Minnesota's

Ground Water Condition: A Statewide View

September 2007

Minnesota Pollution Control Agency

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Minnesota's Ground Water Condition: A Statewide View

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Acronyms

AGQS – Ambient Groundwater Quality Study
BMP – Best Management Practices (BMP)
Ca^{2+} – calcium
CERCLA – Comprehensive Environmental Response, Compensation, and Liability Act
DCEM – Department of Environmental Management
DEHP – di(2-ethylhexly)phthalate
EQB – Environmental Quality Board
GWPA – Groundwater Protection Act
HANS – Hastings Area Nitrate Study
HBV – Health Based Value
HCO_3^- – bicarbonate
HRL – Health Risk Limit
ISTS – Individual Sewage Treatment Systems
MCL – Maximum Contaminant Level
MDA – Minnesota Department of Agriculture
MDH – Minnesota Department of Health
Met Council – Metropolitan Council
Mg^{2+} – magnesium
mg/L – milligrams per liter
MGS – Minnesota Geological Survey
MOA – Memorandum of Agreement
MPCA – Minnesota Pollution Control Agency
N_2 – nitrogen gas
Na^+ – sodium
Organic N – organic form
PCE – tetrachloroethylene
PFC – perfluorinated chemicals
PFoA – perfluoro-octanoate
PFOS – perfluoro-octane sulfonate
PWS – public water supply
RRRWS – Red Rock Rural Water System
RCRA – Resource Conservation and Recovery Act
SO_4^{2-} – sulfate
TCA – trichloroethane
TCE – trichloroethylene
TDS – total dissolved solids
TCAAP – Twin Cities Army Ammunition Plant
THM – trihalomethanes
ug/L – micrograms per liter or ug/L
USDA – United States Department of Agriculture
USEPA – U.S. Environmental Protection Agency
USGS – U. S. Geological Survey
VOC – volatile organic compounds

Executive Summary

One of the goals in the Minnesota Pollution Control Agency (MPCA) 2006 Strategic Plan is to "assess the status or condition of Minnesota's ground water systems" as part of the overall vision calling for "clean and sustainable surface and ground water systems." Accordingly, this report was prepared to provide MPCA managers and others with information about the condition of Minnesota's ground water and Minnesota's progress in implementing ground water condition monitoring. This report refers to "condition" primarily as ground water quality, since the MPCA's mission is to monitor and protect ground water quality. However, ground water quantity is discussed on a limited basis.

Ground water quality data collected in 2004 and 2005 by the MPCA and the Minnesota Department of Agriculture (MDA) serve as the basis for evaluating the condition of Minnesota's ground water. Both agencies conduct statewide ground water quality monitoring in Minnesota's vulnerable aquifers. The MPCA monitors ground water in urban areas for the presence of chloride, nitrate and volatile organic compounds (VOCs); the MDA monitors ground water in agricultural areas for the presence of nitrate and pesticides. The MPCA and MDA monitoring projects comply with the terms of an integrated monitoring strategy that was developed by the MPCA, MDA, and the Minnesota Department of Health (MDH), described in a February 18, 2004 Memorandum of Agreement (MOA). The MDH conducts ground water monitoring for the purpose of regulating public and private water supply wells and public water supplies, and evaluating the risk to human health from contaminants in ground water.

On the basis of the MPCA and MDA statewide ground water quality monitoring project data for 2004 and 2005, the following conclusions about ground water quality in Minnesota's vulnerable aquifers can be made:

1. Ground water quality is generally good and in compliance with drinking water standards. However, human-caused impacts to ground water quality are apparent in many areas of the state.
2. In urban areas, especially the Twin Cities metropolitan area, Rochester and St. Cloud, elevated concentrations of chloride and nitrate and detectable concentrations of VOCs are common.
3. In rural and agricultural areas, nitrate concentrations are frequently elevated or exceed standards; and pesticides and pesticide degradates are commonly detected, though at concentrations that are nearly always less than applicable drinking water standards.
4. Areas of impacted ground water correlate well with land uses that are known to cause the observed quality impacts. The prevalence of elevated nitrate concentrations in ground water in regions dominated by agricultural land uses and in unsewered residential areas is particularly noteworthy.

An important goal of this Ground Water Condition report is to provide sufficient background and technical information to enable the reader to better understand what the MPCA and MDA ambient ground water monitoring data can and cannot reveal about the condition of ground water.

Because the MPCA data are from the first two years of the MPCA condition monitoring project, interpretation of the results is weighted more on the side of evaluation than to making broad conclusions. For example, higher contaminant levels were consistently detected in ground water samples collected by the MPCA from shallower monitoring wells compared to deeper domestic wells. This result adds a level of complication to statements about the overall condition of ground water. Over time, however, having results from both monitoring and domestic wells will be a benefit by enabling a more robust analysis of ground water condition to be made.

For the same reason, the MPCA condition monitoring project is too new to support an evaluation of ground water quality trend. Conducting a trend analysis over a large geographic area such as the state of Minnesota requires a long term and consistent monitoring effort. The MPCA is currently developing a separate trends monitoring network with a supplemental land use monitoring network to assess trends in ground water quality on a shorter timeline.

The MPCA condition monitoring project as presently designed will provide a valuable, long-term record of ambient ground water quality in vulnerable aquifers across Minnesota. This is something Minnesota does not currently have. As stresses on Minnesota's ground water resources increase, a consistent record of ambient ground water quality will become increasingly important to accurate assessment and proper management of Minnesota's most used and most vulnerable ground water resources.

However, ambient ground water quality data alone are generally not sufficient for identifying developing ground water quality issues or localized ground water quality concerns. This is why resource managers need to use other sources of information in conjunction with the results of ambient ground water quality monitoring to better understand and characterize ground water condition.

Considerations for future MPCA ground water quality monitoring efforts include the following:

1. It is important that MPCA managers continue to stay on top of emerging issues that have the potential to impact Minnesota's ground water, to ensure that the MPCA fulfills its charge to monitor and protect the condition of Minnesota's ground water.
2. More studies of land use impacts on ground water quality such as those conducted by the MPCA in the late 1990s and on a limited basis presently are needed to keep up with changing land use practices that have the potential to impact ground water, not only to identify whether impacts are occurring, but also whether the impacts rise to a level of concern. Without this information, it is difficult for the MPCA and other governmental bodies to proactively issue permits, set policy and establish environmental priorities that are protective of ground water.
3. There is a growing need to better incorporate ground water and surface water interaction into water resource management activities. In this report, several examples were provided of Minnesota cities that have struggled to maintain a reliable source of good quality water and found that their ground water quality problems resulted in part from the interaction with impacted surface water. The potential for ground water to improve (or potentially degrade) surface water quality is a factor that should be routinely evaluated as the MPCA undertakes investigation of Minnesota's impaired waters.
4. Many new challenges will be faced by Minnesota's water resource managers as the 21st century unfolds. Chief among these is a changing and less predictable climate, rapid growth of impervious soil cover that reduces the land area where aquifers can be recharged, and an ever increasing demand for potable water. These challenges require that Minnesota water resource managers monitor ground water condition with an eye to the future, and make the critical step of linking land use activities with their impact on ground water, so that practices and guidelines can be developed that will protect this valuable resource.

Introduction

This report was prepared to fulfill the MPCA 2006 Strategic Plan goal to report on the condition of Minnesota's ground water and also Minnesota's progress in implementing ground water condition monitoring. This is the first of an anticipated sequence of reports to be prepared at five year intervals to provide MPCA managers and others with information about the condition of Minnesota's ground water.

Ground water is currently receiving a lot of attention in Minnesota. Public drinking water in several communities in the eastern Minneapolis-St. Paul metropolitan area has been found to be contaminated by low levels of perfluorinated chemicals (PFCs). PFCs are a group of several compounds that only recently have been recognized to be contaminants of concern, and their effect on human health is only partly understood. Residents in communities where ground water has been impacted are grappling to understand the available health risk information on PFCs as they wait for more information to become available and decide whether or not to continue drinking their water.

Meanwhile, the boom in construction of ethanol plants across Minnesota has raised other concerns about ground water. Will the high demand for corn feedstock and more intensive agriculture lead to higher concentrations of nitrate and pesticides in shallow ground water? Will there be enough ground water in parts of the state with fewer ground water resources to supply the ethanol plants without draining aquifers and degrading nearby surface water resources?

These concerns have been the subject of newspaper and television reports in Minnesota over the last year, and with good reason. Ground water supplies 75 percent of Minnesota's population with drinking water (DNR, 2007). Ground water is also an important source of water for commercial and industrial needs.

Given Minnesota's reliance on ground water, the substantial growth in Minnesota's population during the 1990s and its expected continued growth through 2030 is important (Table 1). The number of additional people living and working in Minnesota has increased the demand for water for drinking and basic living needs. There are also more people who expect to enjoy Minnesota's legendary lakes and streams, many of which are fed by ground water.

Table 1: Minnesota Population Statistics

Population Statistics For Minnesota	
Year	**Population**
1990	4,375,665
2000	4,919,479
2005	5,205,091
2010	5,452,500 (projected)
2030	6,268,200 (projected)

(source: Minnesota State Demographic Center, 2002 and 2006)

With these new demands on Minnesota's water resources, and with increasing urbanization and development to accommodate the growing population, Minnesota's generous reserves of high quality ground water can no longer be taken for granted. Recognizing this, the 2005 Minnesota Legislature directed the Minneapolis-St. Paul regional Metropolitan Council (Met Council) to develop a master water supply plan for the region. And in April 2007 the Environmental Quality Board (EQB) completed its water sustainability report (EQB and DNR, 2007) which assesses the availability of the state's water resources to meet long range needs.

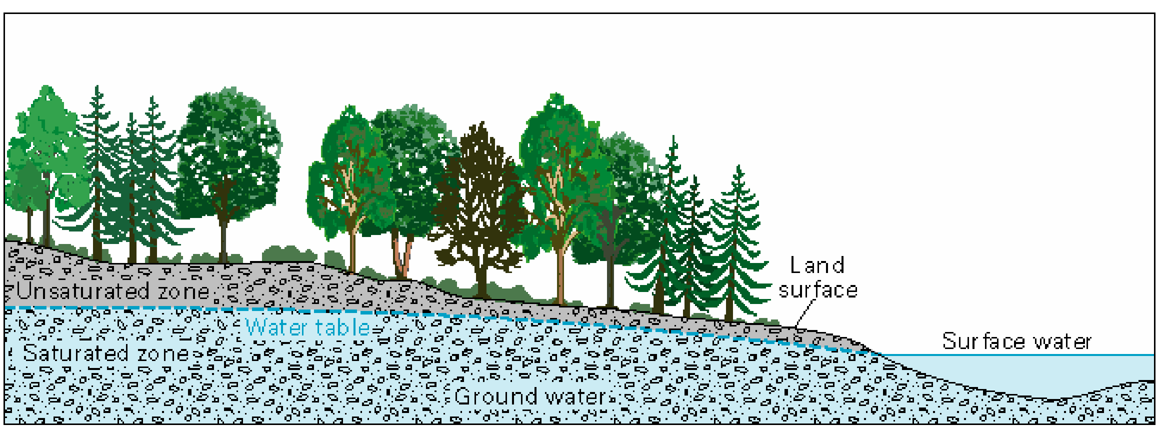


Figure 1. Cross-Sectional View of Ground Water in the Subsurface *(source: USGS, 1999)*

This first MPCA Ground Water Condition report is based primarily on the results of the statewide ground water quality monitoring that is being conducted by the MPCA and MDA. However, because ground water is often a confusing subject to non-hydrogeologists, this report also contains sufficient background and historical information to provide the reader with perspective on both the ground water monitoring project design and the ground water monitoring results.

Map-based and statistical formats are used in the report to display the results of MPCA and MDA ground water monitoring data collected in 2004 and 2005. Other sources of information concerning the monitored contaminants in ground water in Minnesota and nationally are also reviewed, and a brief section on ground water quantity is included. The report concludes with considerations for future monitoring of the state's ground water.

A Brief History of Ground Water in Minnesota

Early Knowledge

The first written knowledge of Minnesota's ground water resources was recorded during exploration of Minnesota's mineral wealth along the North Shore and in the Iron Range during the late 1800s and early 1900s, and later, during investigation of the extensive Paleozoic strata in south and southeastern Minnesota in the early to mid-1900s. The information consisted mostly of observations included in the geologists' field reports (Sims and Morey, 1972).

It was not until the early 1960s that the Minnesota Geological Survey (MGS) began to investigate Minnesota's bedrock aquifers, beginning with aquifers in urban areas. Also during the 1960s, the Minnesota Department of Natural Resources (DNR) collaborated with the United States Geological Survey (USGS) on two studies that focused on ground water supply issues with some attention to ground water quality.

The 1965 DNR-USGS study (Maderak, 1965) compared ground water quality in bedrock aquifers of the Twin Cities between 1899 and 1963. The comparison was made using results from analysis of a limited number of ground water samples for major ions and inorganic parameters. The study concluded that no significant change in water quality had occurred over the 64-year time period, despite the drilling of many new wells and increased withdrawals from the aquifers. The study concluded by cautioning that, "The quality of water in an aquifer can change because of variations in the quality of surface water entering recharge areas and because of large withdrawals that may cause (ground) water of different quality to migrate into the aquifer." This concern remains relevant today.

In 1972, the MGS published a comprehensive survey on the geology of Minnesota on the occasion of its 100th anniversary (Sims and Morey, 1972). The survey noted that "…reliable data on the…areal extent of bedrock aquifers are generally only available for the major urban centers. However, even in the urban areas specific information on the physical and chemical environments of the geologic units generally is poorly known."

The Environmental Era

Concern about the environment in the early 1970s led to enactment of hard-hitting federal legislation designed to protect and improve the nation's air, water and land. The legislation included the Clean Water Act in 1972, the Resource Conservation and Recovery Act (RCRA) in 1976 and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), better known as Superfund, in 1980. In 1983 Minnesota passed its own version of the Superfund program known as "MERLA" (Minnesota Environmental Response and Liability Act) to clean up hazardous waste sites not enrolled in the federal program.

> *During the 1970s and 1980s, the science of ground water monitoring was rapidly evolving. New methods of well construction and installation and new ways of collecting samples were constantly being developed to obtain higher quality, more representative ground water samples. At the same time, analytical laboratories were refining their procedures to develop more sensitive and cost effective techniques for identifying contaminants in water and soil samples.*

As RCRA and CERCLA were being implemented, the MPCA undertook its first ambient ground water monitoring project. The MPCA worked cooperatively with the USGS to prepare a ground water monitoring plan, and in 1978 the MPCA collected the first ground water samples from water supply wells and some springs for analysis of general chemistry, including major cations and anions (Hult, 1979). In 1983, the MPCA ground water monitoring plan was expanded to include analysis for VOCs.

In 1985, the MDA and MDH conducted a survey demonstrating that pesticides and nitrate-nitrogen applied to crops were showing up in ground water and in domestic water supply wells (MDA, 2006a). Consequently, in 1987, MDA began monitoring Minnesota ground water for pesticides.

The results from the MPCA's early ground water monitoring efforts were compiled and published on a number of occasions (MPCA, 1987). However, analysis of the monitoring results was limited by inconsistencies in the data resulting from technical changes, shifting agency priorities and inadequate funding during the life of the program.

Minnesota's 1989 Ground Water Protection Act

By the mid-1980s the presence of ground water contamination around the state and its considerable impact on those affected was becoming well known. Sites such as the Twin Cities Army Ammunition Plant (TCAAP) in Arden Hills served as potent illustrations of the dangers posed by poorly managed hazardous wastes, as residents in communities downgradient of TCAAP saw their private and municipal water supply wells become contaminated in sequence by ground water flowing from the site (Figure 2).

In 1988, a severe drought occurred in Minnesota. The drought created havoc for water-dependent industries such as agriculture, public utilities, forestry and tourism as well as for state residents, many of whom experienced dry wells and dried up lakeshore at their summer cabins.

The difficulties experienced during the drought and growing concern about human impact on ground water quality led the Minnesota Legislature to pass the 1989 Groundwater Protection Act (GWPA) (Helland, 2001). The GWPA resulted in substantive changes and additions to Minnesota's existing body of ground water law and included creation of a Legislative Water Commission to monitor and encourage legislative activity relating to the Act's provisions. The GWPA was viewed as "…a very strong state effort and accolades were received nationwide" (Helland, 2001).

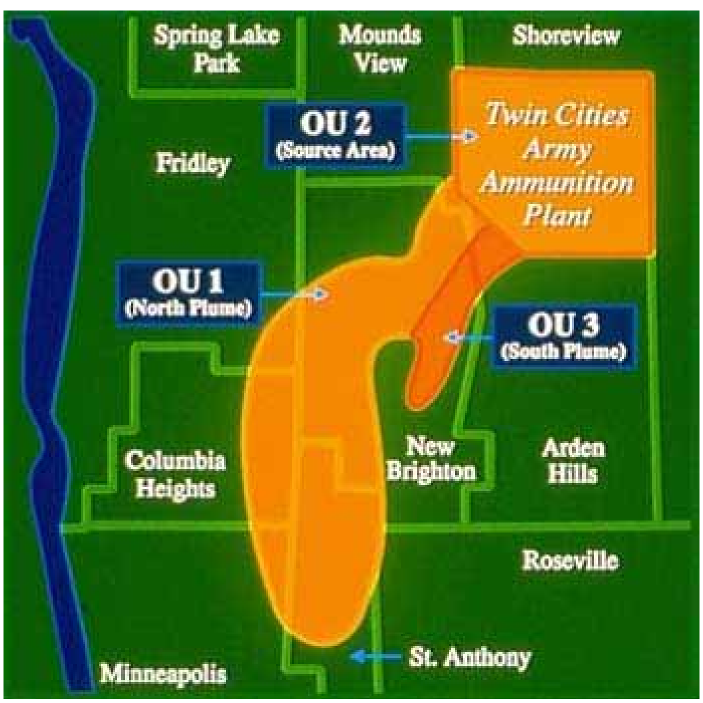


Figure 2: The TCAAP Superfund site in Arden Hills and its Ground Water Contaminant Plume *(source: MPCA, 2006a)*

In 1989, the Legislative Commission on Minnesota Resources (LCMR) awarded the MPCA with a grant to re-design its ambient ground water monitoring activities. The LCMR recognized that Minnesota did not possess quantitative information about the baseline water quality conditions in the State's principal aquifers, without which there was no foundation for developing and evaluating ground water management policies (Myers et. al., 1992).

The LCMR grant resulted in an ambitious ground water monitoring project known as the Baseline Study. The Baseline Study had the following goals:

- establish the ambient or "background" ground water quality in Minnesota's principal aquifers using a statistics-based, randomized sampling design to establish median concentrations for various chemical parameters

- quantify the spatial distribution of water quality parameters in the aquifers
- identify potential ground water quality concerns

The first two years of the project were consumed with developing the project design, setting up field protocols and obtaining the necessary permissions to access and sample wells. Then, between 1992 and 1996 the MPCA collected 954 ground water samples from 954 domestic water supply wells located in 86 of 87 Minnesota counties (no wells were sampled in Lake of the Woods County) (Figure 3). The ground water samples were analyzed for a wide set of analytes, including major cations and anions, trace inorganics, VOCs, total organic carbon, and total and dissolved solids.

The results from the Baseline Study were published in 1998 (MPCA, 1998a), and remain an unrivaled source of information about the ambient ground water quality in Minnesota's principal aquifers. The Baseline Study is distinguished by its comprehensiveness, its statistics-based design, and its consistently implemented methodology, all of which reflect steady funding for the duration of the project.

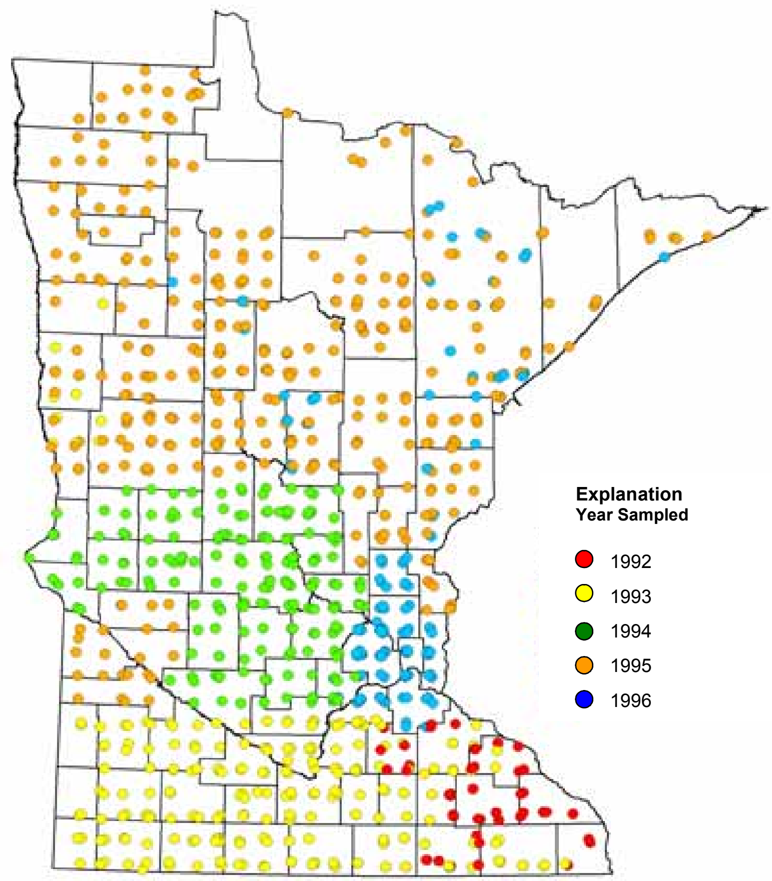


Figure 3. Sampling Grid for the MPCA Baseline Study *(source: MPCA 1998a)*

In the 1990s, Minnesota's economy began to decline, leading to budgetary restraint and cutbacks. To cut costs, the Legislative Water Commission was abolished by the Minnesota Legislature in 1995. In 2001, the MPCA discontinued its ambient ground water monitoring activities, which since about 1996 had focused on studying the impacts of human activity on ground water quality.

The MPCA partially restored funding for its ambient ground water monitoring activities in 2003. The MPCA also began developing an integrated strategy for conducting statewide ambient ground water quality monitoring in collaboration with the MDA and the MDH. On February 18, 2004, the commissioners of each agency signed a MOA stating their intent to carry out the integrated monitoring strategy and to work cooperatively with the other state agencies (MPCA, 2004). The MOA provides for annual review and modification of the agencies' joint monitoring activities, with a five-year timeline for updating the MOA.

Foundation for Current Statewide Ground Water Quality Monitoring Projects

MPCA and MDA Condition Monitoring Projects

The MPCA, MDA, and MDH each have important statutory responsibilities in protecting the quality of Minnesota's ground water, but only the MPCA and the MDA conduct statewide ambient ground water quality monitoring. The MDH conducts ground water monitoring for the purpose of regulating public and private water supply wells and public water supplies, and evaluating the risk to human health from contaminants in ground water.

The purpose of ambient monitoring is to monitor the status or condition of ground water quality and to identify trends in ground water quality over time.

For simplicity, in this report the current statewide ambient ground water quality monitoring projects of the MPCA and the MDA will be referred to as the MPCA and MDA condition monitoring projects.

Fundamental Elements

The MPCA condition monitoring project is designed to build on the results of the Baseline Study and to meet the MPCA's statutory charge to provide information about the statewide impact of hazardous chemicals and other non-agricultural chemicals on ground water resources. The MDA condition monitoring project complements the MPCA condition monitoring project by providing information on the impact of the routine use of pesticides and nutrients on ground water resources (MPCA, 2004).

The MPCA and MDA condition monitoring projects each monitor ground water quality in Minnesota's vulnerable aquifers. Vulnerable aquifers are near-surface aquifers that are most likely to be contaminated by pollutants at the land surface. By monitoring ground water in vulnerable aquifers, the likelihood that human impacts on ground water quality will be detected within a reasonable time frame increases. Deeper aquifers with longer flow paths generally do not reveal changes in ambient ground water quality for many years (Figure 4).

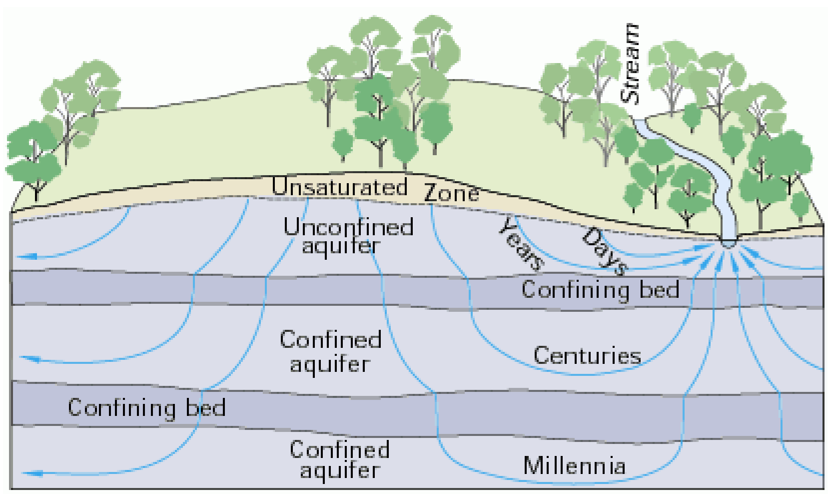


Figure 4. Ground Water Flow Paths and Times of Travel through an Aquifer System *(source: Winter, et. al., 1998)*

In Minnesota, aquifers that meet the designation of "vulnerable" include water table or unconfined aquifers (Figure 4), and the Prairie du Chien, Jordan and Galena bedrock aquifers at locations where there is no significant protective soil cover overlying the bedrock. The water table aquifers are typically composed of unconsolidated sand and gravel that was deposited by glacial activity in recent geologic time; these near surface aquifers occur throughout the state. The Prairie du Chien, Jordan, and Galena bedrock aquifers are considered vulnerable primarily in the Twins Cities and southeast Minnesota, where they outcrop at or near the ground surface. The locations of Minnesota's vulnerable aquifers are shown in Figure 5.

Sampling Design

The MPCA and MDA condition monitoring projects have similar goals and objectives but for a variety of reasons the project designs are different.

The MPCA condition monitoring project targets non-agricultural areas of the state where existing wells are generally plentiful. Using the MGS-MDH's County Well Index database of registered wells, the MPCA has identified more than 10,000 candidate wells that meet the project criteria of: 1) being located in a land use that is not agricultural, and 2) being located in a vulnerable aquifer. From this pool of candidate wells, the MPCA randomly selects about 100 wells each year to be sampled for the condition monitoring project.

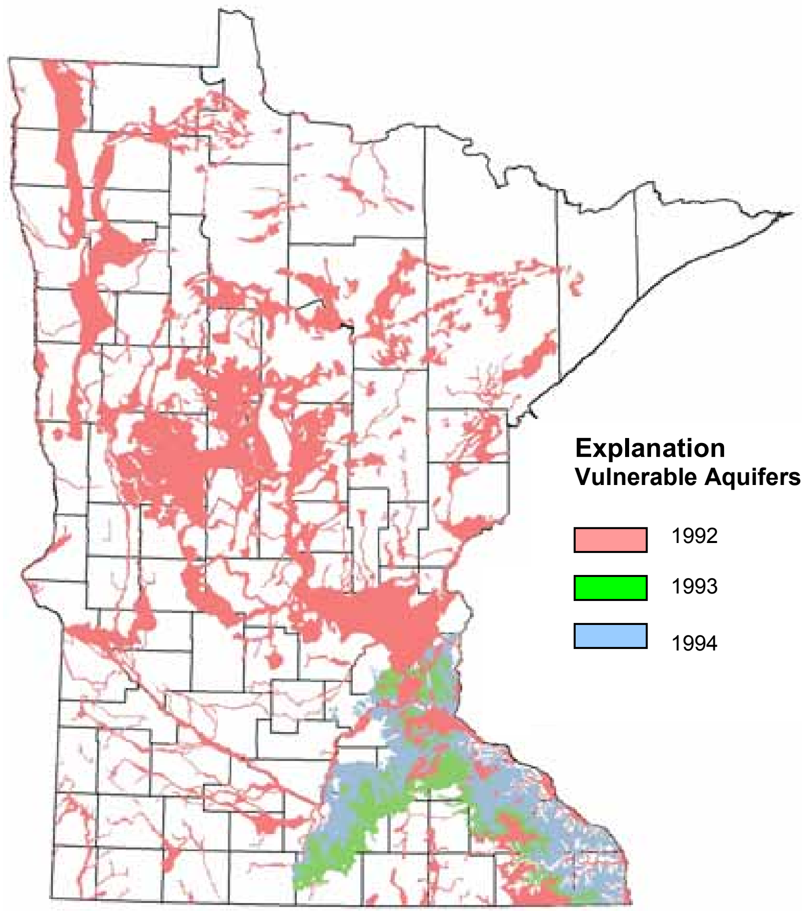


Figure 5. Minnesota's Vulnerable Aquifers
(source: MPCA, 2006b)

The long-term plan for the MPCA condition monitoring project is to reduce the number of wells sampled each year from 100 to about 50 wells. Using the results of the condition monitoring project, the MPCA is constructing a trends monitoring network that will involve repeated sampling of wells that are impacted above a specified concentration. Over the next few years, the trends monitoring network is expected to grow and become the focal point of the MPCA's overall ground water quality monitoring effort, with the condition monitoring project described in this report declining to maintenance level by 2010. The MPCA is also in the early stages of establishing a changing land use monitoring network. More information about the MPCA trends and changing land use monitoring networks is available in the MPCA 2006 sampling plan (MPCA, 2006c).

With its agricultural focus, the MDA cannot make use of existing wells the way the MPCA does. The MDA condition monitoring project uses monitoring wells that are designed and installed by MDA specifically for the purpose of monitoring the impact of agricultural chemicals on ground water quality and evaluating the effectiveness of best management practices (BMPs) employed by farmers to reduce agricultural chemical impacts. MDA selects the monitoring well locations within targeted regions using a randomized grid to retain a random distribution of sampling points.

The MDA condition monitoring project is made up of several individual projects that originated for specific purposes. The oldest and largest is the Central Sands monitoring project, which began in 1999 (MDA, 2006a). MDA defines the Central Sands region to be 12 central Minnesota counties (Becker, Benton, Hubbard, Kandiyohi, Morrison, Otter Tail, Pope, Stearns, Todd, Wadena, Sherburne, and Wright) that share the characteristic of having a sandy subsurface and a shallow water table. Together, these characteristics make the Central Sands region especially vulnerable to pollutants at the land surface. As of 2005, MDA had installed 85 monitoring wells in ten Central Sands counties (all but Sherburne and Wright counties).

In 2004, the MDA began developing its Regional Monitoring program (MDA, 2006a). The purpose of the Regional Monitoring program is to provide ground water quality data from parts of the state outside the Central Sands region for comparison purposes. The MDA plans to install between seven and ten monitoring wells in each primary agricultural region of Minnesota, which by MDA's designation is all but northeast Minnesota and the Twin Cities. As of 2005, four of the six primary agricultural regions had met this goal.

The remaining two components of the MDA condition monitoring project include the monitoring of springs in southeast Minnesota, and the urban pesticide monitoring project (MDA, 2006a).

MDA has monitored six springs in southeast Minnesota since 2003. The springs provide direct access to ground water, which in this part of the state flows erratically through fractures, sinkholes and other karst features that are prominent in the fractured limestone bedrock (Figure 5). The urban pesticide monitoring project is a cooperative sampling effort in which the MDA selects wells in urban or suburban locations for pesticide analysis from the MPCA condition monitoring project's set of randomly selected wells. The MPCA collects the samples and provides them to MDA for analysis.

Sampling Frequency and Sample Analysis

The MPCA and MDA condition monitoring projects differ in the frequency of sample collection. The MPCA collects one ground water sample from each well that is randomly selected for that year's condition monitoring project. The ground water samples are submitted to the MDH laboratory for analysis of chloride, nitrate, and VOCs.

For MDA's Central Sands project, ground water samples are collected on a quarterly basis. Each quarter samples are collected from one of three randomly selected groups consisting of 28 to 29 wells, so that over a period of three quarters each well in the 85 well network is sampled once. Sampling of the three groups rotates regularly through the year (MDA, 2006a and Zabel, 2007).

For MDA's Regional Monitoring project, the wells are sampled once annually in September. The springs in southeast Minnesota are sampled multiple times during the growing season (MDA, 2006a). The urban pesticide monitoring project involves the collection of one sample annually as part of the MPCA condition monitoring project.

The ground water samples collected for the MDA condition monitoring project are analyzed for nitrate and pesticides in the MDA laboratory.

Monitoring Wells versus Domestic Wells

The MPCA and MDA each collect ground water samples from domestic wells and monitoring wells as part of their condition monitoring projects. Because the well type can affect ground water quality results, it is important to be aware of how the wells differ.

Monitoring wells are installed for the sole purpose of monitoring ground water quality. The intake, or screen, of a water table monitoring well is generally less than 15 feet long and is installed to intersect the water table interface, where surface water infiltrating from the ground surface meets the zone of saturation (i.e., the water table) (Figure 6). Ground water samples collected from water table monitoring wells are very sensitive to ground water quality changes caused by infiltrating recharge. This makes water table monitoring wells ideal for evaluating impacts to ground water quality caused by the overlying land use.

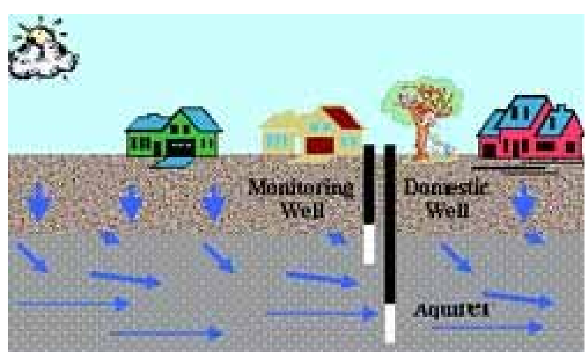


Figure 6. Cross-Sectional View of a Monitoring Well and a Domestic Well in a Water Table Aquifer *(source: MPCA, 2006b)*

Domestic wells, on the other hand, are installed to supply water for drinking and to operate homes and small businesses. The intake or screen for a domestic well is generally installed tens or more feet below the water table and may be tens or more feet in length to maximize the volume of water that can be extracted from the aquifer (Figure 6). Because the intake of a domestic well is separated by distance and time of travel from the water table, ground water samples collected from domestic wells tend to be insulated from quality changes occurring at the water table. Consequently, domestic wells provide a more integrated picture of ambient water quality in the aquifer.

The existing wells sampled by the MPCA condition monitoring project consist of a mix of domestic and monitoring wells, but domestic wells dominate. The MDA condition monitoring project uses monitoring wells almost exclusively. The exceptions are the springs that are sampled in southeast Minnesota and the wells sampled for urban pesticides by the MPCA condition monitoring project.

Handling of MPCA and MDA Ground Water Quality Data

This report reviews ground water quality data collected for the MPCA and MDA condition monitoring projects during the 2004 and 2005 field seasons. Data from the 2006 field season was not available from either the MPCA or MDA early enough to include in this report.

In the next section, the 2004 and 2005 results for the MPCA and MDA condition monitoring projects are displayed geographically by well location. To do this, data sets including wells with more than one analytical result for 2004 and 2005 were averaged to obtain a single representative value to plot. For example, the monitoring wells that are part of the MDA Central Sands project are sampled quarterly on a random basis, and individual wells may have more than one analytical result in a year. To obtain a single result for each well sampled during the two years represented in this report, the following steps were taken: first, the results for individual wells sampled more than once within a year were averaged together; then, the results for the well for each year (i.e., 2004 and 2005) were averaged together to obtain the result for the individual well that is displayed.

The median concentrations for the various data sets that are provided in the report are determined from the average values calculated for the wells as described above.

The Quality of Minnesota's Ground Water

Chloride in Minnesota's Ground Water

About Chloride

Chloride is a key element in seawater, in atmospheric moisture and in the mineral halite (also known as salt or sodium chloride). It is also a major ion in ground water, a status it shares with the sodium (Na^{+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), bicarbonate (HCO_3^{-}) and sulfate (SO_4^{2-}) ions. Together, the total concentration of these six ions normally comprises more than 90 percent of the total dissolved solids (TDS) in ground water, regardless of whether the water is dilute or highly saline (Freeze and Cherry, 1979).

In most areas of Minnesota, good quality ground water containing low concentrations of chloride and TDS is available (Winter, T.C., 1974). However in extreme west, northwest and southwest Minnesota, ground water quality is more variable. In these areas, chloride and TDS concentrations in ground water can be very high, even to the extreme of being saline. The elevated mineral content of the ground water is associated with the Cretaceous-age geologic formations that occur in these parts of the state.

The median concentration of chloride in all Minnesota aquifers as measured by the MPCA Baseline Study is 2.4 milligrams per liter (mg/L) or parts per million (MPCA, 1999). Chloride's generally low background concentration in Minnesota ground water and its prevalence in effluent from individual and municipal septic systems, municipal landfills, agricultural chemicals, animal waste from livestock operations, and road de-icing agents (Panno et.al., 2006) make it a useful indicator of human-induced ground water quality changes.

There is no human health-based drinking water standard for chloride, but U. S. Environmental Protection Agency (USEPA) has established a Secondary Maximum Contaminant Level for chloride of 250 mg/L for taste.

Chloride Results

Chloride concentrations measured in ground water by the MPCA condition monitoring project in 2004 and 2005 are shown in Figure 7. The ground water samples collected from most wells were reported to contain chloride at concentrations of less than 25 mg/L. However, in Minnesota's largest urban areas including Minneapolis-St. Paul (the Twin Cities), St. Cloud (to the northwest), and Rochester (to the southeast) there is a higher occurrence of ground water with clearly impacted (between 25 and 150 mg/L chloride) and elevated (greater than 150 mg/L) concentrations of chloride. This result is consistent with urban land use. The median chloride concentration for the complete set of data is 21 mg/L.

When the chloride results are separated by the type of well they were collected from (i.e., monitoring or domestic), there is a clear distinction in the results.

Figure 8 shows that a higher incidence of clearly impacted and elevated chloride concentrations occurs in the ground water samples collected from monitoring wells in comparison to domestic wells. This is also reflected in the median chloride concentration for each data set: 53 mg/L for the monitoring wells and 12 mg/L for the domestic wells.

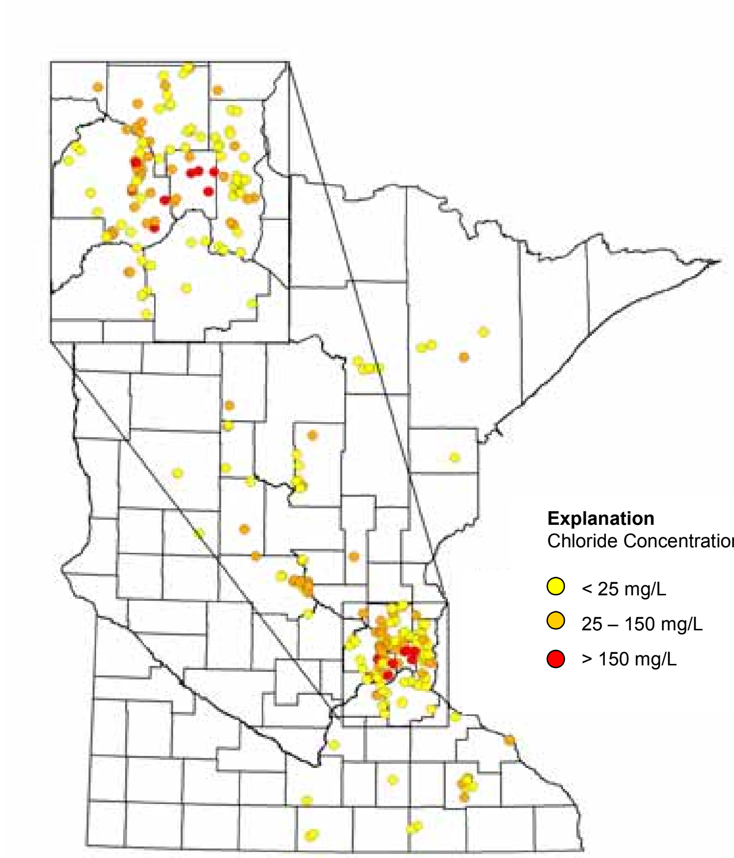
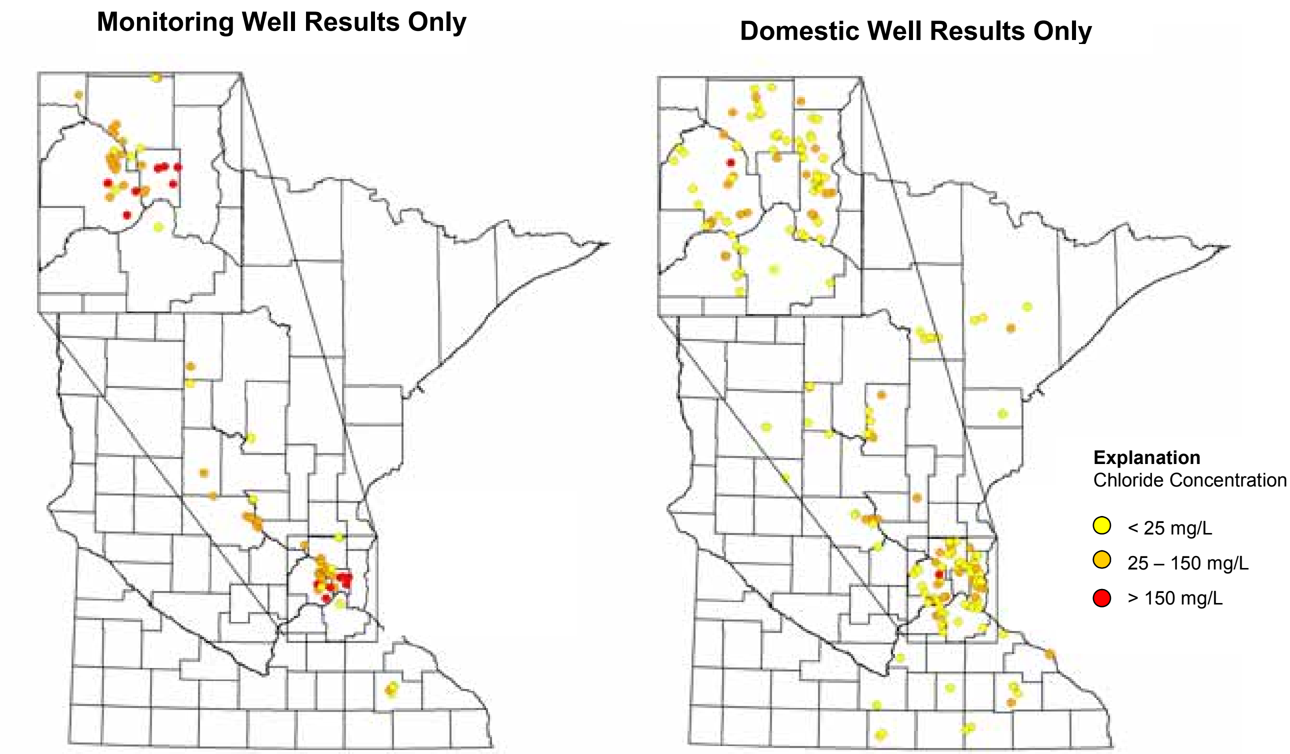


Figure 7. Chloride Concentrations in Minnesota Ground Water

Land use differences do not appear to be a major factor in the different median chloride concentrations, since the monitoring wells and the domestic wells have a similar geographic distribution around the state and in the Twin Cities that is proportional to the number of wells in each group (Figure 8). The higher median chloride concentration obtained for the monitoring well samples likely reflects the monitoring wells' greater sensitivity to quality changes caused by infiltrating recharge relative to the domestic wells.



The median chloride concentration for 67 monitoring well samples is 53 mg/L.

The median chloride concentration for 126 domestic well samples is 12 mg/L.

Figure 8. Chloride Concentrations in Ground Water Collected from Monitoring Wells versus Domestic Wells

Chloride Concentrations in Ground Water Over Time

Identifying trends in ground water quality over a large geographic area such as the state of Minnesota is an immense task. The primary challenges are acquiring data from a sufficient number of sampling locations that will remain comparable over time, and maintaining funding to continue the program over the long term. The MPCA's reinstated condition monitoring project is too new to support an evaluation of trends on a statewide basis.

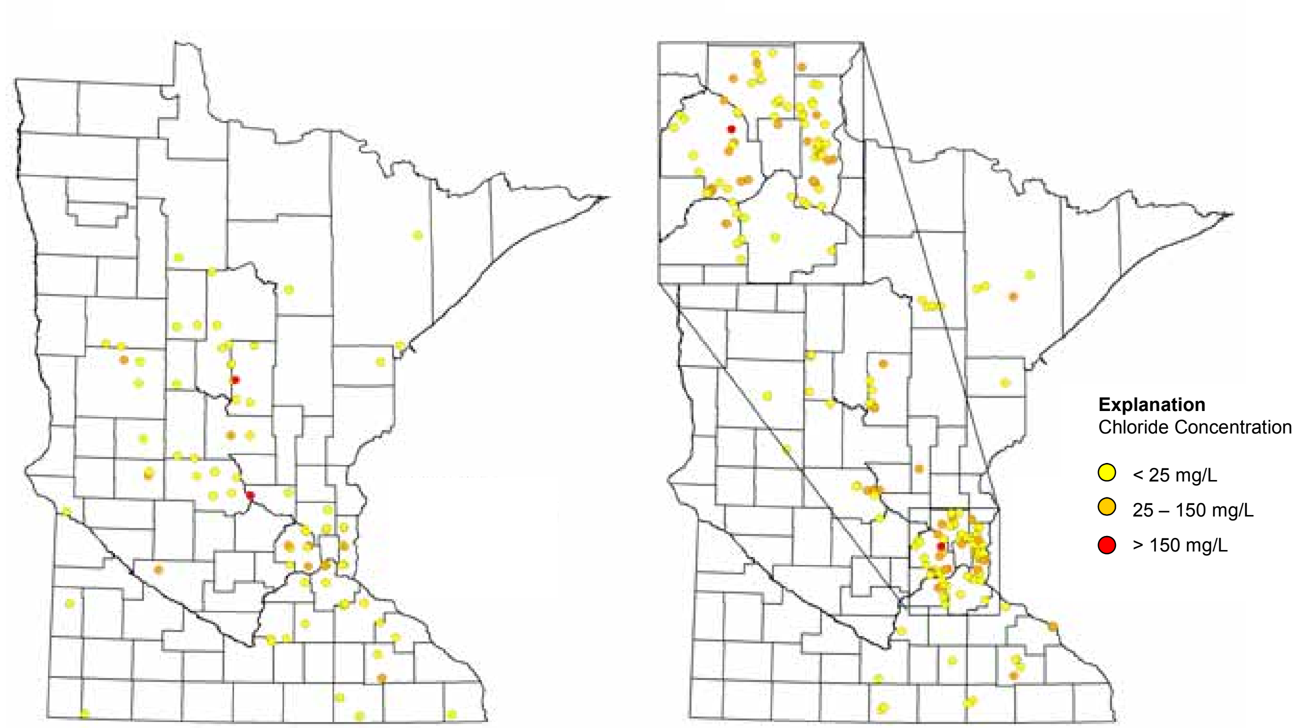
However, an attempt was made to obtain a general indication of ambient ground water quality over time using results from the MPCA Baseline Study and the MPCA condition monitoring project. Both projects include ground water quality data collected from domestic wells installed in vulnerable aquifers, and both projects used the same protocols and types of equipment to collect samples from the wells. The projects were conducted between about 1995 and 2005, or roughly ten years apart.

Figure 9 displays the results for chloride obtained by each MPCA monitoring project. Visually, the data appear similar in terms of the frequency that chloride is detected in each concentration range. However, the median chloride concentration for the condition monitoring project data (12 mg/L) is twice what it is for the earlier Baseline Study data (4.9 mg/L). While this result suggests that chloride concentrations in Minnesota ground water have increased over time, it can be seen in Figure 9 that the condition monitoring project sampled a higher proportion of urban wells compared to the Baseline Study. Because of this, no conclusion can be made concerning the higher median chloride concentration obtained from the condition monitoring project data.

Keep in mind that domestic wells provided the ground water quality data that was used in this comparison. As has been noted, domestic wells are not as likely to show changes in ground water quality over short time frames because of their comparatively deeper construction relative to monitoring wells.

MPCA Baseline Study
1992-1996

MPCA condition monitoring project
2004-2005



The median chloride concentration for 83 domestic well samples is 4.9 mg/L.

The median chloride concentration for 126 domestic well samples is 12 mg/L.

Figure 9. Chloride Concentrations in Minnesota Ground Water Over Time

Chloride Concentrations in Ground Water Beneath Different Land Uses

Between 1996 and 2001, the MPCA conducted several ground water studies to evaluate how land use impacts ground water quality. One of the studies focused on ground water quality beneath different land uses in the rapidly developing area around St. Cloud in east central Minnesota. This area relies heavily on the underlying Anoka Sand Plain Aquifer, a vulnerable aquifer, for its drinking water (Trojan et. al., 2003).

For the study, 23 monitoring wells were installed in areas with the following land uses: non-developed land, irrigated and non-irrigated agriculture, sewered and non-sewered residential development, and commercial land use. Ground water samples were collected from the wells on a quarterly basis for a period of four years between 1997 and 2000. The results of the study showed distinct differences in ground water quality beneath the different land uses. Chloride concentrations were elevated by ten to almost 100 times beneath all land uses compared to non-developed land, where the median concentration of chloride in the ground water was 1.76 mg/L (Trojan et. al. 2003). The highest chloride concentrations were obtained in ground water samples collected beneath residential areas. The chloride results from the study are plotted in Figure 10.

Changes in ground water quality caused by different land uses such as identified in the study described above are not detectable on the scale of a statewide condition monitoring project. To better address the influence of land use and other phenomena on ground water quality, the MPCA is creating a separate trends monitoring network and a supplemental changing land use monitoring network, as described in the previous section. Ground water quality data from the MPCA trends network will be analyzed following collection and qualification of a minimum of three years of data.

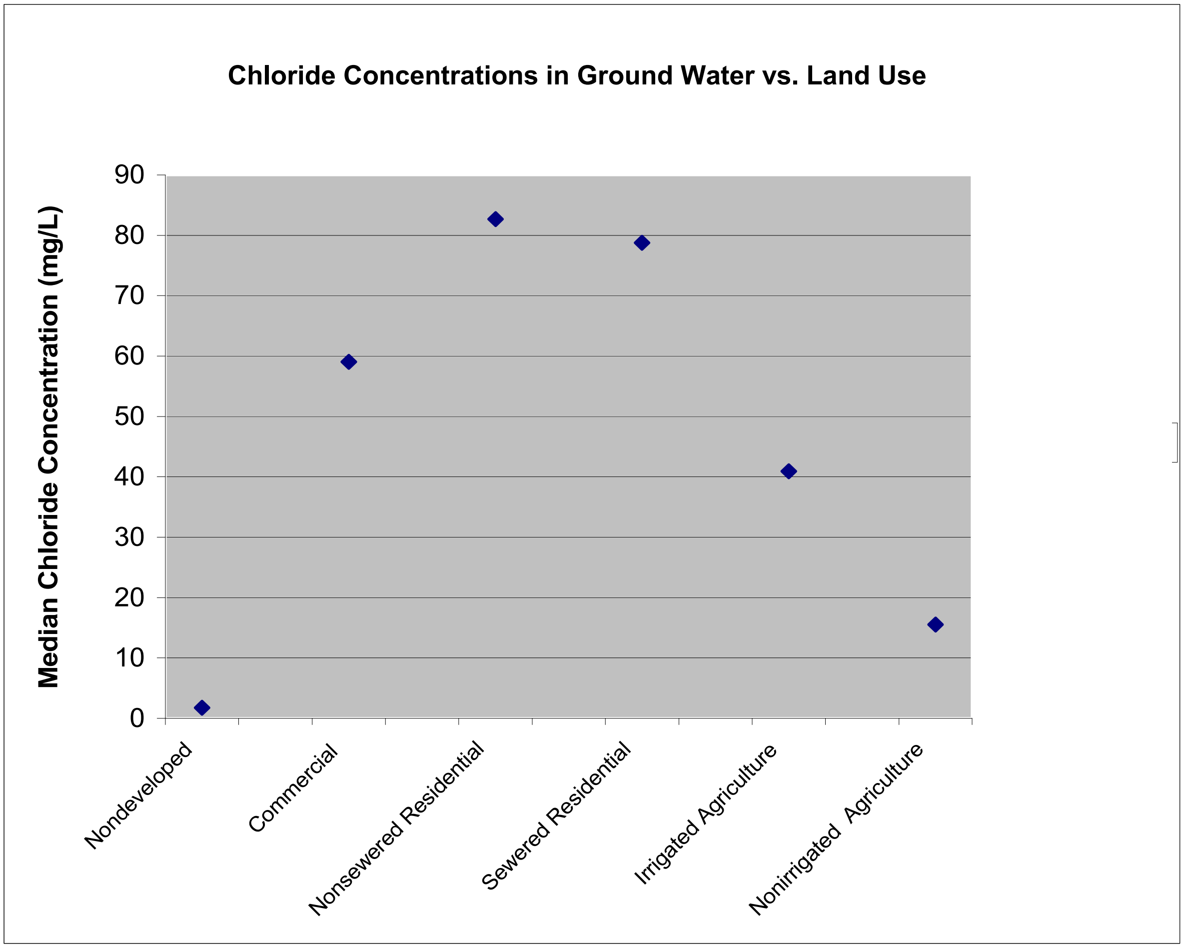


Figure 10. Chloride Concentrations in Ground Water Beneath Different Land Uses, Anoka Sand Plain Aquifer *(source: Trojan et. al., 2003)*

Chloride in Ground Water and Surface Water: National Perspective

A number of recently published studies have documented the dramatic impact to ground water quality from the use of road salt in the snow belt of the United States and Canada. In Illinois and other states, municipal and private water supplies have been adversely affected by elevated chloride concentrations in ground water (Bester et. al., 2005). This can be a serious problem because the removal of chloride from drinking water is generally possible only through desalination, a very expensive process (Panno et. al., 2006).

Figure 11. Synopsis of a Numerical Investigation of Road Salt Impact on an Urban Wellfield *(Bester et. al., 2005)*

A chloride-impacted municipal well field in southern Ontario was evaluated to assess the role of road salt in the overall chloride contamination problem (Bester et. al, 2006). The affected municipality draws its drinking water from a glacially-derived shallow aquifer system similar to aquifers in many areas of Minnesota. Numerical modeling showed that the aquifer system contained a large mass of chloride that accumulated during several decades of road salt use. Well head concentrations of chloride were less than what was actually contained in the aquifer, because of dilution by non-impacted ground water that occurs during pumping. The study results indicate that residual chloride may take decades to flush out of the aquifer system, even if road salt use is discontinued.

In Minnesota, the effects of road salt on ground water quality are relatively unexplored. However, the effects of road salt on surface water quality and aquatic life are evident in some locations. Minnesota's 2006 List of Impaired Surface Waters includes four stream reaches that are impaired by chloride, three of which are in the Twin Cities metropolitan area (MPCA, 2006d).

Nitrate in Minnesota's Ground Water

About Nitrate

Nitrogen makes up 78 percent of the atmosphere by volume as nitrogen gas (N_2) and is a large constituent of living plants and animals in organic form (Organic N). In ground water, nitrogen is primarily present in the form of nitrate (represented chemically as NO_3^-) and occurs naturally at low concentrations of less than 1.0 mg/L (MDH, 1998).

Sources of nitrate to ground water from human activity are abundant. They include nitrous oxides from the combustion of coal and gas; animal manure and other fertilizers used on agricultural crops; individual septic treatments systems (ISTS) used in communities and rural areas without wastewater treatment systems; and fertilizers used at residences and commercially. With this array of sources, it is not surprising that nitrate is one of the most common contaminants of ground water in Minnesota.

Nitrate's behavior in the environment is complicated by its geochemical sensitivity. In oxygenated ground water, nitrate is stable and other forms of nitrogen such as ammonia and nitrite tend to be converted to nitrate. In oxygen-poor or geochemically-reducing ground water, nitrate is often denitrified to nitrogen gas, a process that can reduce or even eliminate the negative impact of nitrate on ground water quality. Because of denitrification, aquifers in locations where sources of nitrate to ground water are abundant do not always develop elevated nitrate concentrations.

Nitrate concentrations in ground water are monitored by both the MPCA and MDA condition monitoring programs because sources of nitrate exist in both rural and urban settings.

The MPCA's involvement with nitrate contamination includes providing standards and a framework for local administration of ISTS programs, and administration of the feedlot and stormwater programs. The MPCA has also conducted several studies of nitrate concentrations in ground water relative to non-agricultural land uses. MDA and MDH work individually and collaboratively on a number of fronts to address nitrate contamination and assist state and local efforts aimed at protecting drinking water supplies and preventing further ground water contamination.

A Health Risk Limit (HRL) of 10 mg/L for nitrate in drinking water has been established by the MDH. The HRL is based on the toxic effect of nitrate on infants less than six months old. Elevated nitrate concentrations in drinking water can also be harmful to livestock.

MDH offers the following classification system as a guide for evaluating human impact on nitrate concentrations in ground water (MDH, 1998):

- Background – Less than 1.0 mg/L
- Transitional – 1.0 mg/L to less than 3.0 mg/L
- Elevated – 3.0 mg/L to less than 10.0 mg/L
- Exceeding standards – 10 mg/L and higher

The 1989 Minnesota Groundwater Protection Act directed the MDH to develop HRLs for substances found to degrade ground water through ground water quality monitoring.

A HRL is the concentration of a ground water contaminant, or a mixture of contaminants, that can be safely consumed daily for a lifetime. A HRL is expressed as a concentration in micrograms per liter, or calculated as a "hazard index." The MDH develops the HRLs using scientific risk assessment methods and data (MDH, 2006a).

In this report, the nitrate results from the MPCA condition monitoring project are reviewed first. Then, the nitrate results from the MDA and MPCA condition monitoring projects are combined to provide a more comprehensive view of the condition of Minnesota's ground water with respect to nitrate.

NOTE: the detection limits for nitrate analysis have varied over time and by laboratory, ranging from 0.5 mg/L for the MPCA Baseline Study, to 0.4 mg/L for the MDA condition monitoring project, to 0.05 mg/L for the MPCA condition monitoring project. For the purpose of this report, all results less than 0.5 mg/L are considered non-detectable.

Nitrate Results

Nitrate concentrations measured by the MPCA condition monitoring project in 2004 and 2005 are shown in Figure 12. The ground water samples collected from most wells were reported to contain nitrate at concentrations of less than 2.5 mg/L. Elevated nitrate concentrations between 2.5 and 10 mg/L were also common, especially in southeast Minnesota, in the east half of the Twin Cities metropolitan area, and in Central Minnesota. The median nitrate concentration for the MPCA condition monitoring project data is less than 0.5 mg/L or non-detectable.

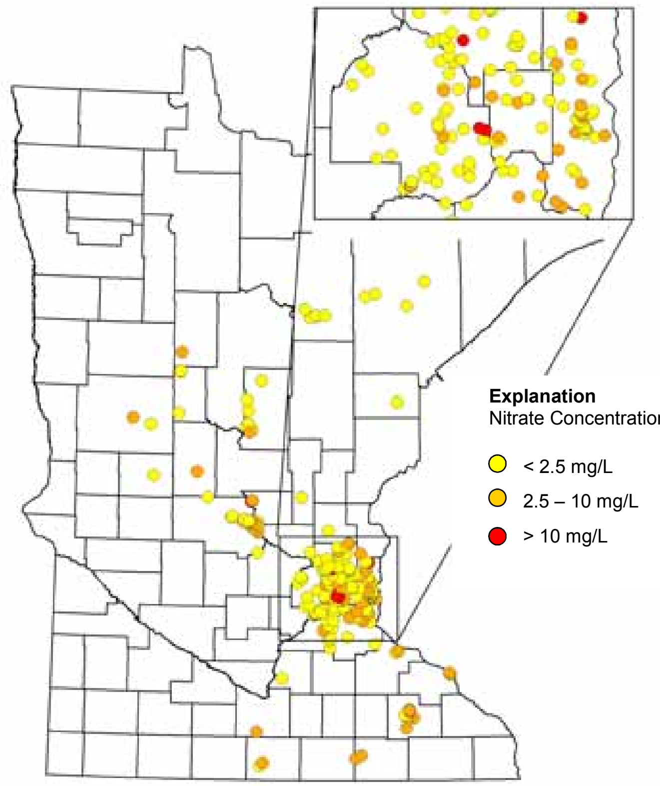
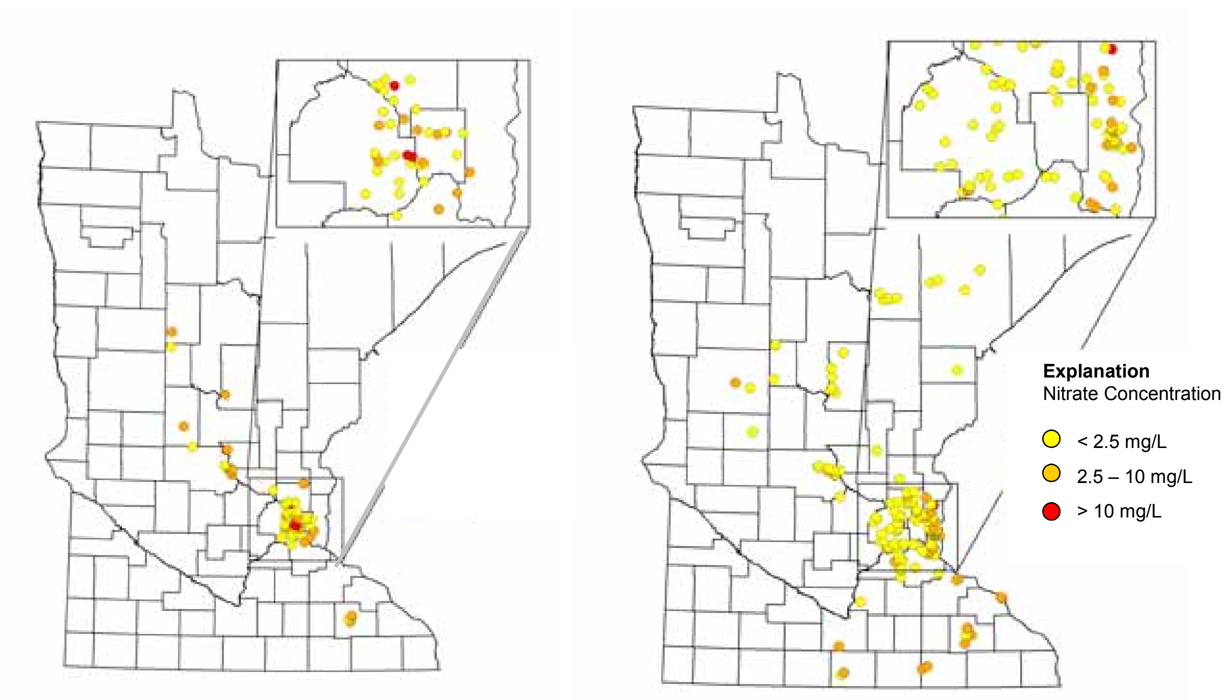


Figure 12. Nitrate Concentrations in Minnesota Ground Water

When the nitrate results are separated by the type of well they were collected from, there is a distinction in the results. Figure 13 shows that samples collected from the monitoring wells have a proportionately higher number of elevated nitrate concentrations compared to samples collected from the domestic wells. This is supported by the median nitrate concentrations of 2.5 mg/L for the monitoring wells and less than 0.5 mg/L (non-detectable) for the domestic wells. The higher median nitrate concentration for the monitoring wells likely reflects their shallower construction and urban sources of nitrate to ground water (i.e., more monitoring wells are located in urban areas than in rural areas). Denitrification may be a factor in the lower median nitrate concentration obtained for the deeper domestic wells, since the potential for denitrication increases with depth, given the appropriate aquifer geochemistry (MPCA and Met Council, 2002).

Interestingly, the nitrate concentrations for the domestic wells in the Twin Cities metropolitan area were mostly less than 2.5 mg/L in the western and central portions of the Twin Cities metropolitan area, but in the eastern portion several domestic wells had elevated (2.5 to 10 mg/L) nitrate concentrations (see map inset, right side of Figure 13). A study conducted by the MPCA and Met Council in 2002 to assess ground water quality in Twin Cities communities served by ISTS showed that many of the aquifers in Washington County in the eastern Twin Cities are sensitive to nitrate; in other words, the aquifer geochemistry is such that denitrification does not occur (MPCA and Met Council, 2002). The elevated nitrate concentrations observed in these wells are likely evidence of Washington County's agricultural heritage and predominantly large lot residential development serviced by ISTS.

Monitoring Well Results Only | **Domestic Well Results Only**



The median nitrate concentration for 75 monitoring well samples is 2.5 mg/L.

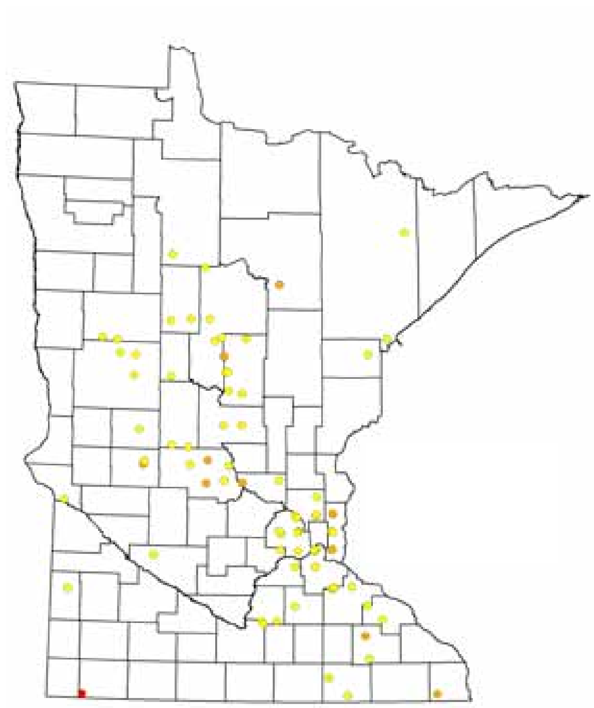
The median nitrate concentration for 126 domestic well samples is <0.5 mg/L.

Figure 13. Nitrate Concentrations in Ground Water Collected from Monitoring Wells versus Domestic Wells

Nitrate Concentrations in Ground Water Over Time

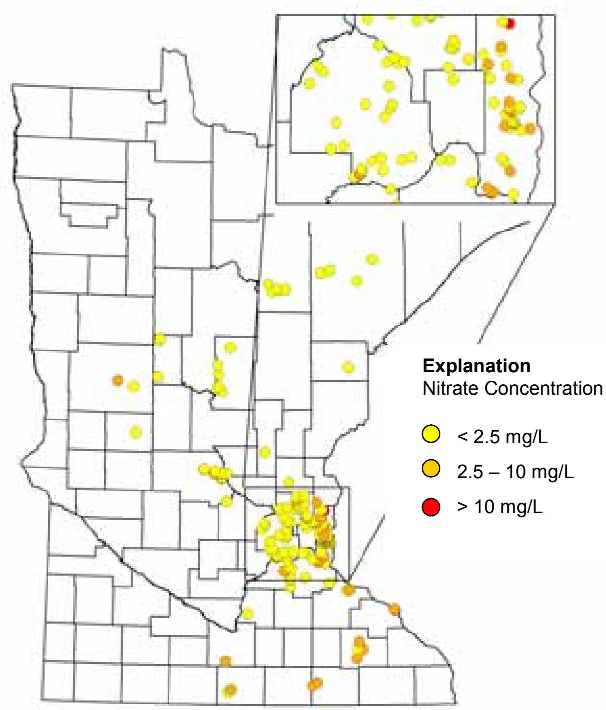
The nitrate results for domestic wells located in vulnerable aquifers obtained for the MPCA Baseline Study and the MPCA condition monitoring project are plotted in Figure 14. No clear difference is apparent in the two data sets, and the median nitrate concentration for both sets of data is less than 0.5 mg/L (non-detectable). Consequently, no comparison of ground water quality over time with respect to nitrate can be made.

MPCA Baseline Study
1992-1996



The median nitrate concentration for 83 domestic well samples is non-detectable (<0.5 mg/L).

MPCA condition monitoring project
2004-2005



The median nitrate concentration for 126 domestic well samples is non-detectable (<0.5 mg/L).

Figure 14. Nitrate Concentrations in Minnesota Ground Water Over Time

Nitrate Concentrations in Ground Water using Combined MPCA and MDA Data Sets

The nitrate results obtained by the MPCA and MDA condition monitoring projects in 2004 and 2005 are plotted in Figure 15. In addition, Figure 15 includes the nitrate results from a survey of drinking water quality in domestic wells conducted by MDA in 2004. The left side of Figure 15 indicates the source of the concentration data that is plotted on the right. The median nitrate concentration for each data set shown on Figure 15 is provided in Table 2.

When the MPCA and MDA condition monitoring data are plotted together, the many locations in the central area of the state where nitrate exceeds the drinking water standard stand out. This area contains the MDA Central Sands monitoring network, which consists of 85 monitoring wells. The median nitrate concentration for the Central Sands wells is 16.1 mg/L, well above the drinking water standard of 10 mg/L.

Elsewhere in the state, elevated nitrate concentrations are most prevalent in southeast Minnesota and in the Twin Cities metropolitan area, particularly the eastern half. Only a few monitoring locations outside of these areas yielded nitrate concentrations that were elevated or exceeded the drinking water standard.

The high median nitrate concentration for the MDA Central Sands region relative to other areas of the state reflects MDA's use of water table monitoring wells that are best suited to detecting nitrate leaching to ground water, and the region's predominantly agricultural land use, much of it irrigated agriculture.

Data Source **Nitrate Results**

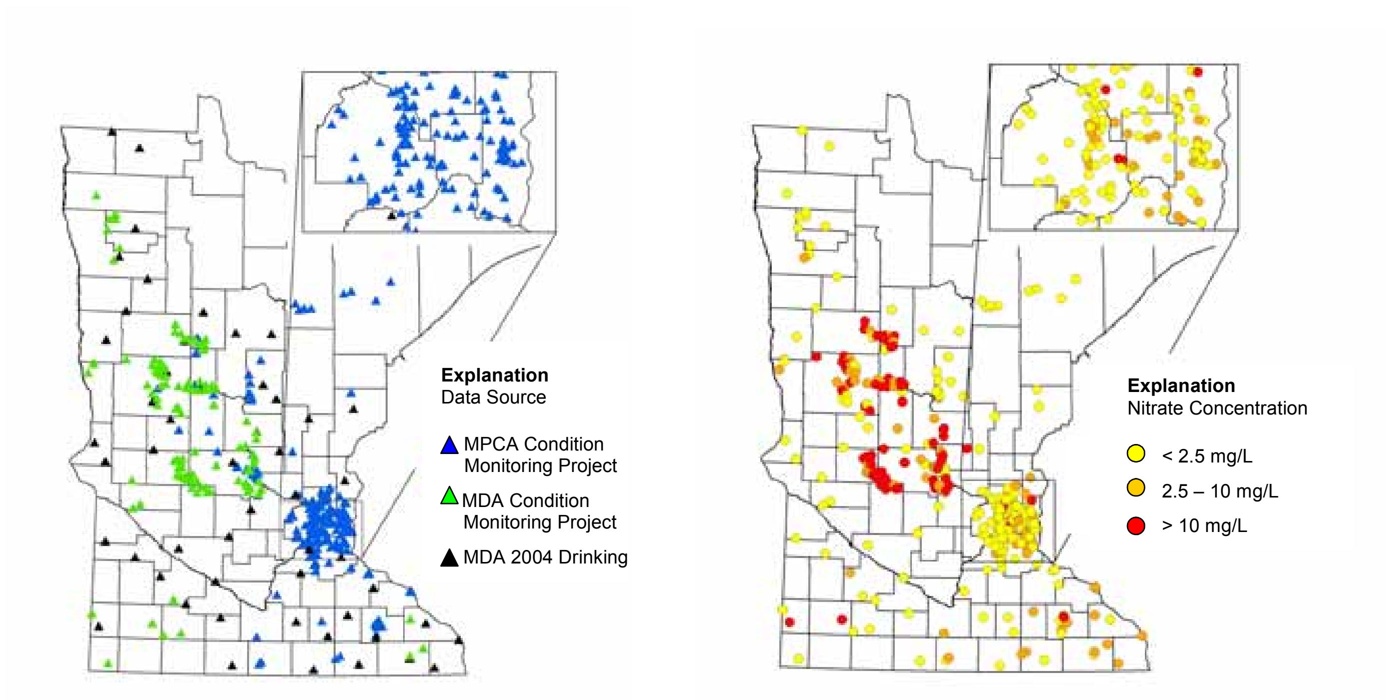


Figure 15. Nitrate Concentrations in Minnesota Ground Water using Combined MPCA and MDA Data Sets

Table 2. Median Nitrate Concentrations for MPCA and MDA Ground Water Data Sets

Data Source	Median Nitrate Conc. (mg/L)	Number of Wells
MPCA Condition Monitoring Project		
All Wells	<0.5	201
Domestic Wells	<0.5	126
Monitoring Wells	2.5	75
*MDA Condition Monitoring Project**		
All Wells	6.0	110
Central Sands	16.1	85
SE Minnesota	3.7	6
All Other Regions	<0.5	19
MDA 2004 Drinking Water Survey		
Domestic Wells	<0.5	71

**MDA condition monitoring project wells are primarily monitoring wells.*

Nitrate Concentrations in Ground Water Beneath Different Land Uses

The MPCA's study of land use impacts on ground water quality in the vicinity of St. Cloud (Trojan et. al., 2003) cited previously also evaluated the impact of land use on nitrate concentrations in ground water. Like chloride, the study results indicated that nitrate concentrations were elevated beneath all land uses compared to those beneath nondeveloped land (Figure 16). The largest increases in nitrate concentration occurred beneath irrigated agriculture and residential land uses serviced by ISTS ("non-sewered" land use). This result is consistent with the MDA condition monitoring project results for the Central Sands region (Figure 15 and Table 2) and other studies that have shown that fertilizer use and ISTS are the primary sources of nitrate to ground water (Gardner and Vogel, 2005).

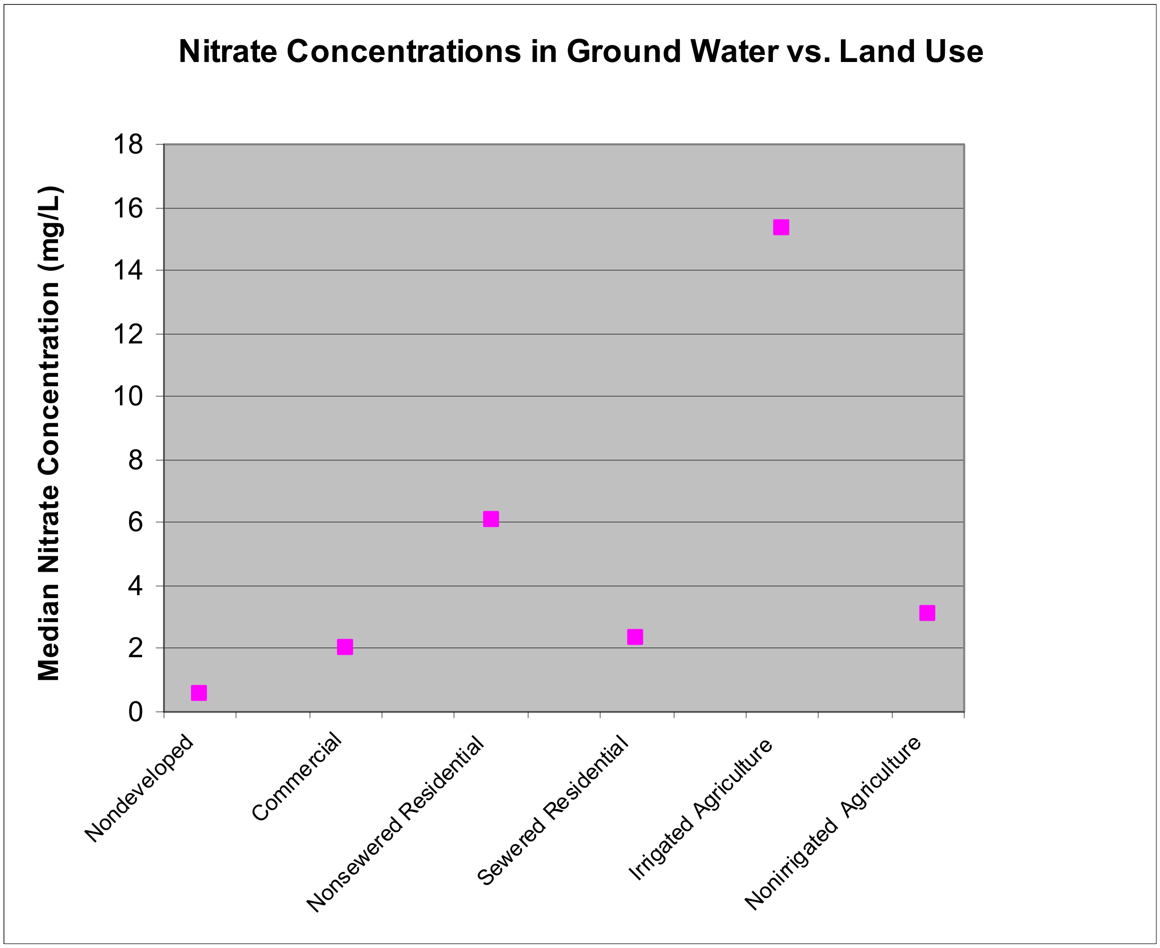


Figure 16. Nitrate Concentrations in Ground Water Beneath Different Land Uses, Anoka Sand Plain Aquifer *(source: Trojan et. al., 2003)*

Nitrate Contamination of Minnesota's Drinking Water

Nitrate contamination of drinking water is a significant problem in Minnesota. It is primarily, but not exclusively a rural issue, and as such it has received substantial attention by both the MDA and MDH. MDH's role is to assist private well owners in understanding the health risks associated with contaminants detected in their well water, and to help local health departments address the human health impacts related to contamination of public and private water supply wells (MPCA, 2004).

According to MDA, seven percent of the more than 400,000 wells in the MGS-MDH County Well Index database of registered Minnesota wells exceed the drinking water standard for nitrate (MDA and MDH, 2007a; and Soule, 2007). MDA and MDH have profiled several communities that are dealing with nitrate contamination of their municipal water supplies in fact sheets that are available on MDA's Web site:

- The city of Mankato, south central Minnesota, which draws its water from wells screened in alluvial sands underneath the Blue Earth River, which is impacted by nitrate (MDA and MDH, 2007b).
- The city of St. Peter, also in south central Minnesota, where tile drainage from agricultural fields percolates rapidly into the aquifers used to obtain the city's drinking water (MDA and MDH, 2003a).
- The city of Perham in Minnesota's west central lakes region, where all five of the city's water supply wells are impacted by nitrate to various degrees (MDA and MDH, 2003b).

Each of these cities has adopted vigorous wellhead protection plans to reduce the impact of agriculture on surface and ground water in the area; each has also investigated or invested in additional measures to reduce the concentration of nitrate in their drinking water.

The solutions for nitrate contamination, all of which are very costly, include:

1) drilling one or more new wells;

2) blending water from different wells to reduce the overall concentration of nitrate in the blended water

3) installation of a water treatment system. Figure 17 illustrates how nitrate in surface water can be drawn into nearby municipal water supplies

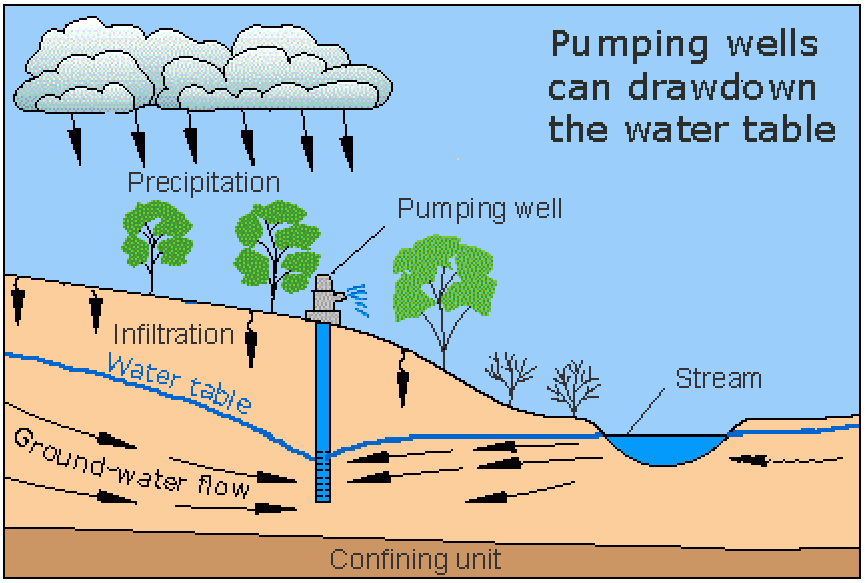


Figure 17. Surface Water Quality Can Impact Nearby Ground Water Quality *(source: USGS, 2007)*

In addition, the Lincoln-Pipestone Rural Water System in the southwest corner of Minnesota, which supplies water to 27 communities and 3,000 rural households, has had to work diligently to provide ground water that meets the drinking water standard for nitrate (MDA and MDH, 2003c). The Lincoln-Pipestone system operates three well fields with a combined well head protection area of 32,000 acres. Two of the well fields are fairly shallow and vulnerable to nitrate contamination. Lincoln-Pipestone blends water from various water supply wells to produce drinking water that meets the drinking water standard of 10 mg/L nitrate, and it has also installed a $2 million nitrate removal system.

Twin Cities metropolitan area communities have also had to deal with the problem of nitrate contamination of their municipal water supplies. The cities of Cottage Grove and the city of Hastings are two such communities. Both cities were primarily agricultural 20 or 30 years ago but are now growing suburban population centers with some ongoing agriculture. Studies conducted by Washington and Dakota Counties in Cottage Grove and Hastings, respectively, led each county to conclude that integrated management of surface and ground water is a necessary ingredient for improving and protecting ground water quality. Dakota County's Hastings Area Nitrate Study (HANS) is a particularly interesting examination of nitrate contamination and ground water – surface water interaction (Figure 18).

Figure 18. Hastings Area Nitrate Study (HANS) *(source: Dakota County, 2003)*

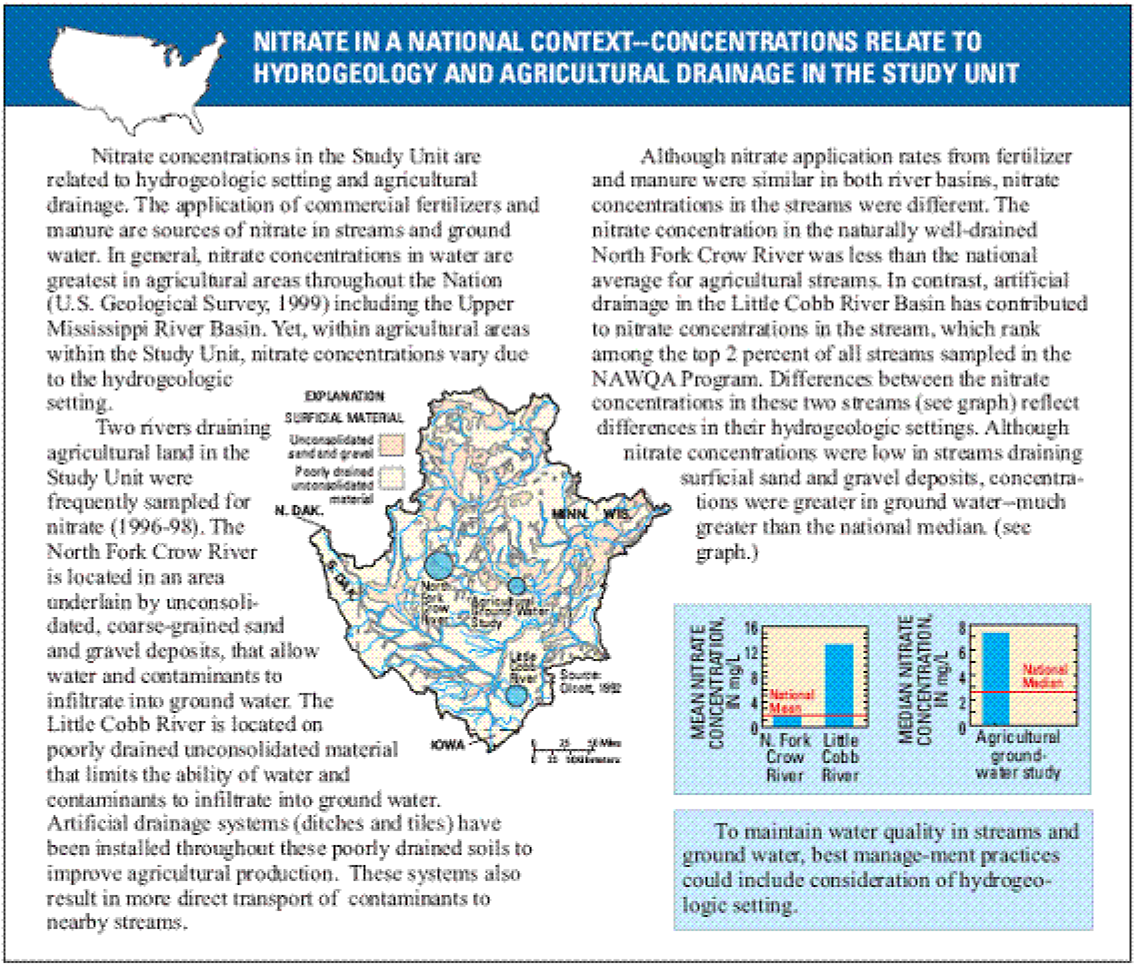
In July 1999, Dakota County obtained a Clean Water Partnership grant in the amount of $75,000 to quantify and map patterns of elevated nitrate in ground water in the City of Hastings and the surrounding townships. Dakota County staff applied for the grant after noticing increasing nitrate levels in the City of Hastings municipal water supply as well as increasing numbers of private drinking water wells with elevated nitrate levels. The City of Hastings and its surrounding townships obtain 100% of their drinking water from ground water. In fact most of the water comes from the deeper bedrock aquifers of the Prairie du Chien and Jordan, a fact that caused some alarm to resource managers.

The study found that the major source of nitrate contamination was row-crop agriculture, although evidence of sewage contamination also was found. Although feedlots were considered a potential source of nitrate, they were eliminated from the study on the basis of the few livestock raised within the study area. The source of the contamination was determined through the very strong association between a well's nitrate concentration and its pesticide concentrations. The study also was able to determine that the Vermillion River, which passes through the study area, carries between 4 to 9 mg/L nitrate and that the Vermillion River loses a significant quantity of its water to ground water. From this, the study concluded that the Vermillion River is a contributor to nitrate in the City's drinking water.

Based on the study, a number of follow up actions and studies have been proposed.

Nitrate in Ground Water and Surface Water: National Perspective

As described in the previous section, several Minnesota communities have discovered that solving the problem of elevated nitrate in ground water requires them also to consider nitrate in surface water and the role of the underlying geology. This is well-illustrated by the USGS in an example from the Upper Mississippi River Basin in Minnesota (Stark et. al., 2000) that is reproduced in Figure 19, below.



NITRATE IN A NATIONAL CONTEXT--CONCENTRATIONS RELATE TO HYDROGEOLOGY AND AGRICULTURAL DRAINAGE IN THE STUDY UNIT

Nitrate concentrations in the Study Unit are related to hydrogeologic setting and agricultural drainage. The application of commercial fertilizers and manure are sources of nitrate in streams and ground water. In general, nitrate concentrations in water are greatest in agricultural areas throughout the Nation (U.S. Geological Survey, 1999) including the Upper Mississippi River Basin. Yet, within agricultural areas within the Study Unit, nitrate concentrations vary due to the hydrogeologic setting.

Two rivers draining agricultural land in the Study Unit were frequently sampled for nitrate (1996-98). The North Fork Crow River is located in an area underlain by unconsolidated, coarse-grained sand and gravel deposits, that allow water and contaminants to infiltrate into ground water. The Little Cobb River is located on poorly drained unconsolidated material that limits the ability of water and contaminants to infiltrate into ground water. Artificial drainage systems (ditches and tiles) have been installed throughout these poorly drained soils to improve agricultural production. These systems also result in more direct transport of contaminants to nearby streams.

Although nitrate application rates from fertilizer and manure were similar in both river basins, nitrate concentrations in the streams were different. The nitrate concentration in the naturally well-drained North Fork Crow River was less than the national average for agricultural streams. In contrast, artificial drainage in the Little Cobb River Basin has contributed to nitrate concentrations in the stream, which rank among the top 2 percent of all streams sampled in the NAWQA Program. Differences between the nitrate concentrations in these two streams (see graph) reflect differences in their hydrogeologic settings. Although nitrate concentrations were low in streams draining surficial sand and gravel deposits, concentrations were greater in ground water--much greater than the national median. (see graph.)

To maintain water quality in streams and ground water, best manage-ment practices could include consideration of hydrogeo-logic setting.

Figure 19. Nitrate in Ground Water and Surface Water in the Upper Mississippi River Basin *(source: Stark et. al, 2000)*

Volatile Organic Compounds in Minnesota's Ground Water

About Volatile Organic Compounds

Volatile organic compounds (VOCs) are a large class of manufactured and refined organic chemicals that have been used extensively in the United States since the 1940s by industry, commerce, households and the military (Zogorski et. al., 2006). VOCs are major components of or additives to many common commercial and household products including gasoline, diesel fuel, carpets, paints, varnishes, glues, and cleaners.

Because of their extensive use in residential and industrial applications, and because of their tendency to persist in the environment, VOCs pose a threat to ground water quality. Many VOCs have documented adverse affects on human health, while many others are suspected to cause adverse effects (Zogorski et. al., 2006).

Several MPCA regulatory programs are focused on the investigation and cleanup of releases of VOCs and other contaminants to the environment. These programs include the Superfund, Hazardous Waste, Closed Landfill, Petroleum Remediation, Voluntary Investigation and Cleanup, and Spills programs. Note that most releases of hazardous substances have occurred due to chemical storage and handling practices that were used prior to knowledge of their environmental impact, or because of deteriorating or abandoned equipment. Education and environmental regulation have eliminated most controllable causes of VOC releases to the environment, however, VOC releases continue to occur as a result of spills and other accidents.

Ground water samples collected for the MPCA condition monitoring project are analyzed for 68 individual VOCs (Table 3). The analytical detection limits for the compounds vary, but most are between 0.1 and 0.5 micrograms per liter or ug/L (equivalent to parts per billion or ppb). Unlike chloride and nitrate, VOCs do not occur naturally in the environment. Therefore, any detection of VOCs in ground water is an indication of contamination from human activities.

The MDH has developed HRLs for many VOCs in drinking water. The HRLs for VOCs range in magnitude from sub-part per billion concentrations (e.g. vinyl chloride) to hundreds of parts per billion (e.g. toluene).

Table 3. List of Volatile Organic Compounds Analyzed by MPCA Condition Monitoring Project

1,1,1-Trichloroethane	Allyl chloride	Methyl tertiary butyl ether (MTBE)
1,1,2,2-Tetrachloroethane	Benzene	Methylene chloride
1,1,2-Trichloroethane	Bromobenzene	Naphthalene
1,1,2-Trichlorotrifluoroethane (Freon 113)	Bromochloromethane	n-Butylbenzene
1,1-Dichloroethane	Bromodichloromethane	n-Propylbenzene
1,1-Dichloroethene	Bromoform	o-Xylene
1,1-Dichloropropene	Bromomethane	p&m-Xylene
1,2,3-Trichlorobenzene	Carbon tetrachloride	p-Isopropyltoluene
1,2,3-Trichloropropane	Chlorobenzene	sec-Butylbenzene
1,2,4-Trichlorobenzene	Chlorodibromomethane	Styrene
1,2,4-Trimethylbenzene	Chloroethane	tert-Butylbenzene
1,2-Dibromo-3-chloropropane (DBCP)	Chloroform	Tetrachloroethene
1,2-Dibromoethane (EDB)	Chloromethane	Tetrahydrofuran (THF)
1,2-Dichlorobenzene	cis-1,2-Dichloroethene	Toluene
1,2-Dichloroethane	cis-1,3-Dichloropropene	trans-1,2-Dichloroethene
1,2-Dichloropropane	Dibromomethane	trans-1,3-Dichloropropene
1,3,5-Trimethylbenzene	Dichlorodifluoromethane	Trichloroethene (TCE)
1,3-Dichlorobenzene	Dichlorofluoromethane	Trichlorofluoromethane
1,3-Dichloropropane	Ethyl benzene	Vinyl chloride
1,4-Dichlorobenzene	Ethyl ether	
2,2-Dichloropropane	Hexachlorobutadiene	
2-Chlorotoluene	Isopropylbenzene	
4-Chlorotoluene	Methyl ethyl ketone (MEK)	

Note: VOCs are analyzed using gas chromatography/mass spectrometry by the MDH Laboratory, according to MDH Method 468.

VOC Results

Only the VOC results obtained by the MPCA condition monitoring project from 2004 are reviewed in this report. While the 2005 VOC results are available, consistent analysis of the combined 2004-2005 dataset is not possible until additional metadata is added to the project database.

The occurrence of VOCs in ground water indicated by the 2004 results from the MPCA condition monitoring project is shown in Figure 20. Note the clusters of wells containing VOCs in the Twin Cities and St. Cloud metropolitan areas. Of the 90 wells sampled for VOCs in 2004, about 20 percent (18 wells) were reported to contain detectable concentrations (i.e., concentrations greater than the laboratory analytical detection limit) of at least one VOC.

In most cases the VOCs were detected at very low concentrations. More than 40 percent of the detected VOCs were present at concentrations of less than 1 ug/L, and more than 75 percent of the detected VOCs were present at concentrations of less than 10 ug/L. Just two of the ground water samples were reported to contain a VOC at a concentration exceeding its HRL. The VOCs exceeding the HRL were tetrachloroethylene (PCE) and vinyl chloride, both chlorinated solvents.

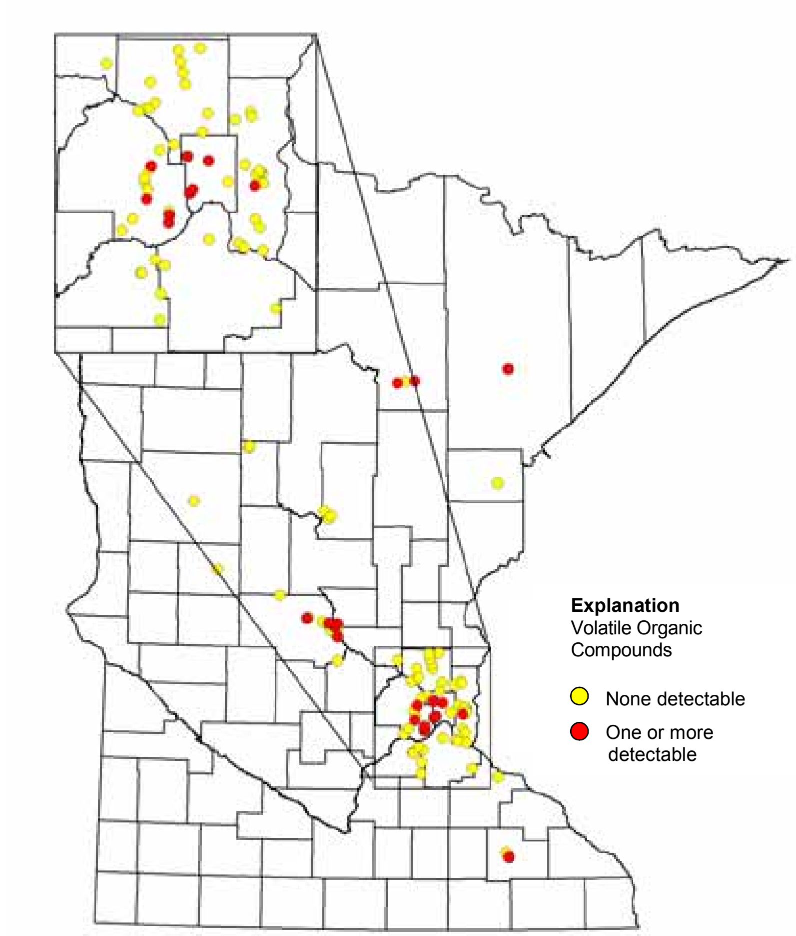


Figure 20. VOCs in Minnesota Ground Water

When the VOC results are separated by well type, there is a distinction in the results (Figure 21). For the monitoring wells, 28 percent were reported to contain detectable concentrations of VOCs, compared to 15.5 percent of the domestic wells. The higher percentage of VOC detections in the group of monitoring wells is consistent with the MPCA condition monitoring project results for chloride and nitrate, which each had higher median concentrations in the results from monitoring wells compared to the domestic wells.

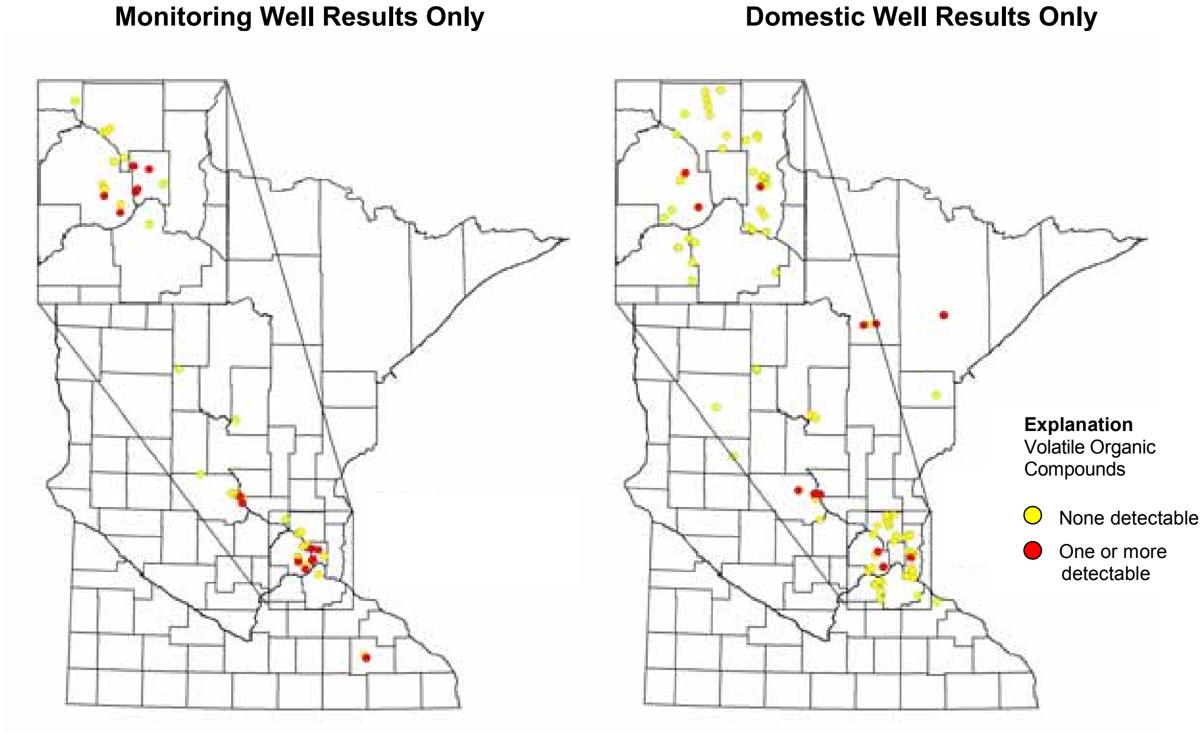


Figure 21. VOCs in Ground Water Collected from Monitoring Wells Versus Domestic Wells

VOCs in Ground Water Over Time

The VOC results for domestic wells in vulnerable aquifers from the MPCA Baseline Study and the MPCA condition monitoring project are plotted in Figure 22. The results show that about 15.5 percent of the samples from the MPCA condition monitoring project contained detectable VOCs (9 of 58 samples), whereas only about 7.2 percent of the samples from the Baseline Study (6 of 83 samples) contained detectable VOCs. While this result suggests that the rate of detection of VOCs in Minnesota's ground water in 2004 is twice what it was in 1992-1996, it can be seen in Figure 22 that the condition monitoring project sampled a higher proportion of urban wells compared to the Baseline Study. Because of this, no conclusion can be made regarding the higher percentage of VOC detections in the condition monitoring project data.

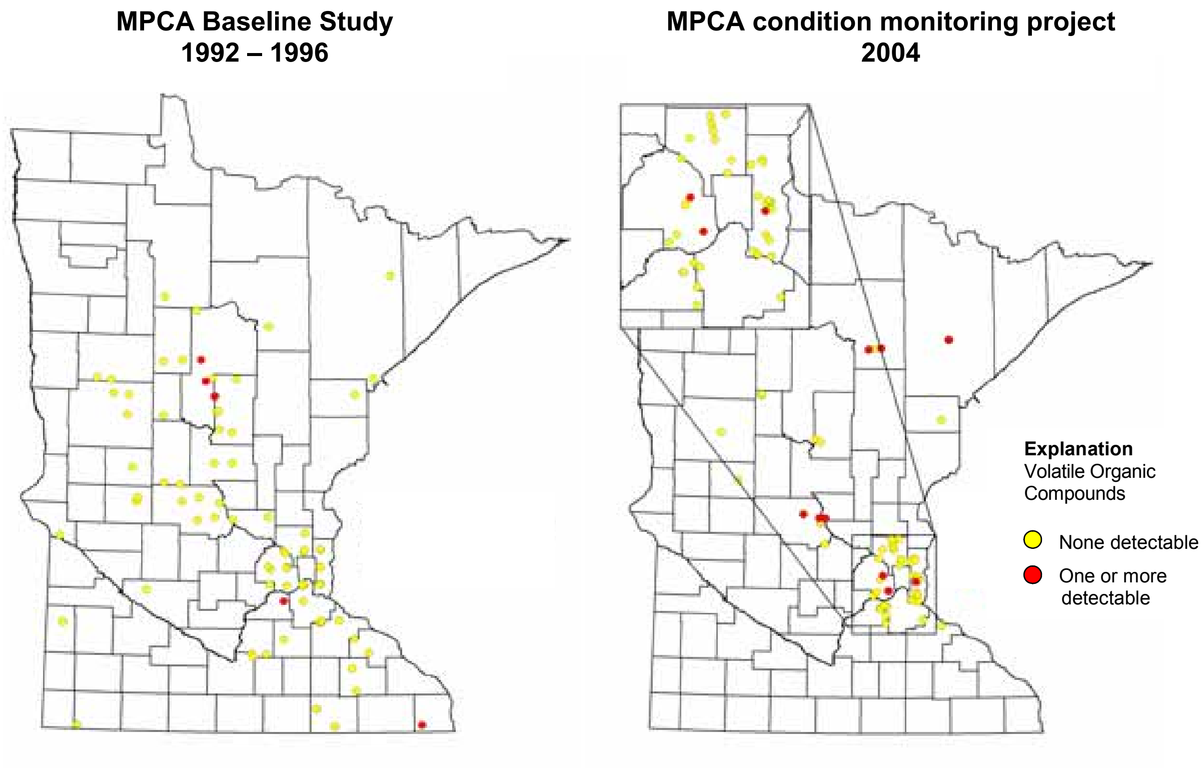


Figure 22. VOCs in Minnesota Ground Water Over Time

For another comparison, the results for all 954 ground water samples collected for the Baseline Study between 1992 and 1996 from domestic wells in all of Minnesota's principal aquifers indicated that 11.8 percent of the samples (113 samples) contained detectable concentrations of at least one VOC. Surprisingly, this is a higher percentage of VOC detections than for the subset collected from vulnerable aquifers (7.2 percent), discussed above.

The condition of Minnesota's ground water with respect to VOCs can be further evaluated using data obtained by MDH from public water supply systems and by the MPCA Remediation Division from contaminated site investigations.

VOCs in Ground Water Supplying Minnesota Public Water Systems

MDH maintains a database to store the results of laboratory analyses of water samples collected from Minnesota's public water supply (PWS) systems. In 2000, the MPCA Remediation Division requested all data from the MDH database for PWS systems that were reported to contain detectable concentrations of contaminants, including VOCs, pesticides, metals, and radionuclides (Delta Environmental Consultants, 2000). This request was made to assist the MPCA Remediation Division in prioritizing its investigations of potential contaminant sources to the PWS wells. The MDH data include analytical results for water samples collected from PWS systems between 1990 and 2000.

> ***Community public water systems*** *serve at least 25 persons or 15 service connections year-round, which includes municipalities, subdivisions, mobile home parks, etc. (MDH, 2006b).*
> ***Noncommunity public water systems*** *are facilities such as schools, factories, restaurants, resorts, and churches that are served by their own supply of water (usually a well). Noncommunity water systems serve either a transient or a nontransient population. A nontransient noncommunity public water system serves the same individuals every day (such as a school, daycare, or factory). A transient noncommunity public water system serves different individuals each day (such as a restaurant, motel, or highway rest area). (MDH, 2006c).*

Although the MDH PWS data is somewhat dated, it provides an alternate set of information for evaluating the condition of Minnesota's ground water with respect to VOCs. The water samples analyzed by MDH are collected from the PWS well head, at the water treatment plant, or from the water distribution system. The MDH PWS data are summarized in Table 4.

When a VOC is detected in a water sample collected from a PWS system, *the frequency of sampling is increased. A PWS system operator must take corrective actions—which include notifying the water users of a problem—if the level of a contaminant exceeds the regulatory limit (usually the MDH HRL or the federal Maximum Contaminant Level). More information about what happens when a contaminant is detected in a PWS system is available at MDH's Web site: http://www.health.state.mn.us/divs/eh/water/com/fs/sampling.html.*

The MDH data indicate that a little over four percent of the almost 1,000 Community PWS systems operating in Minnesota were reported to have at least one record of a sample that contained detectable concentrations of VOCs. For the larger group of about 7,500 Non-community PWS systems, about one percent was reported to have at least one record of a sample that contained detectable concentrations of VOCs. The percentages decrease substantially if only those PWS with at least one VOC detected at a concentration greater than or equal to one-half of its regulatory limit (usually the MDH HRL) are considered (Table 4).

The PWS systems with records of at least one sample with detectable concentrations of VOCs are shown in Figure 23. These 120 PWS systems (40 Community and 80 Non-community) include thirteen PWS systems that were impacted by metals only, and five PWS systems impacted by pesticides only. Seventy-three of the 120 PWS Systems were reported to have a VOC (or pesticide or metal) at a concentration equal to at least 50 percent of its HRL. Many of the PWS with higher concentrations of VOCs were impacted by multiple contaminants.

Table 4. Minnesota Public Water Supply Systems Reporting VOCs[1,2]

	Percent	Number of PWS
Community PWS Systems[3]		954
Municipal		713
Non-municipal (e.g.,trailer park)		241
Number with detectable VOCs*	4.2%	40
Number of VOCs* at 50% of MCL/HRL	1.5%	14
Number with on-going MCL/HRL violations	1.5%	14
Non-Community PWS Systems[4]		7,634
Transient (e.g., restaurant, motels)		6,977
Non-transient (e.g., trailer park)		657
Number with detectable VOCs*	1.1%	80
Number with VOCs* at 50% of MCL/HRL	0.3%	22
Number with on-going MCL/HRL violations	0.01%	1

[1] *Delta Environmental Consultants, 2000.*

[2] *These statistics were calculated after removing PWS systems reported to be impacted by naturally occurring contaminants (i.e., arsenic, radon and/or radionuclides); chlorine disinfection by-products or trihalomethanes; or by di(2-ethylhexly)phthalate (DEHP), a plasticizer that is commonly detected in water system samples. This was done to render the MDH PWS data more comparable to the MPCA condition monitoring project data for VOCs.*

[3] *MDH, 2006b.*

* *VOCs plus a few metals and pesticides*

MCL = Maximum Contaminant Level. The MCL is the federal standard for a contaminant in drinking water. MCLs are developed by the United States Environmental Protection Agency and represent the lowest concentration at which a particular contaminant is believed to be a potential health concern. For many contaminants, the HRL developed by MDH and the MCL developed by USEPA are the same.

[4] *MDH, 2006c.*

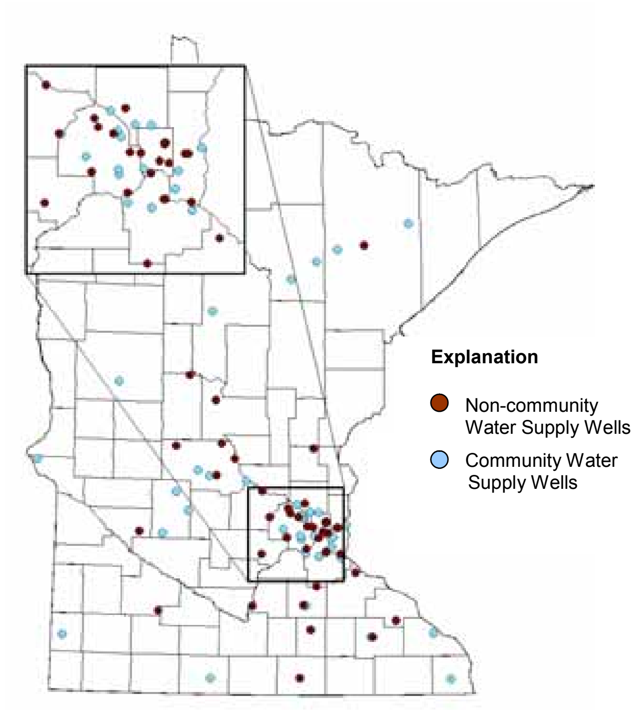


Figure 23. Minnesota Public Water Supply Systems Reporting VOCs *(source: Delta Environmental Consultants, 2000)*

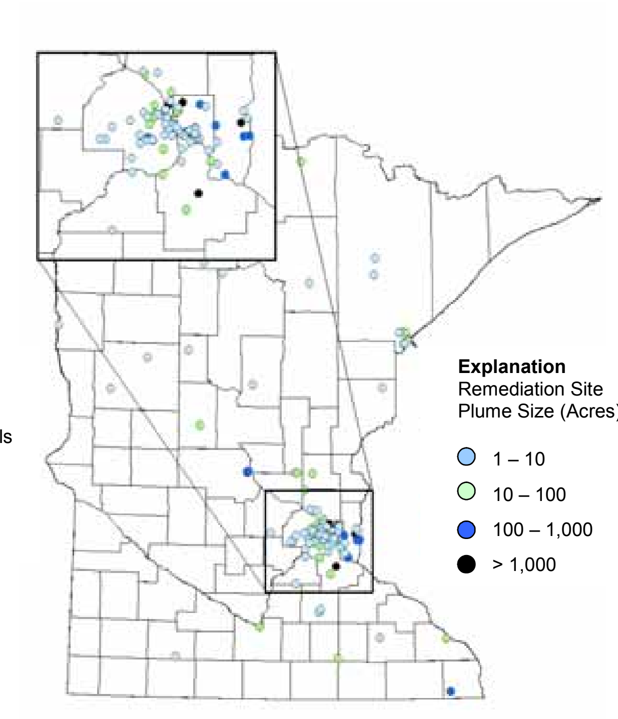


Figure 24. MPCA Remediation Program Sites with Ground Water Contaminant Plumes One Acre or More in Size *(source: MPCA SRS Database, 2006)*

The percentages of Community and Non-community PWS systems with records of water samples having detectable concentrations of VOCs (Table 4) are much lower than what is indicated by the 2004 results from the MPCA condition monitoring project (i.e., about 20 percent of the sampled wells). One factor contributing to the lower rate of VOC detections in the PWS system data is the pre-screening of the PWS system data that was conducted for this report.

The pre-screening involved removal of all records of PWS systems that had VOC detections limited to chlorine disinfection by-products. Chlorine disinfection by-products are more conveniently referred to as trihalomethanes (THMs) and include a number of commonly detected VOCs such as chloroform. THM detections were screened out of the PWS system dataset because of concern that routine use of chlorine disinfection by PWS would be an indicator of the PWS rather than of the water being brought into the PWS (i.e., the ground water). However, the MPCA condition monitoring project results for VOCs include results for THM.

Chlorine disinfection by-products are also known as Trihalomethanes (THMs). THMs include:

- *Chloroform*
- *Bromoform*
- *Chlorodibromomethane*
- *Bromodichloromethane*

MDH studies suggest that three to six percent of public water supplies and about two to four percent of all water supplies in Minnesota contain detectable concentrations of VOCs (MDH, 2006d). Nationally, the USGS reports that 14 percent of the 2,401 domestic wells it sampled for its study of the occurrence of VOCs in ground water contained one or more VOCs (Zogorski et. al, 2006), which is similar to the results from the MPCA Baseline Study of 11.8 percent.

Minnesota PWS systems have a stellar record of supplying drinking water that meets all state and federal standards for quality. The MDH publishes an annual report that summarizes Minnesota drinking water protection activities and the results of monitoring tests; the annual report for 2005 is available on the MDH's Web site (MDH, 2006e).

VOC-Contaminated Ground Water at Minnesota Remediation Sites

The MPCA's Remediation Division receives a large quantity of ground water quality data each year from the investigation and clean up of property contaminated by hazardous substances. Since about 1996, the MPCA Remediation Division has documented selected information about ground water contamination at sites enrolled in the Superfund, Voluntary Investigation and Cleanup, and RCRA programs in an Microsoft Access database. The database, known as the SRS, includes older, closed sites and currently enrolled sites.

The SRS database was queried to obtain a list of sites with entries in the ground water contaminant plume size field. The query identified 178 sites with ground water contaminant plumes that are one acre or more in size. Five of these sites were reported to have a plume size greater than 1,000 acres, and 14 were reported to have a plume size greater than 100 acres. The locations of the remediation sites with ground water contaminant plume sizes greater than one acre are shown in Figure 24.

As is evident in Figure 24, remediation sites with identified VOC contamination are concentrated in the Twin Cities metropolitan area, including the five sites with plumes greater than 1,000 acres. The MDH has set up Special Well Construction Areas around the largest plumes and at other locations in the state where significant contamination of ground water has occurred. Special Well Construction Areas help prevent further spread of contamination that can result from the installation and pumping of water supply wells.

Purifying contaminated ground water for drinking water use is costly:

- *In Edina, replacing a well shutdown in 2002 because of the presence of low levels of vinyl chloride is estimated to cost $800,000.*
- *In St. Louis Park, monitoring and treating ground water contaminated by the nearby Reilly Tar & Chemical Company Superfund site costs the city $500,000 annually.*
- *In Oakdale, 3M Company spent $3,000,000 to build a water treatment plant to remove perfluorinated chemicals from the ground water; the new water treatment plant is estimated to cost $350,000 a year to operate (Shaffer, 2007).*

It should be noted that because the SRS database was developed in 1996 for project management rather than data storage purposes, results from the query presented in this report should be considered representative but not comprehensive information.

Most Frequently Detected VOCs in Minnesota Ground Water

Apart from THMs, the 2004 results from the MPCA condition monitoring project indicate the most frequently detected VOCs in Minnesota ground water are the light-end petroleum hydrocarbons associated with gasoline, and the chlorinated solvents and their breakdown products. The petroleum hydrocarbons include benzene, toluene, xylene, ethyl benzene and many other compounds. The chlorinated solvents include PCE (a drycleaning solvent), trichloroethylene or TCE (an industrial degreaser), and associated breakdown products including cis- and trans-1,2-dichloroethylene, vinyl chloride.

The USGS' 2006 study of VOCs in ground water nationally (Zogorski et. al., 2006) had similar but not identical findings. The USGS results showed that the most commonly detected VOCs not including THMs were, in order: PCE, methyl tertiary butyl ether (a gasoline oxidant that not used widely in Minnesota), TCE, toluene, and dichlorodifluoromethane (a refrigerant) (Zogorski et. al., 2006).

Table 5 lists the most frequently detected VOCs in Minnesota ground water by data source.

Table 5. Most Frequently Detected VOCs* in Minnesota Ground Water By Information Source
(in sequential order from top to bottom)

MPCA Baseline Study 1992 - 1996 (954 Samples)	MPCA Condition Monitoring 2004 - 2005 (140 Samples)	MDH Public Water Supply Systems 1990 - 2000		MPCA Remediation Division SRS Database
		Non-Community PWS (7,634 systems)	Community PWS (954 systems)	
toluene	xylene	PCE	PCE	TCE
benzene	PCE	TCE	TCE	PCE
xylene	toluene	1,4-dichlorobenzene	thallium	cis-1,2-dichloroethene
1,1,1-TCA	TCE	1,2-dichloroethane	vinyl chloride &	Diesel Range Organics
dichlorodifluoro-	benzene	vinyl chloride	1,2-dichloroethane (tie)	benzene
methane			benzene	

**Excluding trihalomethanes*

Key: *Purple font = petroleum hydrocarbon*
Blue font = chlorinated solvent
Orange font = fluorocarbon (refridgerant)
Green font = metal
Black font = fumigant

TCA = trichloroethane
TCE = trichloroethylene
PCE = tetrachloroethylene

When THMs are included, chloroform was the most frequently detected VOC in ground water in the results from the USGS study (Zogorski et. al., 2006), the MPCA Baseline Study and the MPCA condition monitoring project. In all studies, chloroform was typically detected at low concentrations of less than 1 ug/L. According to the USGS, the widespread presence of chloroform in ground water signifies that waters with a history of chlorination such as drinking water and waste water are recharging our aquifers, and this water has now circulated sufficiently to reach domestic and other wells (Zogorski et. al., 2006).

Pesticides in Minnesota's Ground Water

About Pesticides

A pesticide is any substance used to kill or control insects, weeds, fungi, rodents, bacteria, or other unwanted organisms (Gilliom et. al., 2006). Pesticides are released into the environment primarily through their application to agricultural crops. Non-agricultural use of pesticides such as on lawns and gardens, in commercial areas, and on railroad and other rights-of-way is the second major source of pesticides released to the environment (Gilliom et. al., 2006).

The MDA monitors the occurrence and concentration of pesticides and nutrients in both ground and surface water. MDA's monitoring program has the additional goal of evaluating the effectiveness of pesticide and nutrient management plans and BMPs.

A huge variety of pesticides has been developed and are on the market to reduce weed growth and discourage pests. New pesticides are continually being developed to repel emerging and resistant pests and to treat other threats to crops that regularly appear. Meanwhile, older pesticides that are no longer in use, such as DDT, chlordane compounds, and dieldrin, continue to be detected in the environment, primarily in stream bed sediments and fish tissue (Gilliom et. al, 2006).

Once released into the environment, pesticides break down and create degradates. The degradates often have a lower toxicity than the parent pesticide, but some have toxicities that are greater than that of the parent pesticide. New analytical methods must often be developed to detect the newer pesticides and their degradates at the low concentrations generally found in the environment. The analytical methods developed often require the use of sophisticated analytical equipment that is not widely available. For these reasons, the ability to detect the presence of newer pesticides and degradates in the environment typically lags behinds commercial use of the products.

For ground water samples collected in 2004 and 2005 for the MDA condition monitoring project, a list of 26 pesticides and 13 degradate compounds was targeted for analysis or were detected as non-target pesticide analytes (MDA, 2006a). MDA determines a "…'target analyte' list for a given water resource sample based on the relative expectation of detecting the pesticide in the particular water sample. This expectation may depend on the mobility of the pesticide in soil or water, the general use of the pesticide in the monitoring area or other programmatic reasons or concerns." MDA states that this approach helps it focus limited resources on the chemicals of greatest concern to water resources (MDA, 2006a).

Currently, MDA's Commissioner has designated five pesticides "common detection pesticides" in ground water. This means that MDA has determined that the pesticide's detection in ground water is not due to misuse or unusual or unique circumstances, but is likely the result of normal use of a product or practice (MDA, 2005a). Common detection status triggers development of voluntary BMPs for those pesticides. A list of the common detection pesticides and information about their use and regulation in drinking water is included in Table 6.

Table 6. Common Detection Pesticides in Minnesota Ground Water *(source: MDA, 2006b)*

Pesticide Name	Pesticide Type	Trade Name (examples)	Primary Crops	Use Trend	2004 Draft HRL[1] and Trend	Promulgated HRL [1]	Health Based Value (HBV)* for Degradates[1]
Acetochlor	Herbicide	Surpass, Harness	Corn	Steady	2 ug/L (draft)	No previous HRL	50 ug/L
Alachlor	Herbicide	Lasso	Corn, Soy and Dry Bean	Declining	0.7 ug/L (draft)	Down from 4.0 ug/L	40 ug/L
Atrazine	Herbicide	Atrazine, Aatrex	Corn	Steady	4 ug/L (draft)	Down from 20 ug/L	4 ug/L (draft)
Metolachlor	Herbicide	Dual	Corn, Soybean and Potato	Declining	200 ug/L (draft)	Up from 100 ug/L	1,000 ug/L
Metribuzin	Herbicide	Lexone, Sencor	Soybean, Potato	Steady	20 ug/L (draft)	Down from 200 ug/L	20 ug/L (draft)

[1] *Withdrawn by MDH on April 12, 2007. See Table 7 below.*

* *Health Based Value (HBVs) are "interim" Health Risk Limits (HRLs)that are not promulgated in Minnesota Rules and are advisory in nature.*

MDH is in the midst of rules revision that has resulted in several changes to the HRLs and associated HBVs for the common detection pesticides. Table 7 provides current MDH-endorsed HRLs and HBVs for the common detection pesticides and their degradates.

Table 7. Current HRLs for Common Detection of Pesticides in Minnesota Drinking Water

Pesticide Name	**Draft or endorsed HRL** (as of September 10, 2007) [1,2]	**HBV* for Pesticide Degradates** (as of August 20, 2007)[3]
Acetochlor	10 ug/L (HBV)	50 ug/L
Alachlor	2 ug/L	40 ug/L
Atrazine	3 ug/L	(draft of 4 ug/L withdrawn)[3,4]
Metolachlor	100 ug/L	1000 ug/L
Metribuzin	200 ug/L	(draft of 20 ug/L withdrawn) [3,4]

* *HBV = Health Based Values*

[1] *MDH, 2007a.*
[2] *MDH, 2007b*
[3] *MDH, 2007c.*
[4] *MDA, 2006a*

For the purpose of this report, the condition of Minnesota's ground water with respect to pesticides is reviewed using the common detection pesticide atrazine to illustrate some of the findings and issues relevant to pesticides in the environment. Atrazine was selected because it is a well known and widely used herbicide. It is estimated that atrazine was used on 45 percent of the corn acreage in Minnesota during the 2003 cropping season (MDA, 2005b). MDA completed a summary report on the presence of atrazine in Minnesota ground water in 2005 (MDA, 2005b).

In addition, please note that this report was nearing completion when the MDH revised the draft HRL and HBV of 4 ug/L for atrazine and its degradates (Table 6). While the current endorsed HRL for atrazine is 3 ug/L and the HBV for atrazine degradates has been withdrawn (Table 7), the following text and figures will reference the concentration of 4 ug/L that was in effect between 2004 and April 12, 2007.

Pesticide Results

Atrazine was applied to Minnesota corn crops at a rate of about 2 million pounds a year between 1990 and 2004 (MDA, 2006b). MDA has analyzed ground water samples for atrazine and its degradates of deisopropylatrazine and deethylatrazine since the 1990s (Zabel, 2007).

Because the draft HRL for atrazine and the draft HBV for atrazine's degradates of deisopropylatrazine and deethylatrazine were both set at 4 ug/L prior to April 2007, the toxicity of a mixture of atrazine and its degradates could be determined with respect to the drinking water standard by adding the concentrations of the detected compounds together and comparing the summed concentration to the former draft HRL. This is done in the discussion that follows.

The MDA condition monitoring program results from 2004 and 2005 (Figure 25) show that only a few sampling locations in the Central Sands region and southeast Minnesota were reported to contain detectable concentrations of atrazine. The highest concentration detected was 0.20 ug/L, an order of magnitude below the former draft HRL of 4 ug/L for this compound.

When the MDA results for atrazine plus its degradates of deethylatrazine and deisopropylatrazine are plotted, a much higher rate of detection occurs (Figure 26). Overall, 54 percent of the MDA sampling locations yielded detectable concentrations of atrazine plus deethylatrazine and deisopropylatrazine. Most of the sampling locations were in the Central Sands region and southeast Minnesota. In contrast, other MDA regions and the urban pesticide sampling locations in the Twin Cities had primarily non-detectable results for atrazine and its degradates.

While the presence of atrazine and its degradates is much more widespread than for atrazine alone, the combined concentrations for this pesticide were still generally low, less than 0.4 ug/L. The highest concentration of atrazine plus degradates detected at any sampling location was 1.39 ug/L, less than the former draft HRL of 4 ug/L.

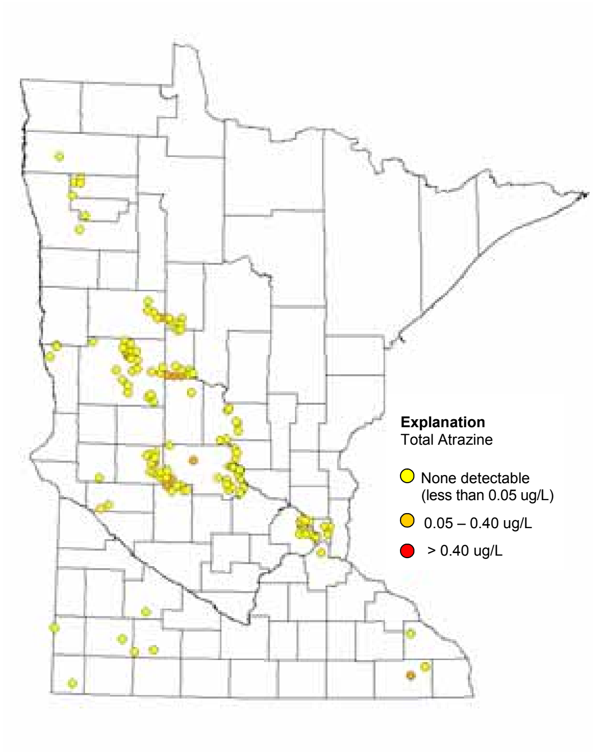


Figure 25. Atrazine in Minnesota Ground Water

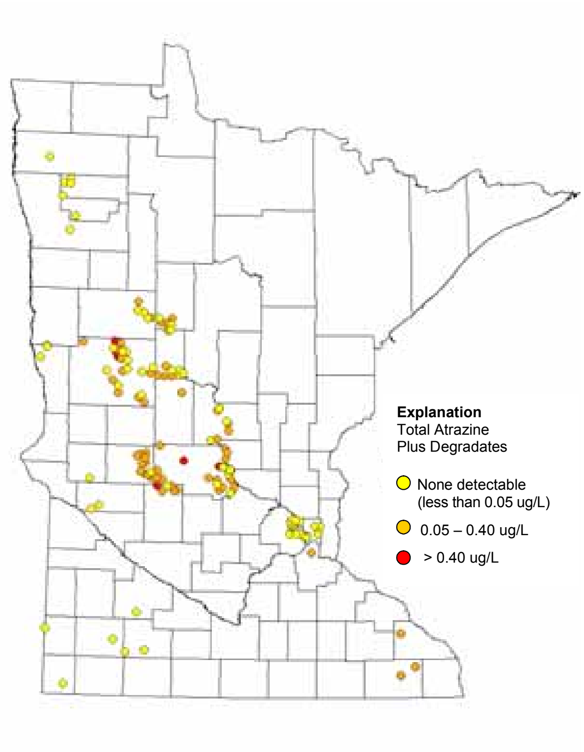


Figure 26. Atrazine Plus Atrazine Degradates in Minnesota Ground Water

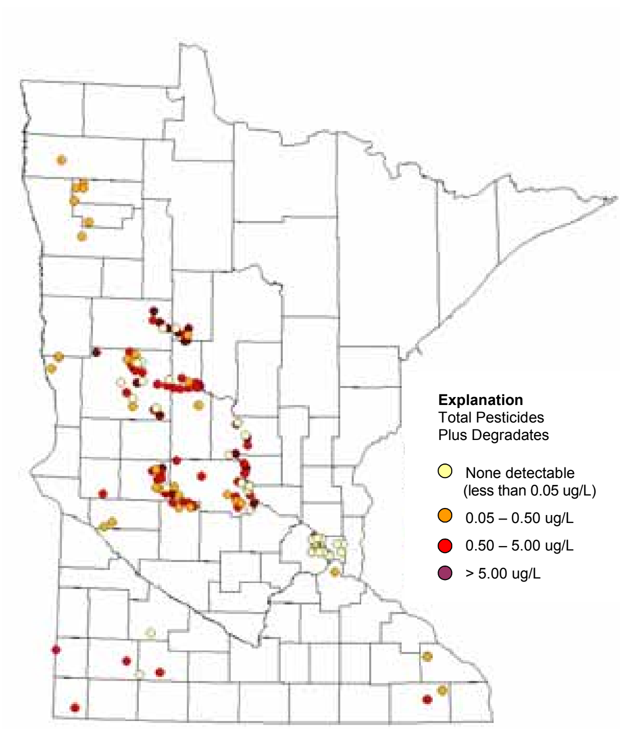


Figure 27. Total Pesticide Concentration in Minnesota Ground Water

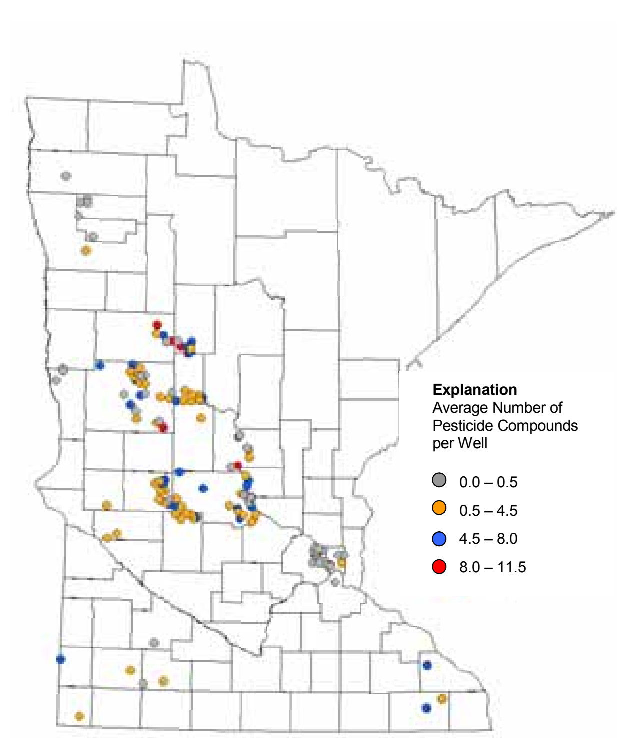


Figure 28. Number of Individual Pesticides in Minnesota Ground Water

When the concentrations of all pesticides and degradate compounds detected in each sample are summed and plotted (Figure 27), the number of samples with detectable pesticide concentrations increases, as does the range of detected concentrations. Overall, 62 percent of the MDA condition monitoring project samples contained detectable concentrations of pesticides or pesticide degradates. Of this group, about half of the samples had total pesticide concentrations that ranged between 0.5 and 5.0 ug/L, with another 20 percent or so having total pesticide plus degradate concentrations greater than 5.0 ug/L. The maximum total pesticide plus degradate concentration at any sampling location was 36.53 ug/L.

Figure 28 shows the results of the MDA condition monitoring project in terms of the number of individual pesticide and degradate compounds detected at each sampling location. For the 62 percent of sampling locations with detectable concentrations of pesticides and degradates, the number of individual pesticide compounds detected ranged from one to 13, with a median of four individual pesticide compounds. The number of individual pesticide compounds detected is of interest because the combined toxicity of a mixture of pesticides in water or other media may be higher than that of any single pesticide compound that is present (Gilliom et. al., 2006).

Looking only at the MDA condition monitoring project results from the Central Sands region for the six common detection pesticides between 2000 and 2005, none of the samples were reported to contain a pesticide or pesticide degradate at a concentration above the former promulgated HRL (Table 6) (MDA, 2006b). However, when the 2004 draft HRLs are applied to the sampling results, exceedences occurred for alachlor and/or its degradates (one exceedence for alachlor; 7 exceedences for alachlor degradates; and 10 for alachlor plus degradates) and atrazine (one exceedence for atrazine plus degradates) (MDA, 2006b).

Pesticides in Dakota County Ground Water

In 1999, Dakota County's Department of Environmental Management (DCEM) initiated the Ambient Groundwater Quality Study (AGQS) (Dakota County, 2006), an ongoing, multi-year study of ground water quality in Dakota County's major drinking water aquifers (Figure 29). The DCEM's motivation to begin this study was the long term trend of increasing nitrate levels in the city of Hastings municipal water supply and also the increasing numbers of private drinking water wells in Dakota County with elevated nitrate levels (Dakota County, 2003). The results of the HANS were highlighted previously in this report (Figure 18).

This chart shows a cross-section of typical geology and aquifers in Dakota County. Depths of the aquifers vary.

The two main sources for drinking water in Dakota County are the Prairie du Chien and Jordan aquifers, for both private wells and municipal (city) wells. Water in sand and gravel below the surface is also a drinking water source in the County.

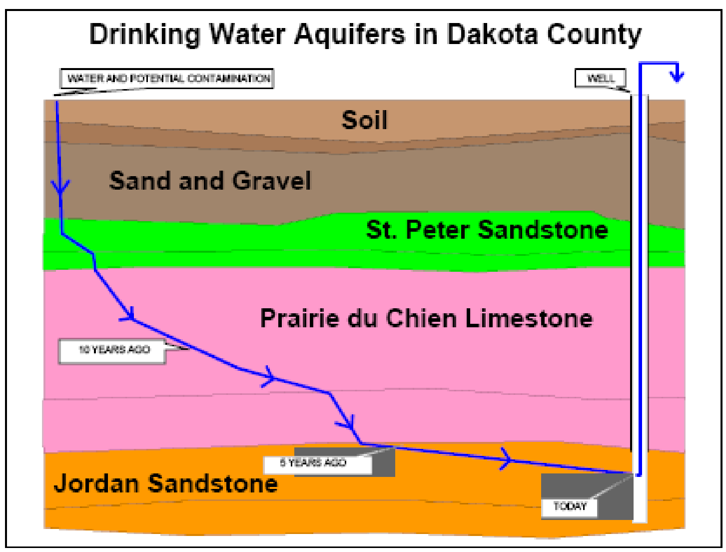


Figure 29. Cross-Sectional View of Drinking Water Aquifers in Dakota County *(source: Dakota County, 2005).* The blue line represents a flow path through the subsurface from the ground surface to the well. Labels indicate the location of a particle of water over time during its journey along the flow path.

In 2004, five years after initiating the AGQS, the DCEM expanded the study by increasing the number of wells that were sampled and by using more advanced analytical techniques for pesticide analysis. The new analytical methods made it possible to test each sample for a longer list of pesticides and to detect the pesticides at lower concentrations. The results obtained for the 2004 AGQS samples using the new analytical methods raised additional concerns about the presence of nitrate and pesticides in Dakota County wells. These concerns were confirmed when the 2005 sample results were received and showed that 82 percent of the 68 private wells sampled for the study contained detectable concentrations of nitrate, pesticides or pesticide degradates. A more specific breakdown of the results is provided in Figure 30.

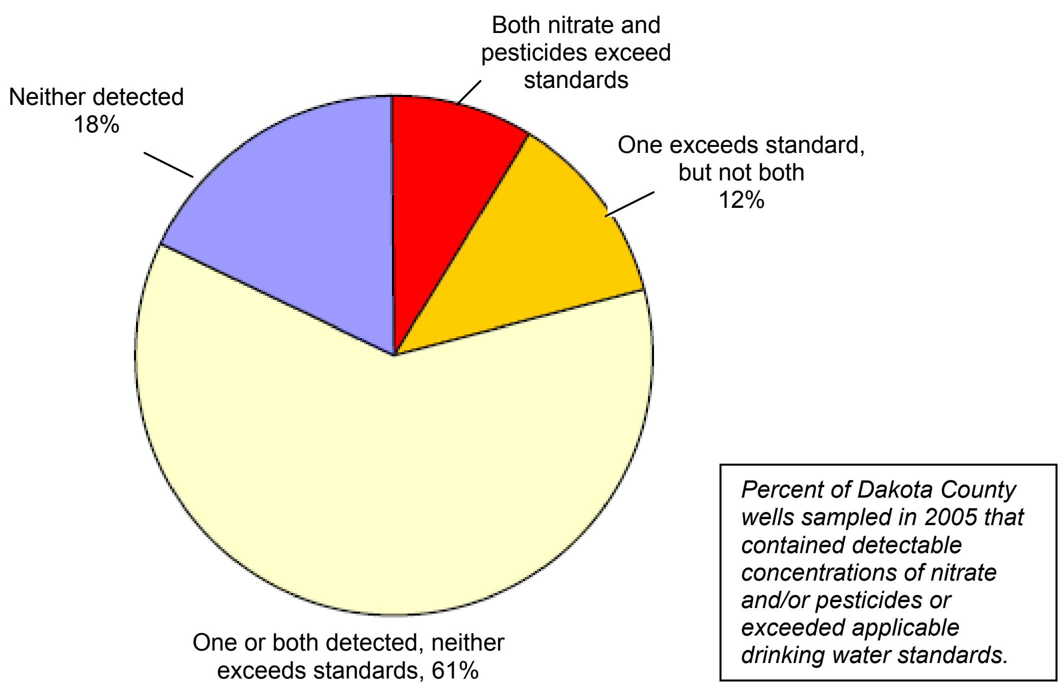


Figure 30. Nitrate and Pesticides Detected in Dakota County Drinking Water Wells, Dakota County Ambient Ground Water Quality Study *(source: Dakota County, 2005)*

A news release sent to more than 8,000 households in Dakota County that rely on domestic wells for their drinking water included the following results from the 2005 AGQS (Dakota County, 2005):

- Of the 15 pesticide parent compounds and 39 degradates tested, 8 pesticide parent compounds and 29 breakdown products were detected. Some of the pesticides associated with the detected compounds have not been sold commercially for several years.
- Alachlor and degradates of cyanazine were detected at concentrations exceeding their drinking water standard (i.e., the HRL). Cyanazine has not been legal for use since 2002, indicating that degradates of this pesticide are persistent in the environment.
- The wells sampled for the AGQS include Dakota County's most commonly used water supply aquifers: unconsolidated sand and gravel deposits, and the Prairie du Chien and Jordan bedrock aquifers (Figure 29).
- Isotope age-dating of ground water from these aquifers indicated that ground water can be as old as 50 years or as recent as one year old, which means that drilling deeper into the aquifer to obtain non-contaminated ground water may not be successful.

Dakota County is the first county in Minnesota to test for pesticides in ground water using methods that have such low detection limits. Although the methodology enables a broader range of pesticides to be analyzed at a lower detection limit, the quality control/quality assurance is less stringent than in the analytical methods employed by MDA.

The 2005 AGQS results for atrazine and its degradates indicate the following: atrazine was detected in 34 percent of the 68 domestic well samples, deethylatrazine was detected in 40 percent of the samples, and deisopropylatrazine was detected in 21 percent of the samples (MDA, 2006b). The rate of detection of atrazine observed in the AGQS results is significantly higher than what was obtained in the MDA condition monitoring project results for the Central Sands region (Figure 25). Like the MDA results; however, the detected concentrations for atrazine and its degradates were low, all being less than 0.40 ug/L.

Pesticides in Surface and Ground Water: National Perspective

The USGS 2006 study of the occurrence of pesticides in the Nation's streams and ground water is based on water samples collected between 1992 and 2001 from more than 186 stream sites and 5,000 wells located across the country (Gilliom et. al., 2006). The water samples were analyzed for a list of 75 of the most heavily used pesticides and 8 pesticide degradates, a fraction of all pesticides currently in use according to the USGS.

The study found that: "Pesticides were less common in ground water than in streams. Nevertheless, more than half of the shallow wells sampled in agricultural and urban areas, and 33 percent of the deeper wells that tap major aquifers and are influenced by a mixture of land uses, contained one or more pesticides or degradates." Ground water is more susceptible to contamination at locations where the subsurface soil is permeable and where agricultural tiling and other structures do not capture and divert recharging water to streams and other surface water bodies.

Echoing previous statements from other studies (see Figure 19), the USGS stresses that, "The entire hydrologic system and its complexities need to be considered in evaluating the potential for pesticide contamination of streams and ground water. Some hydrologic settings where ground water is least vulnerable to contamination are those where streams are most vulnerable, and vice versa (Gilliom et. al., 2006)."

Other Contaminants in Minnesota's Ground Water

In 2005, the MPCA condition monitoring project collected 17 ground water samples from monitoring wells in the Twin Cities and around St. Cloud for analysis of two perfluorinated chemicals or PFCs: perfluoro-octane sulfonate (PFOS) and perfluoro-octanoate (PFOA). These samples were collected because of the relatively new discovery that PFCs are present in some municipal and drinking water wells in eastern portion of the Twin Cities metropolitan area, and the lack of information concerning the presence and extent of PFCs in ground water. The results from the first set of samples revealed that none of the ground water samples contained PFOS or PFOA at concentrations above the laboratory detection limits of 0.5 and 1.0 ug/L respectively. Follow up sampling was conducted in 2006 using an analytical method with a lower detection limit, and this time PFCs were detected.

The MPCA is conducting further investigation of the presence of PFCs in Minnesota ground water, as well as in surface water and fish, as part of an MPCA special study and through the MPCA Remediation Division programs that address clean up of hazardous waste releases. The MPCA is also working cooperatively with the MDH in monitoring domestic, non-community and community wells in the eastern portion of the Twin Cities metropolitan area for PFCs. PFCs are not currently being monitored in ground water as part of the regular MPCA condition monitoring project.

PFCs are an example of human-derived contaminants that fall into the category of "emerging issues." Emerging issues are newly recognized environmental contaminants or concerns that are not fully understood but have the potential to cause adverse ecological and/or human health effects. Because of the limited understanding of their impact on human health and the environment, emerging issues are generally not incorporated into regular environmental protection activities.

Pharmaceuticals and household and industrial use products in Minnesota's rivers, lakes, and ground water are another example of an emerging issue. The MPCA is currently collaborating with researchers at the USGS and St. Cloud State University to monitor and define health effects associated with pharmaceuticals, hormones, and household and industrial products in Minnesota's water resources, to better understand their effects. The USGS, MPCA, and the MDH collaborated previously between 2000 and 2002 in the first state reconnaissance study that showed the presence of industrial and household-use compounds and pharmaceuticals in Minnesota streams, ground water, wastewater and landfill effluents (Lee et. al., 2004). Steroids, nonprescription drugs and insect repellents were the chemical groups most frequently detected, with detergent degradates and plasticizers measured in the highest concentrations.

Pharmaceuticals and household and industrial use products in surface water and ground water are not considered hazardous under existing regulations, and standards for these "emerging" contaminants in drinking water have generally not been developed due to a lack of sufficient toxicological data.

It is important that water resource managers continue to track emerging issues and the developing understanding about their potential effects on human health and the environment, so that this information can be incorporated when appropriate into existing condition monitoring projects.

The Quantity of Minnesota's Ground Water

This report has focused primarily on the issue of ground water quality. The MPCA, MDA, and MDH are specifically charged with carrying out activities designed to protect and improve the quality of Minnesota's ground water. However, quality and quantity are intertwined; both must be protected to ensure the availability of water for its desired use.

The DNR is the state agency responsible for managing Minnesota's ground and surface water resources with regard to quantity. The DNR's map of ground water availability shows that Minnesota's ground water resources are not evenly distributed (Figure 31). Ground water, particularly ground water of adequate quality for drinking and other desired uses, has always been scarce in northwest and southwest Minnesota because of the natural geologic and hydrologic conditions in these areas.

	General Availability of Ground Water by Source		
Area	Surficial Sands	Buried Sands	Bedrock
1	Moderate	Moderate	Good
2	Limited	Moderate	Good
3	Limited	Limited	Good
4	Good	Moderate	Limited
5	Moderate	Limited	Limited
6	Limited	Limited	Limited

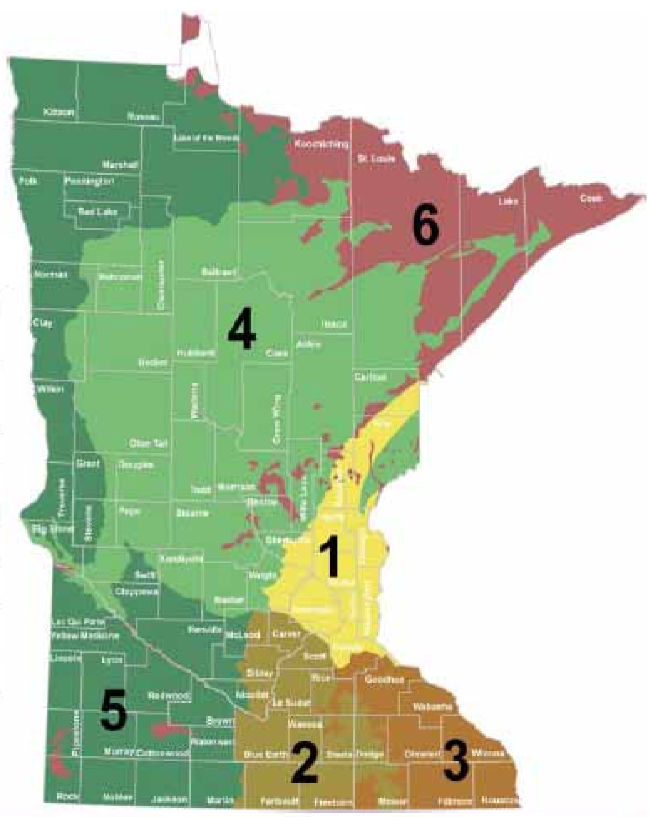


Figure 31. Availability of Ground Water in Minnesota *(source: DNR, 2005)*

To help overcome the difficult problem of finding water of adequate quality and quantity for drinking and other needs, six rural water systems have been constructed in northwest and southwest Minnesota since the 1970s. Three systems currently operate in northwest Minnesota (North Kittson Rural Water in Lake Bronson; Marshall-Polk Rural Water in Warren, and Kittson-Marshall Rural Water in Donaldson); and three systems operate in southwest Minnesota (Lincoln-Pipestone Rural Water in Lake Benton; Rock County Rural Water in Luverne, and Red Rock Rural Water in Jeffers).

The rural water systems are publicly subsidized but the cost for service is still substantial (Figure 32). In many areas of northwest and southwest Minnesota, nitrate contamination of ground water has increased the demand for hook ups and also increased the cost of service, as the rural water systems have been forced to take steps to maintain nitrate concentrations below the drinking water standard (see previous section on Nitrate Contamination of Minnesota's Drinking Water).

Figure 32. Facts about Red Rock Rural Water System (RRRWS)

City of Jeffers, Cottonwood County, Southwestern Minnesota

RRRWS was established 1981, and service began 1985.

<u>The original system:</u> consisted of 2 wells, 1 water tower
supplied 3 communities and 285 rural users

<u>Today:</u> 5 different water sources needed
1,400 miles of pipeline are used to supply 1,360
rural users over portions of 9 counties plus 8 small cities

Original hook up cost for each rural user was $7,178 (RRRWS, 2004).
A hook up fee of $12,000 was approved by Board July 2006 (RRWS, 2006).

As of 2006, the United States Department of Agriculture (USDA) Rural Development had awarded RRRWS $22 Million in low interest loans and grants (USDA Rural Development, 2006).

<u>Just announced</u>: On July 31, 2007, U.S. Senator Norman Coleman announced an additional $12.5 million in low interest loans and grants was awarded to RRRWS to finance a major expansion project to provide service to over 560 new rural users in Nobles and Jackson counties (Coleman, 2007).

The unequal distribution of Minnesota's water resources is becoming better known as the construction of ethanol plants has boomed over the last five or so years. Ethanol plants tend to be built in agricultural areas where corn is grown, which often coincide with regions where water resources are limited (Figure 33). Although the industry is working to reduce its water needs, current ethanol production processes require approximately 4.0 to 4.8 gallons of water per gallon of ethanol produced (MPCA, 2007). Putting this statistic together with the typical ethanol plant capacity of at least 20 million gallons annually (and the trend is towards constructing even higher capacity plants), a huge volume of water, typically ground water, is needed for production. The question remains as to whether this water can be supplied without impacting ground water quality or compromising other higher-level needs for water.

Even the Twin Cities, which are geographically blessed with vast bedrock aquifers and the Mississippi River, are not immune from concerns about water quantity and quality. Suburban cities with growing populations must be mindful of neighboring communities when seeking to expand their municipal water systems (e.g., Woodbury and Afton). The impact of increased ground water pumping on cold water trout streams has also been an issue in several metro area communities (e.g., Brown's Creek in Washington County, the Vermilion River in Dakota and Scott Counties). And communities on the bluffs of the Minnesota River in Dakota and Scott counties have gone through numerous battles involving river bluff development and associated water resource development because of the impact these activities could have on the calcareous fens that occur at the base of the river bluff. The calcareous fens, an artifact of rare hydrogeochemistry, support a unique ecosystem that includes many rare plants that are protected by state law.

As Minnesota's population grows and development continues, it is important to consider how our ground water resources may be impacted. How will additional development and the associated growth in impervious surface affect the recharge areas for our aquifers? Will additional pumping from new and existing water supply wells affect ground water quality? Will construction of an increasing number of storm water infiltration basins intended to prevent degradation of our streams and rivers have a negative impact on the quality of our ground water? Will the increasing number of storm water infiltration basins increase ground water quantity by aiding recharge? And what about climate change? Will the changing weather and precipitation patterns affect recharge to the aquifers that we depend upon more heavily each year, and on which we absolutely rely during times of drought? These are some of the unknowns that face water resource managers at this time.

The EQB recently completed a county by county evaluation of the sustainability of Minnesota's water resources (EQB and DNR, 2007); among the report findings is a call for better understanding of how land use activities and water quality may affect future water supplies.

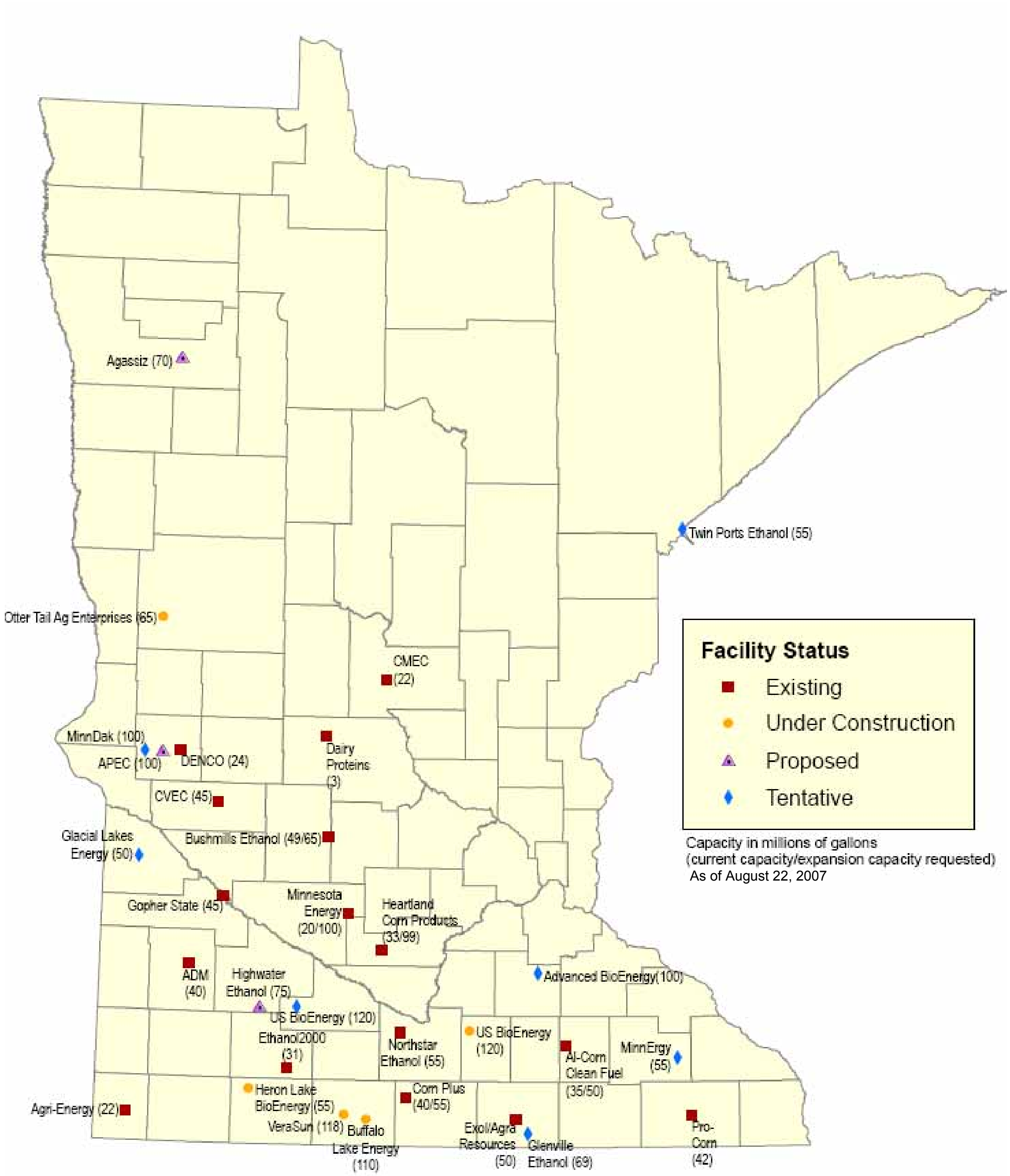


Figure 33. Ethanol Plants in Minnesota, Present and Future *(source: MPCA, 2007)*

Summary of Results and Considerations for Future Efforts

Minnesota is fortunate to have plentiful water resources that have been adequate to supply most needs. However, the state's substantial population increase during the 1990s and projected continued growth has created an increasing demand for water. This raises concerns about whether the quality and quantity of our ground water reserves is adequate to provide for future needs, and whether our current use is sustainable. This report helps address these concerns by providing information about the condition of Minnesota's ground water and progress in implementing ground water condition monitoring.

The MPCA, MDA and other state and local agencies have been monitoring the quality of the state's ground water since the 1970s. During this time, the science of ground water has evolved and changed tremendously, leading to better knowledge and understanding. The MPCA's current condition monitoring project, begun in 2004, appropriately focuses on the state's shallow aquifer systems that are most vulnerable to contamination.

Ground Water Condition Monitoring Results

The MPCA and MDA monitoring data from 2004 and 2005 reveal that ground water quality in Minnesota's vulnerable aquifers is generally good and in compliance with existing drinking water standards. However, human-caused impacts to ground water quality are apparent in many areas of the state. In urban areas, especially the Twin Cities metropolitan area, Rochester and St. Cloud, elevated concentrations of chloride and nitrate, and detectable concentrations of VOCs are common. In rural and agricultural areas, nitrate concentrations are frequently elevated or exceed standards; and pesticides and pesticide degradates are commonly detected, though at concentrations that are nearly always less than applicable drinking water standards.

The MPCA and MDA monitoring results show that the areas where ground water quality impacts were measured correlate well with land uses in those areas that are known to cause the observed quality impacts. The widespread occurrence of elevated nitrate concentrations in agriculture-dominated regions and in unsewered residential areas (Figures 12 through 15) is particularly noteworthy.

The effort to look for trends in ground water quality over time using data from the previous MPCA Baseline Study and the current MPCA condition monitoring project illustrates the challenges involved in conducting trend analysis over an area as large the state of Minnesota. While both the median concentration of chloride and the rate of detection of VOCs doubled in the time between the Baseline Study and the condition monitoring project, the geographic distribution of wells sampled for the condition monitoring project is biased in favor of urban locations that are more likely to be impacted by chloride and VOCs, relative to the Baseline Study. Thus, whether the increases in median chloride concentration and VOC detection are due to the differing geographic distribution of wells or to real changes in ambient ground water quality, or some of both, cannot be determined.

MPCA Condition Monitoring Project

The characteristics that make ground water our most stable and dependable source of high quality water–the vast aquifers in which it resides, its resistance to drought, and the natural cleansing that occurs as it slowly moves through the natural filters of soil and rock–also create challenges for detecting changes in quality that may be occurring. The MPCA's decision to focus ambient monitoring on Minnesota's vulnerable aquifers is an important step forward, and its use of more than 10,000 qualified existing monitoring and domestic wells to obtain a random, statistically sound snapshot of ground water quality each year provides flexibility and economy.

The condition monitoring project's use of both monitoring and domestic wells adds a level of complication to interpretation of the ground water quality results, as was highlighted several times in this report. However, as more ground water quality data is collected over time, a data set that includes results from both monitoring and domestic wells will add value by allowing a more robust analysis of ground water condition to be made.

The two years of ground water quality data from 2004 and 2005 evaluated in this report are not sufficient to support an analysis of ground water quality trend. Conducting a trend analysis using randomized data collected over a large geographic area like the state of Minnesota requires a long term and consistent monitoring effort of at least several years. To address the issue of trend on a shorter timeline, the MPCA is developing a separate trends monitoring network and a supplemental changing land use monitoring network to provide an alternative means of evaluating changing ground water quality.

Note that the trends and changing land use monitoring networks should not replace the ambient monitoring that is currently conducted by the MPCA condition monitoring project. Indeed, the MPCA condition monitoring project as presently designed will provide a valuable, long-term record of ambient ground water quality in vulnerable aquifers across Minnesota. This is something Minnesota does not currently have. As stresses on Minnesota's ground water resources increase, this record will become increasingly important to the accurate assessment and proper management of Minnesota's most used and most vulnerable ground water resources.

When the MPCA first began monitoring ground water quality in the 1970s, hazardous substances in ground water, particularly VOCs, were the focus of concern. Today, other manmade chemicals that have begun to be identified in Minnesota's surface and ground water resources are raising concerns. These include the PFCs that have been identified in drinking water in several communities in the east part of the Twin Cities metropolitan area; and also pharmaceuticals, antibacterial compounds, and surfactants that have been widely detected in surface water downstream of wastewater treatment plants and in ground water. It is important that MPCA managers continue to keep on top of emerging issues such as these and consider potential modifications to the condition monitoring project, as appropriate, to ensure that the MPCA fulfills its charge to monitor and protect the condition of Minnesota's ground water.

Future Efforts

This report emphasizes the need to understand ground water quality data well enough to appreciate what the data can and cannot reveal about condition. Ambient ground water quality monitoring data alone is generally not sufficient for identifying developing ground water quality concerns or localized ground water quality issues. For this reason, it is critical that water resource managers use other information in conjunction with ambient ground water quality monitoring to form their understanding of ground water condition.

An example is the MPCA's pairing of ambient ground water quality monitoring with studies of land use impacts on ground water quality. From about 1996 until about 2001, the MPCA conducted numerous studies - some small in scale, others more involved - to evaluate the impact of ISTS and manure management practices on ground water quality. The MPCA also conducted several studies that looked at how ground water quality changes as land use evolves from a rural to a suburban setting. Currently, the MPCA is conducting two such studies investigating the impact of rain gardens on ground water quality and the impact of land use on ground water temperature in the vicinity of a trout stream.

More studies of this type are needed to keep up with changing land use practices that have the potential to impact ground water, not only to identify whether impacts are occurring, but also whether the impacts rise to a level of concern. Without this information, it is difficult for the MPCA and other governmental bodies to proactively issue permits, set policy and establish environmental priorities that are protective of ground water. The MPCA-managed storm water program is one example of a program that has the potential for substantial impact to ground water quality, yet limited information is available about the effects of common storm water practices on the underlying ground water quality.

There is also a growing need to better incorporate ground water and surface water interaction into water resource management activities. In this report, several examples were provided of Minnesota cities that have struggled to maintain a reliable source of good quality water and found that their ground water quality problems resulted in large part from the interaction with impacted surface water. The potential for ground water to improve (or potentially degrade) surface water quality is a factor that should be routinely evaluated as the MPCA undertakes investigation of Minnesota's impaired waters.

Many new challenges will be faced by Minnesota's water resource managers as the 21st century unfolds. Chief among these is a changing and less predictable climate, rapid growth of impervious soil cover that reduces the land area where aquifers can be recharged, and an ever increasing demand for potable water. These challenges require that Minnesota water resource managers monitor ground water condition with an eye to the future, and make the critical step of linking land use activities with their impact on ground water, so that practices and guidelines can be developed that will protect this valuable resource.

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