal potential.

Figure 30. The influence of a lake is likely to decrease as increase in size down a stream network (reprinted from Jones 2010).

The Cannon River watershed has several headwater lakes that remove approximately 83% of inflowing N loads (Pallardy et al, in review). The Jefferson-German Lake chain (J/G chain) has a relatively small watershed with a watershed area to lake area ratio of approximately 3.5 (Figure 31). Hydraulic loading (0.47m yr<sup>-1</sup>) to this system is low and residence time is a minimum of five years for the major basins in

the chain. The landuse for the J/G chain's watershed is a mix of corn. soybeans, pasture/hay, forest and other minor categories. In 2010, the monitored NO<sub>x</sub>-N flow weighted mean for the tributaries was 11.2 mg/L from March 17 to November 1. It is likely that NO<sub>x</sub>-N loads of tributaries monitored in 2010 were not radically different than that of the past decade. Total nitrogen was not monitored, but it was likely 12-13 mg/L based on organic N levels in other streams in the state. The NO<sub>x</sub>-N concentration of the J/G chain outlet flowing from German Lake was 0.2 mg/L for this same time period. Based on the chlorophyll-a concentration of German Lake in 2010 the TN at the outlet was likely 2.0 mg/L. Based on all the available data and assumptions based on statewide datasets, only 2% of the NO<sub>x</sub>-N and 20% of TN that was loaded to J/G chain was exported in 2010 respectively (Table 7).

Due to the residence times of the individual lakes of the J/G chain that exceed multiple years, multiple years of monitoring would

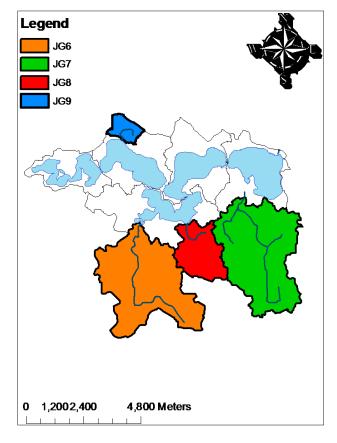


Figure 31. Watershed for Jefferson-German Lakes including highlighted inlets that were monitored in 2010 to estimate nutrient loading. Reprinted and modified from Pallardy et al. (in review).

be needed to confirm that a pulse of nitrate loaded during high flow years is not subsequently released in future years. Based on relatively stable landuse in the watershed, it is likely that  $NO_X$ -N loading to J/G chain has been elevated for many years prior to the 2010 monitoring season.

Table 7. Monitored flow and nitrate loads for the inlets and outlet to Jefferson-German chain for March through November 2010.

Station	Flow rate (hm³/yr)	Nitrate load (kg/yr)	Flow weighted mean (mg/L)
JG6	2.71	46,727	17.2
JG7	2.49	16,406	6.6
JG8	0.78	1,157	1.5
JG9	0.39	6,848	17.9
Sum	6.37	71,138	11.2
Outlet	4.51	801	0.18

## Nitrogen transport in wetlands

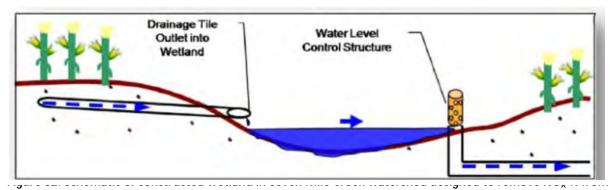
Wetlands are generally considered as aquatic systems with a high capacity to assimilate and ultimately denitrify N inputs. Wetlands have several characteristics that allow for TN removal including abundant labile organic carbon, anoxic sediments, generally long residence times and small watersheds. Mitsch and Day (2006) proposed the creation and restoration of wetlands throughout Mississippi-Ohio-Missouri Basin to intercept field drainage along with diversion wetlands fed by flooding river waters as a means to mitigate eutrophication in the Gulf of Mexico. They based this recommendation on an extensive review of field studies that demonstrated 33% to 95% NO<sub>X</sub>-N retention in wetlands. Flow-through and riparian wetlands must be strategically positioned within a watershed to have the most impact on N transport. Many of the principles discussed in the lake and riverine backwater sections of this chapter also apply to wetlands. For instance, a large wetland receiving a modest load of TN from a small watershed would generally remove more N than a small wetland receiving a large load of TN from a large watershed.

The landscape of much of northern Minnesota has extensive wetlands. Limited monitoring from MPCA's wetland sampling program indicates that  $NO_X$ -N in these wetlands is at or below detection limit and total kjeldahl (organic N + NH<sub>X</sub>-N) is approximately 1.2 mg/L. Certainly N transport in relatively pristine wetlands is both complicated and interesting, but the downstream export of N from these systems is rather small compared to wetlands with excessive N inputs. Concentration of  $NO_X$ -N in the temperate prairies region of Minnesota averages 1.0 mg/L while the median concentration is below detection limit. Given the limited temporal coverage (one sampling visit per wetland) of these wetlands datasets (n=60 wetlands per region) and the general ability of wetlands to remove/assimilate  $NO_X$ -N documented in the literature, we can only conclude that some wetlands in the temperature prairies are receiving more  $NO_X$ -N inputs than can be assimilated.

Completely isolated wetlands which are very valuable for many reasons may indirectly impact transport of N out of watersheds. The impact of isolated wetlands on the hydrology and N transport of watersheds is beyond the scope of this chapter. Certainly if water from an isolated wetland is lost to evapotranspiration or deep groundwater recharge there is a benefit of less water delivered to streams verses an isolated wetland that has been drained or altered to convey water to a nearby stream. The

most practical aspect of N transport regarding wetlands for this chapter is the loss of N in flow-through and riparian wetlands. This is most important where N inputs are excessive and wetlands can potentially remove some N which otherwise would likely to be transported downstream in the absence of wetlands.

Wetlands have been constructed in Minnesota to remove excess nitrate from tile lines (Figure 32). Dr. Bill Crumpton of Iowa State University was brought in to help design and site constructed wetlands. Research indicates that 1 acre of wetland is needed to treat drainage from 100 acres of tile drained field. Constructed wetlands to treat tile outfalls in south-central Minnesota are rare for various reasons, but they are an example of the potential of engineered waterbodies to enhance N removal upstream of stream networks. A constructed wetland (i.e. County Ditch 58 wetland) in the Seven Mile Creek watershed removed about 40% to 70% of  $NO_x$ -N inputs from tile lines from 2005 to 2007 (Figure 33) (Kuehner 2009). Removal rates were lowest during high flow events with relatively cool temperatures. Limited results from a constructed wetland in the Little Cottonwood River watershed achieved 92% removal of  $NO_x$ -N from May 17<sup>th</sup> to October 3<sup>rd</sup>, 2007 (Kuehner 2008). Total nitrogen data was not available for either of the wetlands discussed here. The portion of  $NO_x$ -N lost to denitrification versus the portion that was assimilated by biota is not known. Input N as  $NO_x$ -N assimilated to organic N can still be lost via additional cycling in wetlands especially during extended dry periods when wetlands have no outlet flow.



drain water. Reprinted from Kuehner (2009).

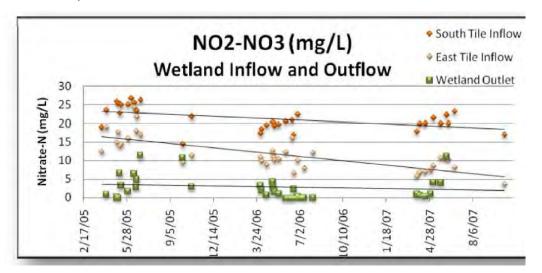


Figure 33. Inlet and outlet NO<sub>X</sub>-N concentration for County Ditch 58 constructed wetland, located in Seven Mile Creek watershed in Minnesota, from 2005 to 2007. East tile inflow was treated by another upstream constructed wetland prior to the County Ditch wetland. Reprinted from Kuehner (2009).

Riparian interception wetlands can mitigate excess water and N from tile lines contributing to streams. Magner and Alexander (2008) found that tile water that was intercepted by a wetland adjacent to Hawk Creek was effective at removing incoming  $NO_X$ -N. Evapotranspiration was the major export pathway for water entering the wetland. The wetland was relatively isolated from Hawk Creek due to the relatively impermeable soils of the Des Moines Lobe till. Low hydraulic conductivity of Des Moines Lobe till which is found throughout southern Minnesota was documented by Komor and Magner (1996). Site selection to maximize N removal and prevent crop damage is an important consideration of interception wetlands (Magner and Alexander 2008).

## Summary

As described in the overview, it is very difficult to generalize transport of N in surface waters for a state such as Minnesota with a myriad of surface waters and watersheds. What is relatively clear is that larger rivers with high TN loads like the Minnesota River deliver most of the annual N load that is delivered to the mainstem of the river from contributing watersheds to downstream surface waters. Cool temperatures and relatively short retention times in the Minnesota River during spring to early summer during the peak of the TN load limit N removal. Even the complex mosaic of habitat types in the Mississippi River downstream of the Twin Cities only facilitates removal of up to 2% of annual TN loads per navigational pool based on estimates for Pools 2 and 3 (LTI 2009). Pool 4, which includes Lake Pepin, is a unique pool on the Minnesota portion of the Mississippi River from LD 1 to the MN/IA border. Total nitrogen removal rates for Pool 4 range from 7% to 10% (LTI 2009, and Lake Pepin mass balance respectively). Collectively, the section of the Mississippi River from LD 1 to the MN/IA border (168 miles) removes 12% to 22% of annual TN inputs based on the approaches outlined in this chapter. Impressive cycling has been documented in this system, but the input load simply overwhelms the capacity of the river to remove the majority TN inputs during most years.

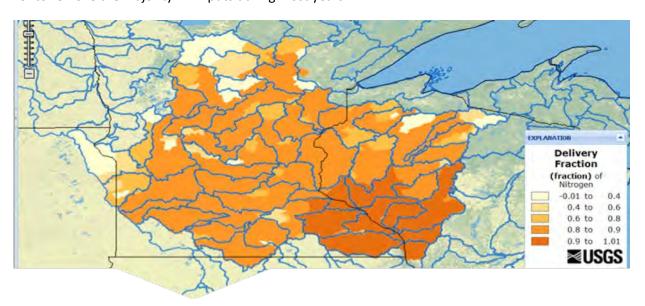


Figure 34. Percent delivery of annual TN loads from SPARROW watersheds to the Mississippi River at the MN/IA border.

The collective removal rate of N loading in Minnesota's lakes, wetlands, ephemeral streams, and headwaters streams is less certain. National models developed for the Gulf of Mexico such as SPARROW can estimate the collective losses of TN for modeled rivers and streams of a given watershed. Figure 34 illustrates the delivery fractions for the SPARROW watersheds upstream of Mississippi River at the

MN/IA border. As noted elsewhere in this report, the SPARROW load estimates do match monitored loads reasonably well. The model was not specifically designed to estimate losses across all aquatic systems in a given SPARROW watershed. Less than 200 lakes and reservoirs are included in the model's stream reaches while the vast majority of natural lakes in Minnesota are not included. Losses in wetlands, headwater streams, and lakes not in the model reaches are accounted for in overland losses. Again, the SPARROW results presented here do not represent the total losses of TN in all aquatic resources, but they are useful to estimate the movement of TN in stream and river networks.

Many factors influence the losses in smaller lotic systems (Table 8). Watersheds with extensive lakes and wetlands and modest N loading certainly remove or transform DIN inputs. Watersheds with extensive tile drainage and limited lakes and wetlands often transport large loads of DIN to watershed outlets with some removal in headwaters. Percentage of delivered DIN load typically increases with proximity to large rivers in all watersheds. Weather and precipitation of any given year certainly influences transport dynamics in any given watershed. Higher precipitation translates into greater loading and increased stream velocity which both contribute to increased downstream transport of DIN. Drought conditions lead to reduced loading and lower stream velocities which contribute to increased losses and transformations of DIN.

Table 8. Positive and negative factors that influence downstream movement of NO<sub>x</sub>-N in Minnesota.

Factor	Conditions that enhance N removal	Example	Conditions that generally reduce N removal	
Streamflow	Low flow	Drought	High flow	Wet periods/spring
Annual precipitation	Low	Western MN	Moderate/high	Eastern MN
Depth	Shallow (inches)	Headwater streams	Deep (9 ft)	Impounded portion of Mississippi River
Carbon content of sediment	High organic content	Backwaters, impoundments, wetlands	"Clean" sand with low organic content	Main channel of large rivers
Input loads/concentration	Low	Northern MN watersheds	High	Southern MN watersheds
Season	Late summer	Low flows and high temperature	Early Spring	High flow and cool temperatures
Riparian area	Natural	Forested stream	Rock or concrete	Urban areas
Riparian wetlands	Common	Northern MN	Few	Ditches in southern MN
Temperature	Warm	Summer	Cold/cool	Winter

Lakes including backwaters of rivers and wetlands can remove and/or assimilate and DIN inputs as long as inputs are not excessive. Long hydraulic residence times in these surface waters along with carbon rich sediments are key to removing DIN inputs. The overall impact of these surface waters on downstream transport of TN from Minnesota is difficult to quantify, but it is certain that existing surface waters of these types currently reduce TN loads to downstream waters.

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## Appendix D2-1.

## Basin summaries of wastewater facilities

Estimated average annual point source nitrogen load per basin from 2005-2009

					_	Annual Load (pounds/year)			
Basin	Area (acres)	Facilities	Domestic	Industrial	Flow (MG)	NHx	TKN	NOx	TN
Upper Mississippi River	12,864,220	260	142	118	105,910	1,245,703	3,399,879	11,300,233	14,742,576
Minnesota River	9,583,767	236	155	81	39,806	279,232	1,102,104	3,629,542	4,717,144
Lake Superior	3,931,107	60	24	36	83,554	421,652	614,397	2,255,984	2,870,381
Lower Mississippi River	4,030,136	121	78	43	27,543	230,725	650,071	2,005,170	2,643,750
Rainy River	7,231,608	28	18	10	25,807	335,418	509,163	1,180,357	1,689,520
Cedar River	665,643	29	21	8	4,497	68,235	144,645	490,599	635,348
Red River of the North	11,315,451	95	78	17	5,749	173,946	168,265	449,607	617,872
St. Croix River	2,249,920	25	21	4	4,164	53,848	121,357	250,692	372,049
Des Moines River	983,753	21	16	5	2,163	10,707	78,498	205,855	284,353
Missouri River	1,141,169	27	22	5	1,051	10,654	27,543	70,893	98,436
Total	53,996,774	902	575	327	300,243	2,830,119	6,815,922	21,838,932	28,671,429

## Estimated annual point source nitrogen yield per basin from 2005-2009

		Yield (lbs/acre)			
Basin	Area (acres)	NHx	TKN	NOx	TN
Upper Mississippi River	12,864,220	0.0968	0.2643	0.8784	1.1460
Minnesota River	9,583,767	0.0291	0.1150	0.3787	0.4922
Lake Superior	3,931,107	0.1073	0.1563	0.5739	0.7302
Lower Mississippi River	4,030,136	0.0572	0.1613	0.4975	0.6560
Rainy River	7,231,608	0.0464	0.0704	0.1632	0.2336
Cedar River	665,643	0.1025	0.2173	0.7370	0.9545
Red River of the North	11,315,451	0.0154	0.0149	0.0397	0.0546
St. Croix River	2,249,920	0.0239	0.0539	0.1114	0.1654
Des Moines River	983,753	0.0109	0.0798	0.2093	0.2890
Missouri River	1,141,169	0.0093	0.0241	0.0621	0.0863
Total	53,996,774				

# Appendix D2-2.

## Major watershed summaries of wastewater facilities

Major Watershed Name	Hydrologic Unit Code	Basin	Facilities	Domestic	Industrial
Mississippi River - Twin Cities	07010206	Upper Mississippi River	85	8	77
Lower Minnesota River	07020012	Minnesota River	53	22	31
St. Louis River	04010201	Lake Superior	39	16	23
Rainy River - Black River	09030004	Rainy River	3	2	1
Zumbro River	07040004	Lower Mississippi River	30	20	10
Mississippi River - St. Cloud	07010203	Upper Mississippi River	18	12	6
Mississippi River - Lake Pepin	07040001	Lower Mississippi River	12	7	5
Mississippi River - Grand Rapids	07010103	Upper Mississippi River	20	14	6
Cannon River	07040002	Lower Mississippi River	26	17	9
Mississippi River - Brainerd	07010104	Upper Mississippi River	15	10	5
South Fork Crow River	07010205	Upper Mississippi River	24	19	5
Minnesota River - Mankato	07020007	Minnesota River	31	16	15
Cedar River	07080201	Cedar River	16	12	4
North Fork Crow River	07010204	Upper Mississippi River	25	21	4
Vermilion River	09030002	Rainy River	8	3	5
Mississippi River - Sartell	07010201	Upper Mississippi River	13	10	3
Upper Red River of the North	09020104	Red River of the North	10	5	5
Lower St. Croix River	07030005	St. Croix River	12	9	3
Des Moines River - Headwaters	07100001	Des Moines River	16	12	4
Root River	07040008	Lower Mississippi River	27	20	7
Shell Rock River	07080202	Cedar River	11	7	4
Redwood River	07020006	Minnesota River	9	8	1
Blue Earth River	07020009	Minnesota River	25	14	11
Long Prairie River	07010108	Upper Mississippi River	10	8	2
Sauk River	07010202	Upper Mississippi River	15	10	5
Otter Tail River	09020103	Red River of the North	15	7	8
Cottonwood River	07020008	Minnesota River	21	16	5
Le Sueur River	07020011	Minnesota River	17	14	3
Mississippi River - Winona	07040003	Lower Mississippi River	18	8	10
Watonwan River	07020010	Minnesota River	14	9	5

Major Watershed Name	Hydrologic Unit Code	Basin	Facilities	Domestic	Industrial
Kettle River	07030003	St. Croix River	8	7	1
Lake Superior - South	04010102	Lake Superior	15	3	12
Chippewa River	07020005	Minnesota River	15	14	1
Minnesota River - Yellow Medicine River	07020004	Minnesota River	26	23	3
Rum River	07010207	Upper Mississippi River	14	11	3
Rock River	10170204	Missouri River	19	16	3
Mississippi River - Headwaters	07010101	Upper Mississippi River	4	2	2
Rainy River - Headwaters	09030001	Rainy River	5	2	3
Lac Qui Parle River	07020003	Minnesota River	8	5	3
Red Lake River	09020303	Red River of the North	8	5	3
Lake Superior - North	04010101	Lake Superior	6	5	1
Crow Wing River	07010106	Upper Mississippi River	6	6	
Pomme de Terre River	07020002	Minnesota River	10	8	2
Snake River	07030004	St. Croix River	4	4	
Redeye River	07010107	Upper Mississippi River	5	5	
Lower Big Sioux River	10170203	Missouri River	6	5	1
Clearwater River	09020305	Red River of the North	7	7	
Buffalo River	09020106	Red River of the North	7	7	
Red River of the North - Grand Marais Creek	09020306	Red River of the North	3	3	
Roseau River	09020314	Red River of the North	2	2	
Wild Rice River	09020108	Red River of the North	10	10	
Mississippi River - La Crescent	07040006	Lower Mississippi River	1	1	
Lower Des Moines River	07100002	Des Moines River	1	1	
East Fork Des Moines River	07100003	Des Moines River	4	3	1
Pine River	07010105	Upper Mississippi River	3	3	
Mississippi River - Reno	07060001	Lower Mississippi River	2	2	
Snake River	09020309	Red River of the North	7	6	1
Red River of the North - Marsh River	09020107	Red River of the North	5	5	
Upper Iowa River	07060002	Lower Mississippi River	5	3	2
Minnesota River - Headwaters	07020001	Minnesota River	7	6	1
Mustinka River	09020102	Red River of the North	6	6	
Rainy River - Baudette	09030008	Rainy River	2	2	
Bois de Sioux River	09020101	Red River of the North	2	2	
Two Rivers	09020312	Red River of the North	4	4	

Major Watershed Name Hydrologic Ur		Basin	Facilities	Domestic	Industrial
Little Fork River	09030005	Rainy River	2	2	
Lake of the Woods	09030009	Rainy River	3	2	1
Red River of the North - Sandhill River	09020301	Red River of the North	4	4	
Big Fork River	09030006	Rainy River	5	5	
Little Sioux River	10230003	Missouri River	2	1	1
Red River of the North - Tamarac River	09020311	Red River of the North	2	2	
Winnebago River	07080203	Cedar River	2	2	
Leech Lake River	07010102	Upper Mississippi River	3	3	
Upper St. Croix River	07030001	St. Croix River	1	1	
Thief River	09020304	Red River of the North	2	2	
Upper/Lower Red Lake	09020302	Red River of the North	1	1	

# Estimated annual average point source load per major watershed from 2005-2009

		Annual Load (pounds/year)				
Major Watershed Name	Flow (MG)	NHx	TKN	NOx	TN	
Mississippi River - Twin Cities	76,149	356,428	2,386,411	8,547,016	10,972,760	
Lower Minnesota River	24,564	121,985	719,124	2,451,801	3,170,968	
St. Louis River	34,211	406,583	590,327	2,130,904	2,721,231	
Rainy River - Black River	14,872	255,072	386,058	879,002	1,265,059	
Zumbro River	9,436	33,308	227,843	733,298	961,146	
Mississippi River - St. Cloud	6,636	171,375	233,049	631,181	864,231	
Mississippi River - Lake Pepin	6,725	110,029	207,295	538,990	746,284	
Mississippi River - Grand Rapids	6,398	97,561	163,936	509,513	672,501	
Cannon River	3,947	47,060	126,113	415,406	541,519	
Mississippi River - Brainerd	2,349	238,443	131,865	351,669	487,618	
South Fork Crow River	2,950	43,287	96,178	339,064	435,234	
Minnesota River - Mankato	4,893	41,892	86,137	358,050	422,285	
Cedar River	2,838	63,720	92,124	299,303	391,530	
North Fork Crow River	2,856	41,566	131,476	250,990	382,466	
Vermilion River	6,176	37,631	109,835	255,684	365,518	
Mississippi River - Sartell	3,924	62,856	101,369	227,557	328,926	
Upper Red River of the North	2,068	57,085	67,470	240,684	308,155	
Lower St. Croix River	3,232	39,701	93,568	202,019	295,587	
Des Moines River - Headwaters	1,904	7,146	70,154	196,108	266,263	
Root River	5,021	17,889	46,505	198,372	244,877	
Shell Rock River	1,641	4,344	52,072	190,320	242,392	

	_		Annual Load (pound	s/year)	
Major Watershed Name	Flow (MG)	NHx	TKN	NOx	TN
Redwood River	1,481	6,113	48,802	177,842	226,644
Blue Earth River	1,611	33,363	50,121	141,855	199,210
Long Prairie River	1,412	135,488	49,579	146,950	196,529
Sauk River	1,439	60,590	40,869	145,011	185,880
Otter Tail River	1,358	74,814	42,639	137,078	179,716
Cottonwood River	1,342	7,660	41,474	125,781	167,255
Le Sueur River	1,114	9,340	36,405	94,964	131,369
Mississippi River - Winona	2,143	14,598	32,372	96,820	129,193
Watonwan River	908	12,234	29,325	93,863	123,289
Lake Superior - South	48,571	218	556	108,457	109,013
Chippewa River	807	7,398	26,876	81,953	108,829
Minnesota River - Yellow Medicine River	1,312	27,947	35,689	57,363	93,052
Rum River	754	11,213	23,302	61,381	84,686
Rock River	646	5,093	18,750	52,832	71,582
Mississippi River - Headwaters	430	15,334	13,906	48,239	62,145
Kettle River	692	8,800	17,320	32,134	49,454
Rainy River - Headwaters	4,590	40,906	8,495	40,495	48,989
Lac Qui Parle River	872	7,836	17,094	24,490	41,584
Red Lake River	671	28,330	16,806	24,416	41,222
Lake Superior - North	772	14,851	23,513	16,623	40,136
Crow Wing River	319	6,645	13,295	21,443	34,739
Snake River	345	6,223	13,099	19,217	32,315
Pomme de Terre River	804	2,650	8,613	19,137	27,770
Redeye River	217	2,852	10,834	14,887	25,721
Lower Big Sioux River	373	5,295	7,997	17,264	25,261
Clearwater River	255	2,059	6,376	11,379	17,756
Buffalo River	282	2,356	7,067	7,067	14,133
Red River of the North - Grand Marais Creek	231	1,927	5,782	5,782	11,563
Roseau River	214	1,787	5,362	5,362	10,724
Wild Rice River	196	1,638	4,913	4,913	9,826
Mississippi River - La Crescent	85	5,060	4,959	7,084	12,043
Lower Des Moines River	187	1,564	4,693	4,693	9,387
East Fork Des Moines River	71	1,996	3,651	5,053	8,704
Pine River	57	1,911	3,344	4,777	8,120
Mississippi River - Reno	115	2,704	3,755	13,699	5,959
Red River of the North - Marsh River	84	705	2,114	3,142	5,257
Upper Iowa River	87	1,090	2,221	2,917	5,138

			Annual Load (pounds	/year)	
Major Watershed Name	Flow (MG)	NHx	TKN	NOx	TN
Minnesota River - Headwaters	98	815	2,444	2,444	4,888
Mustinka River	76	635	1,905	1,905	3,811
Rainy River - Baudette	63	529	1,588	1,588	3,175
Bois de Sioux River	62	513	1,540	1,540	3,080
Two Rivers	61	512	1,537	1,537	3,073
Little Fork River	56	468	1,404	1,404	2,808
Lake of the Woods	16	521	912	1,303	2,215
Red River of the North - Sandhill River	38	318	954	954	1,909
Big Fork River	35	291	873	882	1,755
Little Sioux River	32	265	796	796	1,593
Red River of the North - Tamarac River	31	259	778	778	1,556
Winnebago River	18	171	450	976	1,426
Leech Lake River	19	155	466	555	1,021
Upper St. Croix River	7	62	186	186	372
Thief River	6	54	162	162	324
Upper/Lower Red Lake	2	18	55	55	111

			Yield (pounds/acre/year)				
Major Watershed Name	Hydrologic Unit Code	Area (acres)	NHx	TKN	NOx	TN	
Mississippi River - Twin Cities	07010206	644,320	0.55	3.70	13.27	17.03	
Lower Minnesota River	07020012	1,174,348	0.10	0.61	2.09	2.70	
St. Louis River	04010201	1,831,462	0.22	0.32	1.16	1.49	
Rainy River - Black River	09030004	329,206	0.77	1.17	2.67	3.84	
Zumbro River	07040004	909,363	0.04	0.25	0.81	1.06	
Mississippi River - St. Cloud	07010203	717,374	0.24	0.32	0.88	1.20	
Mississippi River - Lake Pepin	07040001	382,780	0.29	0.54	1.41	1.95	
Mississippi River - Grand Rapids	07010103	1,332,793	0.07	0.12	0.38	0.50	
Cannon River	07040002	940,540	0.05	0.13	0.44	0.58	
Mississippi River - Brainerd	07010104	1,076,295	0.22	0.12	0.33	0.45	
South Fork Crow River	07010205	818,100	0.05	0.12	0.41	0.53	
Minnesota River - Mankato	07020007	861,882	0.05	0.10	0.42	0.49	
Cedar River	07080201	454,029	0.14	0.20	0.66	0.86	
North Fork Crow River	07010204	944,854	0.04	0.14	0.27	0.40	
Vermilion River	09030002	661,296	0.06	0.17	0.39	0.55	
Mississippi River - Sartell	07010201	656,113	0.10	0.15	0.35	0.50	
Upper Red River of the North	09020104	319,533	0.18	0.21	0.75	0.96	
Lower St. Croix River	07030005	585,735	0.07	0.16	0.34	0.50	
Des Moines River - Headwaters	07100001	798,595	0.01	0.09	0.25	0.33	
Root River	07040008	1,061,506	0.02	0.04	0.19	0.23	
Shell Rock River	07080202	157,701	0.03	0.33	1.21	1.54	
Redwood River	07020006	447,531	0.01	0.11	0.40	0.51	
Blue Earth River	07020009	777,240	0.04	0.06	0.18	0.26	
Long Prairie River	07010108	565,076	0.24	0.09	0.26	0.35	
Sauk River	07010202	666,747	0.09	0.06	0.22	0.28	
Otter Tail River	09020103	1,222,024	0.06	0.03	0.11	0.15	
Cottonwood River	07020008	840,782	0.01	0.05	0.15	0.20	
Le Sueur River	07020011	711,113	0.01	0.05	0.13	0.18	
Mississippi River - Winona	07040003	419,200	0.03	0.08	0.23	0.31	
Watonwan River	07020010	558,963	0.02	0.05	0.17	0.22	
Lake Superior - South	04010102	399,371	0.02	0.07	0.21	0.27	
Chippewa River	07020005	1,330,147	0.02	0.03	0.04	0.07	
Minnesota River - Yellow Medicine River	07020004	1,332,769	0.01	0.02	0.05	0.06	
Rum River	07010207	1,013,790	0.01	0.02	0.05	0.07	
Rock River	10170204	582,106	0.03	0.02	0.08	0.11	
Mississippi River - Headwaters	07010101	1,228,884	0.01	0.01	0.03	0.04	

			Yield (pounds/acre/year)				
Major Watershed Name	Hydrologic Unit Code	Area (acres)	NHx	TKN	NOx	TN	
Kettle River	07030003	672,924	0.00	0.00	0.16	0.16	
Rainy River - Headwaters	09030001	1,607,846	0.03	0.01	0.03	0.03	
Lac Qui Parle River	07020003	487,022	0.02	0.04	0.05	0.09	
Red Lake River	09020303	857,496	0.03	0.02	0.03	0.05	
Lake Superior - North	04010101	1,015,865	0.01	0.02	0.02	0.04	
Crow Wing River	07010106	1,268,954	0.01	0.01	0.02	0.03	
Snake River	07030004	643,542	0.01	0.02	0.03	0.05	
Pomme de Terre River	07020002	560,231	0.00	0.02	0.03	0.05	
Redeye River	07010107	572,067	0.00	0.02	0.03	0.04	
Lower Big Sioux River	10170203	326,851	0.02	0.02	0.05	0.08	
Clearwater River	09020305	869,460	0.00	0.01	0.01	0.02	
Buffalo River	09020106	724,094	0.00	0.01	0.01	0.02	
Red River of the North - Grand Marais Creek	09020306	378,808	0.01	0.02	0.02	0.03	
Roseau River	09020314	679,895	0.00	0.01	0.01	0.02	
Wild Rice River	09020108	1,047,065	0.00	0.00	0.00	0.01	
Mississippi River - La Crescent	07040006	60,544	0.08	0.08	0.12	0.20	
Lower Des Moines River	07100002	55,733	0.03	0.08	0.08	0.17	
East Fork Des Moines River	07100003	129,425	0.02	0.03	0.04	0.07	
Pine River	07010105	500,885	0.00	0.01	0.01	0.02	
Mississippi River - Reno	07060001	117,447	0.02	0.03	0.12	0.05	
Red River of the North - Marsh River	09020107	231,541	0.00	0.01	0.01	0.02	
Upper Iowa River	07060002	138,756	0.01	0.02	0.02	0.04	
Minnesota River - Headwaters	07020001	501,739	0.00	0.00	0.00	0.01	
Mustinka River	09020102	550,852	0.00	0.00	0.00	0.01	
Rainy River - Baudette	09030008	196,591	0.00	0.01	0.01	0.02	
Bois de Sioux River	09020101	355,934	0.00	0.00	0.00	0.01	

			Yield (pounds/acre/year)			
Major Watershed Name	Hydrologic Unit Code	Area (acres)	NHx	TKN	NOx	TN
Two Rivers	09020312	704,816	0.00	0.00	0.00	0.00
Little Fork River	09030005	1,198,291	0.00	0.00	0.00	0.00
Lake of the Woods	09030009	736,643	0.00	0.00	0.00	0.00
Red River of the North - Sandhill River	09020301	395,583	0.00	0.00	0.00	0.00
Big Fork River	09030006	1,315,131	0.00	0.00	0.00	0.00
Little Sioux River	10230003	205,753	0.00	0.00	0.00	0.01
Red River of the North - Tamarac River	09020311	567,036	0.00	0.00	0.00	0.00
Winnebago River	07080203	45,649	0.00	0.01	0.02	0.03
Leech Lake River	07010102	857,968	0.00	0.00	0.00	0.00
Upper St. Croix River	07030001	347,719	0.00	0.00	0.00	0.00
Thief River	09020304	671,021	0.00	0.00	0.00	0.00
Upper/Lower Red Lake	09020302	1,241,686	0.00	0.00	0.00	0.00

# Appendix D3-1.

Table 1. Modeled inorganic nitrogen deposition amounts in pounds/acre falling in different watersheds during average, low, and high precipitation years.

ID	HUC8 Watershed Name	Oxidized Wet	Unoxidized Wet	Oxidized Dry	Unoxidized Dry	Avg. precip. Total N Wet + dry	Low precip. Total N Wet + dry	High precip. Total N Wet + dry
1	Lake Superior - North	1.20	1.68	1.47	0.31	4.67	4.21	5.24
2	Lake Superior - South	1.48	2.17	2.10	0.46	6.20	5.62	6.93
3	St. Louis River	1.27	1.99	1.86	0.54	5.66	5.14	6.31
4	Cloquet River	1.37	2.08	1.98	0.52	5.95	5.40	6.64
5	Nemadji River	1.63	2.57	1.95	0.86	7.02	6.34	7.86
7	Mississippi River - Headwaters	1.05	1.78	1.39	0.91	5.14	4.69	5.71
8	Leech Lake River	1.07	1.80	1.36	0.91	5.14	4.68	5.72
9	Mississippi River - Grand Rapids	1.25	2.03	1.60	0.67	5.55	5.03	6.21
10	Mississippi River - Brainerd	1.59	2.82	1.60	1.88	7.89	7.19	8.77
11	Pine River	1.25	2.14	1.45	1.04	5.88	5.34	6.56
12	Crow Wing River	1.18	2.19	1.41	1.77	6.56	6.02	7.23
13	Redeye River	1.17	2.31	1.36	2.40	7.24	6.68	7.94
14	Long Prairie River	1.41	2.79	1.42	2.94	8.57	7.89	9.41
15	Mississippi River - Sartell	2.10	3.73	1.71	3.47	11.01	10.07	12.17
16	Sauk River	1.88	3.50	1.51	4.32	11.20	10.34	12.27
17	Mississippi River - St. Cloud	2.59	4.33	2.08	3.18	12.20	11.09	13.58
18	North Fork Crow River	2.35	4.10	1.76	4.14	12.36	11.33	13.65
19	South Fork Crow River	2.47	4.25	1.81	4.24	12.77	11.70	14.11
20	Mississippi River - Twin Cities	2.88	4.62	3.54	3.07	14.11	12.91	15.61
21	Rum River	2.28	3.68	2.14	1.81	9.91	8.95	11.10
22	Minnesota River - Headwaters	1.36	2.41	1.29	2.91	7.97	7.37	8.72
23	Pomme de Terre River	1.23	2.40	1.32	3.24	8.20	7.62	8.92
24	Lac Qui Parle River	1.62	2.77	1.35	3.33	9.07	8.36	9.94
25	Minnesota River - Yellow Medicine River	1.80	3.22	1.42	4.38	10.83	10.02	11.83
26	Chippewa River	1.44	2.77	1.37	3.67	9.25	8.57	10.09
27	Redwood River	1.81	3.16	1.45	4.41	10.82	10.02	11.81
28	Minnesota River - Mankato	1.95	3.53	1.61	5.06	12.15	11.27	13.24
29	Cottonwood River	1.84	3.26	1.50	4.92	11.52	10.70	12.54
30	Blue Earth River	2.10	3.70	1.68	5.44	12.93	12.00	14.09
31	Watonwan River	2.02	3.65	1.60	5.48	12.74	11.84	13.88
32	Le Sueur River	2.34	4.03	1.81	4.92	13.11	12.09	14.38
33	Lower Minnesota River	2.44	4.18	2.32	4.30	13.23	12.18	14.56

ID	HUC8 Watershed Name	Oxidized Wet	Unoxidized Wet	Oxidized Dry	Unoxidized Dry	Avg. precip. Total N Wet + dry	Low precip. Total N Wet + dry	High precip. Total N Wet + dry
34	Upper St. Croix River	2.01	3.33	1.83	1.04	8.21	7.36	9.28
35	Kettle River	1.76	2.85	1.77	0.93	7.33	6.59	8.25
36	Snake River	2.09	3.39	1.94	1.40	8.83	7.95	9.93
37	Lower St. Croix River	2.75	4.26	2.52	2.04	11.57	10.45	12.98
20	Mississippi River - Lake	2.76	4.64	2.52	4.45	44.05	42.07	45.53
38	Pepin Siver	2.76	4.61	2.53	4.15	14.05	12.87	15.52
39	Cannon River Mississippi River -	2.63	4.37	2.12	4.71	13.83	12.71	15.23
40	Winona	2.91	4.27	2.09	3.76	13.03	11.88	14.46
41	Zumbro River	2.88	4.50	2.13	4.35	13.85	12.67	15.33
42	Mississippi River - La Crescent	2.63	3.48	2.21	3.08	11.41	10.43	12.63
43	Root River	2.54	3.60	2.08	4.16	12.38	11.40	13.61
44	Mississippi River - Reno	2.40	3.23	2.19	3.24	11.06	10.16	12.19
46	Upper Iowa River	2.21	3.18	2.03	4.38	11.80	10.94	12.88
47	Upper Wapsipinicon River	2.10	3.21	1.95	5.71	12.98	12.13	14.04
48	Cedar River	2.26	3.52	2.03	4.75	12.57	11.64	13.72
49	Shell Rock River	2.15	3.46	2.03	4.37	12.01	11.11	13.13
50	Winnebago River	2.20	3.59	1.92	4.80	12.51	11.58	13.66
51	Des Moines River - Headwaters	1.78	3.17	1.57	4.63	11.15	10.36	12.14
52	Lower Des Moines River	1.65	3.01	1.63	5.51	11.80	11.06	12.73
53	East Fork Des Moines River	1.78	3.22	1.59	5.62	12.21	11.41	13.21
54	Bois de Sioux River	1.22	2.35	1.32	3.01	7.91	7.33	8.62
55	Mustinka River	1.22	2.36	1.32	3.14	8.04	7.47	8.76
56	Otter Tail River	1.09	2.16	1.34	2.37	6.96	6.44	7.61
57	Upper Red River of the North	1.07	2.14	1.43	3.08	7.72	7.21	8.36
58	Buffalo River	1.04	2.03	1.39	2.58	7.04	6.54	7.65
59	Red River of the North - Marsh River	0.98	1.92	1.24	2.98	7.12	6.66	7.70
60	Wild Rice River	1.05	2.02	1.30	2.25	6.62	6.13	7.70
00	Red River of the North -	1.05	2.02	1.50	2.23	0.02	0.13	7.23
61	Sandhill River	1.07	2.07	1.21	2.38	6.74	6.23	7.36
62	Upper/Lower Red Lake	1.14	2.00	1.24	0.90	5.28	4.78	5.91
63	Red Lake River	1.17	2.20	1.15	2.03	6.54	6.00	7.21
65	Thief River	1.12	2.11	1.09	1.44	5.76	5.24	6.40
66	Clearwater River	1.16	2.20	1.19	1.73	6.28	5.74	6.95
67	Red River of the North - Grand Marais Creek	1.11	2.16	1.07	2.31	6.65	6.13	7.30
68	Snake River	1.10	2.15	1.01	1.97	6.24	5.72	6.89
69	Red River of the North - Tamarac River	0.99	1.97	0.94	2.18	6.08	5.60	6.67
70	Two Rivers	0.95	1.90	0.94	1.98	5.77	5.31	6.34

ID	HUC8 Watershed Name	Oxidized Wet	Unoxidized Wet	Oxidized Dry	Unoxidized Dry	Avg. precip. Total N Wet + dry	Low precip. Total N Wet + dry	High precip. Total N Wet + dry
71	Roseau River	1.04	2.05	0.97	1.44	5.50	5.01	6.12
72	Rainy River - Headwaters	1.03	1.60	1.57	0.40	4.59	4.17	5.12
73	Vermilion River	0.99	1.50	1.75	0.45	4.69	4.29	5.19
74	Rainy River - Rainy Lake	0.98	1.57	1.30	0.46	4.31	3.90	4.82
75	Rainy River - Black River	1.05	1.83	1.23	0.65	4.75	4.29	5.33
76	Little Fork River	1.00	1.53	1.66	0.52	4.71	4.31	5.22
77	Big Fork River	1.07	1.73	1.45	0.65	4.91	4.46	5.47
78	Rapid River	1.10	1.93	1.24	0.80	5.07	4.58	5.67
79	Rainy River - Baudette	1.12	2.07	1.09	0.84	5.12	4.61	5.75
80	Lake of the Woods	1.13	2.12	0.83	0.79	4.87	4.35	5.52
81	Upper Big Sioux River	1.56	2.73	1.48	3.68	9.45	8.77	10.31
82	Lower Big Sioux River	1.63	3.03	1.51	5.02	11.19	10.44	12.12
83	Rock River	1.62	3.04	1.56	5.47	11.70	10.95	12.63
84	Little Sioux River	1.64	3.06	1.62	5.18	11.50	10.75	12.44

Table 2. Atmospheric deposition estimates of wet+dry inorganic nitrogen falling directly into rivers and streams, marshes/wetlands, lakes, dry-land, and the total onto all land and waters. Results are shown for each HUC8 watershed in Minnesota.

ID	HUC8 Name	Rivers	Marsh	Lakes	Land	Total
1	Lake Superior - North	19,182	182,854	301,631	4,238,004	4,741,671
2	Lake Superior - South	17,175	102,086	12,067	2,344,485	2,475,813
3	St. Louis River	43,837	3,859,744	267,072	6,190,143	10,360,796
4	Cloquet River	9,893	556,977	181,826	2,269,595	3,018,290
5	Nemadji River	8,865	179,056	12,780	1,039,890	1,240,591
7	Mississippi River - Headwaters	13,958	1,088,600	902,133	4,309,974	6,314,665
8	Leech Lake River	7,513	714,060	867,737	2,824,423	4,413,733
9	Mississippi River - Grand Rapids	23,279	2,427,883	450,565	4,497,790	7,399,518
10	Mississippi River - Brainerd	30,972	1,527,410	452,334	6,484,335	8,495,050
11	Pine River	6,069	389,348	366,184	2,185,009	2,946,610
12	Crow Wing River	25,498	736,502	562,014	6,998,316	8,322,330
13	Redeye River	19,706	391,968	62,058	3,667,956	4,141,688
14	Long Prairie River	18,912	288,606	356,160	4,177,958	4,841,636
15	Mississippi River - Sartell	38,612	468,203	145,067	6,569,361	7,221,243
16	Sauk River	44,222	110,769	329,734	6,983,058	7,467,784
17	Mississippi River - St. Cloud	38,896	258,305	270,001	8,181,505	8,748,707
18	North Fork Crow River	46,165	211,573	747,855	10,671,358	11,676,951
19	South Fork Crow River	46,678	116,063	372,917	9,911,898	10,447,555
20	Mississippi River - Twin Cities	33,634	289,587	688,082	8,078,161	9,089,463
21	Rum River	36,446	1,045,295	1,471,647	7,489,333	10,042,722
22	Minnesota River - Headwaters	16,184	59,426	186,887	3,736,698	3,999,196

ID	HUC8 Name	Rivers	Marsh	Lakes	Land	Total
23	Pomme de Terre River	17,119	27,507	337,227	4,210,348	4,592,200
24	Lac Qui Parle River	37,005	19,980	21,193	4,336,731	4,414,910
	Minnesota River - Yellow Medicine	06 700	20.720	457.470	44455 457	44 420 454
25	River	86,788	28,730	157,479	14,155,457	14,428,454
26	Chippewa River	55,684	136,429	594,267	11,513,663	12,300,043
27	Redwood River	27,502	12,579	63,744	4,737,474	4,841,299
28	Minnesota River - Mankato	49,418	109,315	197,359	10,114,728	10,470,820
29	Cottonwood River	60,193	21,971	63,151	9,539,145	9,684,459
30	Blue Earth River	39,189	23,234	136,608	9,849,406	10,048,437
31	Watonwan River	38,335	16,861	93,284	6,973,672	7,122,152
32	Le Sueur River	44,329	90,334	191,544	8,993,149	9,319,355
33	Lower Minnesota River	82,417	205,237	412,026	14,840,895	15,540,575
34	Upper St. Croix River	11,490	557,861	11,352	2,274,915	2,855,617
35	Kettle River	20,011	949,579	83,438	3,877,104	4,930,131
36	Snake River	21,358	780,092	71,907	4,808,473	5,681,831
37	Lower St. Croix River	28,195	437,977	368,374	5,944,629	6,779,174
38	Mississippi River - Lake Pepin	33,609	13,152	148,979	5,181,829	5,377,569
39	Cannon River	79,146	249,839	354,177	12,325,826	13,008,988
40	Mississippi River - Winona	49,509	25,234	29,653	5,357,299	5,461,696
41	Zumbro River	113,547	1,076	26,159	12,456,009	12,596,790
42	Mississippi River - La Crescent	6,323	25,359	13,254	645,590	690,527
43	Root River	120,512	5,696	5,307	13,012,481	13,143,995
44	Mississippi River - Reno	12,140	27,314	17,954	1,241,556	1,298,964
46	Upper Iowa River	17,389	0	489	1,619,870	1,637,748
47	Upper Wapsipinicon River	823	0	0	106,409	107,233
48	Cedar River	33,954	10,365	24,239	5,636,964	5,705,521
49	Shell Rock River	7,199	19,297	57,097	1,810,624	1,894,217
50	Winnebago River	2,732	16,874	11,381	539,913	570,900
51	Des Moines River - Headwaters	47,519	35,983	224,525	8,594,514	8,902,541
52	Lower Des Moines River	3,822	0	972	652,952	657,745
53	East Fork Des Moines River	5,661	0	50,265	1,524,158	1,580,084
54	Bois de Sioux River	14,437	12,582	68,413	2,718,656	2,814,089
55	Mustinka River	25,413	23,774	89,305	4,291,972	4,430,465
56	Otter Tail River	15,828	270,089	1,204,913	7,013,636	8,504,466
57	Upper Red River of the North	12,734	18,630	3,280	2,431,884	2,466,529
58	Buffalo River	23,133	63,359	148,452	4,859,337	5,094,281
59	Red River of the North - Marsh River	9,502	654	1,638	1,637,022	1,648,815
60	Wild Rice River	35,058	253,869	212,659	6,426,256	6,927,843
61	Red River of the North - Sandhill River	16,357	15,060	44,200	2,588,817	2,664,434
62	Upper/Lower Red Lake	18,918	2,446,425	1,584,141	2,511,245	6,560,728
63	Red Lake River	23,811	797,620	18,181	4,768,358	5,607,970
65	Thief River	23,214	1,109,961	154,758	2,575,845	3,863,778

ID	HUC8 Name	Rivers	Marsh	Lakes	Land	Total
66	Clearwater River	29,382	378,888	128,234	4,920,107	5,456,611
67	Red River of the North - Grand Marais Creek	9,525	4,733	3,425	2,501,323	2,519,006
68	Snake River	17,346	54,924	922	3,035,964	3,109,157
69	Red River of the North - Tamarac River	15,809	21,041	11,713	3,397,154	3,445,716
70	Two Rivers	18,079	265,211	4,465	3,777,001	4,064,757
71	Roseau River	21,314	1,130,514	55,991	2,533,911	3,741,730
72	Rainy River - Headwaters	21,313	658,690	976,630	5,730,218	7,386,851
73	Vermilion River	9,209	430,375	387,308	2,272,770	3,099,662
74	Rainy River - Rainy Lake	7,852	446,191	448,652	1,608,381	2,511,076
75	Rainy River - Black River	4,552	1,054,945	297	504,557	1,564,351
76	Little Fork River	20,730	1,706,296	125,729	3,792,184	5,644,939
77	Big Fork River	16,737	2,907,141	270,896	3,263,846	6,458,619
78	Rapid River	14,532	2,379,493	583	664,976	3,059,583
79	Rainy River - Baudette	5,718	550,915	1,705	447,547	1,005,885
80	Lake of the Woods	8,528	929,398	1,473,364	1,174,219	3,585,510
81	Upper Big Sioux River	2,327	0	0	247,819	250,146
82	Lower Big Sioux River	36,539	1,856	1,465	3,617,679	3,657,540
83	Rock River	62,910	0	4,462	6,742,999	6,810,371
84	Little Sioux River	10,621	5,528	77,184	2,272,828	2,366,161

# Appendix E2-1.

Maps showing the spatial pattern of explanatory variables in the best regression models:

# Percent of Watershed in Tile Drainage (Estimated)

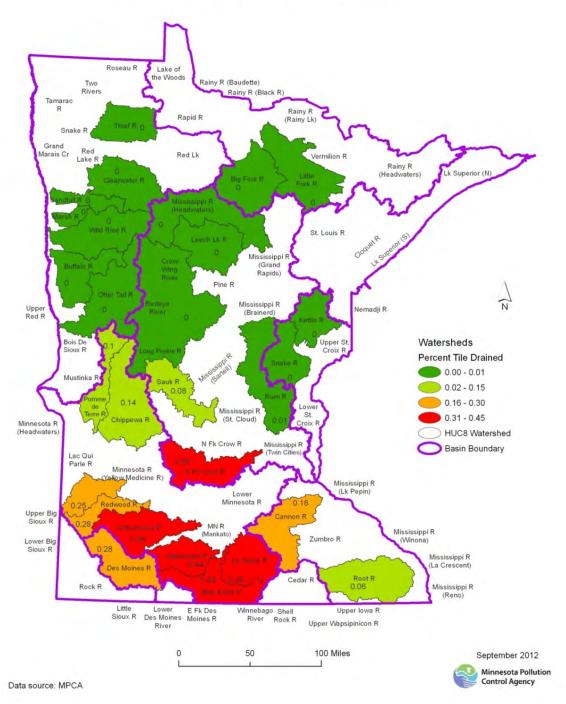


Figure E2-1-1. Fraction of watershed estimated to be tile drained for each of the 28 assessed watersheds analyzed in chapter E2.

## Percent of Watershed with Row Crop over Shallow Depth to Bedrock (<= 50 Feet) or Sandy Soils (>= 85%)

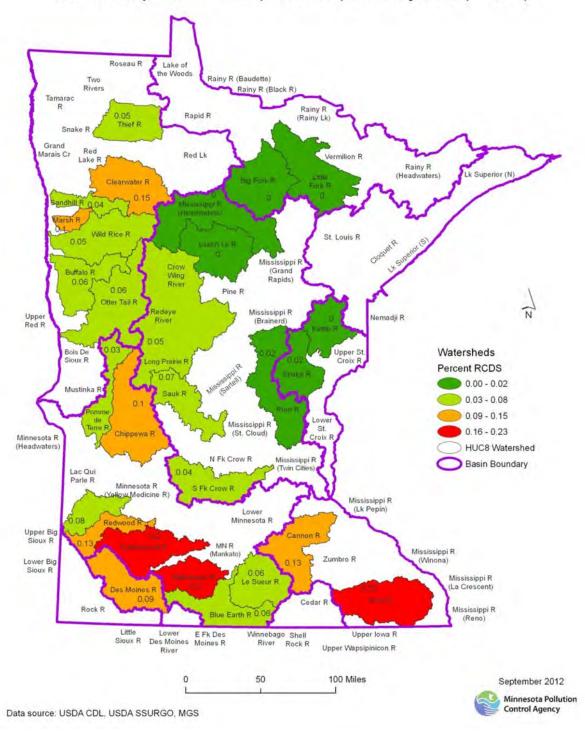


Figure E2-1-2. Fraction of watershed with a depth to bedrock estimated to be less than 50 feet plus fraction with sandy soils (>85% sand in subsoils) for each of the 28 assessed watersheds analyzed in chapter E2.

# **Precipitation in Minnesota**

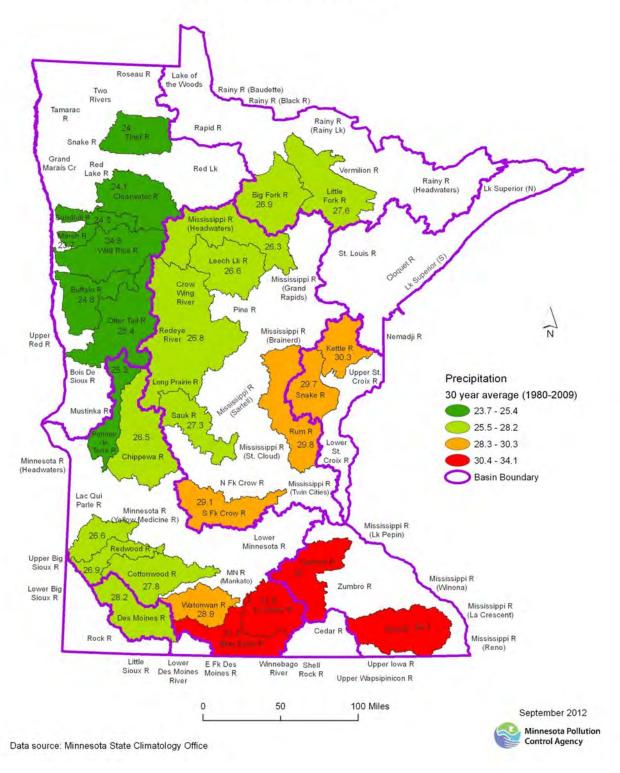


Figure E2-1-3. Average annual precipitation in each HUC8 Watershed (1980-2009).

# Appendix E2-2.

Geographically weighted regression coefficients for the explanatory variables included in the multiple regression analysis in Chapter E2.

# Rainy R (Baudette) Rainy R (Black Rainy R (Headwaters) (Grand Rapids) deye 3.68 Watersheds **TD Coefficients** 1.60 - 2.52 2.53 - 3.31 3.32 - 4.21 4.22 - 4.91 Minnesota R (Headwaters) 4.92 - 5.74 Basin Boundary 50 Miles 25 Sioux R Des Moines R River Upper Wapsipinicon R. November 2012 Minnesota Pollution Control Agency

#### Nitrite + Nitrate-N Yield GWR Coefficients

Figure E2-2-1. Geographically weighted regression coefficients for the tile drain explanatory variable for nitrite+nitrate-N yield included in the multiple regression analysis in Chapter E2.

#### Nitrite + Nitrate-N Yield GWR Coefficients

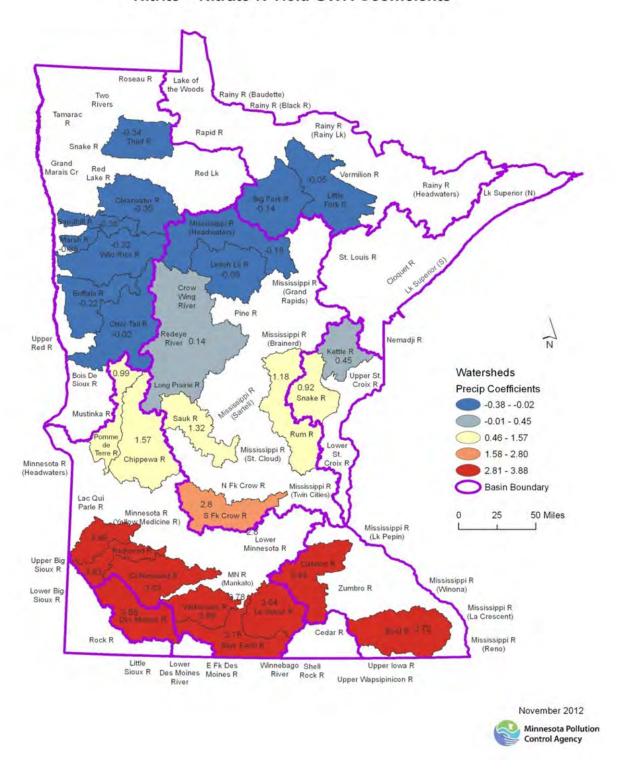


Figure E2-2-2. Geographically weighted regression coefficients for the precipitation explanatory variable for nitrite+nitrate-N yield included in the multiple regression analysis in Chapter E2.

# **Total Nitrogen Yield GWR Coefficients**

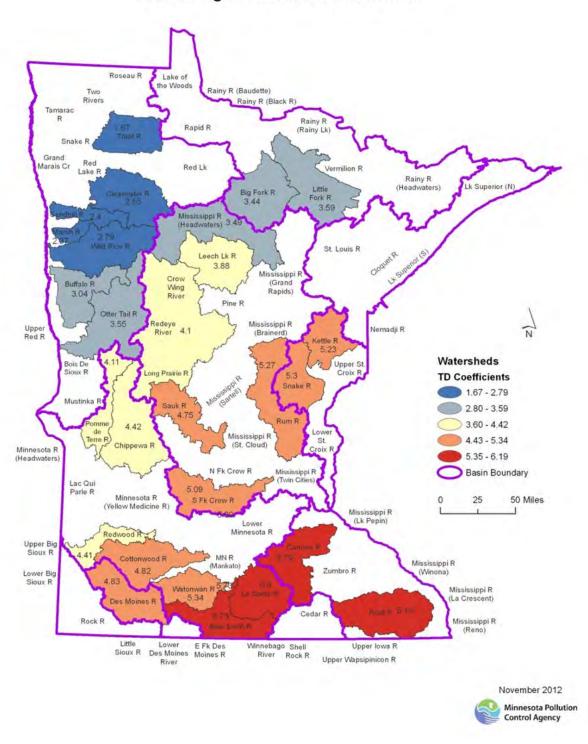


Figure E2-2-3. Geographically weighted regression coefficients for the tile drainage explanatory variable for TN yield included in the multiple regression analysis in Chapter E2.

# **Total Nitrogen Yield GWR Coefficients**

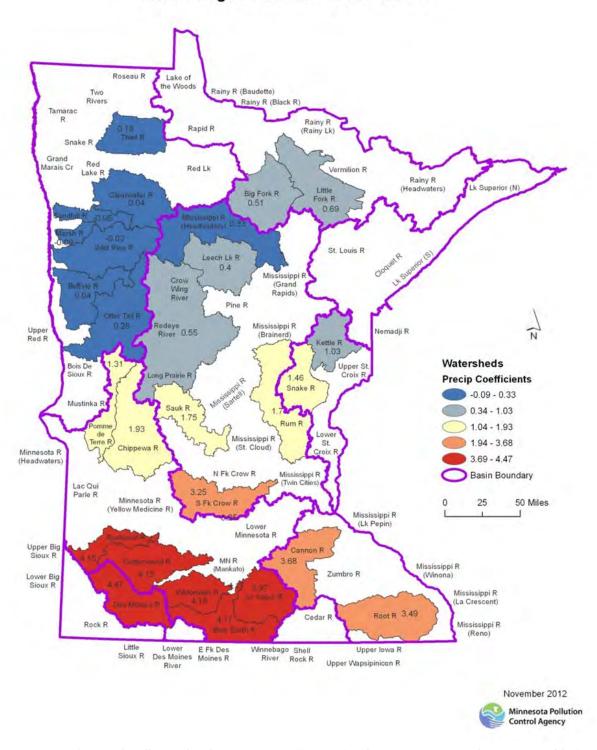
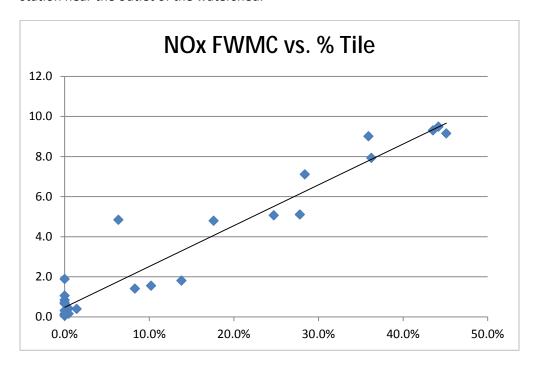
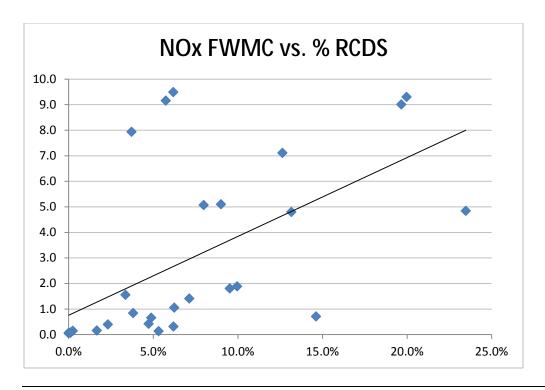


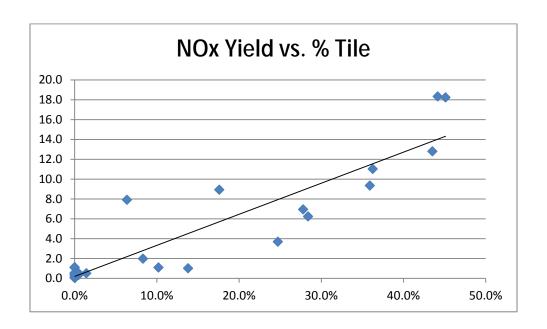
Figure E2-2-4. Geographically weighted regression coefficients for the precipitation explanatory variable for TN yield included in the multiple regression analysis in Chapter E2.

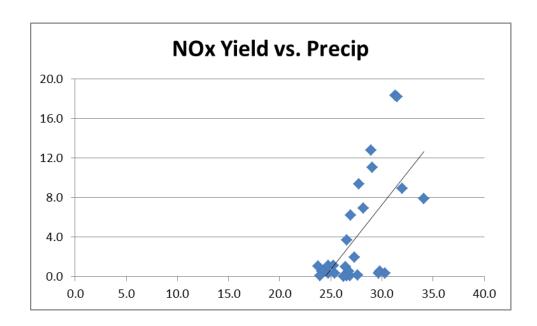
# Appendix E2-3.

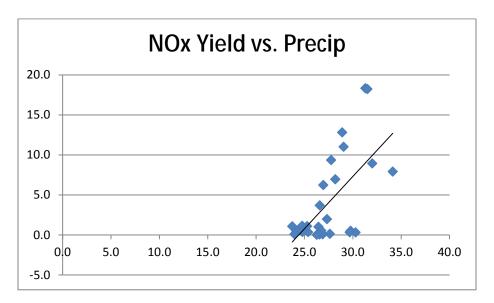
Scatter plots showing how individual explanatory variable results used in the best statistical models in Chapter E2 compare with stream nitrite+nitrate-N (NOx) and TN FWMCs and yields in Chapter E2. FWMCs are in mg/l. Yield is average pounds/acre across the lands contributing N to the monitoring station near the outlet of the watershed.

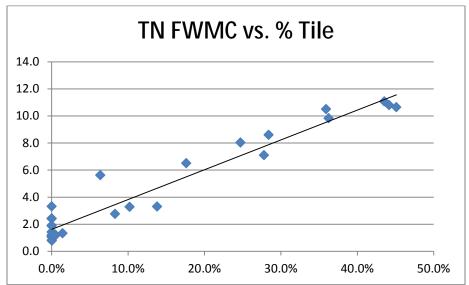


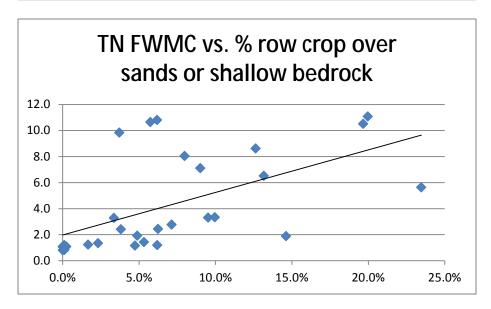


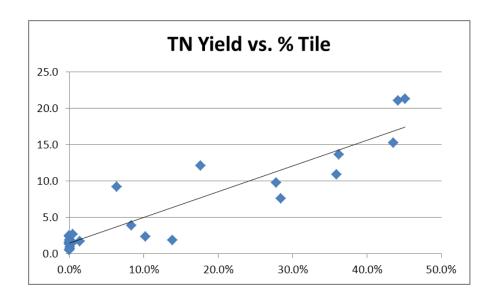


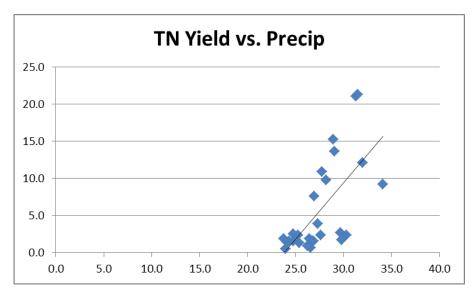












# Appendix F1-1. Effectiveness of Best Management Practices for Reductions in Nitrate Losses to Surface Waters in Midwestern U.S. Agriculture

Authors: Karina Fabrizzi and David Mulla, University of Minnesota

#### **Abstract**

Several best management practices (BMPs) are available to reduce NO<sub>3</sub>-N loading from agricultural lands to surface water. These management practices are classified into three main categories: hydrologic, nutrient management, and landscape diversification BMPs. A literature review was conducted to identify the range of effectiveness of these BMPs in the Midwestern U.S. region in general, and Minnesota in particular. Hydrologic BMPs include practices to reduce discharge from subsurface tile drainage systems, such as changes in spacing or depth of tile drain systems, or installation of controlled drainage (CD) and bioreactors. Nutrient management BMPs consist of practices to reduce the impact of nitrogen (N) fertilizer, including reductions in rate of N applied, use of nitrification inhibitors, changes in timing of application, and split applications. Landscape diversification BMPs include alternative cropping systems that include perennial crops, use of cover crops or riparian buffer strips, and restoration of wetlands. Hydrologic BMPs can reduce nitrate loadings at the edge of field by an average of from 43-63%. Reductions at the watershed scale will be less than this; because not all land is suitable for these BMPs. Nutrient management BMPs can reduce nitrate loadings at the edge of field by an average of from 19-27%. Landscape diversification can reduce nitrate loadings at the edge of field by an average of from 42-73%.

# Best management practices for nitrogen

Nitrogen from agriculture sources is a key contributor to the hypoxia in the Gulf of Mexico (Burkart and James, 1999). Nitrate (NO<sub>3</sub>-N) entering the Gulf of Mexico through the Mississippi-Atchafalaya Rivers has led to nutrient over-enrichment, causing detrimental effects such as growth of phytoplankton, reduction in oxygen concentrations, fish migration, and mortality of some species (Mulla, 2008).

Several agricultural BMPs have been proposed to reduce  $NO_3$ -N losses into the surfaces water. The Gulf of Mexico Hypoxia Task Force set a goal to reduce the area of the hypoxic zone by 30% by 2015 (Mitsch et al. 2001). A BMP can be defined as a practice or combination of practices which are economically and technologically effective to reduce pollutant loads by nonpoint sources and reach water quality goals (EPA, 1980). Best management practices fall into three main categories: hydrologic, nutrient management, and landscape diversification practices (Figure 1).

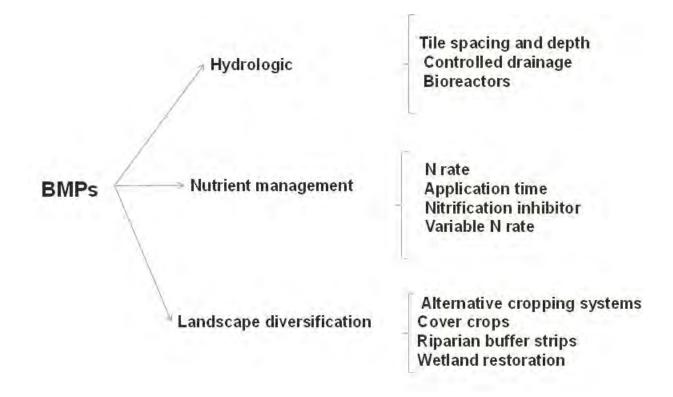


Figure 1. Best management practices to reduce N loading to surface water. Adapted from Mulla (2008).

# 1. Hydrologic best management practices

Agricultural drainage is an important practice in Minnesota implemented by farmers to facilitate trafficability of the fields and cropping systems operation such as crop planting and harvesting, reducing standing water on the fields during the growing season (Strock et al. 2010). Subsurface drainage is typically practiced on flat poorly drained soils with limited internal drainage due to an impermeable clay layer deep in the soil profile. In these cases, subsurface drainage may boost crop yields by as much as 30%.

Subsurface drains are typically installed at spacings of 20 to 30 meters (m) and depths of from 1 to 2 m in Minnesota. These systems were first installed using clay pipes during the 1920s after the advent of widespread construction of ditches throughout southern Minnesota. As these systems age, they are being replaced by more modern corrugated plastic pipes which became popular during the 1980s. New subsurface drain tile installations can be designed with environmental as well as production goals, the idea being that shallower tile installations could be used along with narrower spacings to maintain crop productivity while enhancing denitrification and reducing losses of nitrate to the environment.

In Minnesota, Sands et al. (2006) conducted a field experiment with a corn-soybean rotation designed to evaluate flow and nitrate-N losses from subsurface tile drains installed at depths of 0.9 or 1.2 m, and at spacings of roughly 10 or 20 m. They found an 18% reduction in annual flow and a 15% reduction in nitrate-N losses for the 0.9 m depth in comparison with the 1.2 m depth, without significant differences in nitrate-N concentrations. These results show that reductions in nitrate-N losses were largely attributed to reduced drainage flows at shallower tile depths.

Nangia et al. (2005a) used the Agricultural Drainage and Pesticide Transport (ADAPT) model to investigate the influence of subsurface tile drain depth and spacing on discharges of water and nitrate-N from tile drains under a corn-soybean rotation using a 50 year record of climatic conditions in southern Minnesota. The ADAPT model was calibrated and validated using a 10 year dataset for flow and nitrate-N losses from a 21 ha corn-soybean field in southern Minnesota. Baseline conditions for simulations included a tile spacing of 27 m, a tile depth of 1.2 m, and a fall application of 123 kg/ha N fertilizer. For a subsurface tile depth of 1.2 m, increasing the tile spacing from 27 to 100 m reduced nitrate-N losses from 43.1 to 9.5 kg/ha, a reduction of 78%. Reductions in nitrate-N losses are also possible by decreasing depth of tile drains, at a spacing of 27 m, reducing tile depth from 1.5 m to 0.9 m reduced nitrate-N losses from 43.1 to 17.5 kg/ha, a reduction of 59%.

#### 1.1 Controlled drainage

Controlled drainage is one of the BMPs proposed to reduce nutrient loading to surface water. Controlled drainage consists in placing a water control structure near the outlet of the drainage systems such as stop logs or float mechanisms that can regulate the level of the water table. Controlled drainage has been used as a BMP in North Carolina for reducing N and P loadings to surface waters, and recently research has indicated that CD is an effective BMP to reduce N losses under different soils and climatic conditions (Skaggs and Youssef, 2008). In Ontario, Canada Drury et al. (1996) reported a 43% decrease in the total annual NO<sub>3</sub>-N loading on a clay loam soil when comparing CD, sub irrigation and drainage treatments. In Quebec under a silt loam soil, Lalonde et al. (1996) found a reduction in NO<sub>3</sub> losses of 76% and 69% in 1992, and 62% and 96% in 1993, under water table control levels of 0.25 and 0.50 m above the drain, respectively, in the CD compared to subsurface drainage system. Thorp et al. (2008) using the RZWQM-DSSAT hybrid model simulated the effect of conventional drainage and CD over 25 years across 48 locations in the Midwestern of U.S. on drain flow and N losses. They reported a longterm average simulated reduction in drain flow of 53% and a 51% reduction in N losses. Drain flow reductions were offset by increases in surface runoff and evapotranspiration, and N loss reductions by increases in soil N storage, denitrification and plant uptake, so a more conservative percentage of NO<sub>3</sub> reduction would be 31% to consider these other effects. Fausey (2005) reported reductions of 41% in drain flow and 46% in N losses for a study conducted in Ohio. Tan et al. (1998) found greater reduction in NO<sub>3</sub> losses under CD treatments than in free drainage (FD) systems. NO<sub>3</sub> losses were reduced by 14% under conventional tillage and 25.5% under no-tillage systems, when comparing CD and FD systems. In lowa, Kalita and Kanwar (1993) reported a reduction in NO<sub>3</sub> losses of 39% using a drainage water management system. In Ontario, Canada, under a sandy loam soil in a study conducted on corn, Ng et al. (2002) found that the cumulative drainage water volume from CD and sub irrigation treatments were 8% greater than for free tile drainage, but the flow weighted mean of nitrate concentration was reduced by 41% with the CD treatments, so the total nitrate loss was reduced by 36% compared with free tile drainage treatments. In Ontario Canada, Drury et al (2009) compared CD systems and controlled drainage systems with subsurface irrigation (CDS) with unrestricted tile drainage under a corn-soybean rotation. Reductions in NO<sub>3</sub>-N of 44% and 66% were reported for CD and CDS when 150 kg N ha<sup>-1</sup> was applied to corn, and no N was applied to soybean. They found that nitrate losses were reduced by 31% and 62% for CD and CDS when 200 kg N ha<sup>-1</sup> was applied to corn, and 50 kg N ha<sup>-1</sup> was applied to soybean.

Woli et al. (2010) conducted a field study in Illinois comparing CD and FD systems. Controlled drainage had greatly reduced  $NO_3$ -N removal (17 kg N ha<sup>-1</sup> yr<sup>-1</sup>) compared to FD systems (57.2 kg N ha<sup>-1</sup> yr<sup>-1</sup>) averaged over three years, representing an overall reduction of 70% with CD systems. Recently, Feser (2012) reported a 25% reduction in  $NO_3$ -N yields in a field study in Southwest Minnesota comparing conventional FD and CD in a loam texture soil.

Most of the cited studies indicated a positive response to the implementation of the CD systems in improving water quality. However some limitations are still in need for more research on this system. One of the limitations is that CD is only economically feasible on flat landscapes with less than 1% of surface slope. Also, this system requires maintenance by farmers after installation, including removal or adjustments to the weir boards according to the time of the year (Feser, 2012).

#### 1.2 Bioreactors

In the Midwest, the use of bioreactors has potential to reduce N loads from agricultural drainage. Denitrification is the main mechanism to remove N through bioreactors. Bioreactors and denitrification walls are designed to intercept drainage water before leaving the field, and increase denitrification using a C source (Greenan et al. 2009). Nitrate in the drainage water is converted to N gas (dinitrogen,  $N_2$ ) by denitrifying bacteria present in the soil and bioreactor. These bacteria use the carbon source added to the bioreactor (woodchip, sawdust, compost, paper fibers, etc.). There are two main characteristics that need to be considered when a bioreactor is designed; one is the volume of discharge that will circulate through the bioreactor, the second is having a long enough retention time to allow bacteria to convert the nitrate to  $N_2$  (Christianson et al., 2009). Efficiency of bioreactor removal decreases during high flow periods such as spring runoff.

Some of the advantages of using bioreactors are: 1) no modification of current practices is needed, 2) No land has to be taken out of production, 3) there is no decrease in drainage effectiveness, 4) bioreactors require little or no maintenance, 5) carbon sources in bioreactors can last for up to 20 years (Cooke et al., 2008). As a new technology, still there are some concerns with its implementation related to 1) export of methyl mercury when water is retained in bioreactors for long periods of time, 2) discoloration of the outflow water, and 3) the production of nitrous oxide, a greenhouse gas, if the denitrification process is not complete (Christianson and Helmers, 2011).

Early research showed a reduction in  $NO_3$ -N concentration using bioreactors containing a C source to enhance denitrification (Blowes et al. 1994; Robertson and Cherry, 1995; Schipper and Vojvodić-Vuković, 1998, 2001).

More recent research also shows that bioreactors are effective at reducing the amount of  $NO_3$ -N reaching surface waters. In a laboratory study, Greenan et al. (2009) found a 100, 64, 52, and 30% efficiency of  $NO_3$ -N removal for flow rates of 2.9, 6.6, 8.7 and 13.6 cm d<sup>-1</sup>, respectively, using column bioreactors that contained woodchips as a C source. The authors also state that denitrification was the main mechanisms for  $NO_3$ -N removal, and the denitrification process ( $NO_3$  to  $N_2$ ) was complete since the production of nitrous oxide was insignificant (0.003 to 0.028% of N denitrified). Chun et al. (2009) using a laboratory scale bioreactors reported a range of  $NO_3$ -N removal depending on the retention time. High retention time results in 100%  $NO_3$ -N removal, while low retention time produced a 10-40% removal of  $NO_3$ -N. Greenan et al. (2006) compared different C sources in a laboratory study, and found greater  $NO_3$ -N removal with cornstalks followed by cardboard fibers, wood chips with oil, and wood chips alone. For all C sources, denitrification was the main pathway of  $NO_3$ -N removal.

Chun et al. (2010) observed a 47% removal of  $NO_3$ -N in a field-scale bioreactor using woodchips as C source and a retention time of 4.4 h in Decatur, Illinois. This is a greater amount removed than those reported in laboratory scale bioreactors with similar retention time (Chun et al. 2009). A pilot-scale evaluation of a bioreactor was performed in lowa by Christianson et al. (2011). The authors observed that from 30 to 70% of  $NO_3$ -N was removed with a retention time ranging from 4 to 8 h. In Illinois under a corn soybean-rotation, Woli et al. (2010) showed that  $NO_3$ -N loading could be reduced by 33% for a bioreactor associated with CD.

Verma et al. (2010) evaluated the performance of bioreactors to remove  $NO_3$ -N from tile drainage in three experimental sites located in Illinois. Percentages of load  $NO_3$ -N reduction were 42, 54 and 81% for a loading density (acres/100 sq. feet of bioreactor area) of 1.25, 4, and 8.5 in 2007-08, respectively, and 48 and 98 % for loading densities of 8.5 and 1.25, respectively, in 2008-09. The authors presented a relationship between load reduction and loading density (bioreactor efficacy curve) which showed that  $NO_3$ -N reductions decreased as loading density increased. The relationship between these two parameters could help to improve the design of bioreactors.

In Ontario, van Driel et al. (2006) tested two bioreactor designs using alternating layers of fine and coarse wood particles as a labile carbon source in a corn field (lateral flow design) and golf course (upflow design). NO<sub>3</sub>-N removal averaged 33% and 53% for the corn field and golf course sites, respectively. Authors also estimated that carbon consumption from denitrification was less than 2%, which indicates that these reactors can be used for several years without replenishment of the C source. Thus, it appears that bioreactors have a great potential for use as a BMP to control N loading, are relatively cheap, and have low maintenance.

Jaynes et al. (2008) compared  $NO_3$  losses from a conventional drainage system and two alternative systems: deep tile (DT) and a denitrification wall (DW) in a corn-soybean rotation in Iowa, reporting an annual  $NO_3$ -N reduction of 55% with the denitrification wall over a 5 year period; however DT treatments did not lower  $NO_3$ -N concentrations or mass loss in drainage.

Ranaivoson et al (2012) evaluated the performance of two woodchip bioreactors in Minnesota. At Dodge County site, nitrate loading reduction was of 26 and 10% during snowmelt period in 2010 and 2011, respectively. During rainfall season reductions were 48 and 21% in 2009 and 2010, respectively, and the differences between years could be related to the greater rainfall in 2010. In Rice County site, the bioreactor presented an overall nitrate loading reduction of 47%.

Table 1. Effectiveness of hydrological management practices to reduce nitrate ( $NO_3$ -N) concentrations under tile drainage management.

Type of study	Reference	Site	% Reduction in NO <sub>3</sub> -N loss	
	Sands et al. (2006)	Minnesota	15%	
	Nangia et al. (2010)	Minnesota	59 to 78%	
	Kalita and Kanwar (1993)	Iowa	39%	
	Lalonde et al. (1996)	Quebec, Canada	62 to 96%	
	Drury et al. (1996)	Ontario, Canada	49%	
	Drury et al. (2009)	Ontario, Canada	31 to 44%	
ge	Thorp et al. (2009)	Midwestern U.S.	31%	
Drainage	Tan et al. (1998)	Ontario, Canada	14 to 26%	
۵	Fausey (2005)	Ohio	46%	
	Feser 2012	Minnesota	25%	
	Ng et al. (2002)	Ontario, Canada	36%	
	Woli et al. (2010)	Illinois	70%	
	Range of % reduction		14 to 96%	
	DI (400 t)	0 (0 . 1)	2004	
	Blowes et al. (1994)	Ontario (field)	99%	
	Roberson and Cherry (1995)	Canada (septic systems)	58 to 96%	
	Schipper and Vojvodić-Vuković (1998)	New Zealand (field)	60 to 88%	
	Schipper and Vojvodić-Vuković (2001)	New Zealand (field)	>95%	
	Greenan et al. (2009)	Laboratory experiment	30 to 100%	
	Greenan et al. (2006)	Laboratory experiment	80 to 96%	
	Chun et al. (2009)	Laboratory experiment	10-40 to 100%	
ors	Chun et al. (2010)	Illinois (field)	47%	
Bioreactors	Christianson et al. (2011)	Iowa (field)	30-70%	
iore	Verma et al. (2010)	Illinois (field)	42 to 98%	
<u>α</u>	Woli et al. (2010)	Illinois (field)	33%	
	van Driel et al. (2006)	Ontario (field)	33 to 53%	
	Jaynes et al. (2008)	Iowa (field)	55%	
	Robertson et al. (2000)	Ontario (field)	58%	
	Ranaivoson et al. (2012)	Minnesota (snowmelt+ rainfall-field)	31 to 74%	
	Ranaivoson et al. (2012)	Minnesota (field)	47%	
	Range of % reduction		10 to 99%	

### 2. Nutrient management best management practices

#### 2.1. Nitrogen rate

Reducing N rates from fertilizer or manure, shift in time of application and use of nitrification inhibitors are some of the BMPs available to reduce N loading to surface water. Several studies in the Midwest on tile drained lands have shown that reducing N fertilizer rates for corn resulted in decreased NO<sub>3</sub>-N concentrations in tile discharge (Kladviko et al., 2004; Buzicky et al., 1993; Nangia et al., 2005; Gowda et al., 2006a, Jaynes et al., 2004a).

In Minnesota, Buzicky et al. (1983) reported a 28% reduction in  $NO_3$ -N losses from tile drainage by reducing spring-applied N rates from 202 to 134 kg ha<sup>-1</sup>. Using the ADAPT model, Nangia et al. (2005a) estimated a reduction of 12% to 15% in nitrate-N losses at the field scale when reducing N rates from 180 to 135 kg N ha<sup>-1</sup> under a corn soybean rotation. Nangia et al. (2010), using the ADAPT model in Seven Mile Creek, Minnesota, estimated that decreasing N rates from 179.3 to 112 kg N ha<sup>-1</sup> could reduce nitrate losses by 23% (28.2 to 21.8 kg  $NO_3$ -N ha<sup>-1</sup>).

Besides N rate reductions, cropping systems also had an influence on the amount of  $NO_3$  losses on tile drainage. Losses were greater under continuous corn than under corn-soybean rotations, which could be explained by the frequency of annual fertilization. Under continuous corn, N is applied to corn every year, however, in corn-soybean rotations N is applied every other year, reducing the total amount of N entering the system. Several researchers showed decreases in  $NO_3$ -N losses when cropping systems were shifted from continuous corn to corn-soybean (Wee and Kanwar, 1996; Kanwar et al. 1997; Bakhsh et al. 2005; Randall et al. 1997). Kladivko et al. (2004) reported a reduction of 70% in the concentration of  $NO_3$ -N (28 to 8 mg  $NO_3$ -N  $L^{-1}$ ) in tile drainage during a 14 year period with such a shift in cropping system. This reduction could also be attributed to decreases in N rate over time and the inclusion of a winter cover crop in the SC rotation.

In summary, there is a potential to reduce  $NO_3$  losses through tile drainage by reducing N application rate if producers are currently applying N at rates greater than the maximum net economic return, however at the optimum N rate producers will face an economic reduction to achieve lower  $NO_3$ -N concentrations in tile drainage (Sawyer and Randall, 2008).

Table 2. Effectiveness of N management practices to reduce nitrate (NO₃-N) concentrations under tile drainage management.

Type of study	Reference	Site	% of Reduction in NO <sub>3</sub> -N loss
	Buzicky et al. (1983)	Minnesota	28%
	Nangia et al. (2005a)	Minnesota (model)	12 to 15%
	Gowda et al. (2006)	Minnesota (model)	11 to 14%
	Jaynes et al. (2004a)‡	Iowa	30%
N rates	Baksh et al. (2004)	Iowa	17%
Z	Nangia et al. (2010)	Minnesota (model)	23%
	Kladivko et al. (2004)†	Indiana	70%
	Range of % reduction		11 to 70%
-			
Ş			
N application time and Inhibitors	Smiciklas and Moore (1999)	Illinois	58%
nhik	Randall and Mulla (2001)	Minnesota	36%
n pu	Gowda et al (2006)	Minnesota	34%
ле а	Nangia et al. (2005b)	Minnesota	6%
n tin	Randall et al (2003)	Minnesota	17 to 18%
atio	Randall and Vetsch (2005)	Minnesota	10 to 14%
plic			
ар	Range of % reduction		10 to 58%
	Randall et al. (2003)	Minnesota	13%
Split applications	Jaynes et al. (2004)	Iowa	30%
	Range of % reduction		13 to 30%

This reduction also includes the effect of changing crop rotation and adding cover crops plus changing N rate over time. ‡ This reduction is also related to changing time of application.

#### 2.2. Nitrogen application time, split applications and use of inhibitors

Shifting from fall to spring N fertilizer application is a BMP to reduce  $NO_3$  losses to surface water. This practice is, however, challenging for farmers because it implies a greater risk due to a narrow time window for applying spring fertilizer. In spring, soils are typically wet, and rainfall is frequent. Thus some producers want to avoid the risk of failing to have enough time to apply N fertilizer in spring, and do not want to risk a loss of crop

Randall and Mulla (2001) reported a 36% reduction in nitrate losses when comparing fall to spring application in Minnesota. For two Minnesota watersheds, Gowda et al (2006) estimated a 34% reduction in nitrate losses by switching from fall to spring application. Randall et al. (2003) evaluated the influence of time of N application and use of nitrapyrin on nitrate losses in a corn-soybean rotation at Waseca, Minnesota from 1986-1994. They showed that  $NO_3$ -N losses in drainage were reduced by

18% with fall N + NP and by 17% in spring, and by 13% for split-applications relative to fall N application without NP. Randall and Vetsch (2005) reported that for the period from 1993 to 2000,  $NO_3$ -N losses were reduced by 14% with spring N applications, and by 10% with late fall + NP application.

Split applications of N are another alternative to reduce NO<sub>3</sub>-N losses through tile drainage. With split applications, N use efficiency by crops should increase due to better synchronization in the amount of N available and crop uptake (Randall and Sawyer, 2008). Jaynes et al. (2004) evaluated the effect of using the late spring nitrate test (LSNT) in corn and reported that in two of the four years, LSNT significantly reduced N applications, and annual NO<sub>3</sub>-N concentrations for the last two years were 11.3 mg N L<sup>-1</sup> for LSNT and 16 mg N L<sup>-1</sup> for the control subbasins. The authors concluded that a reduction of 30% in NO<sub>3</sub>-N losses in tile drainage could be attained if LSNT programs are adopted. The LSNT method is not, however, widely used in Minnesota. As mentioned before, Randall et al. (2003) also reported a 13% reduction for split-applications relative to the fall N without NP treatments. However, some studies reported higher losses of NO<sub>3</sub>-N with split applications under continuous corn (Baker and Melvin, 1994).

# 3. Landscape diversification best management practices

#### 3.1 Buffers

Conservation buffers are defined as areas of permanent vegetation that intercept and slow runoff, improve infiltration and overall water quality. Conservation practices such as field strips, riparian forest buffers, and riparian herbaceous cover, conservation cover, contour buffer strips, alley cropping, grassed waterways, and vegetative barriers are considered buffers (Helmers et al. 2008). Riparian buffers help to regulate the stream environment, controlling sediments and contaminants carried in surface runoff, including nitrate in shallow groundwater moving to the streams (Lowrance et al. 2000). The effectiveness of riparian buffers to remove nitrate will depend on the proportion of the groundwater moving in or near the biologically active root zone, the residence time, the site and weather conditions as well buffer design (Helmers et al. 2008). Nitrate in shallow groundwater can be removed by several mechanisms: including dilution (Hubbard and Lowrance, 1997; Spruill, 2000), plant N assimilation (Lowrance, 1992; Hubbard and Lowrance, 1997; Mayer et al. 2007); or denitrification (Jacobs and Gilliam, 1985; Addy et al. 1999, Gold et al. 1998). In the Midwestern region, the use of these buffers has not been effective in removing NO<sub>3</sub>-N in tile drained soils, since tile discharge bypasses the buffers and goes directly into surface water; however alternative strategies to treat tile discharge with buffers are under current study (Isenhart and Jaynes, 2012). Riparian buffers generally have lower flow rates, less buildup of organic C in soils, and higher redox potential than wetlands (Mitsch et al. 2001).

In North Central Minnesota, Duff et al. (2007) evaluated three well transects from a natural, wooded riparian zone adjacent to the Shingobee River. The authors reported a reduction in groundwater  $NO_3$ -N concentrations from 3 mg N  $L^{-1}$  beneath the ridge to 0.01 to 1 mg N  $L^{-1}$  at wells 1 to 3 m from the channel, which represents a 67 to 99% efficiency. However, an increase in  $NO_3$ -N due to cultivation could result in an increased in  $NO_3$ -N movement to the channel.

Petersen and Vondracek (2006) evaluated the effect of buffer width on sediment, N, phosphorus, and runoff in the Karst region of Minnesota using a spreadsheet model. The authors reported that buffers around sinkholes could contribute to the reduction of sediment and nutrients in Minnesota, with buffers 15 m wide being more cost effective in relation to the cost of the Conservation Reserve Program management practice.

Table 3. Effectiveness of landscape diversification management practices to reduce nitrate (NO<sub>3</sub>-N) concentrations.

Type of study	Reference	Site	% Reduction NO <sub>3</sub> -N
	Barfield et al. (1998)	Kentucky	95 to 98%
	Blanco-Canqui et al (2004a)	Missouri	94%
	Blanco-Canqui et al (2004b)	Missouri	47 to 69%
<b>.</b> S	Dillaha et al (1989)	Virginia	54 to 77%
Riparian Buffers*	Magette et al. (1989)	Maryland	17 to 72%
n B	Schmitt et al. (1999)	Nebraska	57 to 91%
aria	Lowrance and Sheridan (2005)	Georgia	59 to 78 %
Rip	Duff et al (2007)	Minnesota	67 to 99%
	Range of % reduction		17 to 99%
	Appelboom and Fouss (2006)		37 to 83%
S	Kovacic et al. (2000)	Illinois	33 to 55%
Wetlands	Crumpton et al. (2006)	Iowa	25 to 78%
Vetl	Hunt et al. (1999)	North Carolina	70%
>	Xue et al. (1999)	Illinois	19 to 59%
	Iovanna et al. (2008)	Iowa	40 to 90%
	Range of % reduction		19 to 90%

<sup>\*</sup>Note: none of the riparian buffer studies referenced here were at sites with subsurface tile drainage.

#### 3.2 Wetlands

Wetlands are saturated or inundated areas in landscape depressions. In the Midwest, wetlands are an alternative management practice to reduce nitrate concentrations in tile drained areas before nitrates are transported to surface waters. Some of the mechanisms that cause wetlands to act as a "sink" of N are:1) NH<sub>4</sub> is the predominant form of N in most flooded wetlands soils and can be taken up by the vegetation through roots, or can be immobilized and transformed in organic matter (Mitsch et al. 2001), and 2) NO<sub>3</sub> can be used as the terminal electron acceptor for oxidation of C sources under anaerobic conditions and denitrification and 3) dissimilatory reduction of NO<sub>3</sub> to NH<sub>4</sub> can occur, with NH<sub>4</sub> being absorbed by plants (Bowden, 1987). Several factors influence the effectiveness of wetlands to remove nitrate: scale, landscape position, geographic location, ratio of runoff volume to storage volume of the wetland, the extent of subsurface tile drainage, resident time of the water, water temperature, vegetation type, N loading rates and forms of N (NO<sub>3</sub> vs. NH<sub>4</sub> or organic N), and soil characteristics (texture, permeability) (Mulla, 2008, Crumpton et al. 2008).

Kovacic et al. (2000) evaluated the effect of constructed wetlands to reduce N in Illinois. They reported that in a three year period 37% of the incoming N (most of as  $NO_3$ ) was removed and if a buffer strip was between the wetland and the river, an overall efficiency removal rate of 46% was achieved. Crumpton

et al. (2006) reported annual  $NO_3$ -N removal rates of 25, 68, and 78% in three wetlands in lowa. Xue et al. (1999) evaluated the capacity of constructed wetlands to remove  $NO_3$ -N on tile drained soils in Illinois. The authors found that the ratio of denitrification capacity and mean  $NO_3$ -N loads ranged from 19 to 59 % with an average of 33%.

Constructed wetlands on tile drained lands are being considered as a potential BMP to improve water quality in the Corn Belt. In 2001, lowa initiated a conservation program (Conservation Reserve Enhancement Program) to promote the adoption of practices that could reduce the effects of tile-drained lands on water quality; wetlands are one option being implemented. To date, 27 wetland pools have been constructed, and monitoring data suggest that 40 to 90% of the NO<sub>3</sub>-N can be removed (Iovanna et al. 2008).

Although more research is needed to determine the effectiveness of the wetlands to reduce N loadings in tile drained lands (design, maintenance, size, amount of N load into the wetland), the main constraint for adoption is related to the cost associated with the restoration and construction of the wetlands and land taken out of production (Crumpton et al. 2008).

#### 3.3 Alternative cropping systems

The use of alternative cropping systems has shown advantages to reduce nitrate losses. Randall et al. (1997) reported a reduction of 7% in NO<sub>3</sub>-N flux over a 4-year period involving a shift from continuous corn to a corn-soybean rotation. In the same study, greater reductions were achieved when alfalfa was included in the rotation (97%) and with the implementation of the Conservation Reserve Program (98%). Including perennials in the rotation implies that crops are actively growing for a longer time and had greater evapotranspiration than annual crops, which would contribute to greater N uptake and less drainage. Also perennial crops receive less N input through fertilization than annual cropping systems, thereby reducing NO<sub>3</sub>-N leaching potential.

#### 3.4 Cover crops

Cover crops are planted before or after crop harvest. Cover crops such as rye, small grains, and clover can accumulate N during the fallow period, thus preventing leaching of the residual soil N. Other advantages of using cover crops are related to improved soil quality, increasing soil organic matter and protecting soil from erosion (Lal et al., 1991, Kaspar et al., 2001). Kladivko et al. (2004) found over a 15 year period annual NO<sub>3</sub>-N losses from tile drained soil were reduced by 60% (38 to 15 kg ha<sup>-1</sup>) when continuous corn was replaced by a corn-soybean rotation with a fall cover crop of winter wheat. Strock et al. (2004) evaluated the effect of autumn winter rye to reduce NO<sub>3</sub>-N losses in subsurface tile drainage under a corn-soybean rotation at Lamberton, Minnesota. The authors reported a 13% reduction in NO<sub>3</sub>-N losses with corn-soybean and a rye cover crop. Also, for southwestern Minnesota, Feyereisen et al. (2006) showed that NO<sub>3</sub>-N losses could be reduced by 30% or 11% depending on the planting day of the cover crop (September 15 or October 15, respectively). Kaspar et al. (2007) reported a decrease in NO<sub>3</sub>-N loads (4 year average) of 61% in subsurface drainage water using a rye winter cover crop, but no differences were observed with the inclusion of gammagrass (Tripsacum dactyloides L.) in the corn-soybean rotation.

Winter cover crops have the potential to reduce N loadings because they decrease water flow, nitrate concentrations and N loading to surface waters (Kaspar et al. 2008), thereby improving soil and water quality. However, their general adoption is affected by some limitations that affect the development of cover crops as a function of climate (lack of rainfall), poor soil conditions and delays in planting time of the cover crop.

Table 4. Effectiveness of landscape diversification management practices to reduce nitrate ( $NO_3$ -N) concentrations under tile drainage management.

Type of study	Reference	Site	% Reduction in NO <sub>3</sub> -N loss
6	Randall et al. (1997)	Minnesota	7 to 98%
pino	Boody et al. (2005)	Minnesota	51 to 74%
Alternative cropping systems	Simpkins et al. (2002)	Iowa	5 to 15%
ative cro systems			
rnat sy	Range of % reduction		5 to 98%
Alter			
	Kladivko et al. (2004)	Indiana	<60%
ps	Feyereisen et al. (2006)	Minnesota	11 to 30%
Cover crops	Strock et al. (2004)	Minnesota	13%
ver	Jaynes et al. (2004b)	Iowa	60%
3	Kaspar et al. (2007)	Iowa	61%
	Range of % reduction		11 to 60%

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