

A2. Nitrogen in Waters: Forms and Concerns

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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_3), 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.

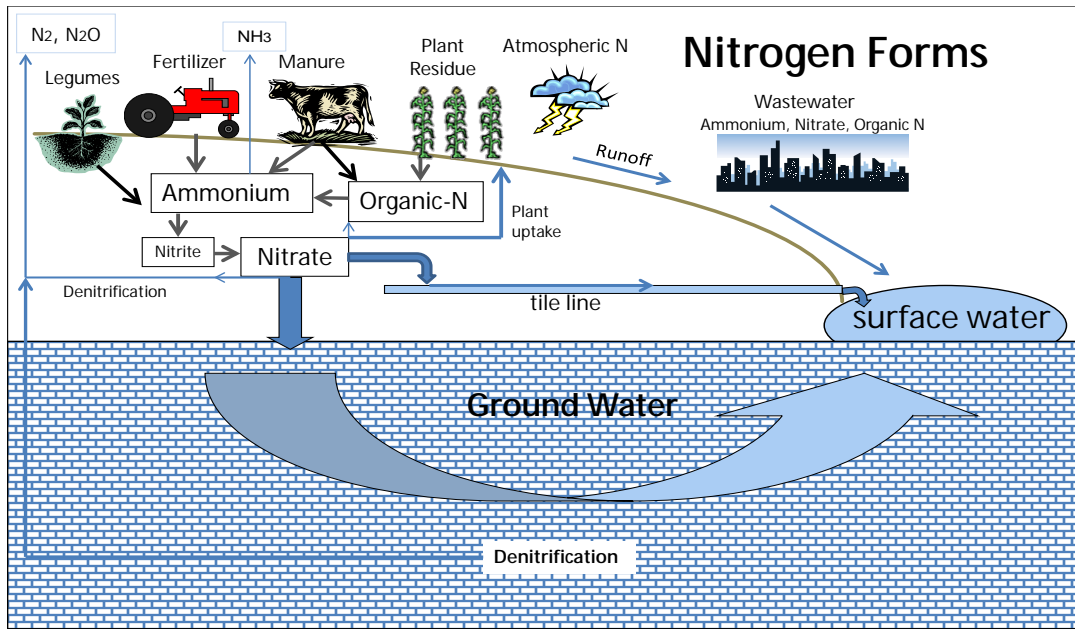
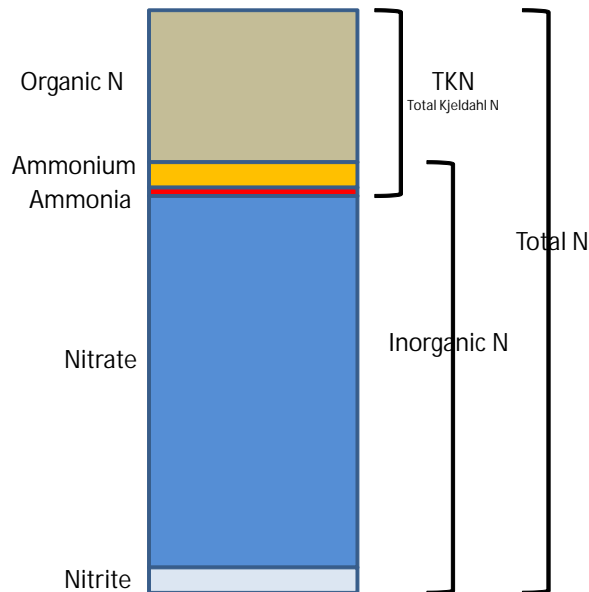


Figure 1. Nitrogen cycle, showing primary N sources, forms and routes to surface waters.

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 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 NH ₃ +NH ₄ is in the NH ₄ form. But NH ₃ 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 (NO₃) and nitrite (NO₂)

Nitrate (NO₃) 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 (NO₂) 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, NO₂+NO₃-N, NO_x-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 residence 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 (NH₃) is toxic to fish and other aquatic organisms. Ammonium (NH₄), the predominant form in the pH range of most natural waters, is less toxic to fish and aquatic life as compared to NH₃. 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 in-home 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.

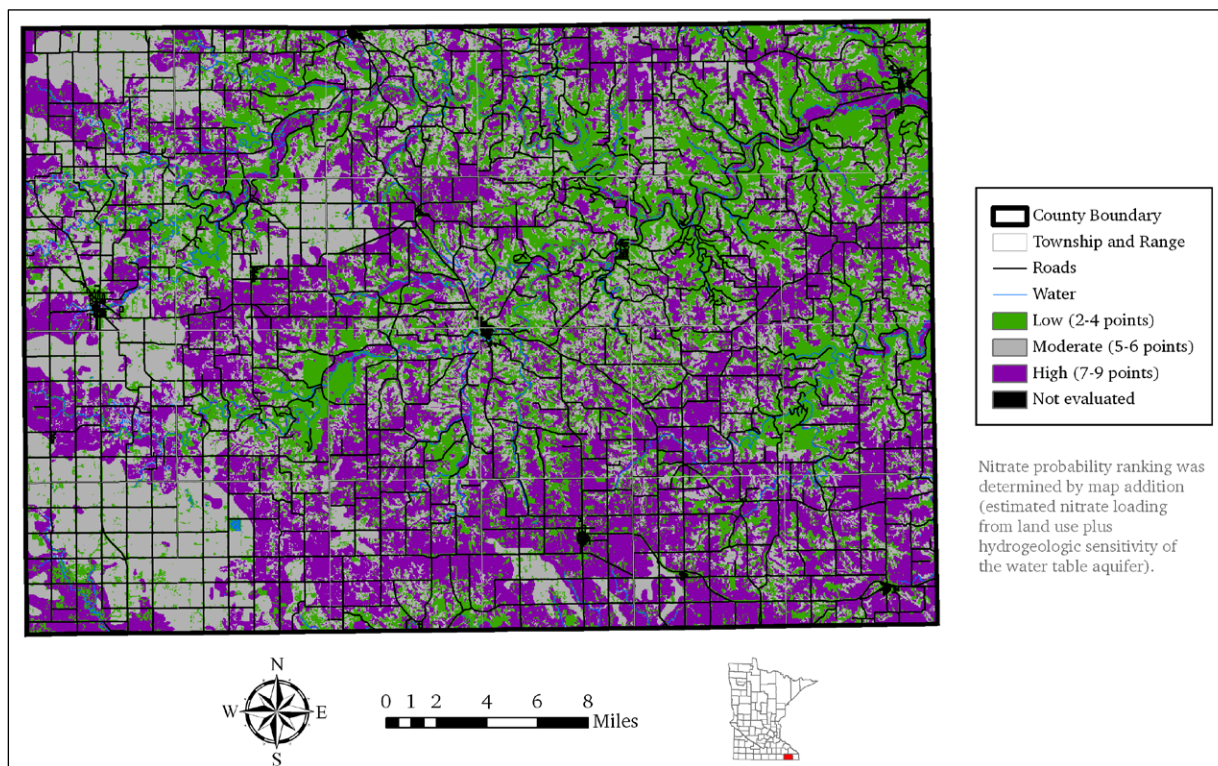


Figure 3. Fillmore County Nitrate Probability Map, showing areas with high (purple), moderate (gray) and low (green) probability of elevated nitrate in the water table aquifer (from MDH).

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_3 or un-ionized ammonia) to its less toxic form ammonium (NH_4), depending on temperature and pH. The pH and temperature of water samples are required to determine the NH_3 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 $16 \mu\text{g/L}$ (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 th	<0.005	0.008	0.288
10 th	<0.005	0.011	0.417
25 th	<0.005	0.015	0.537
50 th	<0.005	0.024	0.807
75 th	<0.005	0.045	1.341
90 th	0.012	0.182	2.435
95 th	0.110	0.276	4.026

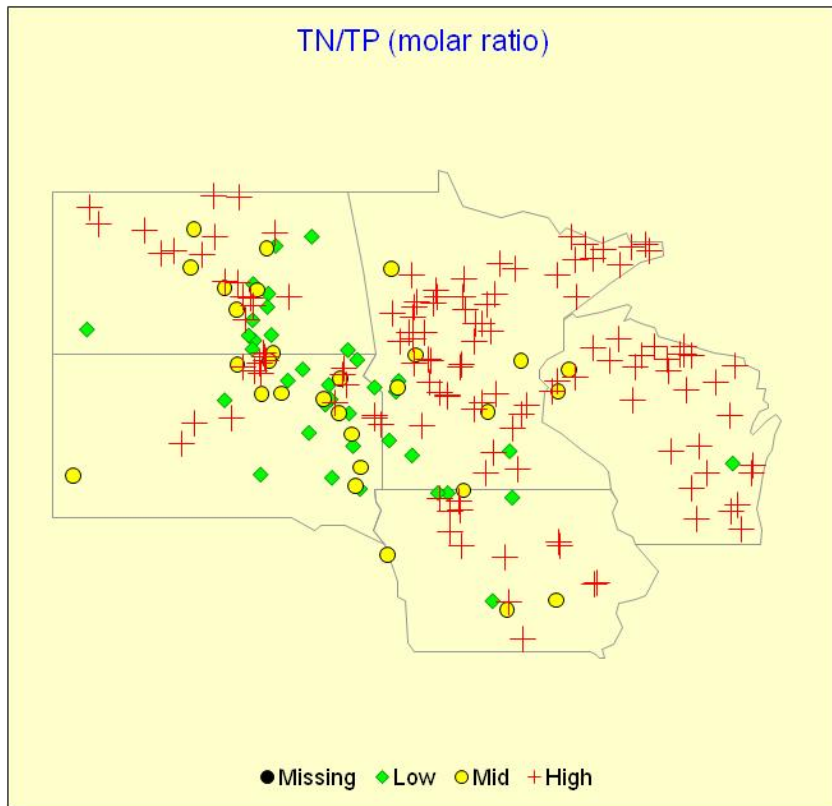


Figure 4. Total nitrogen to TP ratios in Minnesota Lakes, showing locations of “low” (<10:1), “Mid” (10:1 to 17:1) and “High” (>17:1) ratios. From Heiskary and Lindon (2010).

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 mid-summer 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: www.gulfhypoxia.net/Overview/

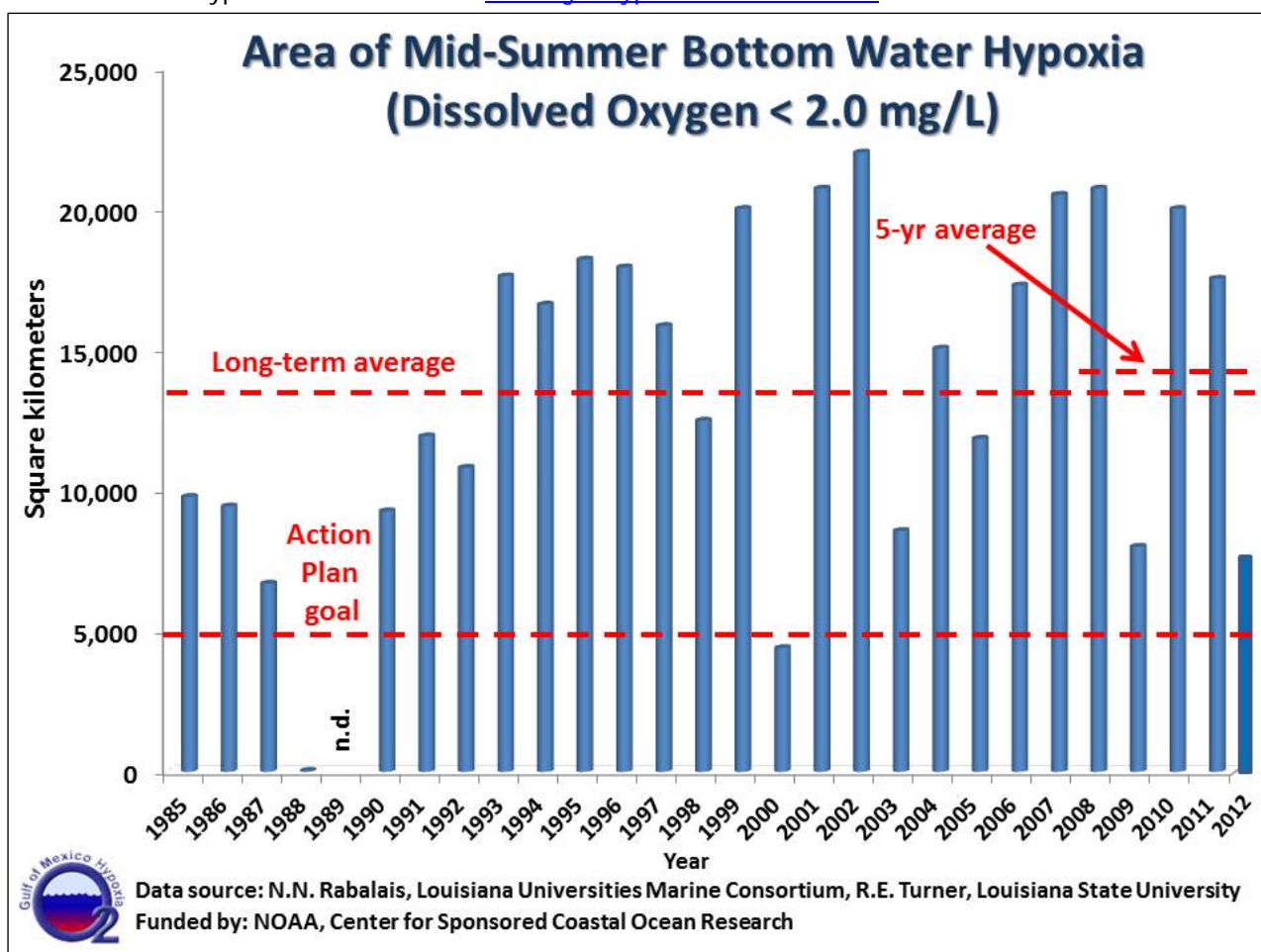


Figure 6. The size of mid-summer bottom water hypoxia areas in the Gulf of Mexico in square kilometers between 1985 and 2011.

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 Iowa, 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 N₂, a harmless common gas. The atmosphere is approximately 78% N₂ 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 (HNO₃), 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 (PM_{2.5}), and in most locations ammonium sulfate and ammonium nitrate are the largest components of PM_{2.5} (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.

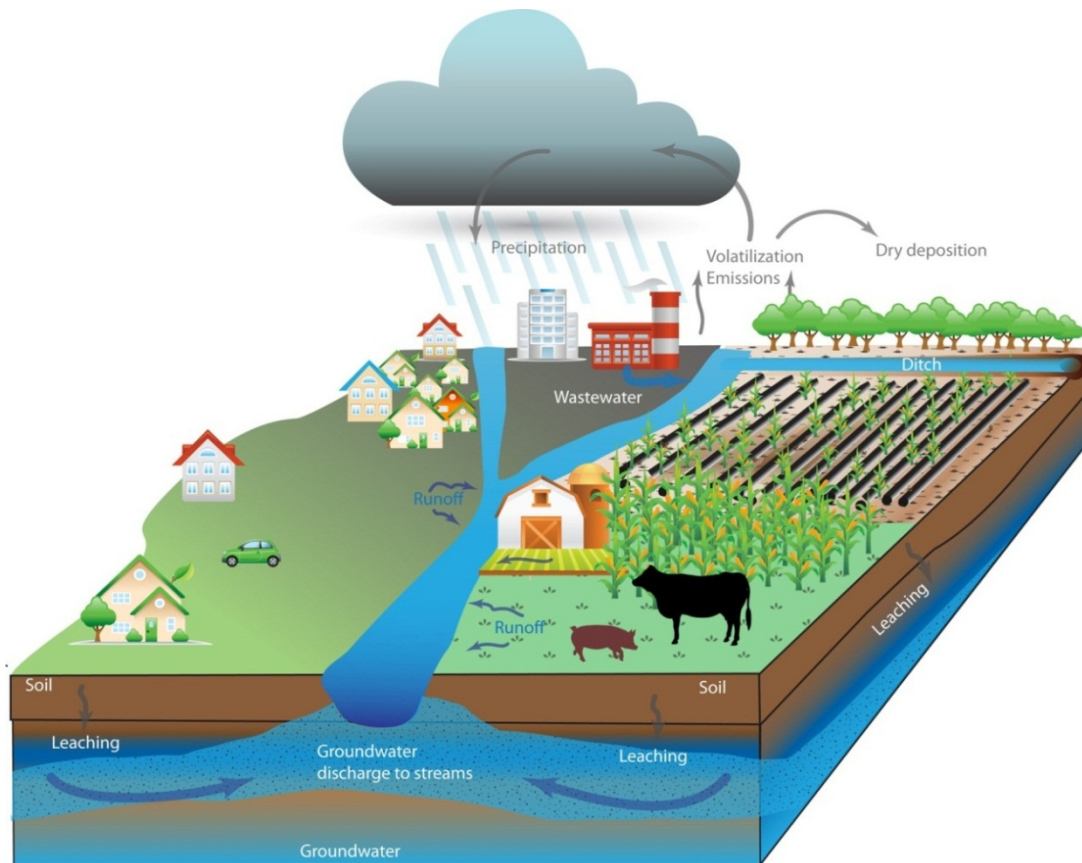


Figure 7. Nitrogen sources and pathways to streams, including direct discharges, runoff, leaching to groundwater, subsurface tile drainage to ditches, and precipitation directly into waters.

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.

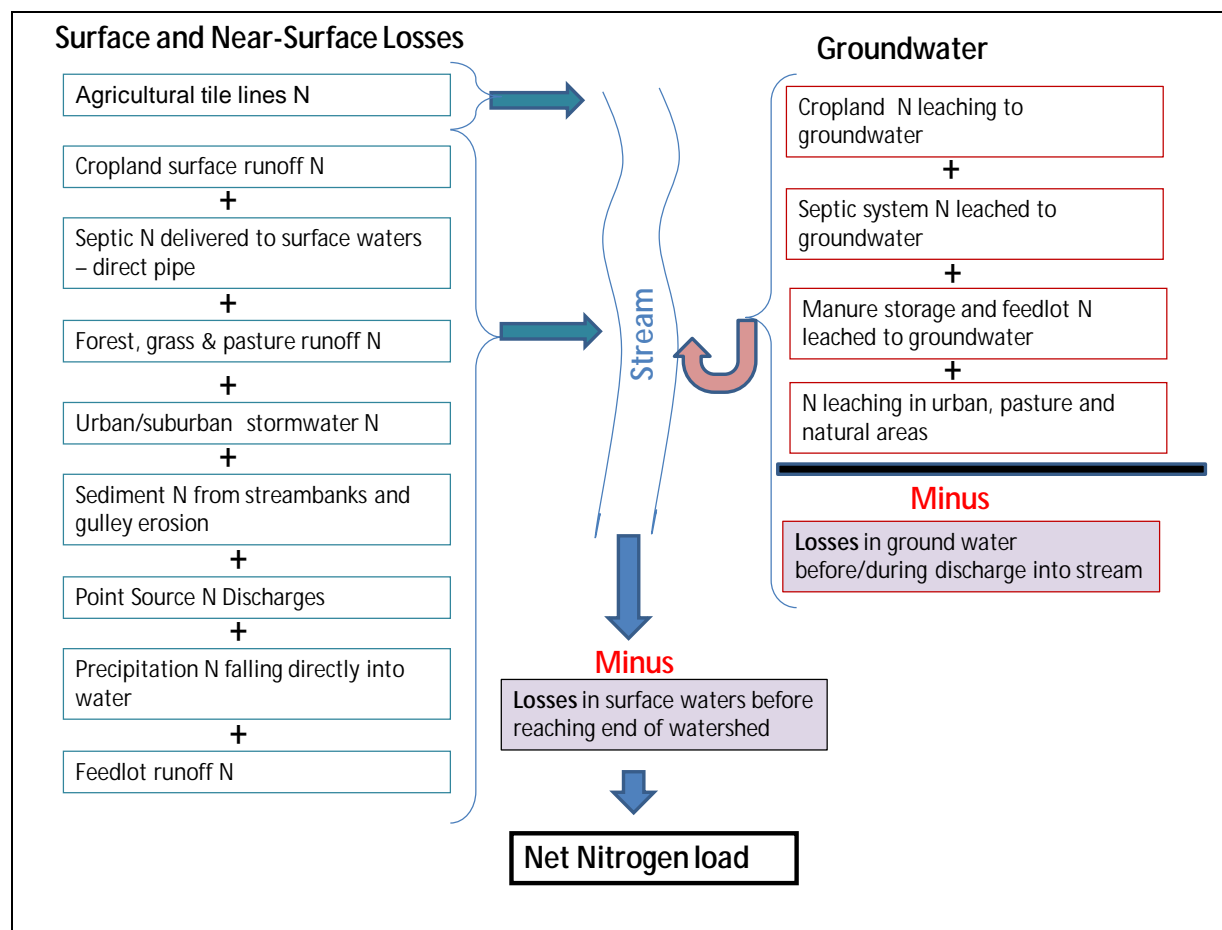


Figure 8. Conceptual diagram of potential N sources, pathways and losses which affect the net N load at the end of the watershed. Denitrification losses are represented by the shaded boxes.

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