Nitrate in Minnesota Ground Water

A GWMAP PERSPECTIVE

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Minnesota Pollution Control Agency
Ground Water Monitoring and Assessment Program

MINNESOTA POLLUTION CONTROL AGENCY
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Abstract

In 1991, a Nitrogen Task Force consisting of staff from several state agencies produced a report on nitrogen in Minnesota ground water. Informational needs related to nitrogen were identified. Between 1991 and 1997, the Minnesota Pollution Control Agency's (MPCA) Ground Water Monitoring and Assessment Program (GWMAP) collected considerable information related to the distribution of nitrate in Minnesota ground water. This information fills some of the informational gaps identified by the Nitrogen Task Force.

Much of the GWMAP's nitrate data comes from two separate studies. The first, called the baseline study, was designed to assess nitrate concentrations in the principal aquifers of Minnesota. The second study is an on-going effort in St. Cloud to determine the effects of land use on ground water quality. Results from these two studies were used to determine background concentrations of nitrate in Minnesota's principal aquifers and under different land uses, and to identify factors resulting in elevated concentrations of nitrate and elevated potential risk to drinking water receptors. Extensive literature reviews on the fate of nitrogen in the environment were completed and this information is included in the report.

Nitrate stability was an important factor affecting the distribution of nitrate in ground water. Nitrate-stable waters are defined as those in which nitrate will not undergo denitrification. Ground water in which dissolved oxygen concentrations exceeded 0.50 mg/L, Eh was greater than 20 mV, and iron concentrations were less than 1.0 mg/L were considered to represent nitrate-stable conditions. Nitrate will rapidly undergo denitrification in nitrate-unstable waters. Background concentrations of nitrate in nitrate-unstable samples from the baseline study were very low in all aquifers, generally below 0.10 mg/L and often below 0.010 mg/L. Median concentrations in nitrate-stable samples ranged from below the reporting limit of 0.5 mg/L in the Precambrian, buried Quaternary, and St. Peter aquifers to 8.6, 7.1, and 2.7 mg/L in Cretaceous, Galena, and water table Quaternary aquifers, respectively, but these differences were not statistically different. Concentrations of nitrate and potential risk to drinking water receptors was significantly greater in nitrate-stable wells compared to nitrate-unstable wells.

Physical factors that affect the occurrence of nitrate-stable conditions in ground water, such as recharge rate and soil organic matter content, are only briefly discussed. Low concentrations of total organic carbon were an important factor contributing to nitrate stability in Quaternary aquifers. Decreased distance to upper bedrock and decreased thickness of confining units were important factors contributing to nitrate stability in the Prairie du Chien, Jordan, St. Peter, and Franconia-Ironton-Galesville aquifers. Shallow well depth was an important factor contributing to nitrate stability in Cretaceous aquifers. There was no measured attribute which accounted for increased nitrate stability in the Precambrian and Upper Carbonate aquifers, possibly because these may represent highly dynamic systems (fractured bedrock).

Statistically, concentrations of nitrate in shallow ground water from the St. Cloud study followed the pattern: irrigated agriculture > unsewered residential > nonirrigated agriculture > sewered residential = commercial > undeveloped. Background concentrations in undeveloped, commercial, sewered residential, nonirrigated agriculture, unsewered residential, and irrigated agricultural land uses were approximately 0.60, 1.0, 2.0, 4.6, 8.0, and 13 mg/L, respectively. Potential risk to drinking water receptors was extremely high under irrigated agriculture, moderate under unsewered residential, and low under remaining land uses. There was no strong correlation between any measured parameter and nitrate concentration in shallow ground water, indicating the quantity of nitrate available for leaching is the primary factor affecting nitrate concentration in shallow ground water. Consequently, well construction, nitrogen application rates, and hydrologic controls such as rate, quantity, and timing of recharge will be the primary factors affecting nitrate concentration in most shallow ground water systems.

There were no significant differences in baseline nitrate concentrations between aquifers, considering only nitrate-stable samples. This provides further evidence that in sensitive hydrologic settings, where recharge readily occurs and creates conditions favorable for nitrate stability in ground water, the controlling factor on nitrate concentration in ground water is the amount of nitrate available for leaching.

Concentrations of nitrate and potential risk to drinking water receptors was significantly greater in large diameter (> 16 inches) wells compared to small diameter

(< 12 inches) wells. Large diameter wells were considered to represent poor construction because they were dug wells and subject to leakage along casing joints. In addition to direct transport of nitrate from the unsaturated zone to the well, poor construction provides a mechanism for transporting oxygen-rich water, thus increasing the nitrate stability within the well. Effects of poor construction are probably limited to individual wells, unless the overall aquifer nitrate-susceptibility is high.

There were no significant differences in nitrate concentrations between sampling quarters for the St. Cloud study. Nitrate concentrations in baseline wells sampled in June were greater than in other months. June represents a time when nitrogen concentrations in soil are elevated and when spring recharge may still be occurring. Data from the St. Cloud land use study showed that nitrate concentrations decreased following snowmelt due to dilution, but concentrations increased during the summer in response to large precipitation events. Additional sampling is recommended to assess seasonal effects, since only one year of data exist for the St. Cloud study.

The results indicate that shifts in land use may lead to significantly greater nitrate concentrations and potential risk to drinking water receptors. Aquifer-wide assessments should be conducted when the following land use changes are occurring over an aquifer which is susceptible to contamination:

- Nonirrigated to irrigated;
- residential development within irrigated agriculture;
- unsewered residential development;
- conversion of undeveloped land to agriculture or unsewered residential;
- siting of feedlots or application sites for animal waste; and
- shifts in agriculture to more nitrogen-intensive crops, such as potatoes.

A ground water assessment includes three components:

1. Utilizing geochemical information to assess aquifer nitrate susceptibility;
2. conducting predictive modeling and assessing sensitivity of physical, chemical, and land use factors on nitrate distribution in ground water; and
3. estimating the probability of exceeding drinking water or surface water criteria.

Hydrologic information, such as recharge rate, aquifer conductivity, and aquifer dispersivity, can assist interpretation of geochemical information to assess nitrate susceptibility of an aquifer.

The GWMAP has begun two new studies related to nitrate distribution in ground water. The first is a study of the effects of septic systems on water quality. The second is a study of the effects of manure storage systems on ground water quality. These studies include the three aquifer assessment criteria presented above. Annual or summary reports will be prepared for each study.

[1]Introduction

The Minnesota Ground Water Protection Act of 1989 required the Minnesota Pollution Control Agency (MPCA) and the Minnesota Department of Agriculture to prepare a report on nitrate and related nitrogen compounds in ground water. The report, published in 1991, was prepared in consultation with the Board of Soil and Water Resources and University of Minnesota Agricultural Experiment Station. Other agencies were consulted while writing this report.

Several objectives were addressed during preparation of the report.

1. Existing data and literature were examined to provide legislators, policy makers, planners, and managers with information necessary to respond to the issue of nitrogen in ground water.
2. An overview of nitrogen characteristics and health effects was included.
3. Nitrogen inputs and causes of nitrogen contamination, best management practices (BMPs), and policy associated with the primary nitrogen sources were discussed.
4. Federal, state, and local response to the issue of nitrogen in ground water was examined to make feasible recommendations for appropriate state and local response.

The final report, *Nitrogen in Minnesota Ground Water* (Minnesota Pollution Control Agency and Minnesota Department of Agriculture, 1991), included several recommendations. Some of these are summarized below.

1. Long-term monitoring is needed to assess nitrate trends over time in the principal aquifers of the state. This monitoring should be focused in high priority or problem areas or aquifers. An important objective of this monitoring is to determine the effectiveness of state and local programs in nitrogen management. Monitoring programs should include rigorous sampling and data analysis procedures.
2. Data management is needed for nitrogen and includes establishment of statewide standards for collection and analysis of data, a statewide database for nitrate, and increased technical assistance, particularly at the local level.

[1] **ABBREVIATIONS**: MPCA, Minnesota Pollution Control Agency; VOCs, volatile organic compounds; GWMAP, Ground Water Monitoring and Assessment Program; CWI, County Well Index; HRL, Health Risk Limit; MCL, Maximum Contaminant Level; QA/QC, Quality Assurance/Quality Control.

3. Nitrogen management plans for cropland include establishing realistic yield goals, taking proper credits for manure nitrogen, properly managing and operating feedlots, and accurately accounting for irrigation water in crop management.
4. Research needs include understanding the fate of manure nitrogen, developing BMPs for specialty crops such as potatoes, and identifying appropriate lot sizes in unsewered areas.
5. Health risk assessments should be made in areas where there are potential nitrate contamination problems and ground water receptors are present (i.e., infants).

The MPCA's GWMAP conducts ground water studies related to some of these recommendations. The GWMAP studies provide water resource managers with information for making decisions that minimize risk to human and ecological receptors. Since 1991, the GWMAP has collected information on the distribution of nitrate in Minnesota's principal aquifers. This information can be used to establish background concentrations of nitrate under natural and anthropogenic conditions, determine if and where aquifers have been impacted above background concentrations or to levels that represent a risk to receptors, and identify factors affecting the distribution of nitrate in ground water. Management strategies can then be developed to minimize impacts of human activity on ground water and surface water.

Information on distribution of nitrate is derived primarily from two studies. The first is the statewide baseline study, initiated in 1992, in which 954 primarily domestic wells were sampled from Minnesota's principal aquifers. The second study, begun in 1996, is designed to assess impacts of land use on water quality of a surficial sand and gravel aquifer in the St. Cloud area. Additional studies, initiated in the past year, examine the effects of manure management and septic systems on ground water quality.

The following report presents a compilation of information on nitrogen in Minnesota ground water collected by GWMAP between 1991 and 1997. Information from the baseline study (see Section 2.1) can be used to establish background nitrate concentrations in principal aquifers, identify aquifers where nitrate contamination is a potential concern, and identify some causal factors for distribution of nitrate in principal aquifers. Current studies (see Section 2.2) being conducted by GWMAP will help identify differences in nitrate concentration under different land uses, aid in understanding the behavior of nitrate in ground water, and provide information about risk to ground water receptors in nitrate-susceptible aquifers. As a result of these studies, the GWMAP has developed protocols for data and sample collection and for data analysis that may be useful in developing statewide standards.

1. Nitrogen in the Environment

The form of nitrogen in the environment is controlled by oxidation-reduction reactions, most of which are microbiologically mediated. In aqueous systems with oxidizing conditions (oxygen is present), nitrogen will occur as a gas (NO or N_2O) or as the dissolved ions nitrate (NO_3^-) or nitrite (NO_2^-). Under reducing conditions nitrogen occurs as ammonia (NH_4^+-NH_3) or in organic forms. Nitrogen gas (N_2) is relatively inert. Other forms of nitrogen, such as cyanide, are less common and generally not persistent.

Nitrate can represent either a drinking water concern or a threat to ecological environments as a result of nutrient enrichment. The Health Risk Limit (HRL) for nitrate is 10 mg/L ppm and the target endpoint is the cardiovascular/blood system (Minn. Rules 4717.7100-4717.7800). The human health risk is associated with infants age six months or less. Nitrite has similar health effects, but concentrations of nitrite are generally very low in ground water. In surface water, nitrate is often limiting to algae growth, and increased inputs lead to excessive growth of algae, resulting in oxygen depletion. Ammonia does not have a health-based drinking water criteria, although there is a Lifetime Health Advisory level of 30 ppm. Ammonia may have significant impacts on aquatic life, however. Some organic compounds containing nitrogen, such as nitrosamines, are suspected carcinogens. It is unclear to what extent these occur naturally and if they are more likely to form in the presence of elevated nitrate concentrations, but they are rarely found at concentrations which represent a potential health concern. Consequently, nitrate is the nitrogen form of greatest concern in drinking water, although the relationships between reduced and oxidized forms of nitrogen cannot be ignored.

1.1. Assessing Nitrate Available for Leaching

Humans have dramatically altered the nitrogen cycle. Globally, release of nitrogen from combustion of fossil fuels has led to environmental concerns such as acid rain. Ground water and surface water have been impacted locally by large inputs of nitrogen into the environment, such as with cultivation (oxidation of organic matter), fertilization, and waste management (human and livestock).

Nitrogen concentrations of most aquifer materials are insignificant. Consequently, nitrogen must leach through the soil and vadose zones to reach ground water. Ammonia and organic forms of nitrogen are attenuated in the vadose zone and will not reach ground water in appreciable quantities unless there is a large source of reduced nitrogen, as might occur under a feedlot. Nitrate is mobile in soil and will leach to ground water unless taken up by plants or denitrified under reducing conditions before reaching the aquifer. Three conditions which enhance nitrate leaching to ground water are therefore ground water recharge, oxidizing conditions in the vadose zone, and nitrogen inputs (e.g. fertilizer, manure, etc.).

1. Recharge rate considers both the quantity of annual recharge and the rate at which an aquifer is recharged. Greater quantities of recharge deliver more nitrate to an aquifer, but if the rate is sufficiently slow, aquifer dilution may keep nitrate concentrations at acceptable levels. Uniform, coarse-textured soils with a shallow water table are conditions most conducive to leaching of nitrate.
2. Nitrate will be converted to nitrogen gas (denitrified) in the absence of oxygen and presence of a food source (organic carbon). Under oxidizing conditions, nitrate will be stable and reduced forms of nitrogen will be converted to nitrate. Nitrate cannot be attenuated below the root zone in soils with a low moisture-holding capacity and low concentrations of organic carbon. These conditions occur in coarse-textured soils.
3. In soils with large quantities of rapid recharge and oxidizing environments, the most important factor affecting the amount of nitrate leached to ground water will be the quantity of nitrogen available in the soil. Based on condition 2 above, the form of nitrogen is not important. For example, nitrate concentrations will be greater beneath a septic drainfield than beneath a nonirrigated agricultural field, although the area impacted by leached nitrate will be smaller under the drainfield.

1.2. Assessing Fate of Nitrate in Ground Water

The primary mechanisms of nitrate attenuation in ground water are dilution and denitrification. Dilution will occur through recharge with water that has a lower nitrate concentration than the concentration in the aquifer. This can be an important mechanism when nitrate is introduced into ground water as a point source, such as a septic system or a feedlot, but it less important for nonpoint sources. Dilution will be most important on coarse textured soils with a shallow water table, since recharge will be greatest under these conditions. Dilution does not remove nitrate from ground water, however.

Denitrification can occur in ground water but requires presence of a food source (organic carbon) and absence of oxygen. Denitrification is a process that removes nitrate from ground water, since nitrate is converted to nitrogen gas. Shallow ground water often has low concentrations of organic carbon and contains oxygen, so denitrification is limited in shallow ground water. Under these conditions, nitrate is considered to be stable in ground water and these aquifers or portions of these aquifers are susceptible to nitrate contamination. If conditions are conducive for denitrification, nitrate is not stable and these aquifers or portions of these aquifers are not susceptible to contamination. Consequently, when examining nitrate information, it is important to determine if the sample represents nitrate-stable or nitrate-unstable conditions.

The GWMAP uses the following criteria to define ground water as nitrate-stable:

- Eh is greater than 250 mV;
- dissolved oxygen concentration is greater than 0.50 mg/L; and
- dissolved iron concentration is less than 0.70 mg/L.

It is important to note that nitrate-stability varies with both time and space. For example, during spring recharge, oxygenated water is introduced into an aquifer and the portion of an aquifer in which nitrate will be stable may be larger than at other times of the year. Fractured bedrock and aquifer mixing, such as occurs with heavy pumping, are also factors which increase the likelihood a portion of an aquifer will have nitrate-stable conditions. Consequently, it is important to identify portions of an aquifer that are nitrate-unstable and nitrate-stable, but it is equally important to identify factors which may change the nitrate stability of an aquifer.

This paper primarily focuses on assessing fate of nitrate in ground water rather than on determining nitrogen available for leaching. Hydrogeologic factors affecting the leaching of nitrate to ground water are briefly discussed, particularly the results from the St. Cloud study.

2. Methods

2.1. Statewide Baseline Study

The statewide baseline study was initiated shortly after GWMAP was created in 1991. The GWMAP was established to provide consistent and comprehensive ground water quality information. The baseline study was designed to provide baseline or "background" water quality in Minnesota's principal aquifers. Specific objectives of the statewide baseline study were to:

1. Determine median and 95th percentile concentrations of selected chemicals in Minnesota's principal aquifers;
2. identify locations where water quality problems existed; and
3. determine the spatial distribution of chemical concentrations in Minnesota's principal aquifers.

A statewide grid was established, with a spacing of eleven miles between grid nodes. Centered at each node was a nine-square mile area (three miles by three miles) in which one well was sampled from each identified principal aquifer. Each selected well had a County Well Index (CWI) well log. Wells which were grouted were considered to represent good construction and were preferentially selected. Wells were purged until field temperature, pH, and specific conductance stabilized. Data were stored in a FoxPro database until being analyzed in 1997. Field collection and data analysis methods are described in MPCA (1996) and MPCA (1998a), respectively. Specific methods employed during the baseline study are described in MPCA (1998b). Because nitrate in an individual well may represent a source related to human activity, spatial analysis was not performed.

2.2. St. Cloud Land Use Study

The St. Cloud land use study was initiated in 1996 in response to numerous questionnaires and other information which indicated ground water managers and legislators wanted information on the effects of human activity on ground water quality. The objectives of the study are to:

1. Determine if water quality differs beneath different land uses;
2. evaluate overall water quality and risk to ground water receptors in a variable and changing land use setting;
3. evaluate seasonal and annual variability in water quality beneath several land uses; and
4. determine trends in water quality in areas where land use changes.

Construction of a monitoring network was initiated in autumn 1996, and was completed the following spring. The final network consists of 23 monitoring wells screened across the water table, 21 deeper domestic or monitoring wells screened at different depths within the unconfined water table and underlying buried artesian sand and gravel aquifers, and two surface water sampling points in the Sauk River. At three locations, shallow monitoring wells are nested with deeper wells. Three monitoring wells are located in each of six different land uses: undeveloped, unsewered residential, sewered residential, commercial/industrial, nonirrigated corn, and irrigated corn. The remaining five monitoring wells are located in transitional areas which are undergoing changes in land use. The deeper wells are scattered across the study area. Four shallow monitoring wells are instrumented with continuous water level recorders. Two continuous surface water level recorders are instrumented on the Sauk and Mississippi Rivers. A permanent National Weather Service station is located at the St. Cloud municipal airport. In addition to a wide range of chemicals, sampling has been conducted for tritium,

nitrogen-15, and for aquifer attenuation characteristics. An extensive geoprobe study was completed across the study area in spring 1998. Geoprobe samples were collected at approximately one mile spacings under several land uses at the water table and at depths of seven and one-half and 15 feet below the water table. Detailed information regarding the design, sampling, data analysis, and interpretations for the St. Cloud land use study can be found in MPCA (1998c) and MPCA (1998d).

2.3. Analytical Methods

Data collection, analytical methods, and information on Quality Assurance/Quality Control (QA/QC) are described in MPCA (1996) and MPCA (1998a). Laboratory samples were analyzed by the University of Minnesota Research Analytical Laboratory. Quality Assurance/Quality Control information, laboratory methods, and reporting limits are provided in Appendix A.

Helsel's Robust Method, a curve-fitting technique, was used to calculate mean and upper 95 percent confidence interval concentrations of nitrate. This method assumes a log-normal distribution and works well for sample sizes of 20 or more (Helsel, 1990; Newman et al., 1995). Group tests included the Kruskal-Wallis (more than two groups) and Mann-Whitney (two groups) tests and were used to compare nitrate concentrations between different aquifers, well diameter classes, land use, nitrate-stability classes, year of sampling, month of sampling, and quarter of sampling. Nitrate correlations with other chemical parameters, sampling date, well depth, depth to bedrock, static water elevation, depth to water, and thickness of confining units were calculated using the Spearmann rho method. A significance level of 0.05 was used to identify significant relationships. Statistical methods are discussed in Appendix B.

3. Results and Discussion

3.1. Background Concentrations of Nitrate in Ground Water

Before "nitrate-impacted" ground water can be identified, background nitrate concentrations must be established. Establishing background concentrations of nitrate in ground water is complicated by three factors. First, data from aquifers in which nitrate is stable and in which it will be denitrified must be separated prior to analysis. Second, within nitrate-stable ground water with no anthropogenic nitrogen inputs, natural concentrations will vary between different physical settings. For example, nitrate concentrations directly beneath a hardwood forest are likely to differ from those under grassland. Third, concentrations vary with human activity. For example, nitrate concentrations under continuous nonirrigated corn may be greater than natural background concentrations but lower than under irrigated potatoes. This last factor is important when considering long-term sustainability of ground water resources, since some human activities may impact ground water, but at levels where risk to receptors is low. To illustrate the relationship between these three factors, consider a shallow sand and gravel aquifer beneath a grassland on sandy soils. Natural concentrations of nitrate at the top of this aquifer might be about 0.50 mg/L. Deeper in the aquifer, where denitifying conditions exist, the concentration may be 0.050 mg/L. Beneath nonirrigated continuous corn on the same soil, the concentration may be 5.0 mg/L. If a well were randomly sampled from this aquifer and the nitrate concentration was 3.5 mg/L, we could assume the sample came from a nitrate-stable portion of the aquifer, the concentration was greater than natural background, but the concentration was not greater than background for an agricultural setting.

The first step in establishing background concentrations was to examine the baseline data set and separate data into nitrate-stable and nitrate-unstable samples. This procedure was outlined in Section 1. Although data can be separated by the method described in Section 1, the reporting limit for nitrate during most of the baseline study was 0.50 mg/L ppm. This resulted in almost 80 percent of the samples being below the reporting limit. Thus, in nitrate-unstable (denitrification is likely) samples, this reporting limit is too high. Precise mean concentrations cannot be calculated for nitrate-unstable waters. With some simple assumptions, however, rough estimates of mean nitrate concentrations in nitrate-unstable waters can be calculated. These assumptions are outlined below.

1. Most sampled wells represent nitrate-unstable water.
2. The distribution of nitrate in an aquifer can be described by a logarithmic distribution.

3. The effect of conditions under which assumption 1 fails is minor.

Table 1 presents a summary of total samples collected, by aquifer, and the number of samples in which nitrate-stable conditions were encountered. The second assumption cannot be validated with existing data. The natural distribution of most chemicals in ground water is well described by a log-distribution (MPCA, 1998b). Results from Helsel's method showed correlation coefficients exceeding 0.900 for all regressions, indicating the log model described the data adequately. The assumption that most sampled wells represent nitrate-unstable conditions appears reasonable for Cretaceous and most Precambrian and Quaternary aquifers, but not for other bedrock aquifers. When assumption one fails, estimated nitrate concentrations will exceed the true concentration. There were 192 samples collected in which the nitrate reporting limit was 0.10 ug/L or less. These data were used for comparison with the results from the Helsel method. Using the data with lower reporting limits for the Prairie du Chien aquifer, which had the highest percent of nitrate-stable samples, the mean concentration was calculated to be about 0.005 mg/L, which indicates the curve-fitting error was about 0.60 mg/L. Using a similar analysis for Cretaceous samples, where the extent of nitrate stability was much less, the mean concentration decreased from 0.056 to 0.016 mg/L. A plot of the percent non-detections versus estimated mean concentration indicates a tendency for higher mean concentrations as the percent decreases. This is reasonable, since detections may represent nitrate-stable conditions, thus violating assumption 1.

Although the assumption that all samples were from nitrate-stable conditions may lead to errors of 0.50 mg/L, the error for most aquifers will be much less. The effect of these potential errors is relatively insignificant. Concentrations of nitrate estimated by applying Helsel's method are well below drinking criteria and below background concentrations observed in nitrate-stable wells. The concentrations of nitrate in nitrate-unstable wells are thus very small. Data from the St. Cloud land use study (MPCA, 1998c) verifies this. Using a nitrate reporting limit of 0.010 mg/L, the median concentration of nitrate in domestic wells completed deeper (more than 30 feet below the water table) in the water table and buried aquifers were 0.030 and < 0.010 mg/L, respectively. Data from the St. Cloud geoprobe study showed that nitrate concentrations within seven and one-half and 15 feet of the top of the underlying sand and gravel aquifer were 0.45 and 0.040 mg/L, respectively, even when concentrations at the water table were several parts per million. From a practical standpoint, nitrate is absent in aquifers under conditions in which nitrate would be expected to be denitrified. Nitrate concentrations under nitrate-unstable conditions are very low, probably less than 0.10 mg/L.

Aquifer	**CWI Aquifer Code**	**No. of samples**	**No. of nitrate-stable samples**
Franconia	CFRN	27	9
Franconia-Ironton-Galesville	CFIG, CRFR, CIGL	40	10
St. Peter	OSTP	23	9
Prairie du Chien	OPDC	36	19
Jordan	CJDN	31	13
St. Peter-Prairie du Chien-Jordan	OSTP, OPDC, CJDN	90	41
Mt. Simon-Hinckley	CMSH, CMTS, PHMN	26	5
Cretaceous	KRET	39	5
Galena	OGAL	22	3
Crystalline Precambrian	PCCR, PCUU	29	4
North Shore Volcanics	PMNS	23	8
Proterozoic Metasedimentary units	PMUD	23	6
buried Quaternary artesian aquifers	QBAA	386	47
unconfined buried Quaternary aquifers	QBUA	104	38
buried undifferentiated Quaternary aquifers	QBUU	22	3
Quaternary water table aquifers	QWTA	119	36
Cambrian aquifers	CXXX	102	29
Ordovician aquifers	OXXX	87	33
Precambrian aquifers	PXXX	80	23

Table 1: Aquifers considered in this report.

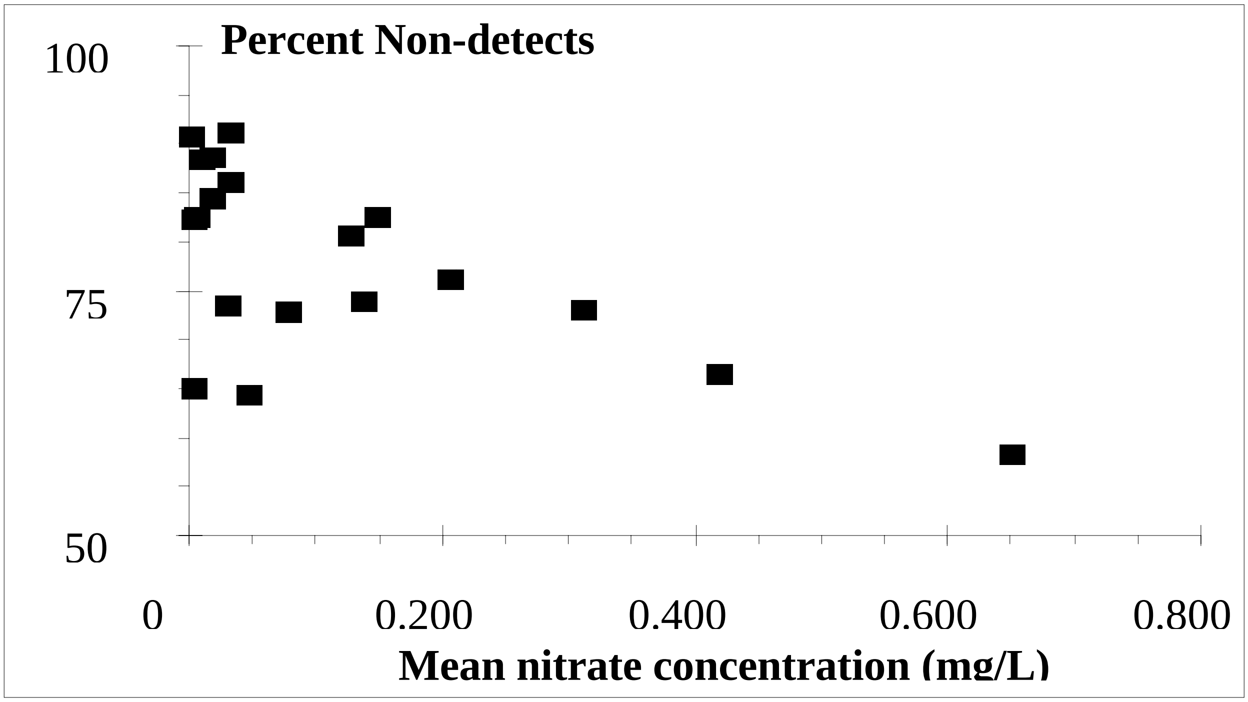

Figure 1: Relationship of mean nitrate concentration estimated using the Helsel Robust Method and the percent of samples below the reporting limit.

Using the three assumptions stated above, Helsel's Robust Method (Newman et al., 1995) was utilized to estimate mean concentrations in the state's principal aquifers. This technique employs curve-fitting procedures utilizing detected values, the reporting limit, and an assumption of a logarithmic distribution. The method works best for sample sizes of 20 or more. The aquifers included in the analysis are therefore restricted by this size limitation and include those illustrated in Table 1. Mean concentrations of nitrate in these aquifers are illustrated in Table 2, along with sample size and the number of values below the detection limit. These concentrations represent background nitrate concentrations in these aquifers under conditions in which nitrate is not stable - i.e. nitrate will be denitrified.

From a nitrate management perspective, nitrate-unstable conditions do not represent a potential health concern. If these aquifers are contaminated with nitrate, either a continual contaminant point source exists or the stratification which was responsible for presence of nitrate-unstable conditions has changed. Factors which may lead to a change in this stratification included recharge, which will introduce oxygen-rich water to an aquifer; pumping, which can draw water from oxygen-rich portions of the aquifer to deeper portions of the aquifer; and poor well construction, which results in the introduction of oxygen-rich water to the aquifer in the vicinity of the well. Water with high concentrations of ammonia and organic nitrogen may become enriched in nitrate if oxygen is introduced to the water prior to consumption, as might occur in the case of a municipal well. Considering these factors, it is important to manage these nitrate-unstable portions of the aquifer to avoid changes which could lead to nitrate-stability. For example, installation of high-capacity wells deep into an aquifer may introduce oxygen-rich water from the top of the aquifer into the lower portion of the aquifer, thus making the entire aquifer susceptible to nitrate contamination.

Aquifer	No. of Samples	No. of Nondetections	Mean (mg/L)
Franconia	27	20	0.147
Franconia-Ironton-Galesville	40	33	0.002
St. Peter	23	19	0.146
Prairie du Chien	36	21	0.649
Jordan	31	20	0.045
St. Peter-Prairie du Chien-Jordan	90	60	0.418
Mt. Simon-Hinckley	26	21	0.127
Cretaceous	39	33	0.016
Galena	22	19	0.031
Crystalline Precambrian	29	24	0.003
North Shore Volcanics	23	15	0.002
Proterozoic Metasedimentary units	23	21	0.030
buried Quaternary artesian aquifers	386	342	0.009
unconfined buried Quaternary aquifers	104	76	0.076
buried undifferentiated Quaternary aquifers	22	20	0.001
Quaternary water table aquifers	119	87	0.310
Cambrian aquifers	102	78	0.205
Ordovician aquifers	87	64	0.029
Precambrian aquifers	80	71	0.017

Table 2: Summary of samples and mean concentrations for selected aquifers.

The remaining discussion focuses on nitrate-stable ground water. These data represent hydrologic and geochemical conditions that result in an aquifer being susceptible to nitrate contamination. Considering nitrate-stable ground water, mean, median, and maximum concentrations of nitrate in 19 aquifers with sample sizes of at least 20 wells are illustrated in Table 3. The percentage of total samples in which nitrate was stable varied widely between aquifers. The greatest percentages of nitrate-stable samples were observed for the Prairie du Chien (53 percent), Jordan (42 percent), and St. Peter (39 percent) aquifers. This may reflect a tendency to complete wells in the uppermost aquifer in southeast Minnesota, since the cost of drilling bedrock wells can be high. This tendency was supported by a qualitative review of well logs. The uppermost aquifer receives more direct recharge than deeper, buried aquifers, and direct recharge water is typically oxygen-rich and therefore nitrate-stable. Another potential explanation for the high percentage of nitrate-stable samples is that these aquifers are heavily utilized and local pumping may break up the stratification of nitrate-stable and -unstable portions of the aquifer. Less than 20 percent of wells sampled from the buried Quaternary, Cretaceous, Galena, crystalline Precambrian, and Mt. Simon-Hinckley aquifers had nitrate-stable conditions.

Median concentrations of nitrate were below the reporting limit of 0.50 mg/L for the Precambrian (North Shore volcanics, crystalline, and Proterozoic Metasedimentary units, not including the Sioux Quartzite), buried confined Quaternary, and St. Peter aquifers. Except for the St. Peter aquifer, these represent aquifers in which nitrogen inputs should be low because they are in nonagricultural areas, although there may be localized inputs from septic systems, animal storage areas, and dumps. Mean concentrations were estimated at 0.27 and 0.32 mg/L for the Precambrian and buried confined Quaternary aquifers, respectively. The highest median nitrate concentrations were observed for the Cretaceous (8.6 mg/L), Galena (7.1 mg/L), and water table Quaternary (2.7 mg/L) aquifers. For the Cretaceous and Galena aquifers, there were only five and three samples in which nitrate was considered to be stable, respectively. The very high nitrate concentrations in these wells suggest rapid response to percolating recharge water. For example, Cretaceous samples sensitive to nitrate contamination were locations where Cretaceous aquifers are close to the land surface (Patterson and Bradt, personal communication), since Cretaceous aquifers are generally deep, anaerobic, and therefore not susceptible to nitrate contamination. Similarly, the Galena aquifer is generally not susceptible to contamination where it is covered by at least 100 feet of drift or younger bedrock, but in locations where it is the uppermost bedrock, karst topography may result in a system which is highly susceptible to contamination by nitrate.

Aquifer	Total samples	Stable samples	Median	Mean	Max.	75th quartile	No. above HRL
Franconia	27	9	1.040	1.224	7.850	2.300	0
Franconia-Ironton-Galesville	40	10	0.935	1.020	7.850	2.240	0
St. Peter	23	9	< 0.500	0.777	7.320	1.800	0
Prairie du Chien	36	19	1.860	1.555	15.700	3.415	1
Jordan	31	13	1.420	1.272	9.200	1.990	0
St. Peter-Prairie du Chien-Jordan	90	41	1.320	1.217	15.700	2.935	1
Mt. Simon-Hinckley	26	5	1.300	ins	4.000	-	0
Cretaceous	39	5	8.625	ins	23.300	-	3
Galena	22	3	7.060	-	30.460	-	1
Crystalline Precambrian	29	4	< 0.500	ins	3.900	-	0
North Shore Volcanics	23	8	< 0.500	ins	16.700	-	1
Proterozoic Metasedimentary	23	6	< 0.500	ins	8.100	-	0
buried Quaternary artesian	386	47	< 0.500	0.321	33.240	1.725	4
unconfined buried Quaternary	104	38	1.000	1.109	47.900	6.650	8
buried undifferentiated Quaternary	22	3	< 0.500	-	10.870	-	1
Quaternary water table	119	36	2.650	2.101	18.130	6.100	4
Cambrian aquifers	102	29	1.300	1.205	9.200	2.060	0
Ordovician aquifers	87	33	1.800	1.408	30.460	3.300	2
Precambrian aquifers	80	23	< 0.500	0.274	16.700	1.055	2

Table 3: Summary data from nitrate-stable samples for the 19 major aquifers. Concentrations are in mg/L or parts per million.

Except for the aquifers discussed above, the aquifers shown in Table 3 are exposed to a wide variety of nitrogen inputs. It is thus difficult to establish “background” concentrations, since the samples from these aquifers probably represent a range of land uses. This point is discussed further in the Recommendations section. It is useful to understand the distribution of nitrate in these aquifers so that extremes in measured concentration can be identified. Nitrate concentrations below the upper quartile represent 75 percent of the nitrate distribution. Upper quartile concentrations are illustrated in Table 3. Again, there is a range in the data. The unconfined Quaternary samples had upper quartile concentrations greater than 6.0 mg/L. It appears that nitrogen inputs into these aquifers are greater than into the other aquifers. The data in Table 3 cannot be taken as representative of background concentrations in those aquifers that are likely to have anthropogenic sources of nitrogen. Differences in nitrate concentration between aquifers will be examined more closely in Section 3.2.3.

Data from the St. Cloud monitoring wells are illustrated in Table 4. Included in this table are data from a variety of literature sources. The following should be considered when reviewing data from these literature sources.

- Most data are from surficial sand and gravel aquifers.
- For some studies, an overall median concentration was used to represent data from more than one sample location.
- Concentrations from plumes or directly below contaminant point sources were not included. This is most relevant for unsewered data, in which concentrations of nitrate in septic plumes are often between 15 and 50 mg/L depending on local conditions and distance from the drainfield (Bicki and Brown, 1991; Brown, 1980; Harmon et al., 1996; Robertson et al., 1991; Walker et al., 1973; Wilhelm et al., 1994).
- Most data for agricultural land uses is for continuous corn or corn-soybean rotations, but some data is from vegetable crops (irrigated) and either small grains or alfalfa rotations (nonirrigated). Most agricultural data does not include manure application. Manure application typically results in slightly higher nitrate concentrations compared to nonmanured fields (Angle et al., 1993; Chang and Entz, 1996; Chang and Janzen, 1996; Jemison and Fox, 1994; Motavalli et al., 1989).
- Most undeveloped data represents woodland (deciduous) with some wetland or unfertilized pasture mixture also represented.

- All data are from shallow ground water in which direct recharge occurs and in which nitrate is stable.
- The data are from papers in which sampling methods, monitoring design, and quality assurance methods were documented.

Adjusting for different land use practices within each of the six land use categories would add considerable variability to the data. For example, nitrate leaching may differ beneath conventional and conservation tillage (Angle et al., 1993; Chang and Janzen, 1996; Levanon et al., 1993; Randall and Iragavarapu, 1995) or beneath different crops (MPCA, 1998d).

The information in Table 4 is useful for identifying background concentrations of nitrate under different land uses. First, the median concentrations reflect a range of nitrate concentrations. Undeveloped areas show the lowest concentrations, with each of the remaining land uses showing nitrate concentrations greater than undeveloped areas (significant at the 0.05 level). Irrigated agriculture had the greatest concentrations. Unsewered areas had greater concentrations than sewered areas (including commercial). Nonirrigated agriculture had concentrations less than unsewered and irrigated areas, but greater than sewered areas. Second, the standard deviations are relatively low for all land uses except the commercial areas, indicating fairly narrow ranges in nitrate concentrations within each land use. Finally, data from the St. Cloud land use study fall within the ranges from other studies. Consequently, median concentrations from Table 4 seem reasonable as “typical” background concentrations from each of the six land uses.

Because the St. Cloud data fall within the ranges indicated in Table 4, it will be used in much of the remaining discussion. Although the aquifer underlying the St. Cloud study area is a sand and gravel aquifer, the previous discussion of the environmental fate of nitrogen suggests that differences in nitrate concentration between aquifers within the same general land use should be negligible if nitrogen inputs are relatively uniform for that land use. This is because the amount of nitrate reaching ground water is most importantly a function of the amount of nitrogen available for leaching. The amount of nitrogen available for leaching will vary most importantly with nitrogen inputs, but also with vegetation (plant uptake), recharge (nitrate will accumulate in soil during dry years), and soil (nitrogen in ammonia or organic forms will be more highly retained as clay and

Study	Unsewered	Sewered	Commercial	Nonirrigated	Irrigated	Undeveloped
St. Cloud, MN	4.415	1.365	0.405	2.480[1]	13.390[1]	0.470[6]
St. Cloud, MN	1.575	1.970	0.580	3.350[1]	23.605[1]	0.790[6]
St. Cloud, MN	7.880	1.970	6.720	5.225[1]	26.715[1]	1.370[4]
St. Cloud, MN	9.555	-	0.470	-	-	-
Miller	2.000	-	-	-	-	-
Miller	13.000	-	-	-	-	-
Cain et al.	-	-	2.500	2.400[3]	4.500[1]	0.625
MSEA study - Minnesota	-	-	-	-	20.000[1]	-
MSEA study - Minnesota	-	-	-	-	30.000[2]	-
Kitchen et al.	-	-	-	4.750[1]	-	-
Kitchen et al.	-	-	-	4.500[1]	-	-
USGS Upper Miss. NWQA	-	1.400	-	-	-	-
Taraba, et al.	-	-	-	4.750	-	0.750
Ayers et al.	-	-	-	-	31.000	-
Eckhardt and Stackelberg	7.000	5.000	-	-	8.500	0.300
Hamilton and Helsel	-	-	-	2.900	9.200	0.100
Hamilton and Helsel	-	-	-	8.200	6.700	0.100
Hamilton and Helsel	-	-	-	-	7.500	0.100
Harmson	7.000					
Nolan et al.	-	-	-	4.200	-	1.000
Walker et al.	10.000	-	-	-	-	0.750
Hantzsche and Finnemore	11.700	-	-	-	-	-
Hantzsche and Finnemore	13.900	-	-	-	-	-
Hantzsche and Finnemore	9.600	-	-	-	-	-
Hantzsche and Finnemore	10.400	-	-	-	-	-
Quan et al.	8.000	1.000	-	-	-	-
Bauder et al.	-	-	-	2.300	-	-
Haycock and Pinay	-	-	-	7.000	-	0.800[4]
Piskin	-	-	-	3.000	12.000	-
Creed et al.	-	-	-	-	-	0.800[5]

Study	Unsewered	Sewered	Commercial	Nonirrigated	Irrigated	Undeveloped
Schnabel et al.	-	-	-	-	-	0.200[4]
Schnabel et al.	-	-	-	-	-	0.800[5]
Clawges and Vowinkel	-	2.500	1.600	1.800	-	0.500[6]
Anderson	4.200	-	-	2.000	5.300	0.220[6]

Jacobs and Gilliam	-	-	-	7.600	-	0.100
Peterjohn and Correll	-	-	-	6.500	-	0.600
Lowrance	-	-	-	-	13.520	0.810
Altman and Parizek	-	-	-	5.000	-	0.060
Randall and Iragavarapu	-	-	-	13.400[7]	-	-
Randall and Iragavarapu	-	-	-	12.000[7]	-	-
Geron et al.	-	2.700[8]	-	-	-	-
Median	8.000	1.970	1.090	4.625	12.695	0.600
Standard deviation	3.730	1256	2432	3.196	9.349	0.348

[1] continuous corn and corn-soybean rotations
[2] corn-potato rotation, during growing season
[3] cropping practice unknown or varies
[4] grassland
[5] hardwood forest
[6] predominantly forest but mixed
[7] poorly-drained soil
[8] turfgrass

Table 4: Median nitrate concentrations, in mg/L, in shallow ground water beneath different land uses.

organic matter increase). However, considering 'typical' land uses on coarse-textured soils overlying sensitive aquifers, soil and aquifer effects are of secondary importance. Soil and aquifer effects on nitrate concentrations can be very important for those conditions where there are rapid transport mechanisms (e.g. large diameter wells, karst) or poorly drained soils (which lead to denitrification). Aquifer comparisons are presented in Section 3.2.3.

3.2. Identifying Impacted Ground Water

Once background concentrations are established, impacts to individual aquifers can be assessed. Impacts can be identified within or between land uses. For example, within a land use we could compare nitrate concentrations beneath nonirrigated corn and soybean fields, while between land uses we could compare nitrate concentrations beneath nonirrigated and irrigated corn fields. A second objective of assessing impacts is to identify the probability that wells will be impacted above the drinking water criteria of 10 mg/L. Impacts to surface water receptors cannot be quantified with the existing GWMAP data, although future work will include ecological risk assessment.

3.2.1. Nitrate Stability

Nitrate-stable aquifers or portions of aquifers in which nitrate is stable are susceptible to contamination when there is a source of nitrogen to the aquifer. Median concentrations of nitrate in individual aquifers are shown in Table 5 for nitrate-stable and unstable samples. Mean and 75th quartile concentrations are also shown for nitrate-stable samples but could not be calculated for nitrate-unstable samples since there were very few detections of nitrate in these wells. As would be expected, concentrations of nitrate were significantly greater in nitrate-stable samples compared to nitrate-unstable samples for all aquifers for which there was sufficient sample size for comparison.

Aquifer	Nitrates Stable			Nitrates Unstable		
	Median	Mean	75th quartile	Median	Mean[1]	75th quartile
Franconia	1.040	1.224	2.300	< 0.500	-	< 0.500
Franconia-Ironton-Galesville	0.935	1.020	2.240	< 0.500	-	< 0.500
St. Peter	< 0.500	0.777	1.800	< 0.500	-	< 0.500
Prairie du Chien	1.860	1.555	3.415	< 0.500	-	< 0.500
Jordan	1.420	1.272	1.990	< 0.500	-	< 0.500
St. Peter-Prairie du Chien-Jordan	1.320	1.217	2.935	< 0.500	-	< 0.500
Mt. Simon-Hinckley	1.300	ins	-	< 0.500	-	< 0.500
Cretaceous	8.625	ins	-	< 0.500	-	< 0.500
Galena	7.060	-	-	< 0.500	-	< 0.500
Crystalline Precambrian	< 0.500	ins	-	< 0.500	-	< 0.500
North Shore Volcanics	< 0.500	ins	-	< 0.500	-	< 0.500
Proterozoic Metasedimentary	< 0.500	ins	-	< 0.500	-	< 0.500
buried Quaternary artesian	< 0.500	0.321	1.725	< 0.500	-	< 0.500
unconfined buried Quaternary	1.000	1.109	6.650	< 0.500	-	< 0.500
buried undifferentiated Quaternary	< 0.500	-	-	< 0.500	-	< 0.500
Quaternary water table	2.650	2.101	6.100	< 0.500	-	< 0.500
Cambrian aquifers	1.300	1.205	2.060	< 0.500	-	< 0.500
Ordovician aquifers	1.800	1.408	3.300	< 0.500	-	< 0.500
Precambrian aquifers	< 0.500	0.274	1.055	< 0.500	-	< 0.500

[1] Means could not be calculated because there were an insufficient number of samples above the reporting limit.

Table 5: Summary data from nitrate-stable and nitrate-unstable samples for the 19 major aquifers. Concentrations are in mg/L or parts per million.

The percent of samples exceeding the HRL in nitrate-stable wells was 11.5, compared to 0.4 in nitrate-unstable wells. Nitrate stability greatly enhances the potential risk to ground water receptors.

3.2.2. Land Use Effects

Table 4 showed that sewered and unsewered development, nonirrigated agriculture, and irrigated agriculture all lead to significant impacts to aquifers compared to undeveloped land use. Human activity in general, results in nitrate-impacted ground water.

The following comparisons were considered using information from the St. Cloud study:

- Sewered versus unsewered;
- irrigated versus nonirrigated;
- all land uses versus undeveloped; and
- agriculture versus residential.

An important aspect of these four situations is the rate at which ground water trends from the undeveloped concentrations to the final concentrations under the established land use. Current GWMAP studies include long-term monitoring in areas undergoing transitions in land use. This information will not be available for several years.

Median nitrate concentrations are summarized in Table 6 for the six land uses in the St. Cloud land use study. Nitrate concentrations which differed between land uses are indicated with different letters. Nitrate impacts in the St. Cloud study area can thus be assessed as follows:

- Nitrate concentrations under irrigated agriculture are significantly greater than concentrations under nonirrigated agriculture;
- nitrate concentrations under unsewered residential developments are greater than concentrations under sewered residential developments;
- nitrate concentrations under sewered residential developments and commercial areas are equal;
- nitrate concentrations under unsewered residential and nonirrigated agriculture are equal;
- nitrate concentrations under sewered residential and nonirrigated agriculture are equal;

- nitrate concentrations under all land uses are greater than under undeveloped areas; and
- nitrate concentrations in surface water are much lower than in ground water.

Parameter	Non-irrigated	Irrigated	Sewered	Unsewered	Commercial	Undeveloped	Surface Water
Median (mg/L)	3.145 bc	18.860 d	2.225 b	6.080 c	1.365 b	0.820 a	0.070
% of samples exceeding HRL	0	100	0	22	7	0	0

Table 6: Median nitrate concentrations and percentage of samples exceeding the HRL for nitrate under different land uses. Data are from the St. Cloud land use study. Different letters indicate median concentrations which differed between land uses at a confidence level of 0.05.

In terms of ground water management, these results identify ground water which is impacted or not impacted relative to the land uses being compared. For example, a new residential development in a previously undeveloped area will lead to significantly greater nitrate concentrations in ground water if the development is not sewered. As stated earlier, caution must be utilized in drawing these conclusions, since factors such housing density would need to be considered in assessing impacts.

There were significant differences (at the 0.05 level) between wells (intrawell comparisons) within the sewered, unsewered, commercial, and undeveloped land uses. Median concentrations for each well (1997 data from St. Cloud) within a land use are illustrated in Table 7. Letters identify wells, within a land use, in which nitrate concentrations differ. These results are somewhat problematic, because they indicate that more than three or four wells are needed to quantify the variability in nitrate concentrations within a land use. The variability in nitrite concentrations between land uses (standard deviation = 6.963), however, is greater than the variability within land uses (standard deviation = 3.616), which indicates that land use is a more important factor affecting nitrate concentrations than individual wells within a land use. Nevertheless, the differences between wells within land uses reflect either a natural variability in the data or some factor (e.g. nitrogen inputs, geochemistry) which leads to higher nitrate concentrations in some wells compared to others. Some of these potential factors are explored in Section 3.3.

Parameter	Non-irrigated	Irrigated	Sewered	Unsewered	Commercial	Undeveloped
Well 1	2.480	13.390	1.365 a	4.415 a	0.405 a	0.470 a
Well 2	3.350	23.605	1.970 b	1.575 a	0.580 a	0.790 ab
Well 3	5.225	26.715	1.970 b	7.880 ab	6.720 b	1.370 b
Well 4	-	-	-	9.555 b	0.470 a	-

Table 7: Median concentrations of nitrate, in mg/L, in each well, separated by land use, from the St. Cloud land use study. Different letters within a column indicate wells which had significantly different nitrate concentrations at a probability of 0.05.

A second objective of assessing impacts is to quantify the likelihood of receptors being impacted. While a specific land use may result in higher nitrate concentrations compared to another land use, the risk to receptors may not be increased. Comparisons of nitrate concentration with drinking water criteria are illustrated, by land use, in Table 6. All samples from irrigated agriculture exceeded the drinking water standard of 10 mg/L. There were two and one exceedance of the drinking standard in the unsewered and commercial areas, respectively, and no exceedances in the remaining land uses. The criteria for identifying impacts (increased concentrations versus increased risk) must be determined by the appropriate planning or management group.

For the St. Cloud data, ecological receptors cannot be evaluated directly, but surface water nitrate concentrations are very low in the Sauk River, which runs through St. Cloud. The Sauk River is well oxygenated and nitrates should be stable in the river. The concentrations are well below values typically thought to lead to nutrient enrichment of surface water (approximately 1.0 mg/L). The low values also indicate that ground water, which is enriched in nitrate, does not appear to impact surface water. The reasons for this are unclear, but one explanation is that nitrates are denitrified prior to reaching the river. This is plausible in the study area, since the Sauk River has extensive riparian buffering along much of its length, primarily as deciduous forest. It is also possible that nitrates are being used by plants, primarily algae, within the Sauk River.

The following conclusions, based on results from the St. Cloud study, can be offered in terms of land use:

- Irrigation will lead to significantly increased nitrate concentrations and potential risk to drinking water receptors in shallow ground water compared to all other land uses;
- unsewered development will lead to increased nitrate concentrations and potentially greater risk to drinking water receptors than sewered development;
- sewered or commercial development, or nonirrigated agriculture will lead to significant increases in nitrate compared to undeveloped land use, but will not significantly increase potential risk to drinking water receptors.

3.2.3. Aquifer Effects

Median concentrations of nitrate for different aquifers under nitrate-stable conditions were illustrated in Table 3. The data are difficult to analyze statistically because there were values below the reporting limit of 0.50 mg/L. The nonparametric Kruskal-Wallis test provides weak evidence that median nitrate concentrations differ between aquifers ($p = 0.057$). The Cretaceous and Galena aquifers, however, had small sample sizes and may represent rapid flow systems due to poor well construction (Cretaceous aquifer) or karst limestone (Galena aquifer). If these two aquifers are removed from the data and the nonparametric test is rerun, no significant differences exist between aquifers ($p = 0.21$). This is an important conclusion, since it indicates that for nitrate sensitive ground water, there were no differences in nitrate concentration between aquifers. The data probably reflect a wide variety of nitrogen inputs, but despite this, aquifer effects do not occur. The conclusion is that nitrogen inputs are the only factor likely to effect nitrate concentrations in aquifers where nitrate will be stable. This result is supported by data from the St. Cloud land use study, in which no significant correlations other than land use were found for nitrate in monitoring wells, even though nitrate concentrations varied widely in the wells. In shallow, oxygenated ground water, nitrogen input is the only factor controlling nitrate concentrations above natural background concentration. Those natural background concentrations appear to be between 0.50 and 1.0 mg/L based on data from the St. Cloud study.

The above discussion focuses on the nitrate stability of an aquifer, but no inferences are made relative to hydrologic controls on nitrate stability. Nitrate stability in an aquifer, however, is the result of physical and human forces. It is thus important to determine the hydrologic factors that control nitrate stability. Some of the human factors, which apply to all aquifers, are increased pumpage (which mixes nitrate-stable water with nitrate-unstable water) and well construction, which introduces oxygen-rich water to an aquifer in the vicinity of the well. Physical factors which affect nitrate stability are discussed briefly below.

- Recharge controls the amount of oxygenated water reaching an aquifer. The greater the quantity of recharge, the deeper the nitrate-stable zone is likely to be in an aquifer. Since recharge occurs only during short periods during the year, thickness of the nitrate stable zone will vary in response to recharge.
- Total organic carbon leached to an aquifer controls the amount of food available to microbes. Without food, microbes cannot utilize oxygen. Aquifers with low concentrations of organic carbon will have greater thickness of nitrate-stable zones.
- Hydraulic conductivity of an aquifer, which is related to the three-dimensional distribution of geologic materials, affects the rate at which nitrate-stable water will be transported in an aquifer. The depth to which oxygen-rich water will penetrate is also a function of the vertical hydraulic conductivity.

None of these human or physical factors was extensively investigated for this report. While it is important to identify portions of an aquifer which have nitrate-stable conditions, it is equally important to understand the mechanisms which control nitrate-stability. The data indicates that if the unsaturated zone and the upper portion of an aquifer are oxygenated and recharge to the aquifer occurs annually, nitrogen in the unsaturated zone will leach to ground water as nitrate.

3.2.4. Well Construction Effects

Poorly constructed wells may result in degradation of ground water quality within the vicinity of the well. Large diameter wells (greater than 16 inches) are often poorly constructed and may provide a direct conduit for water to move from the unsaturated zone into ground water. In addition to providing a mechanism for nitrates to enter ground water, these wells introduce oxidized water to the aquifer in the vicinity of the well. Nitrates will thus be stable in the vicinity of the well.

Median concentrations of nitrate in small (less than 12-inch) and large (more than 16-inch) diameter wells are illustrated in Table 8. Concentrations are much greater in large diameter wells. The percentage of wells exceeding the drinking water standard is also greater in large diameter wells. Poor well construction leads to significant increases in nitrate concentration in individual wells and to increased potential risk to drinking water receptors in these wells.

Well type	No. of wells	Median (mg/L)	Q75 (mg/L)	% greater than HRL
Small diameter	199	0.700	3.215	9
Large diameter	11	10.550	19.195	55

Table 8: Summary data for small and large diameter wells.

3.2.5. Seasonal Effects

Comparisons of nitrate concentration by quarter within each land use and overall are summarized in Table 9 for the St. Cloud study. No significant differences were observed between quarter of sampling. Caution must be exercised with this data. The data represent only one year of results and there are some trends in the data which are consistent with expected differences in nitrate concentrations between different seasons. Concentrations in agricultural land uses were greater (though not statistically) in fall and winter, which is consistent with most data from the literature. Concentrations in residential areas were greater (though not statistically) in spring and summer, when fertilization of grass would be expected. Concentrations in undeveloped land use were consistent throughout the year, as would be expected under conditions of no human inputs of nitrogen. Figure 2 indicates that, in St. Cloud samples, nitrate decreased in concentration during spring recharge but increased, except under unsewered land use, during a period of summer recharge. Spring snowmelt probably represents a condition that dilutes the upper portion of an aquifer, while summer recharge will leach nitrate left in the soil from spring application. Additional years of sampling will help identify if these patterns are statistically significant and under which land uses seasonal effects are most important.

Quarter	Non-irrigated	Irrigated	Sewered	Unsewered	Commercial	Undeveloped	Overall
Winter	3.985	25.390	1.580	-	0.360	-	3.680
Spring	2.365	16.310	1.725	3.605	2.710	0.710	2.420
Summer	2.625	15.350	2.840	7.880	2.365	0.850	3.090
Fall	3.720	22.960	2.480	7.790	0.800	0.790	2.560

Table 9: Median nitrate concentrations in mg/L, by sampling quarter, from the St. Cloud land use study.

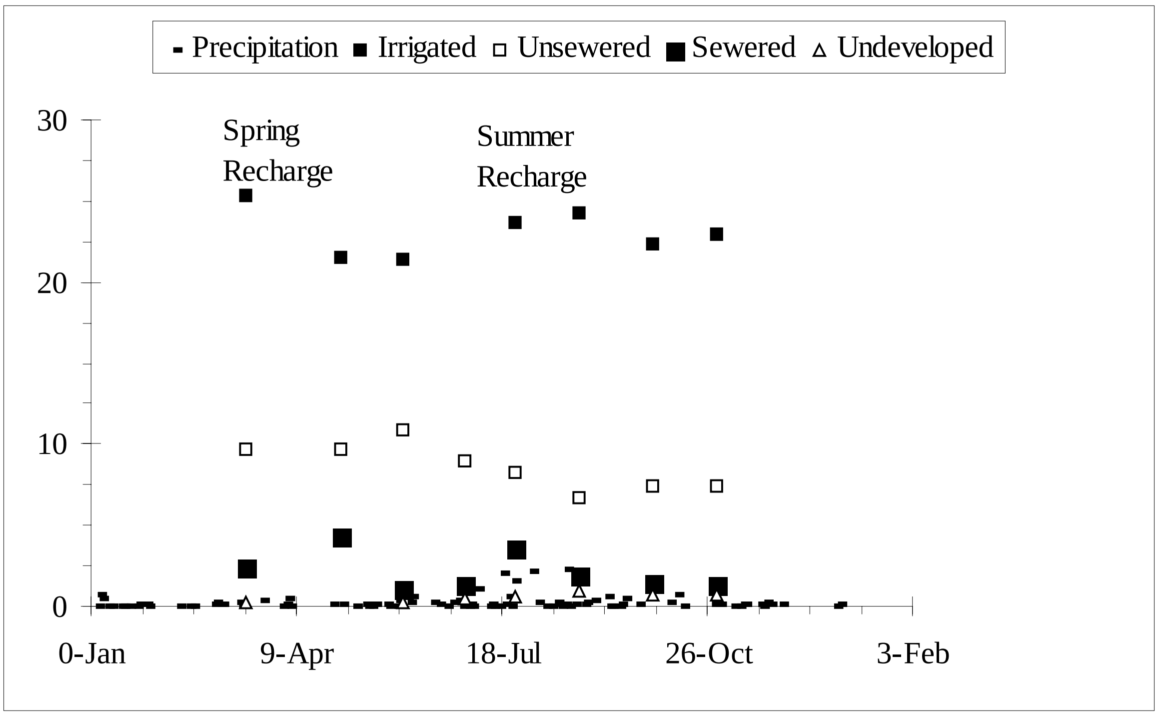

Figure 2: Concentrations of nitrate under different land uses in response to precipitation. Nitrate concentrations are in mg/L ppm and precipitation is in inches.

The baseline data, although not sampled for purposes of identifying seasonal differences, can be examined to determine if nitrate concentrations differed by month of sampling. Median concentrations of nitrate in nitrate-stable ground water are illustrated in Table 10. Concentrations which differed between sampling months are indicated with different letters. Concentrations appeared relatively uniform throughout the year, except for high concentrations in June. The drinking water standard was most commonly exceeded between May and July. Potential reasons for these monthly effects are discussed in Section 3.3.4.

Month	No. of samples	Median (mg/L)	% greater than HRL
January	5	1.310 ab	0
April	4	0.800 ab	0
May	17	1.300 ab	12
June	52	3.450 b	29
July	40	0.850 ab	13
August	47	< 0.500 a	0
September	13	0.600 ab	0
October	12	0.830 ab	8
November	6	1.455 ab	0
December	16	< 0.500 a	0

Table 10: Median concentrations of nitrate by sampling month. Data are from the baseline study. Different letters indicate concentrations which differed at a significance level of 0.05.

3.3. Factors Affecting Nitrate Impacts to Ground Water

In Section 3.2, the following nitrate impacts were identified.

1. Within an individual aquifer, wells in which nitrates were stable had greater concentrations of nitrate than wells in which nitrates were not stable.
2. Nitrates differed between land uses.
3. Nitrates differed with well diameter.
4. Nitrates differed between sampling month.

A variety of factors may be responsible for these differences. The most important factors which can be evaluated in this report are nitrogen inputs, well depth, and geochemical controls. Additional factors not included in this discussion may include specific nitrogen application methods, well location with respect to nitrogen sources (e.g. septic drainfield), cropping practices, fertilizer practices in residential areas, and ground water recharge.

3.3.1. Nitrate Stability

Although nitrate-stable aquifers or portions of aquifers in which nitrate is stable are susceptible to contamination when there is a source of nitrogen to the aquifer, there are different reasons why some aquifers are nitrate-stable. It is important to identify the reasons why an aquifer or a portion of an aquifer is susceptible to nitrate contamination because this information can be used in aquifer management.

Aquifers receiving direct recharge are potentially susceptible to nitrate contamination because recharge water is often oxygenated and may contain nitrates leached from the soil zone. Even these aquifers, however, may not be susceptible if there is sufficient carbon in the aquifer to allow for microbial activity. For example, the distribution of nitrate-stable ground water in baseline samples for the buried and surficial Quaternary aquifers indicates no specific geographic pattern (Figure 3). Concentrations of total organic carbon were significantly greater in nitrate-unstable samples than in nitrate-stable samples for both aquifers ($p < 0.0001$ and $p = 0.0010$, respectively). In many Quaternary aquifers of Minnesota, there appears to be insufficient organic carbon to initiate the microbial activity needed to consume oxygen. The same relationship was noted for the Cambrian and Ordovician aquifers, although the relationships were not as strong as for the Quaternary groups ($p = 0.013$ and 0.045, respectively).

Data from the St. Cloud geoprobe study (MPCA, 1998d) further illustrates the importance of organic carbon in ground water. The median concentration of carbon at the water table of the underlying surficial sand and gravel aquifer was 2.3 mg/L, but increased to 3.1 and 7.8 mg/L at depths of seven and one-half and 15 feet, respectively. Over this same depth range, concentrations of dissolved oxygen and Eh decreased by 0.028 mg/L/feet and 1.7 mv/feet, respectively. Since soil is the most likely source of organic carbon but concentrations were lower at the water table than at depth, microbes are active in the upper ten feet of the aquifer. Nitrates over this depth range decreased from a median concentration of 5.6 mg/L at the water table to 0.045 mg/L at 15 feet. This is an important conclusion and further research is needed to identify aquifers where carbon may be a limiting factor in nitrate attenuation. Numerous researchers suggest approximately 5 mg/L of organic carbon is needed to initiate microbial activity.

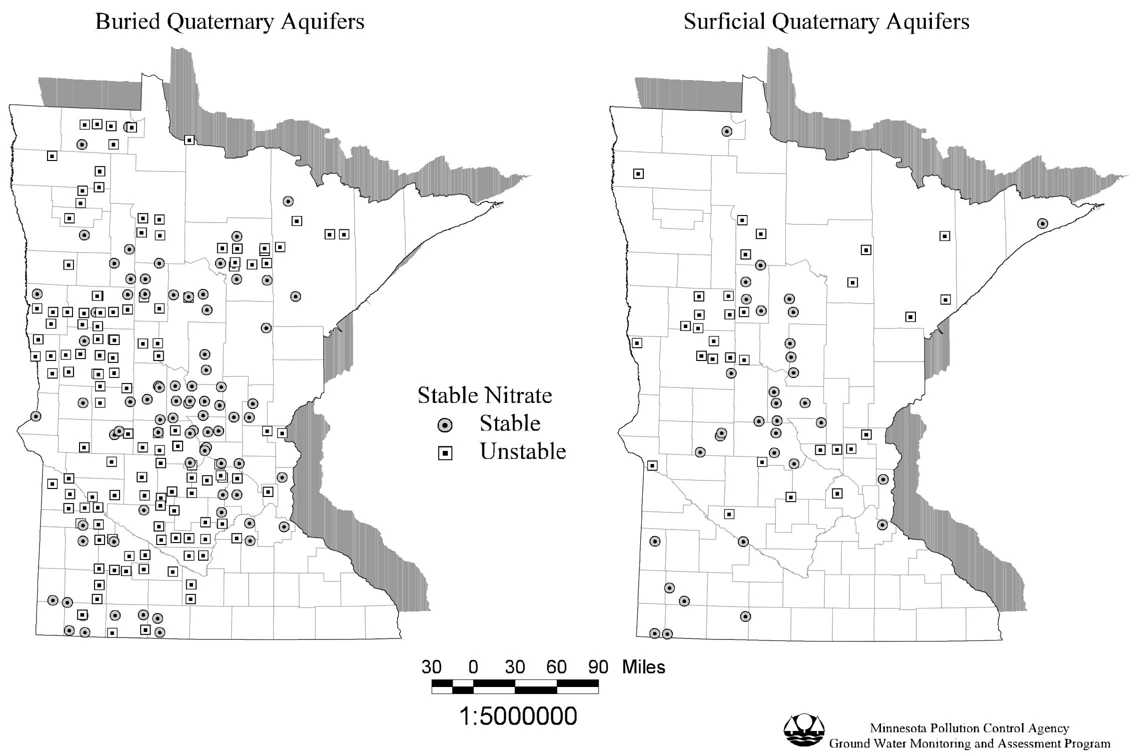

Figure 3: Distribution of nitrate-stable and nitrate-unstable samples in buried and surficial Quaternary wells.

The distribution of nitrate-stable samples in the Prairie du Chien, Jordan, and St. Peter aquifers appears strongly related to geographic location (Figure 4). Nitrate-stable samples were observed primarily along the eastern portion of these aquifers, where they are likely to be first bedrock and may outcrop or have a thin cover of glacial material or loess. Similar conditions may exist along the western edge of these aquifers. The results suggest there may be a relationship between the occurrence of nitrate-stable conditions and depth to bedrock, depth to aquifer, or thickness of confining units. One complication in the analysis of nitrate stability is the low iron content of these aquifers, which confounds the interpretation of nitrate stability. If all low oxygen-low Eh samples were plotted in Figure 4, the pattern of nitrate stability would be more evident, since these samples lie primarily in the western portions of the aquifers. Iron concentrations in most samples, however, were below 1.0 mg/L, even in the oxygen-depleted samples.

Static water elevations were greater in the nitrate-stable wells for these aquifers (p = 0.0413) compared to the unstable wells, although well depth and static water elevation are not necessarily good indicators of where the top of the aquifer is located with respect to the land surface or whether ground water is unconfined. Well logs were examined for these three aquifers to evaluate which aquifer was closest to the land surface, what the effect of total confining thickness was on nitrate concentrations, and what effect depth to bedrock had on nitrate concentrations.

- Nitrate stability was unaffected regardless of whether an aquifer was the first bedrock encountered or a deeper aquifer overlain by other aquifers.
- Nitrate-stable conditions were more likely to occur than nitrate-unstable conditions in wells with shallow depths to first bedrock. Nitrate concentration was correlated with depth to first bedrock, as illustrated in Figure 5. Nitrates were not detected in wells in which depth to bedrock exceeded 125 feet.
- Cumulative thickness of confining layers had no effect on likelihood of nitrate-stable conditions in a well. Nitrate concentration, however, was significantly correlated (p = 0.003) with cumulative thickness of confining units, as illustrated in Figure 6. Figure 6 shows that nitrates decrease rapidly as confining thickness increases to about 75 feet. Few samples had detectable nitrates at thicknesses greater than 75 feet. This result is supported by Walsh (1992), who observed a decline with depth in the percent of samples containing tritium. Little tritium was detected below approximately 100 feet. Waters containing enriched concentrations of tritium are post-1953 and are more likely to contain oxygen than older waters.

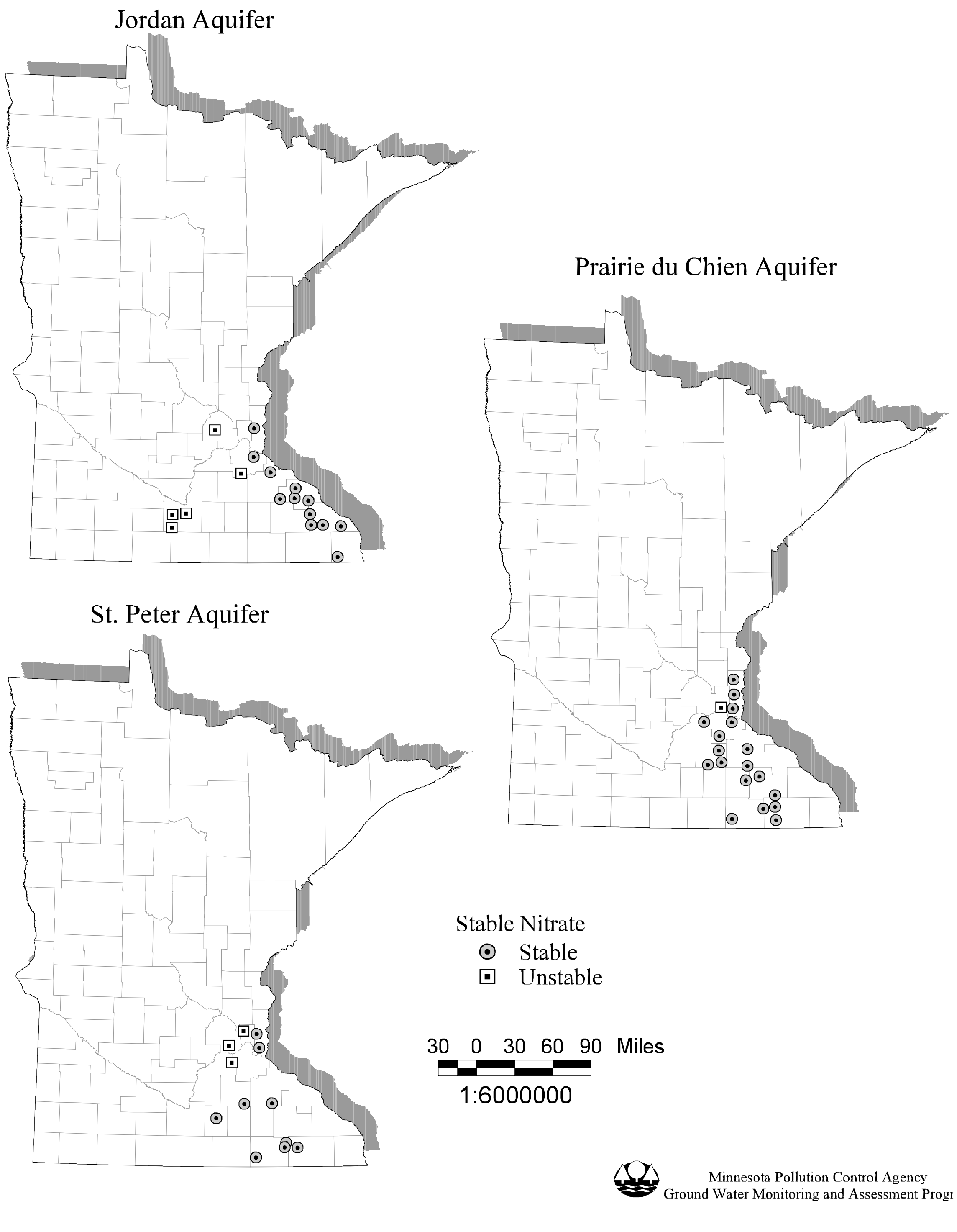

Figure 4: Distribution of nitrate-stable and nitrate-unstable samples in Prairie du Chien, Jordan, and St. Peter aquifers.

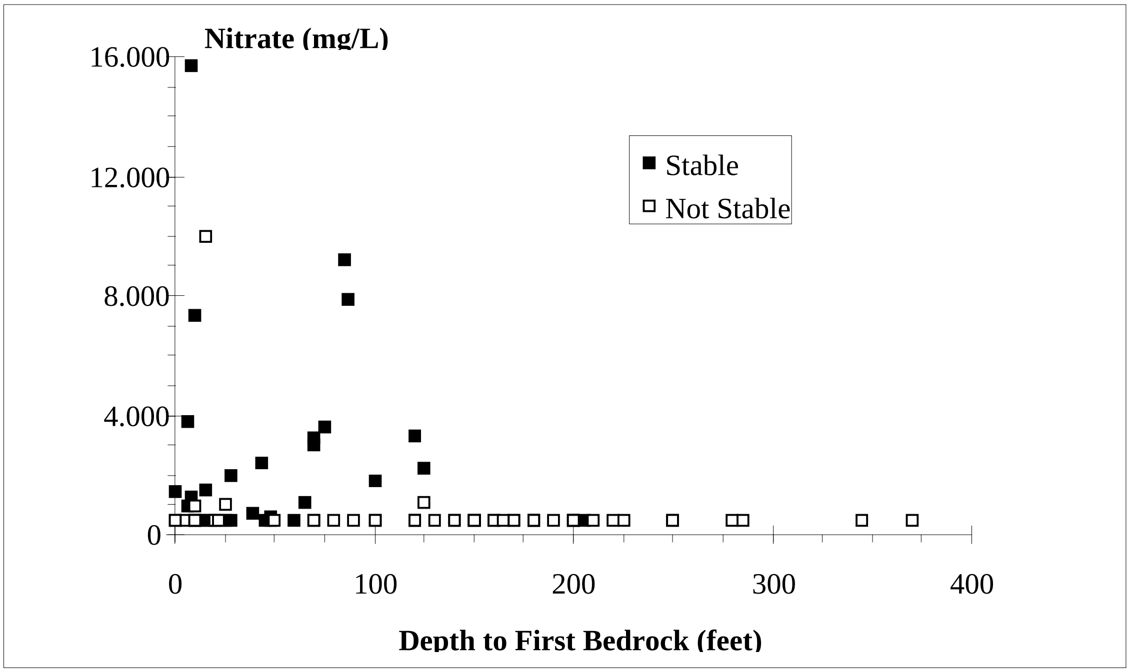

Figure 5: Relationship of nitrate concentration and depth to first bedrock for nitrate-stable and nitrate-unstable samples.

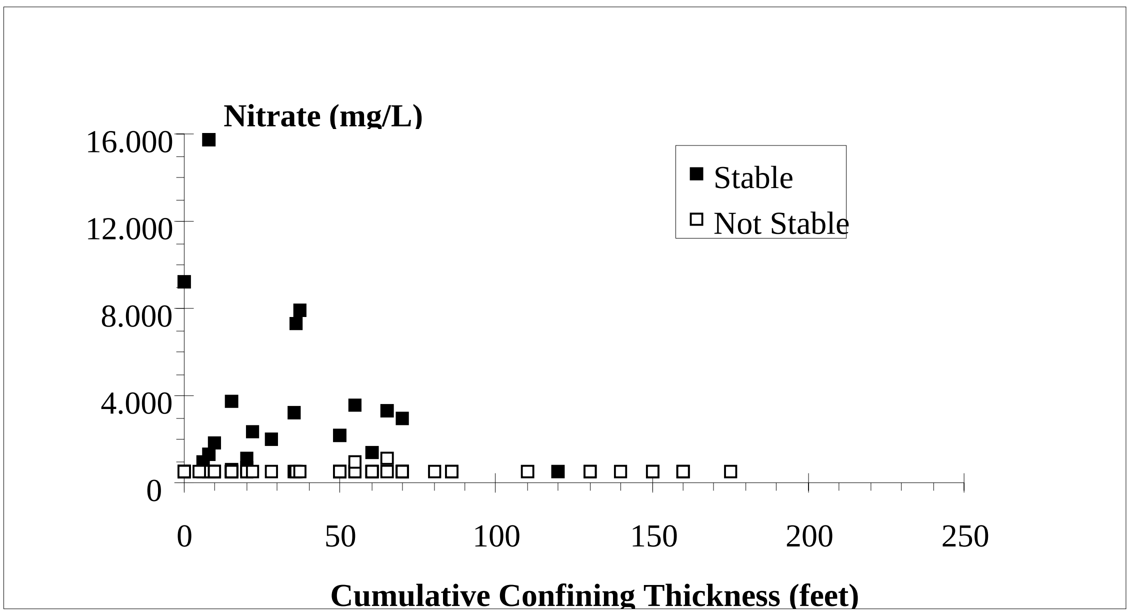

Figure 6: Relationship of nitrate concentration and cumulative thickness of confining layers in nitrate-stable and nitrate-unstable samples.

Cretaceous aquifers are commonly overlain by thick layers of low-permeability till. However, there were five Cretaceous wells in which nitrate was considered to be stable. These differences were not attributed to geographic location (Figure 7), well construction (there were no differences in well diameter between stable and unstable wells), or to the concentration of total organic carbon. Well depth was significantly greater ($p = 0.0245$) in nitrate-unstable wells compared to nitrate-stable wells, with median well depths of 285 and 129 feet in the two groups, respectively. The primary control on nitrate-stability and hence, concentrations of nitrate in the Cretaceous aquifer, is depth to the aquifer. A potentially contributing factor which could not be examined with the baseline data is the relationship between underlying bedrock and the slope of the Cretaceous surface. In locations where underlying Precambrian bedrock is near the land surface and has significant vertical slope, percolating water may be rapidly transported along the Precambrian surface and eventually discharge into Cretaceous deposits. This water would be expected to be rich in oxygen and therefore susceptible to high nitrate concentrations.

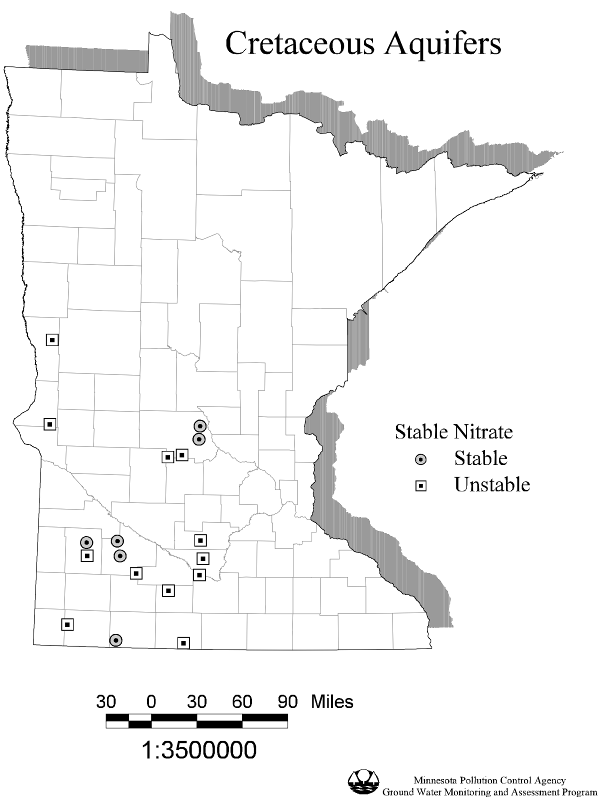

Figure 7: Distribution of nitrate-stable and nitrate-unstable samples in Cretaceous aquifers.

No relationships were observed for the Precambrian aquifers, including lack of a spatial pattern to the nitrate-stable samples (Figure 8). This makes some sense for the baseline data, since hydrogeologic information for each well is insufficient to determine why nitrates would be stable in a particular well. Precambrian aquifers would be expected to be susceptible to contamination with nitrate when they are close to the land surface and highly fractured, which allows for rapid transport of water and solutes.

No relationships were observed for the Upper Carbonate samples (Figure 8). These aquifers appeared to be relatively well protected. This was somewhat surprising because these aquifers are mapped as hydrologically sensitive when they are fractured or dissolved (karst). Most wells sampled may be drilled deeper in the Upper Carbonate formations, since well construction requirements limit construction of wells in active, near-surface karst. As Figure 8 shows, many of the wells sampled from these aquifers were located further west than other Ordovician wells. These are locations where active karst is unlikely and overlying, low-permeable tills are thicker.

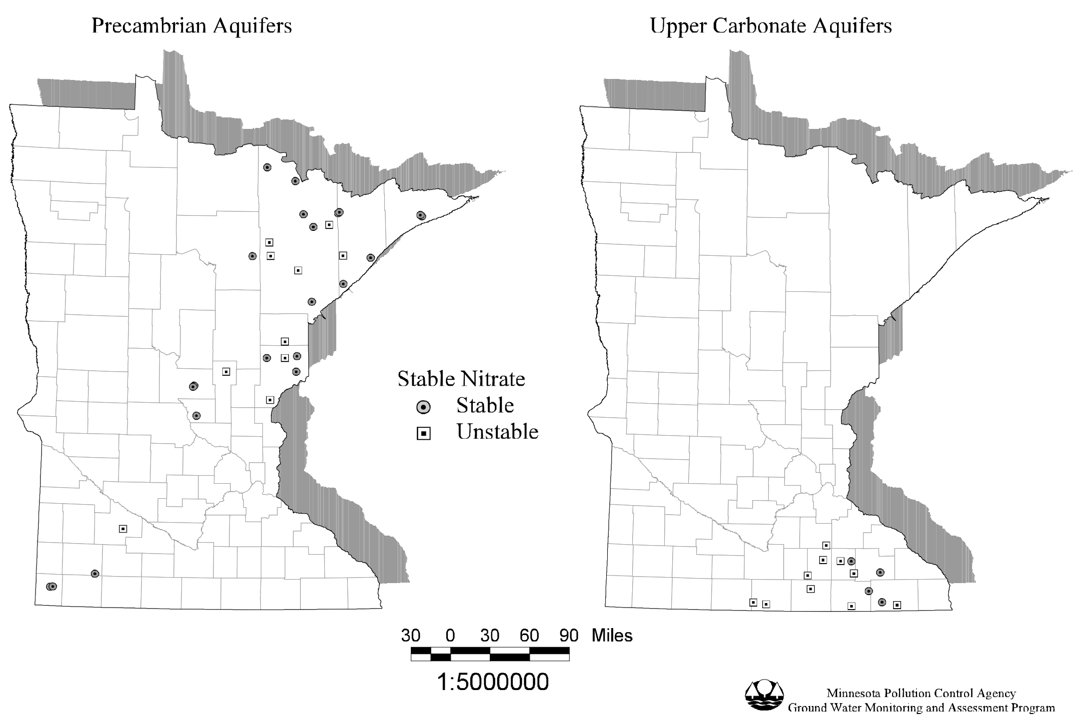

Figure 8: Distribution of nitrate-stable and nitrate-unstable samples in Precambrian and Upper Carbonate aquifers.

The distribution of nitrate-stable and -unstable samples is illustrated in Figure 9 for the Mt. Simon, Hinckley, Franconia, Ironton, and Galesville aquifers. The pattern for the Franconia, Ironton, and Galesville aquifers is similar to that for the Prairie du Chien, Jordan, and St. Peter aquifers, except that the distribution of nitrate-stable samples is located further east. As with the Prairie du Chien and Jordan aquifers, nitrate stability appears closely related to thickness of overlying deposits. No pattern is evident for the Mt. Simon and Hinckley aquifers, although nitrate-stable wells were clustered in the northeastern portion of these aquifers where regional recharge originates.

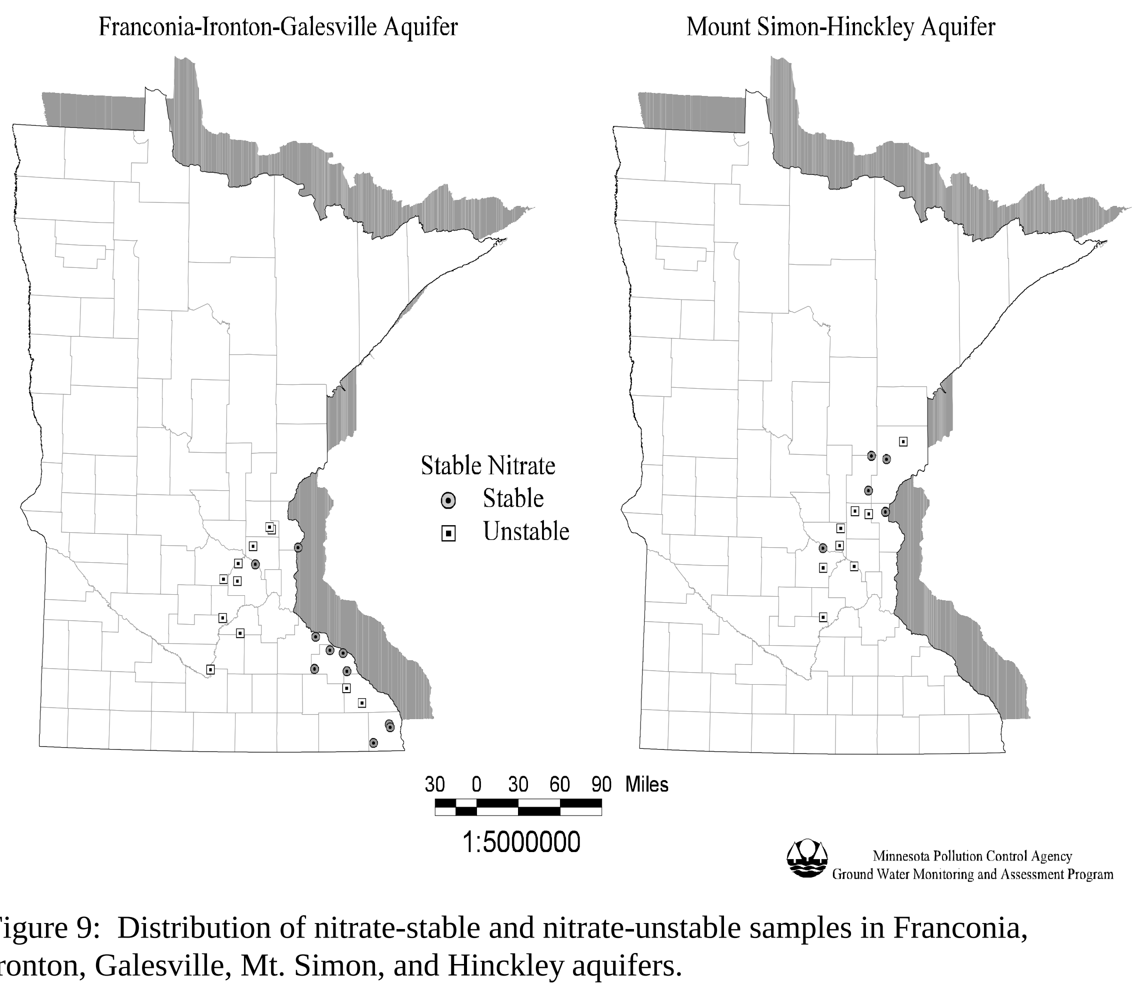

Figure 9: Distribution of nitrate-stable and nitrate-unstable samples in Franconia, Ironton, Galesville, Mt. Simon, and Hinckley aquifers.

3.3.2. Land Use

Results from one year of monitoring in St. Cloud indicate significant differences in ground water quality between different land uses. Correlation tests were run between nitrate and all sampled chemical parameters, well depth, depth to water, and geographic location. There were no strong correlations between any of these parameters and nitrate. All hydrologic factors being equal, the primary factor controlling nitrate concentration beneath a land use is the amount of nitrogen available for leaching to ground water. However, these results were significant only for the monitoring wells screened at the water table. There were significant correlations between nitrate concentration and well depth (negative correlation), oxidation-reduction potential (positive), dissolved oxygen (positive), and dissolved iron (negative) in wells deeper than 25 feet. Additional work was conducted in Spring, 1998, to characterize nitrate concentrations in the upper 15 feet of the aquifer under different land uses (MPCA, 1998d). Overall nitrate concentrations decreased rapidly, from a median concentration of 5.6 mg/L at the top of the water table to 0.54 mg/L at a depth of seven and one-half feet to 0.054 mg/L at a depth of 15 feet below the water table. Nitrate concentrations at the water table differed significantly between land uses, but did not differ at the seven and one-half or 15 foot depths. This illustrates the importance of geochemical conditions within the aquifer. Land use effects, which are very important in the upper portion of the aquifer and are related to the amount of nitrogen available for leaching, are not evident at depths where denitrification occurs.

3.3.3. Well Construction

Well construction, as indicated by large diameter (greater than 16 inches) and small diameter (less than 12 inches) wells, had significant impacts on nitrate concentration. While poorly constructed wells may act as direct conduits for nitrogen, another important effect of well construction is to introduce oxygenated water in the vicinity of the well. This is illustrated in Figure 10, using data from the baseline study. Concentrations of dissolved oxygen and Eh (a measure of redox potential) were much greater in large diameter wells, while concentrations of iron were much less. There were no differences in depth to water and well depth between large and small diameter wells. These results are important when considering the impact of poor well construction on aquifer water quality. In most circumstances, well construction will only impact water quality in the vicinity of the well, as opposed to the entire aquifer. Consequently, when conducting regional water quality assessments, data from poorly constructed wells should be separated in the data analysis.

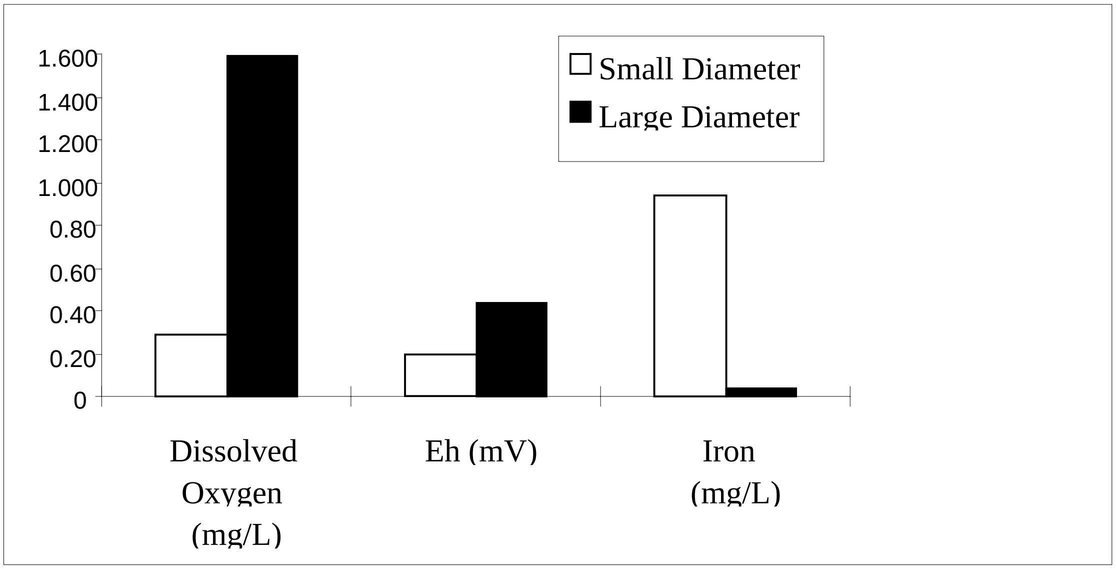

Figure 10: Comparison of dissolved oxygen, Eh, and iron in large and small diameter wells.

3.3.4. Seasonal Effects

Results from the baseline study showed greater concentrations of nitrate in June compared to other months, while the St. Cloud data indicate no effect of sampling season on nitrate concentration. These compare with information from the literature which suggests that the greatest nitrate concentrations will occur in autumn and winter, prior to recharge, since recharge tends to dilute an aquifer. Long-term data from the Minnesota Department of Agriculture (unpublished) indicates no seasonal effect on nitrate concentrations in shallow sand and gravel or in karst aquifers.

Reasons for the elevated concentrations in June for the baseline data are not clear. There was no correlation between sampling month and the percent of wells sampled from particular aquifers, during particular years, or with the percent of nitrate-stable wells sampled. Concentrations of dissolved oxygen and Eh were greater in autumn and winter and dissolved iron concentrations were less in autumn and winter compared to spring.

These conditions would be more conducive to elevated nitrate concentrations in autumn and winter, which is contrary to the results. Wells sampled in spring were shallower, depth to water was less, and chloride concentrations were greater compared to wells sampled in autumn and winter. This may suggest more rapid response to recharge in the wells sampled during spring. Data from the geoprobe study suggest that nitrate concentrations and geochemical conditions in the upper portion of an aquifer are transitory, particularly in spring. Figure 11 shows that oxygen concentrations increase in spring during a time when ground water elevations also increase, presumably in response to recharge. Figure 2 showed that nitrate concentrations decreased during spring recharge (snowmelt) but increased during summer recharge (precipitation). These results suggest that recharge leads to oxygenated conditions in an aquifer, which increases its susceptibility to nitrate contamination. When nitrate is available in soil, as it usually is under agricultural land use in June and July, it will leach to ground water, where it will behave as a conservative solute.

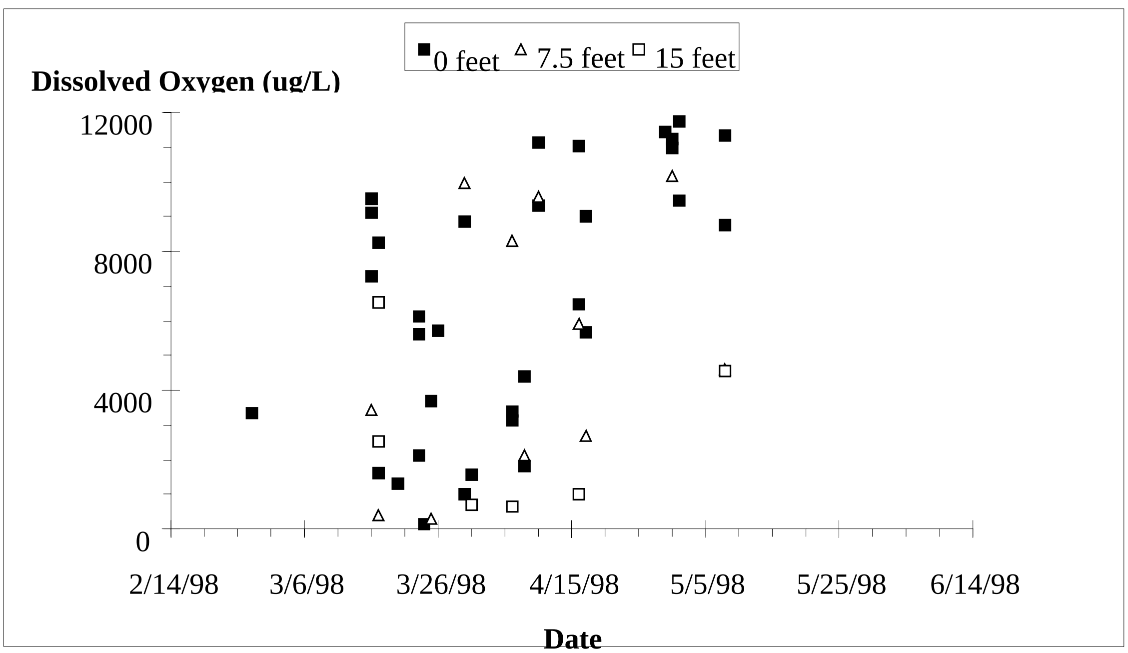

Figure 11: Change in median ground water elevations and median dissolved oxygen concentrations from monitoring wells in St. Cloud. The reference elevation is one foot.

4. Summary and Conclusions

1. Background concentrations of nitrate in ground water vary with stability of nitrate and with land use. Nitrate stability is a function of hydrologic and human factors, including recharge, organic carbon concentration in leachate water, aquifer conductive properties, aquifer mixing from pumping of high capacity wells, and well construction. In portions of aquifers defined as not susceptible to nitrate contamination because denitrification is likely, concentrations of nitrate are very low, generally less than 0.10 mg/L and often less than 0.010 mg/L. In nitrate-susceptible aquifers, natural background concentrations of nitrate are between 0.30 and 1.0 mg/L, with 0.50 to 0.70 mg/L being about average. These concentrations do not differentiate between different natural settings, such as woodland, prairie, or wetland. Within broad land use categories, background nitrate concentrations are approximately 1.0 to 2.0 mg/L in sewered residential and commercial areas, 4.5 mg/L in nonirrigated agricultural areas (primarily corn or corn-soybean rotations), 8.0 mg/L in unsewered areas, and greater than 10 mg/L in irrigated agricultural areas.
2. Factors which result in differences in concentrations of nitrates within or between aquifers are summarized below.
   2.1. Nitrate Stability. Concentrations of nitrate were greater in ground water in which nitrate is stable (will not be denitrified). These are aquifers in which oxygen is present in sufficient quantity to limit the activity of nitrate-consuming bacteria. Nitrate stability in many Quaternary aquifers is controlled by low concentrations of total organic carbon, which represents the food source for microbes. Nitrate is stable in the Prairie du Chien, Jordan, and St. Peter aquifers where bedrock is close to the land surface and the cumulative thickness of confining geologic materials is less than 75 feet. These conditions are encountered more frequently near the eastern and western edges of the aquifer. Nitrate is stable in the Cretaceous aquifer when the aquifer is located close to the land surface. There were no observed relationships which explained the likelihood of nitrates being stable in Precambrian or Upper Carbonate aquifers. Nitrate stability greatly increases the potential risk to drinking water receptors.

2.2. Land Use. Concentrations of nitrate followed the order: irrigated agriculture > unsewered residential > nonirrigated agriculture > sewered residential = commercial > undeveloped. The primary control on nitrate concentrations in shallow, oxygenated ground water under different land uses is the quantity of nitrogen available for leaching. The potential for increased risk to drinking water receptors is high under irrigated agriculture, moderate under unsewered development, and low under the remaining land uses.

2.3. Aquifer Effects. There were no significant differences in nitrate concentrations between different aquifers when considering only samples in which nitrate was considered to be stable. These data indicate that a source of nitrogen is present and aquifer conditions are conducive to nitrate stability, nitrate concentrations are independent of the aquifer.

2.4. Nitrogen Inputs. Although no direct data supports the effect of nitrogen inputs, the lack of significant differences in nitrate concentrations between aquifers and the significant differences between different land uses suggests that in shallow, nitrate-susceptible ground water, nitrogen inputs are the most important factor affecting nitrate concentrations.

2.5. Well Construction. Large diameter wells, which are likely to be poorly constructed, had significantly greater concentrations of nitrate than smaller diameter wells, which are considered to be properly constructed. The reason for this is that poorly constructed wells often leak along cracks or joints in the casing, thus introducing oxygen-rich water from the unsaturated zone or the upper portions of an aquifer. If there is a source of nitrogen in this water, it will exist as nitrate and persist in the vicinity of the well. Consequently, poor well construction may represent an increased health risk in individual wells, but may have minor impacts on overall nitrate concentrations in an aquifer if the aquifer is not susceptible to nitrate contamination.

2.6. Seasonal Effects. There were no significant differences in nitrate concentration between sampling quarters, although greater nitrate concentrations were observed during June for the baseline data. These results are based on a single year of data from the St. Cloud land use study and should therefore be viewed with caution, since they conflict with some research results, primarily from agricultural studies, in which greater nitrate concentrations have been observed in winter prior to spring recharge. There appeared to be decreased concentrations following spring snowmelt and increased concentrations during summer recharge. Additional years of data within individual land uses are needed to determine seasonal effects on the distribution of nitrate.

5. Recommendations

The following planning and management recommendations are based on data presented in this report.

1. Unsewered development should be accompanied by a ground water assessment (see recommendation 6).
2. Conversion of nonirrigated land to irrigated land should be accompanied by a ground water assessment.
3. Conversion of undeveloped land to agriculture or unsewered development should be accompanied by a ground water assessment.
4. Residential development within irrigated agricultural land use requires a ground water assessment.
5. Installation of high capacity wells within drinking water aquifers which have nitrate susceptible areas should be accompanied by a ground water assessment.
6. Ground water assessments are not site specific but are based on physical information about the aquifer of concern and information on land use effects collected from various studies. Assessments are aquifer-wide. For example, if there is significant unsewered development occurring over a mapped, hydrologically sensitive aquifer, the ground water assessment would be conducted for the aquifer, not specific locations where unsewered developments are occurring. An important component of this is determining geochemical conditions in the upper portion of the aquifer. This includes three components.

6.1. The nitrate susceptibility of the aquifer should be evaluated by measuring Eh, dissolved oxygen concentration, dissolved iron concentration, and total organic carbon concentration, and by determining the nitrogen available for leaching. The stable-unstable boundaries for Eh, dissolved oxygen, and dissolved iron are approximately 250 mV, 0.50 mg/L, and 0.70 mg/L respectively, although different researchers may have slightly different boundaries. This assessment should be conducted three-dimensionally within the aquifer. A one time sample event similar to the baseline study (no long-term monitoring) will be sufficient to define general nitrate-stability of an aquifer, although at specific locations within the aquifer, nitrate-stability will vary in response to hydrologic controls such as vetical dispersivity and recharge. It is unclear what concentration of total organic carbon is required to initiate microbial activity, although some researchers suggest a concentration of approximately 5.0 mg/L. Estimating the quantity of nitrogen available for leaching may be very difficult, particularly in agricultural settings. Data from the literature for a particular land use will provide a good first approximation. **NOTE: The field measurement of oxidation-reduction potential must be converted to Eh. The conversion includes a correction for the type of electrode used (approximately 200 to 250 mV) and for temperature. Consult the manufacturer or instrument manual for determining the proper corrections.**

6.2. Modeling is used to simulate nitrate concentrations in ground water under different development (nitrogen input) scenarios and to assess the sensitivity of different physical and management factors. Several unsaturated and saturated zone models are available which simulate solute transport. Inputs for ground water models include the aquifer dimensions, nitrate leachate concentrations, aquifer hydraulic and attenuation properties, recharge, and sources and sinks. Unsaturated zone models are designed to predict the quantity of leachate and concentration of nitrate in the leachate. Inputs therefore include hydraulic properties, attenuation characteristics, and nitrogen inputs, although additional parameters may be required to simulate plant uptake, volatilization, and so on.

With each modeling effort, sensitivity analysis should be conducted for physical and chemical properties of the aquifer, and for chemical inputs (management effects).

6.3. Risk assessment is used to estimate the probability that a drinking or surface water criteria will be exceeded at the receptor (compliance) point. Examples of receptor points include a well or a lake.

There are gaps in understanding the distribution of nitrate in ground water of Minnesota. The following recommendations will help fill some of these gaps.

1. Nitrate susceptibility of hydrologically sensitive aquifers should be assessed. The procedures outlined in planning recommendation 6.1 above can be used. Department of Natural Resources Atlas and Regional assessments and other hydrologic investigations such as Clean Water Partnership diagnostic projects can be used to identify the hydrologically-sensitive aquifers in the state. Areas where nitrogen inputs are significant, such as agricultural areas or expanding urban areas, should be prioritized first.
2. Additional information is needed from unsewered developments to quantify nitrogen loading under different unsewered scenarios. The primary factor affecting nitrogen loading will be lot size (i.e. density) and usage patterns (e.g. seasonal vs. nonseasonal, and average family size). An important component of these studies will be determining trends in water quality following unsewered development or following sewering of an unsewered development.
3. Additional information is needed from agricultural areas in which cropping patterns are changing. The primary factor will be the extent of irrigation, although crops grown, rotations used, and fertilizer application practices may also be important. These studies will primarily involve long-term aquifer monitoring coupled with site-specific quantification of nitrate inputs.
4. Impacts of high capacity wells on aquifer geochemistry as they relate to nitrate stability should be evaluated. A monitoring network can be established within these aquifers to determine if Eh and concentrations of dissolved oxygen, dissolved iron, total organic carbon, and nitrate change in response to high-capacity pumping.

Since ground water is largely managed at the local and regional level and because nitrate contamination problems appear correlated with regional hydrogeologic or land use factors, the following region-specific recommendations were developed.

1. In Southwest Minnesota, nitrate is often stable in shallow ground water, potential nitrogen inputs from agriculture are high, and the hydrogeology is complicated. Additional investigation is needed to:
   - Identify sensitive surficial aquifers;
   - determine geochemistry, including total organic carbon, of sensitive surficial aquifers;
   - quantify nitrogen inputs to shallow ground water from fertilizer and from point sources, such as feedlots, coupled with additional information on nitrate stability in different aquifers;
   - determine if impacts to buried drift aquifers from dug wells occur just within the vicinity of the well or if there are more widespread impacts to the aquifer;
   - assess seasonal variation in nitrate concentrations in Quaternary wells; and
   - complete a regional assessment of nitrate within the entire Sioux Quartzite aquifer, including factor analysis and a risk assessment. Portions of the Sioux Quartzite have been studied, but additional work is needed and results from all studies need to be compiled into an overall aquifer assessment.
2. In Southeast Minnesota, nitrate is generally not stable in deeper ground water. However, nitrate is present in bedrock aquifers when bedrock is close to the land surface. Additional investigation is needed to:
   - identify and quantify correlations between various geologic and hydrologic factors and the distribution of nitrate. Additional data from other sources should be included in the analysis; and
   - test hydrologic sensitivity maps for this area.
3. In the sand plain regions of central Minnesota, nitrate may rapidly enter ground water as a result of leaching. Land use is changing rapidly in many locations, including urbanization and increased irrigation and potato farming. Additional investigation is needed to:

- Quantify nitrogen loading under different land uses and as a result of changes in land use;
- determine patterns of geochemistry within the upper portion of these aquifers;
- determine the seasonal variability in nitrate concentrations in ground water;
- determine the fate of nitrate in surficial aquifers; and
- determine the effectiveness of confining geologic units for underlying buried Quaternary aquifers.

Nitrate contamination is not limited to these three regions, but contamination in other locations is less extensive. Also, understanding the distribution of nitrate in these three areas will greatly increase the understanding of its distribution in other areas of the State.

6. Future Work

Much of GWMAP's work now focuses on investigation of specific issues related to ground water quality (e.g. septic systems, manure management, effectiveness of Best Management Practices). The objective of new studies is to conduct monitoring in ground water which is potentially impacted by a specific land use. Examples of these studies include the St. Cloud land use study, an investigation of the effect of septic systems on nitrate concentrations in ground water and surface water, and the effect of manure storage basins on ground water quality. These studies are much smaller in scope than the baseline study, covering areas of less than 30-square miles and in some cases, less than a square mile. However, all these studies are conducted in areas considered to be representative enough to transfer information to other similar physical settings.

These studies include rigorous methods for field sampling, drilling, network design, data analysis, and product delivery. Hydrologic and geochemical interpretations, modeling, and risk analysis are components of each study.

For the St. Cloud land use study, quarterly sampling will be conducted through the year 2000. The sampling schedule will be evaluated at that time. In addition to nitrates, sample parameters include major cations and anions, total Kjeldahl nitrogen, dissolved and total organic carbon, volatile organic compounds, and pesticides. An annual report is prepared. An extensive geoprobe study was completed in spring, 1998. Approximately 35 geoprobe samples were collected from eight different land uses across the 30 square-mile study area. Samples for the above mentioned parameters were collected at the water table. At half these locations, additional samples were collected seven and one-half and 15 feet below the water table. This information will be useful in understanding the three-dimensional distribution of nitrate across the study area, in relation to both land use and aquifer geochemistry. The geoprobe report is scheduled for release in September, 1998.

A septic system study was initiated in Baxter (located in north-central Minnesota) in spring, 1998. The objectives of the study are to determine the three-dimensional distribution of nitrate across an unsewered area, determine the chemistry of several septic plumes, determine septic nitrate loading and impacts to two lakes in the area, assess trends in nitrate concentration following changes from unsewered to sewered land use, and develop a predictive model for estimating impacts of septic systems on ground water quality. Each of these objectives will be conducted as a separate component of the overall study. Aquifer geochemistry and hydrogeology will be rigorously studied for each component. Reports will be prepared for each study component. The information will be useful for identifying risk to surface water and ground water receptors resulting from septic systems and should provide planning authorities with information useful in land use planning.

A study of the effect of manure storage systems on ground water quality was initiated in fall, 1997. Initial monitoring networks have been established at two sites around manure storage systems. Eventually, as many as six to ten sites are likely to be investigated. Most sites are located on sandy soils overlying shallow, sensitive aquifers. These studies are long-term investigations which include quarterly sampling for nitrogen species and geochemical parameters. This information will be useful for understanding the fate of nitrogen from these systems, since these may locally be high-impact point sources for nitrogen. The study results can be used to guide management of manure in sensitive hydrologic environments.

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Appendix A - Summary of QA/QC Analysis

The University of Minnesota Research Analytical Laboratory performed nitrate analysis of the GWMAP baseline ground water samples. Cadmium reduction was the laboratory method utilized, with a reporting limit of 0.50 mg/L for most of the data. Field duplicates were collected for 82 samples (8.6 percent of the samples). Nitrate was below the reporting limit of 0.50 mg/L in 61 of the 82 primary samples for which duplicates were also collected. Nitrate was undetected in the duplicates for these 61 samples. There was no significant difference ($p = 0.910$) in nitrate concentrations for prime and duplicate samples. The correlation coefficient for prime and duplicate samples was 0.972, which was significant at a level of less than 0.001. The standard deviation for samples with detectable nitrate was 10.41 and 10.37 for the prime and duplicate samples, respectively.

Laboratory splits were conducted on 105 samples (11.0 percent of the samples). There were 75 samples in which both the field sample and the split sample had no detectable nitrate. For two samples in which the laboratory split had no detectable nitrate (< 0.50 mg/L) the field samples had concentrations of 0.50 and 756 mg/L. This last sample was viewed as an extreme value and deleted from the analysis. It is possible this sample was contaminated by accidentally adding nitric acid to the anion sample bottle. For the 28 samples with detectable nitrate in both field samples and lab splits, the correlation coefficient of 0.777 was significant at $p < 0.001$. There was no significant difference ($p = 0.704$) in nitrate concentration between the two types of samples. Standard deviations were 10.89 and 11.24 for the lab splits and field samples, respectively.

A laboratory spike performed on 10 November, 1994, resulted in 93.75 percent recovery of the nitrate added to the spike sample. Laboratory checks throughout the sampling period showed concentrations within 1 percent of the expected concentration for spiked samples.

Charge balance was performed on each sample. The percent of samples exceeding 5 and 10 percent was 27.6 and 11.9, respectively. The overall charge balance was 2.1 percent. The largest potential contributing factor to discrepancies in charge balance is use of laboratory rather than field alkalinity, which underestimates the bicarbonate contribution by approximately 10 percent. Over 90 percent of the large imbalances (> $\pm$10 percent) were due to excess positive charge.

A final check on data considered the relationship between total dissolved solids and total ions or specific conductance. The ratio of total dissolved solids to specific conductance for all samples was 0.696, which is within the acceptable range of 0.55 to 0.76 (Hounslow, 1995). Many individual sample ratios were outside the acceptable range, but field measurement of specific conductance may not be reliable because of occasional difficulties with the field instrument. The greatest deviations from the acceptable range occurred for samples with total dissolved solids less than 100 mg/L. The overall difference between lab-measured total dissolved solids and calculated total dissolved solids (sum of ions and silica) was 2.3 percent.

Appendix B - Discussion of Statistical Methods

Analytical methods are described in MPCA (1996) and MPCA (1998a). GWMAP employs rigorous statistical methods during data analysis. The methods discussed in this section include curve-fitting techniques, normality and other data checks, nonparametric analysis, and correlation testing.

Curve-fitting techniques were utilized for data in which there were values below the reporting limit (nondetects). These data are censored, which means an arbitrary value less than the reporting limit is assigned to each nondetect. For example, with nitrate, if the reporting limit is 0.50 mg/L, all nondetects were assigned a value of 0.49 mg/L. Curve-fitting techniques treat these censored values as missing data. In a curve-fitting program, the values for which there was a value reported are used to fill in the curve below the reporting limit. To do this, the data are assumed to fit either a normal or log-normal distribution. The values below the reporting limit can be “fit” with a mathematical equation, provided the normality assumption is correct, the reporting limit is known, and the number of censored values is known. The computer software used to fit the data completes the routine and returns the slope and intercept of the curve, which can then be used to fill in the censored values. Helsel’s Robust Method was employed for nitrate. This method assumes a log-normal distribution and works well for sample sizes of 20 or more (Helsel, 1990; Newman et al., 1995).

Data checks include testing the assumption of normality, independent samples, and equal variance. Ground Water Monitoring and Assessment Program primarily employs nonparametric methods, which do not require these assumptions for the data. In cases where parametric methods are used (some ANOVA testing, establishing means and confidence limits, some regression methods), these data checks must be performed. Normality is tested using the Komologorov-Smirnov test for samples sizes greater than 20 and the Shapiro-Wilks test for sample sizes of 20 or less. The Pearson chi-square test or other similar methods of association are used to test the assumption that samples are independent of each other. The Levene test is used to test the assumption that variances of different groups are equal. For all statistical tests, a p-value of 0.05 is used as the decision criteria. P-values less than 0.05 indicate the assumption is not valid. Data may then be transformed (e.g. log transform) and the data checks rerun. The most common procedures employed by GWMAP in which these data checks must be conducted include establishing means and confidence limits, and in conducting regression analysis.

Nonparametric methods refer to methods of statistical analysis which do not require assumptions of normality, independence, or homogeneity of variance. For most environmental analyses, nonparametric methods have been proven to be almost as powerful as parametric methods when data are truly normally distributed, and they are much more powerful than parametric methods when the data are not normally distributed. The most common nonparametric procedure utilizes a ranking approach. Data are simply ordered from high to low (or vice versa) values, and the statistical tests are then run on the ranked data. Ties are assigned equal values. Censored data are therefore treated as ties. These methods work well provided the number of ties is not excessive. The Kruskal-Wallis, Mann-Whitney test, and Spearmann correlations are the most common nonparametric tests conducted by GWMAP.

Correlations test the strength of a linear relationship between two or more parameters. For example, nitrate may be related to iron concentrations. A correlation test can be used to determine if such a relationship is significant. A p-value of 0.05 is used to identify significant correlations. The correlation coefficient quantifies the fraction of variability in the dependent variable attributable to the independent variable. For example, if the correlation between nitrate and iron has a p-value of 0.02 and the correlation coefficient is -0.750, then we assume the relationship is significant (0.02 is less than 0.05), 75 percent (0.75) of the variability in nitrate concentrations can be explained by iron concentrations, and the relationship is negative (nitrate concentrations decrease as iron concentrations increase). Ground Water Monitoring and Assessment Program typically employs the nonparametric Spearmann method for correlation analysis. Linear regression is a parametric procedure which tests the correlation between a dependent variable and one or more independent variables. This statistical technique is therefore subject to data checks for normality, equality of variance, and independence.