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NITRATE IN MINNESOTA GROUND WATER - A GWMAP PERSPECTIVE

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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

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

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.

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.

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

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.

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]

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.

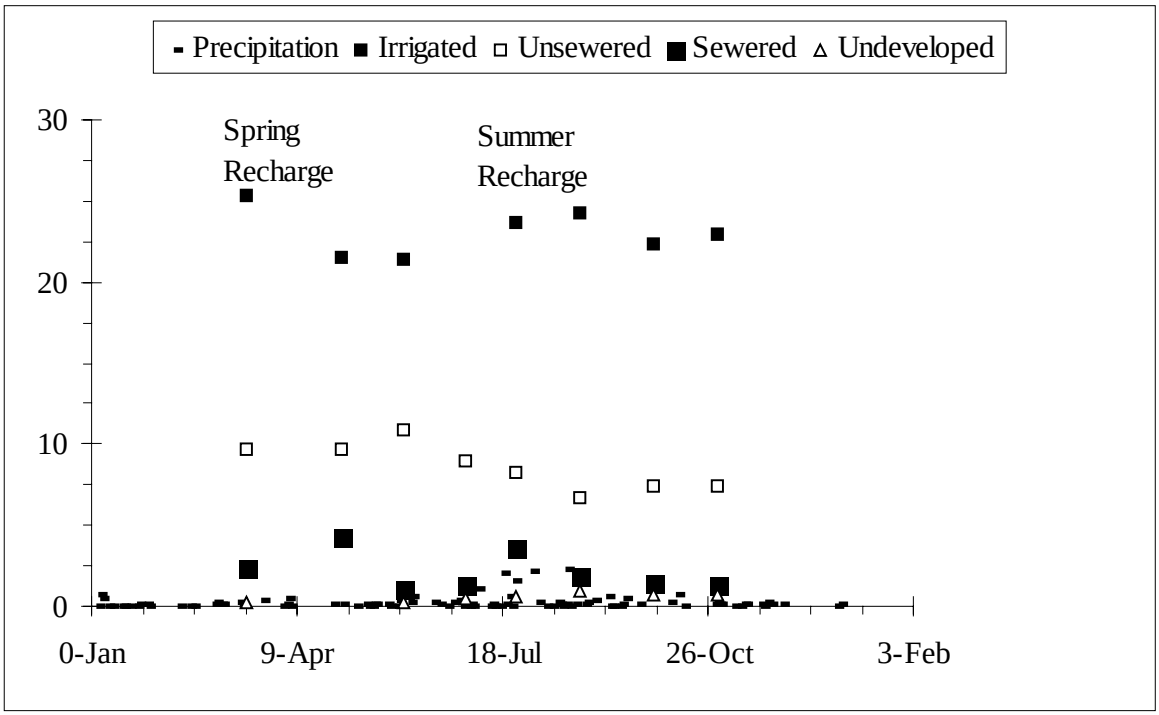

Figure 2: Concentrations of nitrate under different land uses in response to precipitation. Nitrate concentrations are in mg/L ppm and precipitation is in inches.

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.

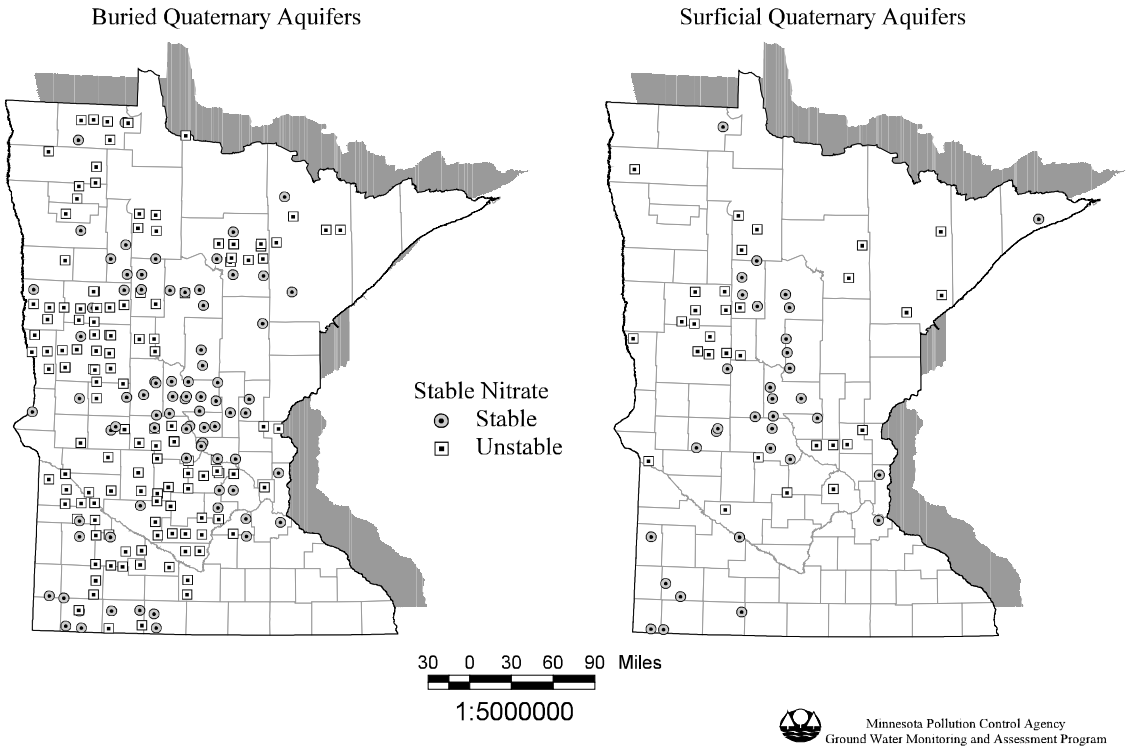

Figure 3: Distribution of nitrate-stable and nitrate-unstable samples in buried and surficial Quaternary wells.

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.

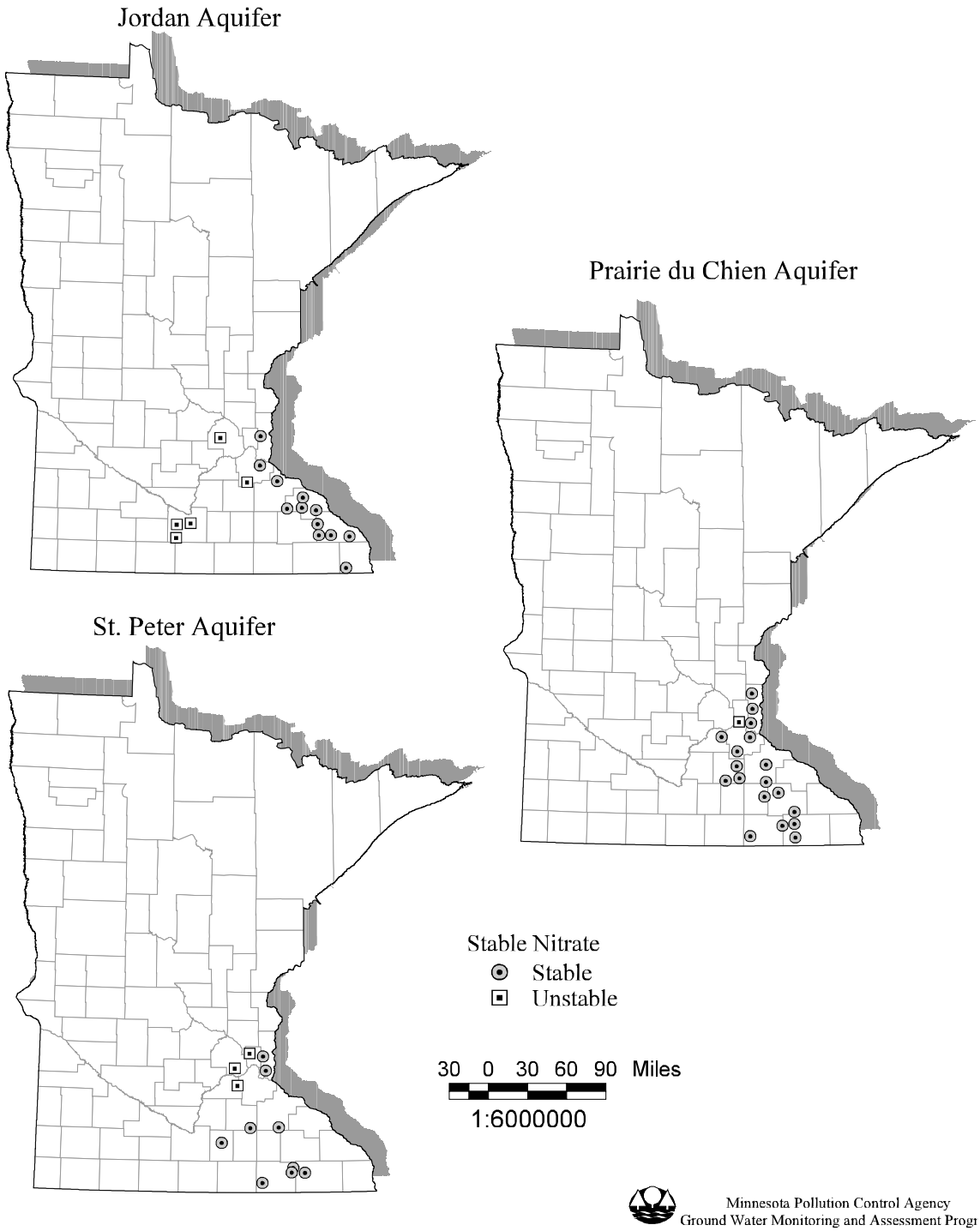

Figure 4: Distribution of nitrate-stable and nitrate-unstable samples in Prairie du Chien, Jordan, and St. Peter aquifers.

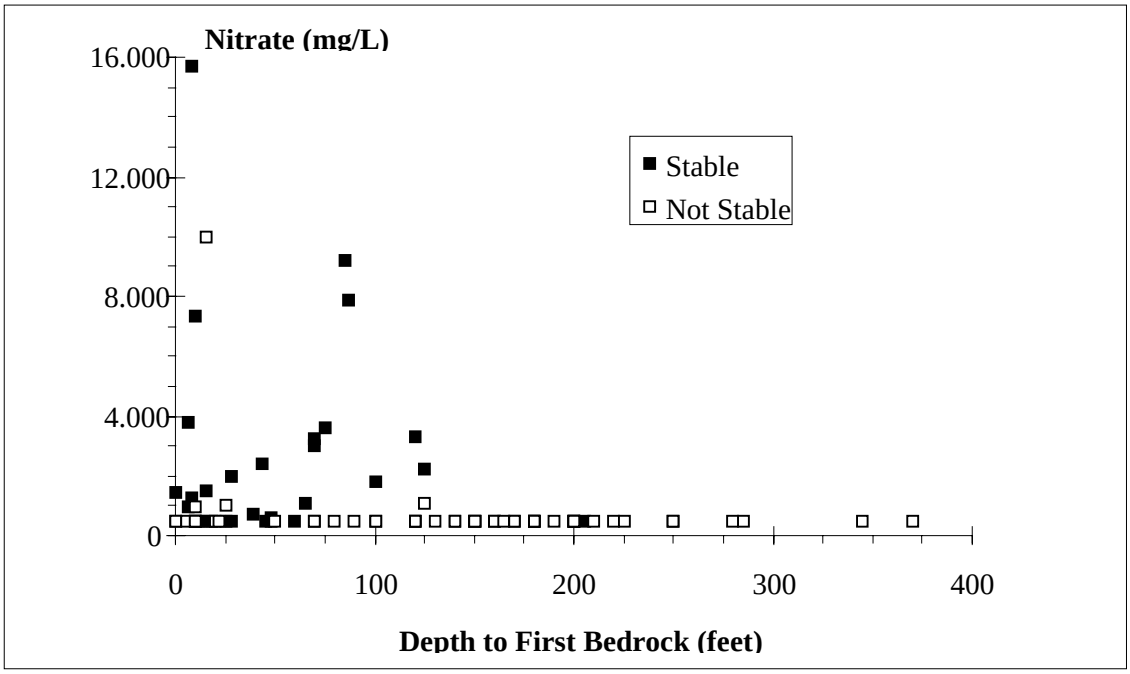

Figure 5: Relationship of nitrate concentration and depth to first bedrock for nitrate-stable and nitrate-unstable samples.

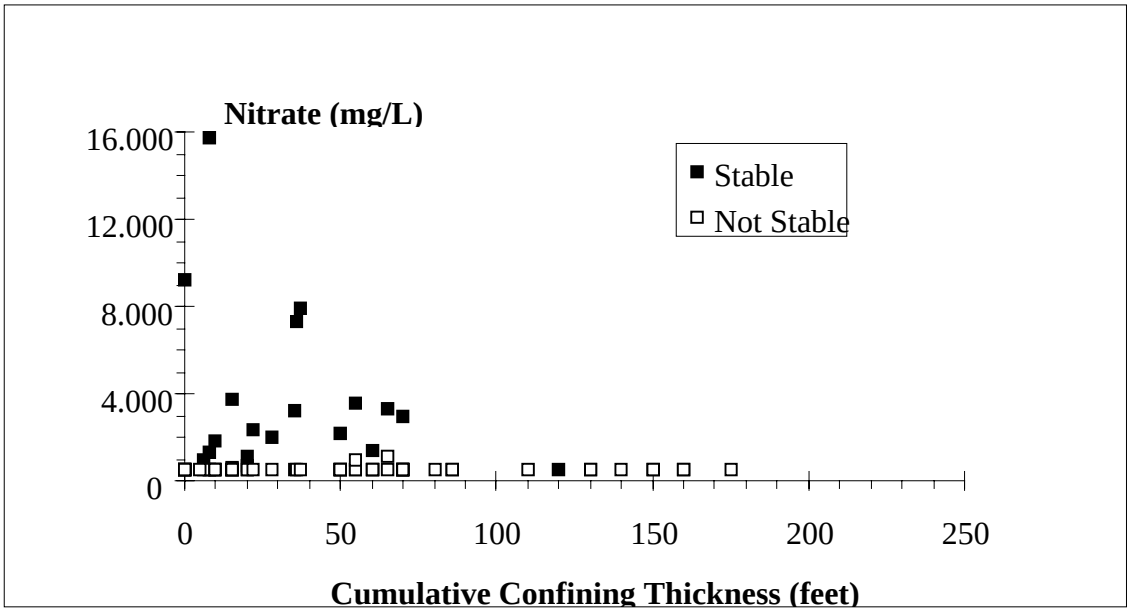

Figure 6: Relationship of nitrate concentration and cumulative thickness of confining layers in nitrate-stable and nitrate-unstable samples.

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.

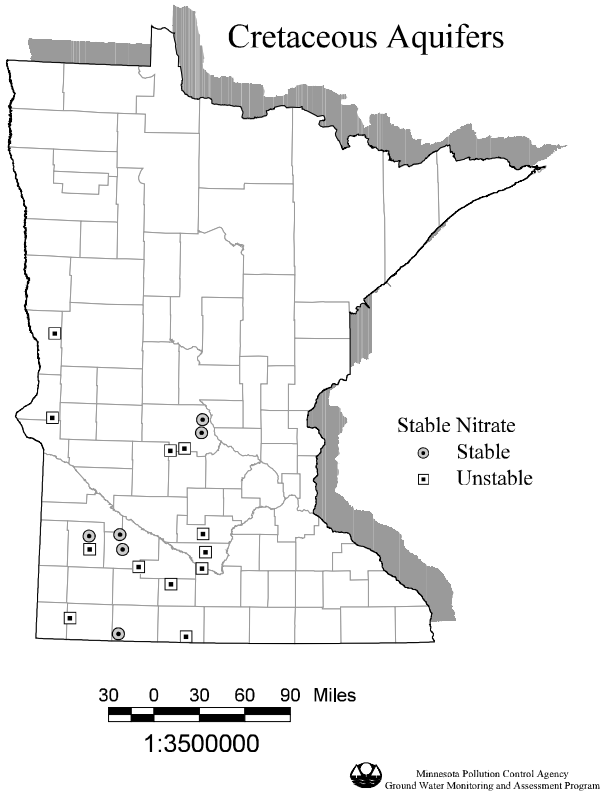

Figure 7: Distribution of nitrate-stable and nitrate-unstable samples in Cretaceous aquifers.