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 75th 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 Iowa 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 Iowa, 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 Iowa, 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.

<table>
<thead>
<tr>
<th>Input source</th>
<th>Inputs (tons of N Iowa)</th>
<th>Iowa Percent of total inputs</th>
<th>Minnesota Percent of total inputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fertilizer</td>
<td>984,000</td>
<td>25%</td>
<td>30%</td>
</tr>
<tr>
<td>Legumes</td>
<td>762,000</td>
<td>20%</td>
<td>14%</td>
</tr>
<tr>
<td>Wet Deposition</td>
<td>363,000</td>
<td>9%</td>
<td>4%</td>
</tr>
<tr>
<td>Soil N</td>
<td>1,014,000</td>
<td>26%</td>
<td>38%</td>
</tr>
<tr>
<td>Manure</td>
<td>493,000</td>
<td>13%</td>
<td>10%</td>
</tr>
<tr>
<td>Human</td>
<td>16,000</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Dry Deposition</td>
<td>254,000</td>
<td>7%</td>
<td>4%</td>
</tr>
<tr>
<td>Industry</td>
<td>2800</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Total</td>
<td>3,888,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Output categories</th>
<th>Outputs (tons of N)</th>
<th>Iowa percent of total outputs</th>
<th>Iowa percent of total if soil N storage not included</th>
<th>Minnesota percent of total outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harvest</td>
<td>1,565,000</td>
<td>40%</td>
<td>53%</td>
<td></td>
</tr>
<tr>
<td>Grazing</td>
<td>172,000</td>
<td>4%</td>
<td>6%</td>
<td>63%</td>
</tr>
<tr>
<td>Crop Volatilization</td>
<td>353,000</td>
<td>9%</td>
<td>12%</td>
<td>15%</td>
</tr>
<tr>
<td>Soil N (storage)</td>
<td>1,014,000</td>
<td>26%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Manure Volatilization</td>
<td>249,000</td>
<td>6%</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>Fertilizer Volatilization</td>
<td>17,000</td>
<td>&lt;1%</td>
<td>1%</td>
<td>6%</td>
</tr>
<tr>
<td>Denitrification</td>
<td>413,000</td>
<td>10%</td>
<td>14%</td>
<td>10%</td>
</tr>
<tr>
<td>Waters</td>
<td>198,000</td>
<td>5%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>Total</td>
<td>3,981,000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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, Iowa, 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 Iowa watersheds and average stream nitrate concentrations. By comparing stream nitrate levels with row crop production acreage in 25 Iowa watersheds, the authors concluded that mean annual stream nitrate-N concentrations in Iowa 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 Iowa, 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 Iowa 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).

Iowa'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.
References


