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#### WATER QUALITY AND SENSITIVITY OF THE PRAIRIE DU CHIEN-JORDAN

#### AQUIFER IN WESTERN WINONA COUNTY

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Minnesota Pollution Control Agency Water Quality Division

June 1991

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#### EXECUTIVE SUMMARY

This study was conducted as part of a multi-agency Legislative Commission on Minnesota Resources funded study related to assessing sensitivity of ground water resources in Minnesota. The Minnesota Pollution Control Agency (MPCA) Water Quality Division focused on water quality of the Prairie du Chien-Jordan aquifer in a 100 square mile area of west-central Winona County. This report discusses the results from two rounds of samples taken from 22 Prairie du Chien (PDC) wells and 32 Jordan Formation wells during the spring and summer of 1990. Primary goals of the study were to determine the variability of water chemistry within the formations, relate the water quality and variability to geologic sensitivity, and assess the factors affecting water quality and residence times within the aquifer. Nearly 90 percent of sampled wells had an associated well log and were completed in the PDC or Jordan Formation. Water from all wells was analyzed for nitrate and field parameters, and most wells were analyzed for other major ions, dissolved organic carbon and silica. Tritium (age dating) analysis was conducted on water from 22 wells and pesticides were analyzed in six wells. Geologic information was obtained largely from the Winona County Geologic Atlas, supplemented with downhole geophysical logging analyses performed by the Minnesota Geological Survey.

The Minnesota Department of Natural Resources ranked the geologic sensitivity throughout most of the project area as high or very high based on soil parent materials (level 1 assessment). Elevated nitrate, tritium and chloride concentrations in many wells throughout the project area suggest that portions of the Prairie du Chien-Jordan aquifer are indeed sensitive to surface contamination. However, great variability in nitrate, tritium, and other parameter concentrations was found throughout the project area.

In general, the water chemistries varied much less between Jordan wells as compared to water chemistry differences between PDC wells. While several PDC wells have water chemistries and quality similar to Jordan wells, PDC wells had higher nitrate, chloride, sodium, calcium, and bicarbonate and lower pH than Jordan wells, on the average.

The maximum detected chloride and sulfate concentrations in both formations were far below secondary drinking water standards. Nearly 50 percent of the 22 Prairie du Chien wells sampled had nitrate-N in excess of 10 mg/l. Older PDC wells and PDC wells not protected by overlying shale tended to be more greatly impacted by nitrate and other dissolved solids. Nearly 75 percent of Jordan wells had nitrate-N in the range of one to seven mg/l. The highest nitrate-N concentrations found in Jordan wells were 10 mg/l in a municipal well and 11 mg/l in a domestic well. The water chemistry of the 1945 constructed municipal well indicated that the well was likely drawing much of its water from the PDC rather than the Jordan, due perhaps to a poor seal and high capacity pumpage.

Tritium analysis results showed that while some Jordan wells withdrew water which had more recently entered the aquifer, other Jordan wells were withdrawing water that had entered the ground prior to the mid 1950's. Of five PDC wells analyzed for tritium, three had recent water (post-1954) and two wells had a mix of older and recent water. The two mixed age PDC wells had nitrate-N concentrations averaging 2.4 and 0.36 mg/l. Of sixteen Jordan wells with tritium data, six wells have older water (pre-1954), six wells have recent water (post-1954) and four wells have mixed water. Four of the older water wells had nitrate-N concentrations less than 0.01 mg/l, and the other two older water wells had nitrate-N averaging 3.2 and 1.2 mg/l. The low nitrate concentrations in the pre-1954 water suggest that either very little nitrate was entering ground water before the mid-1950's or that nitrate entering ground water was lost through denitrification, or a combination of the two. The potential for denitrification, based on redox potential, dissolved organic carbon and dissolved oxygen measurements, was high in the four nitrate-free wells and somewhat lower for the older water wells with measurable nitrate. A third round of sampling conducted in April 1991 will provide additional information to aid in further understanding residence times, nitrate levels and denitrification potential in the study area. The third round of data will be incorporated into a 1992 report to EPA.

Geophysical logging information, combined with well drillers log information and water chemistry results, show that higher nitrate concentrations and younger water is found in the PDC formation and upper Jordan formation. Since the Jordan Formation is divided into several geozones by lower permeability units, significant differences in water chemistry exist vertically within the Jordan. The lower part of the Jordan, especially where the Sunset Point Mb is present, is much less sensitive to surficial contamination compared to the PDC and upper Jordan. It is recommended that new wells in the area be cased at least 30 to 55 feet into the Jordan, where possible.

Vertical and lateral variability in water quality and residence times understood when detailed geologic information is available. Relying on well driller's logs alone is insufficient for accurately defining geologic sensitivity in this region. The Minnesota Geological Survey produced a sensitivity map based on a number of geologic factors. Nitrate concentrations from this study corresponded fairly well with the sensitivity rankings. A minimum of a level 2 assessment (MDNR guidelines) should be used to evaluate sensitivity in similar areas of southeastern Minnesota. Geologic sensitivity assessments utilizing detailed geologic information appear to be a reasonable means of prioritizing where to implement Best Management Practice efforts (e.g. nitrogen fertilizer and pesticide management).

Due to the likelihood of denitrification in the deeper part of the Jordan Formation, and the relatively low residence times of water in the PDC and much of the upper Jordan, the nitrate situation could significantly improve in the PDC-Jordan aquifer within one generation following reductions in nitrate loading into the aquifer.

#### INTRODUCTION

#### Purpose and Scope

This study was conducted as part of a Legislative Commission on Minnesota Resources (LCMR) funded multi-agency study on assessing geologic sensitivity of ground water resources in Minnesota. The primary goals of the multi-agency project were to: 1) develop and evaluate guidelines and criteria for identifying areas sensitive to ground water pollution; 2) conduct aquifer and water quality studies to support criteria and guidelines development; and 3) prepare a ground water planning handbook to assist local governments, water planning officials, and citizens in the development of local programs for ground water protection. The overall project coordination was provided by the Minnesota Department of Natural Resources (MDNR).

The Minnesota Pollution Control Agency (MPCA) Western Winona County Ground Water Study component was conducted primarily to help meet the second stated objective. The U.S. Geological Survey (USGS) has conducted aquifer studies in Hennepin, Olmsted, and Dakota counties as part of this project, focusing most of their work on the Prairie du Chien-Jordan aquifer. The Minnesota Geological Survey (MGS) mapped the Prairie du Chien aquifer and assessed factors that affect the sensitivity of the aquifer. Other groups involved in the overall project included Metropolitan Council, the University of Minnesota, and Dakota County.

One of the reasons for choosing western Winona County as one of the aquifer study areas was that much information was learned about the ground water system/quality in the area from work conducted by MPCA, MGS, Minnesota Department of Agriculture (MDA), and Winona County Extension (WCE) between 1981 and 1989. Since 1981, the eastern half of the currently-studied area has been part of the Garvin Brook Rural Clean Water Project (RCWP) area. The Garvin Brook RCWP was one of 21 experimental programs in the country to evaluate the social, economic and technical aspects of controlling nonpoint source pollution. The Garvin Brook RCWP is further described in Wall, et al. (1989).

While much information was obtained from past studies, a lot of the water quality data in past work was either from: 1) wells that had very little known about well construction and underlying geology; 2) wells which were in aquifers too deep to reflect recent land use conditions; or 3) vadose zone sampling.

By sampling wells with associated well logs, the major goals and objectives of this ground water study (conducted from 1989 to 1991) were to:

- Determine the variability of well water chemistry and quality withdrawn from the Jordan Sandstone and determine the geologic, hydrologic, and other factors controlling the observed variability;
- 2. Characterize differences between water withdrawn from the Prairie du Chien Dolomites Formation and the Jordan Sandstone Formation, including nitrate concentrations, general chemistry and residence times; and
- 3. Assess the sensitivity of the Prairie du Chien-Jordan Aquifer to contamination in this area of the state, and compare ground water monitoring results to sensitivity rankings.

Other more minor objectives of this study were to:

- i) Assess the potential for denitrification (nitrate loss) to occur in the Prairie du Chien-Jordan Aquifer; and
- ii) Compare the water quality of high capacity Jordan municipal wells to those of lower capacity domestic wells in the Jordan.

LCMR funding of the Winona County study was limited to \$20,000, which was sufficient for the first two rounds of sampling. This report represents results from these two rounds. Additional funding was provided by EPA to conduct a third round of sampling in the spring of 1991. A final report will be completed in 1992 that will incorporate results from all three rounds of sampling.

#### Previous Investigations

A geologic atlas for Winona County was published by MGS in 1984. The glacial deposits, bedrock stratigraphy, ground water flow, and karst geology are described in the atlas. The geologic atlas information for the study area, in addition to MPCA geologic/hydrogeologic interpretation for the study area, is described in the section of this report entitled "Geology and Hydrogeology."

The MPCA, MDA, and WCE conducted ground water and soil water monitoring in the Garvin Brook RCWP area since 1981, with increased monitoring efforts since 1987. The data collected has been analyzed to look at general water quality trends and sources of nitrate and pesticide contamination. A description of the many individual ground water quality studies conducted, along with results from these studies, is described in Wall, et al., 1989. The boundaries of previous study efforts are shown in Figure 1. Some results and conclusions from previous ground water quality related work in this area are listed below.



Figure 1 Map showing location of Garvin Brook Watershed and the adjacent Ground Water Recharge Area. Together, these two areas comprise the Garvin Brook RCWP Project Area, which was the boundary for previous monitoring efforts.

#### Nitrate - Previous Studies

- About 35 to 40 percent of over 160 wells sampled in the area had nitrate-N concentrations in excess of 10 mg/l. A greater percentage of wells exceeding 10 mg/l nitrate-N were found to the west in the ground water recharge area. This was believed to be largely due to the great number of wells developed in the fractured carbonate Prairie du Chien Formation in the ground water recharge area.
- 2. From 38 wells believed to draw water out of the Prairie du Chien formation, the median nitrate-N concentration was 11.7 mg/l. The Jordan formation wells had varied, but generally much lower, nitrate-N concentrations, with a median of 2.2 mg/l. Wells in deeper aquifers, below one or more confining units, were found to have consistently very low nitrate concentrations (usually < 0.01 mg/l).</p>
- 3. While nitrate concentrations in some Jordan formation wells had < 0.01 mg/l nitrate-N, other nearby Jordan wells had nitrate concentrations in the range of 4 to 7 mg/l. The one Jordan well that was analyzed for tritium, showed nitrate < 0.01 mg/l and water that predated atomic bomb testing (before the mid 1950's). The Jordan well with the highest nitrate was a municipal well in Lewiston.</p>
- 4. Temporal variability of nitrate concentrations throughout the year was much greater in the Prairie du Chien wells than in Jordan wells, but could not be correlated in most wells to climatic events or season.
- 5. No correlation was found between nitrate concentrations and proximity of domestic wells to sinkholes. Nitrate concentrations in water moving to ground water via sinkholes varied greatly, being very low in sinkholes surrounded by hay, grassland, or woodland and very high in sinkholes surrounded by corn fields.
- 6. A comparison of nitrate concentrations determined from water collected at the same places and times at three different laboratories showed significant and consistent differences in reported concentrations. Therefore, long-term trends analyses of nitrate were made by only comparing data from the same laboratory. Nitrate trends began to show some decline in 1988 and 1989 compared to years 1983 to 1987.
- 7. Nitrate-N concentrations in percolating water below four cornfields was in the range of 20 to 50 mg/l, even after a couple of years of nitrogen fertilizer BMPs implemented through the Garvin Brook RCWP. It is likely to take several years before nitrogen management BMPs in soils of this area show their full potential to reduce nitrate leaching. Nitrate-N concentrations in percolate under control grassland sites were between 0 and 7 mg/l.

#### Pesticides - Previous Studies

1. Of 21 domestic wells sampled in 1988 and 1989 for 18 to 25 different pesticides, 16 (76 percent) have had at least one detection of the herbicide atrazine. All but two of the wells had detections less than the drinking water standard of 3 ppb, and many of the detections were in the range of 0.05 to 0.20 ppb. The only wells with other pesticides detected

were the same two wells with atrazine above 3 ppb. These two wells are Prairie du Chien wells and are located on the eastern fringes of the city of Lewiston.

- Atrazine concentrations were very low or nondetectable in most Jordan wells sampled. The highest atrazine concentrations of all wells in the Jordan or lower aquifers was found in one of the city of Lewiston's municipal wells (0.27 to .77 ppb).
- 3. Relatively high concentrations of four pesticides were found to be entering sinkholes just south of Lewiston. These pesticides were believed to originate from the city of Lewiston, where very high pesticide concentrations were found in soils around a couple of commercial pesticide applicator facilities. Effects from pesticide management BMPs may be undetectable in some areas due to "point" source related pesticide problems.
- 4. Evidence of some leaching of pesticides, mostly cyanazine and atrazine, below cropland and in adjacent sinkholes was found.

#### Bacteria - Previous Studies

- 1. Of 143 wells sampled for coliform bacteria in June 1989, 20 percent had detectable bacteria (at least 2.2 MPN/100 ml).
- 2. Coliform bacteria were found in certain wells from all aquifers, but were least prevalent in Jordan wells.

#### Description of Study Area

#### Location

In the area studied from 1981 to 1989, there are relatively few Prairie du Chien or Jordan wells that had an associated well log, and thus, well information was largely from owner's recollection. In order to include the desired number of wells with associated well logs in the monitoring network and study a greater diversity of geologic conditions, the study area was expanded beyond the bounds of previous (1985-1989) investigation. The area under investigation for this study includes the western edge of Garvin Brook Watershed, most of the Garvin Brook Ground Water Recharge Area, and the area between Utica and St. Charles (see Figure 2). The entire study area covers about 100 square miles.

#### Climate

Winona County has an average daily temperature of 16°F in the winter and 70°F in the summer. Average annual precipitation is 31 inches, with over 75 percent of the total falling from April to September. Figure 3 shows the monthly precipitation departure from normal for the period 1986 to 1991. 1986 was a wet year. This was followed by a normal year in 1987, a very dry year in 1988, and a dry year in 1989. The dry trend reversed in 1990 with above normal rainfall. April, 1991 was a very wet month.

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### Figure 2





Figure 3 Departure from monthly average precipitation in Winona County for the years Jan/1986-April/1991 compared to the historical average (1951-1980) in Winona County.

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#### Soils

Soils in the project area consist mostly of silt loams, ranging generally from 3 to 40 feet thick, which are underlain by glacial till, outwash, or bedrock (see surficial geology section). The project area is characterized by broad ridges (one to two miles wide) with narrow drainageways throughout, and narrow valleys (25 to 75 feet wide). Native vegetation for most of the soils was prairie. Most of the area is nearly level to gently sloping. However, areas of steeper slopes do exist.

The two soil associations prevalent in the project area are the Rockton-Channahan-Atkinson and the Mt. Carrol-Port Byron-Joy. Soils of the Rockton-Channahan-Atkinson association are underlain by carbonate bedrock in a region of karst topography. Rockton and Atkinson formed over a moderately thick covering of loamy glacial drift and in the underlying clayey residuum over limestone bedrock. These soils formed at the upper end of drainageways and on the sloping parts of summits and side slopes. Rockton has a loam surface soil and loam or sandy clay loam subsoil. Channahan has a silt loam surface soil and silty clay loam subsoil. Atkinson soils developed in shallower loamy glacial drift and have a loam surface soil and silt loam subsoil underlain by limestone bedrock. Soils of this association are well drained.

Soils of the Mt. Carrol-Port Byron-Joy association formed in thick silty loess covered uplands that overlie glacial till or carbonate bedrock. Mt. Carrol and Port Byron soils are well drained and found on summits and sideslopes. Joy soils are in drainageways and are somewhat poorly drained. Most soils in this association have silt loam surface and subsurface soil texture.

#### Land Use

Between 75 and 90 percent of the studied area is cropped, with about half of that land planted to corn. Soybeans, alfalfa, and oats are also grown on much of the remaining half of the cropped land. Many dairy farms exist in the project area, and commercial fertilizers and manure are applied extensively. Three cities are found within the studied area, including Utica, Lewiston and St. Charles.

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#### GEOLOGY AND HYDROGEOLOGY

Within this section of the report, an overview of the surficial, bedrock and hydrogeology are provided based on the Winona County Geologic Atlas, Geology of Minnesota Centennial Volume, ongoing work by MSG and personal observations. The geology is discussed further, especially as it pertains to the water chemistry, in the section of the report entitled "Geologic Influences on Water Quality."

#### Surficial Geology

Pleistocene glacial deposits cover the entire Western Winona County study area. These unconsolidated sediments overlie the bedrock formations and comprise the surficial materials, except for a few small areas of alluvium and colluvium. Hobbs (1984) maps four prevalent units in the study area: rtl, loess-covered till and bedrock residuum; scs, outwash and till; scp, loess-covered bedrock; and scl, loess-covered till, as shown in Figure 4.

#### Map Unit Descriptions

The map unit rtl (loess-covered till and bedrock residuum) covers the easternmost part of the study area. Figure 4 shows that rtl occupies the area east of Lewiston and is bounded on the west side by a contact with scl. Hobbs (1984) dates rtl as Pleistocene, possibly Pre-Illinois. The typical glacial stratigraphy for this unit from bottom to top is: bedrock residuum, loess, till, and loess. The lower three layers appear to be absent in downcutting drainages, while the uppermost loess layer tends to drape into the drainages. The bedrock residuum is made up of sandy and clayey material formed by the weathering of the underlying bedrock formations. In the study area, the residuum is generally less than five feet thick and patchy. The till component of rtl ranges in texture from clay to clay loam and sandy clay to sandy clay loam. The pebble fraction of this till is dominated by weathered igneous rock fragments. Chert and sandstone fragments are found locally and carbonate fragments are absent. The till is usually less than ten feet thick and is thickest on the drainage divides and thin or absent near the drainages. The loess layers are composed of unbedded brownish silt loam. These layers were originally calcareous, but the carbonate material has been leached from the top five to eight feet. The loess layers are greater than ten feet thick on the drainage divides and thin or absent in the valleys.

The map unit scp (loess-covered bedrock) covers the southwestern part of the study area and delineates the region of highest elevation. In this region, the resistant limestone of the Galena Formation caps the more easily erodible Glenwood Formation and St. Peter Sandstone. The surficial stratigraphy in this area consists of a single layer of loess underlain by a thin layer of calcareous till which has been eroded down to thin remnants, scattered pebbles and boulders on the bedrock surface. The loess layer varies from one to ten feet in thickness and is similar in composition to the loess of the rtl unit.

The map unit scs (outwash and till) makes up most of the central part of the study area. The unit consists of a single unit of thin gray calcareous till less than ten feet thick, with localized patches of outwash. The till is typically loam to clay loam, and contains pebbles, cobbles, and boulders. The till is usually less than ten feet thick and brown and non-calcareous where exposed to the surface. Granitic fragments of the Canadian shield dominate the very coarse sand fraction. Sand and coarser size particles of limestone and dolostone can be doubd where the till has not been leached.



Figure 4 Surficial Geology Map

The map unit scl (loess-covered till) covers most of the northern part of the study area. It is bounded to to south primarily by scs. The unit consists of a lower layer of till and an upper layer of loess. The till component is equivalent to the till in unit scs, and the loess component is similar to the loess component in unit scl. According to Hobbs (1984) the three units: scl, scs, and scp are of Pleistocene, possibly Pre-Illinoian age, and are stratigraphically higher than the unit rtl.

#### Thickness of Glacial Cover

Lithologic information from well logs suggest that the thickness of glacial material over the bedrock does not vary greatly in the study area. Figure 5 shows that, generally, the glacial cover varies in thickness from five to forty feet. The glacial material does not systematically thicken in any one direction, rather the the variation in thickness is probably attributable to the erosional irregularities in the underlying bedrock surface.



#### Bedrock Geology

#### **Overview**

The stratigraphic units encountered in the study area range in age from Upper Cambrian to Middle Ordovician. During this time a shallow continental sea covered Winona County, and widespread layers of sand, clay and lime mud accumulated. These layers were eventually compacted and lithified into the presently observed sedimentary sequence. The sequence is summarized in a stratigraphic column constructed by Mossler and Brook (1984), shown in Figure 6. The formations approximate planar tabular bodies which have a regional dip of only one sixth of a degree to the west-southwest. These Paleozoic stata probably overlie Precambrian granitic genisses which have been observed east of the study area.

Since the focus of this report is the Prairie du Chien-Jordan Aquifer, geologic descriptions of the formations below the Jordan Sandstone will not be included. The Jordan Sandstone represents the youngest Cambrian sediments in the study area. The Prairie du Chien Group caps the Jordan throughout the area, except in some drainages and valleys in the eastern part of the study area. The Jordan is a laterally continuous sandstone that varies in thickness from approximately 100 to 110 feet in the study area (Setterholm, 1991).

#### Jordan Sandstone

In Western Winona County the Jordan Sandstone can be divided into three members, namely the Van Oser Mb, the Waukon or Sunset Point Mb, and the Norwalk Mb (Setterholm, 1991). The Van Oser Member makes up most of the upper 90 to 100 feet of the Jordan. It is characteristically a medium-grained, white to yellow, quartzose sandstone, although grain size varies from coarse to fine sand (Webers, 1972). Very fine-grained, felspathic, dolomitic, well cemented beds of sandstone and interbedded siltstone are found within the Van Oser Member (Odom and Ostrom, 1978). Setterholm (1991) suggests that these strata are analogous to the Waukon Member of northeastern Iowa and southwestern Wisconsin and the Sunset Point Member of south central Wisconsin. These very fine-grained beds range in thickness from 2 to 30 feet and can be traced up to eight miles along strike (Setterholm, 1991). The Norwalk Mb is the lowermost strata and is generally 10 feet thick. It is typically described as a very fine-grained dolomitic feldspathic sandstone (Odom and Ostrom, 1978) which may contain layers of siltstone in the study area (Setterholm, 1991).

The Van Oser Mb is overlain by a unit of interbedded dolomitic sandstones, sandy dolostones, sandstones, and lesser amounts of siltstones, shales, and cherts. This heterogeneous unit has been called the Coon Valley Mb by Odom and Ostrom (1978). The unit's distinctive lithology is not characteristic of either the Jordan Sandstone or the Prairie du Chien Formation. For this reason, the Coon Valley Mb is considered by some as part of the Jordan Sandstone, while others include it as part of the Prairie du Chien Formation. Work performed by the Minnesota Geological Survey suggests that the Coon Valley Mb may be laterally continuous and is 25 to 30 feet thick in the western Winona County study area.

SYSTEM SERIES	G F(	ROUP OR DRMATION NAME	SYM- BOL	LITHOLOGY	THICK- NESS (feet)	DESCRIPTION						
CIAN	F	GALENA ORMATION	Og		60	Fine-grained fossiliferous limestone. Many shale partings in basal 15-20 feet						
ordovie	DEC PLA GLI	ORAH SHALE ITEVILLE Fm ENWOOD Fm	0d		45 20 4	Shale and thin interbeds of limestone. Commonly fossiliferous Fine-grained fossiliferous limestone Sandy shale						
MIDDLE	Si	ST. PETER ANDSTONE	Os	fe fe	90 to 100	Fine- to medium-grained, poorly cemented, quartzose sandstone; basal contact minor erosional surface. Upper surface commonly iron crusted. Generally massive and unbedded						
DVICIAN	EN GROUP	SHAKOPEE FORMATION	Ops		90 to 115	Thin-bedded and medium-bedded dolomite with thin sandstone and shale beds. Basal 20 to 30 feet is fine-grained quartzose sandstone. Local red iron staining. Basal contact minor erosional surface						
LOWER ORDO	RAIRIE DU CHI				160 to 180	Thick-bedded to massive dolomite. Some sandy dolomite in basal 10 to 20 feet. Vugs filled with coarse calcite in upper part. Minor chert nodules. Upper part near contact with Shakopee commonly brecciated						
	Sŕ	JORDAN ANDSTONE	€j		100 to 120	Sandstone. Top 30 feet is thin bedded and well cemented by calcite. Middle part is medium- to coarse-grained quartzose sandstone: generally uncemented and iron stained in outcrop. Basal 35 to 40 feet is very fine to fine-grained sandstone						
	ST. F	LAWRENCE <sup>1</sup> ORMATION	€s		50 to 75	Thin-bedded dolomitic siltstone. Minor shale partings						
AN	FF FC	ANCONIA <sup>1</sup> DRMATION	£f	G G G G M G M G G G G G G G G G G M G M	140 to 180.	Thin-bedded, dolomite-cemented glauconitic sandstone. Very fine to fine , grained. Contains minor dolomite beds near base and shale partings throughout						
er cambri	lF G SA	IRONTON & GALESVILLE SANDSTONES		IRONTON & GALESVILLE SANDSTONES		IRONTON & GALESVILLE SANDSTONES		RONTON & Carlos Control			90 to 120	Ironton: Poorly sorted, silty, fine- to medium-grained quartzose sandstone with minor glauconite Galesville: Fine- to medium-grained, well- sorted quartzose sandstone
UPPE	E4 F(	AU CLAIRE <sup>2</sup> ORMATION	€e	6 6 6 6 6 6 6 6 6	90 to 125	Very fine to fine-grained sandstone and siltstone. Some is glauconitic. Interbedded shale						
	M SA	MT. SIMON <sup>2</sup> SANDSTONE		MT. SIMON <sup>2</sup> SANDSTONE Cm		290 to 350	Fine- to very coarse grained, poorly cemented sandstone. Contains pebbles in basal 20 to 40 feet. Sandstone generally moderately to well sorted. Greenish-gray shale mottled with grayish-red in basai third of formation. Basal contact major erosional surface					
PF	RECA	MBRIAN <sup>3</sup>	D€	P. M. C.		Biotitic granite gneiss in eastern part. Poorly known in west						

St. Lawrence and Franconia Formations undivided on map. Symbol: Est

<sup>2</sup>Eau Claire Formation and Mt. Simon Sandstone undivided on map. Symbol: €em

<sup>3</sup>Precambrian shown only on sections

· .

from Mossler & Book,1984

Figure 6 Stratigraphic sequence of bedrock materials

#### Prairie du Chien Group

The Prairie du Chien Group lies above the Coon Valley Mb. The Prairie du Chien has a maximum thickness of approximately 270 feet, however since it is usually the uppermost bedrock in the study area, in many places some of its original thickness has been removed by erosion. All formations in the Prairie du Chien Group are laterally continuous in the study area. The Prairie du Chien Group is divided into the lower Oneota Dolomite and the upper Shakopee Formation (Davis, The Oneota Dolomite is thick-bedded, light brownish gray to buff, fine 1966). to medium-grained dolostone with a silt size dolomite matrix (Austin, 1972). It is approximately 120 feet thick in the study area. The Shakopee Formation is divided into the lower New Richmond Mb and an upper Willow River Mb. The New Richmond Mb is approximately 50 feet thick in the study area and consists of fine-grained quartzose sandstone and sandy dolostone with minor amounts of shale (Austin, 1972). The bottom 10 feet of the New Richmond Mb consists of interbedded dolostone, sandy dolostone, and sandstone (Setterholm, 1991). The Willow River Mb is composed of thin to thick-bedded dolostone, sandy dolostone, sandstone and some grayish-green shale (Austin, 1972) and may exceed thicknesses of 100 feet in the study area (Setterholm, 1991).

#### Bedrock Geology Map

As previously stated, the Prairie du Chien Group is the shallowest bedrock encountered in most of the study area. However, Figure 7 shows that the area near and to the south of St. Charles is subcropped by younger bedrock. The remaining bedrock sequence in this area from bottom to top is: the St. Peter Sandstone, the Glenwood Fm, the Platteville Fm, the Decorah Shale, and the Galena Fm. These formations can add up to 230 feet of thickness to the bedrock stratigraphy. For this reason, the surface elevations in this area are higher than in adjacent areas. Brief geologic descriptions of these units can be found in the stratigraphic column in Figure 6.

#### Hydrogeologic Characteristics

The Prairie du Chien-Jordan Aquifer is the target of this study and the principal source of ground water in the region. The aquifer may reach thicknesses of up to 400 feet in the study area. The upper part of the aquifer is the predominantly carbonate Prairie du Chien Group. The porosity of this unit is said to be post-depositional or secondary. After the Prairie du Chien Group was deposited, geologic stresses caused the unit to become fractured. This mechanical deformation was later enhanced by chemical dissolution. Ground water moving through the fracture networks dissolved the bounding limestone and dolostone creating cavities, and in some cases, caverns (Kanivetsky, 1984). The Jordan Sandstone makes up the bottom 100 feet of the aquifer. Much of the porosity of the Jordan Sandstone is primary and attributable to void spaces between the sand grains. Since these pore spaces are sufficiently interconnected, water is able to travel through the rock by moving through these pores (intergranular flow). It is possible, however, that the porosity of the Jordan was increased by fracturing resulting in both primary and secondary porosities, at least in some areas.

The Coon Valley Mb is a 30 feet thick unit which lies between the Prairie du Chien Group and the Jordan Sandstone. Most of the porosity in this unit is probably secondary, however, there is a possibility of intergranular flow, particularly in the more sandy and silty beds (Setterholm, 1991).



#### Potentiometric Levels

Water in an aquifer flows from areas of high hydraulic potential to areas of low hydraulic potential. Water pressure gradients in an aquifer are assessed by the measurement of static water levels. The elevation to which water rises in a single aquifer well is a direct reflection of the hydraulic potential in the aquifer at that location. Static water level elevations are computed by subtracting the depth to the water table from the land surface elevation.

Kanivetsky (1984) constructed a hydrostatic pressure or potentiometric map for the Prairie du Chien-Jordan Aquifer in Winona County. In addition, the MPCA collected static water elevations at 16 wells during November 1990 in order to see if major changes were evident since 1984 and to obtain measurements at locations that were previously not measured. For the most part, the static water elevations collected by the MPCA were within a few feet of those illustrated by the map of Kanivetsky (1984). The supplemental points aided in creating a modified version of Kanivetsky's 1984 map (Figure 7). The solid lines in Figure 7 represent points of equal of hydraulic potential within the Prairie du Chien-Jordan Aquifer. In general, water flows towards the north around St. Charles and to the northeast near Utica and Lewiston.

The highest potentials are found in an elliptical area extending from St. Charles to one mile south of Utica. This area approximately correlates with the area subcropped by bedrock units younger than the Prairie du Chien Group. In this region, the static water level elevations exceed the the elevation of the contact between the Prairie du Chien Group and the St. Peter Sandstone. This suggests that the Prairie du Chien-Jordan Aquifer may be confined by the basal shale beds of the St. Peter Sandstone in this area. North and east of this region the hydraulic potential of the water in the aquifer is lower than the top of the Prairie du Chien Group. Here the Prairie du Chien Group is the uppermost bedrock and thus can not be confined by any overlying bedrock units. Since the glacial material does not appear to be an effective confining layer, the Prairie du Chien-Jordan Aquifer is unconfined or under water table conditions in these Static water levels in the Prairie du Chien-Jordan Aquifer decrease areas. substantially with increasing distance from the confined area. East of Lewiston the Prairie du Chien Group is so greatly dewatered that most wells must penetrate into the Jordan Sandstone to obtain sufficient yields. Static water level information seems to indicate that the Prairie du Chien Group and Jordan Sandstone are hydrologically connected and should be treated as one aquifer within the study area.



Figur ) Potentiometric Map of Prairie Du hien-Jordan Aquifer

#### WATER QUALITY MONITORING PROCEDURES

#### Sampling Site Selection

It was the original intent of this study to choose wells for sampling that 1) had an associated well log on file, 2) were completed in the Prairie du Chien or Jordan aquifer, and 3) were located in the Garvin Brook RCWP Ground Water Recharge Area and western edge of Garvin Brook Watershed. Because only ten wells met the three conditions, it was decided to expand the sampling area to include much of west-central Winona County. Another reason for expanding the sampling area to the west was to include an area of greater diversity of geologic conditions.

Within this area, we attempted to find a series of wells along a flow tube, but were unable to find a suitable area to effectively analyze water chemistry as it moves from recharge areas towards discharge. Forty-five wells with associated well logs were chosen for analysis in the expanded study area; 17 Prairie du Chien Formation wells, 26 Jordan Formation wells, and two Prairie du Chien-Jordan wells that were cased almost, but not completely, through the Prairie du Chien (Figure 10). The two Prairie du Chien-Jordan wells (#226524 and #219251) are usually listed with the Jordan wells in this report.

Data from other wells were also included in this report, including:

- Eight wells without well logs that were sampled in previous years (1988 and 1989) and resampled for select parameters in this study, plus one very old well that was not previously sampled;
- 2. Water chemistry data from the city of Lewiston's two municipal Jordan wells sampled in August 1990; and
- 3. Tritium and water chemistry data from three wells sampled by the University of Minnesota/Minnesota Department of Health (two of these wells were sampled also by MPCA during 1990 for General Chemistry).

Table 2 on page 20 lists the well location and known construction information for each well analyzed in this study. With the exception of the two municipal wells (240797 and 219156) and two commercial wells (226533 and 219103), all wells sampled were domestic water supply wells. Wells will be referenced in this report by their unique well number.

#### Parameters Analyzed

All wells were sampled for nitrate and field parameters, including dissolved oxygen, temperature, pH, specific conductance, alkalinity, and redox potential. Most of the study wells were analyzed for the following additional parameters:

<u>Anions</u> Chloride	<u>Cations</u> Sodium	<u>Other</u> Silica
Sulfate T. alkalinity	Potassium Calcium	Dissolved organic carbon
it ainainity	Magnesium	

## Figure 10 West-Central Winona County Ground Water Study Unique Well Numbers



				r		
	Total # Sampled 1990	# Sampled with Well Logs 1990	# Sampled for Major Ions 1990	# Sampled for Major Ions 1988-90	<pre># Sampled for Tritium 1988-90</pre>	<pre># Sampled for Pesti- cides 1990</pre>
Prairie du Chien	22	17	18	22	5	1
Jordan	32	31	32	32	17	5
TOTAL	54	48	50	54	22	6

The number of wells analyzed for various parameters are shown in Table 1.

Number of wells sampled for various parameters

Following the first round of sampling, 17 wells were chosen for tritium analysis. The wells were chosen with consideration to proximity to other network wells, nitrate concentrations, redox and dissolved oxygen concentrations. Three wells were sampled for tritium by the University of Minnesota during 1990. Two other wells were sampled for tritium in 1988.

#### Sampling Dates

Table 1

The first round of sampling was during April 1990 (actual sampling dates were April 17, 18, 19, 23, 24). Sampling dates for the second round of sampling were over an eight week period. Seventeen wells analyzed for tritium and general chemistry were sampled on June 26 and 27, 1990. The other wells in the network were sampled on August 21 and 22, 1990. The June and August sampling dates will be referred to as the summer sampling for 1990. The wells sampled during June can be distinguished from the August sampled wells in table 3 (page 21, second column from the left).

#### Sampling Protocol

Prior to sample collection, water ran into a flow through chamber until the water temperature, conductivity, pH, and redox were fairly stable. The dissolved oxygen often did not stabilize completely. It was usually necessary to run the water for a period of five to twenty-five minutes in order to reach stabilization. After stabilization, it was assumed that the water being withdrawn was from the aquifer rather than the casing.

The following equipment was used for measurement of field parameters:

Field Parameter	Equipment	Standardizing/Calibration
Specific Conductance	YSI 3000 TLC meter	Two times daily with 1000 micromohs/cm at 25°C standard
Temperature	YSI 3000 TLC meter	Checked with thermometer
Dissolved oxygen	YSI 5700	Calibrated 4 times daily with air calibration and results were verified with a Winkler kit
рН	Beckman meter, Orion probe	Standardized with 7 and 10 pH buffers at least between every 3 wells
Redox	Beckman meter, Orion platinum probe in silver chloride solution	Standardized in late August – with Zobells solution numbers were adjusted
Total Alkalinity	Hach colormetric $H_2$ SO <sub>4</sub> titration	

Redox potential measurements were taken without standardization. During late August, the probe was checked in a standard solution of (450 mv) and was found to be reading 130 mv too low. The numbers were adjusted by 130 mv. Therefore, while the redox values should give a general approximation of the true redox, the redox numbers in this report should be used with discretion. The April redox measurements should be used to check redox differences between wells. Redox measurements were taken using two standards in April 1991. These results compared reasonably well with the adjusted 1990 values.

Cleaned polyethylene bottles were used for inorganics sampling. Nitric acid was added as a preservative for Calcium and Magnesium. Hydrochloric acid was added as a preservative to the bottle for the nitrate and organic carbon analyses. The Minnesota Department of Agriculture provided cleaned one-liter amber bottles with Teflon-lined caps for pesticide analysis. The University of Minnesota provided glass bottles for tritium analysis. With the exception of the pesticide bottles, all bottles were triple rinsed with sample water before filling. All bottles were placed in a cooler and kept below 4°C with ice.

#### Laboratories

Most analyses for everything except tritium and pesticides were conducted at the Minnesota Department of Health Laboratory. Samples from selected wells and split samples were analyzed at the University of Minnesota Geology Department Laboratory. The six samples for pesticide analysis were conducted at the Minnesota Department of Agriculture laboratory. Tritium analyses were conducted at the University of Ontario at Waterloo laboratory.

#### WATER CHEMISTRY RESULTS

The well information and all results are listed in Tables 2, 3, 4 and 5.

Table 2 - Well location and construction Table 3 - Field measured parameters Table 4 - Major ions Table 5 - Nitrate, tritium, DOC, silica, redox, D.0.

Water quality results are summarized in this section of the report. In the following section, water quality results are discussed in more detail as they relate to the geologic formation, the hydrogeology, geologic sensitivity, and well construction.

#### Nitrate

Nitrate-N was shown from previous studies to be a common contaminant in Central Winona County, exceeding the drinking water standard of 10 mg/l in over one-quarter of all wells sampled (Wall et al. 1990). Major sources of nitrogen release in the project area are from animal waste and commercial fertilizer. Nitrogen from legume crops, septic systems, and municipal wastewater treatment ponds also contribute nitrogen to ground water in the project area.

All nitrate concentrations in this report will be referred to as nitrate-nitrogen (nitrate-N) for which the drinking water standard is 10 mg/l. The primary health concern associated with exposure to nitrate is methemoglobinemia, commonly known as "blue baby syndrome." This condition can occur in infants less than six months of age, causing an oxygen deficiency in the bloodstream. This condition can also occur in livestock at higher concentrations. While adults rarely, if ever, have any toxic effects associated with nitrate, there is a potential for nitrate to contribute to production of N-nitrosamine compounds shown to be carcinogenic in animal tests. Nitrate in well water can indicate a well with susceptibility to other surface contaminants.

Great variability in nitrate concentrations were found between wells throughout the study area (Figure 11). Ten wells (18 percent) sampled in 1990 had nitrate-N concentrations in excess of ten mg/l and four wells had nitrate-N less than 0.01 mg/l. Six of the ten high nitrate wells were constructed prior to 1965 and may, therefore, be improperly sealed. The lower percentage of high nitrate wells compared to previous studies can be explained by 1) a much larger proportion of wells sampled in the current study have been more recently constructed, and 2) many of the wells sampled for this study are located further west, which is closer to the recharge area and less geologically sensitive. A bar graph of the distribution of nitrate concentrations in the Jordan and Prairie du Chien (PDC) is shown in Figure 12. Most of the Jordan wells have nitrate-N concentrations between 1 and 7 mg/l, whereas nearly half of the PDC wells have nitrate-N in excess of 10 mg/l. There are, however, six PDC wells with lower nitrate-N (1-4 mg/l).

Table 2	. Well	location	and	construction	information	for	sampled	wells.
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UNIQUE WELL #	AQUIFER	YEAR CONST	TOWN- Ship	RANGE	SECT	. 1/4 SECT.	DEPTH CASED	TOTAL WELL DEPTH	GROUND SURF. ELEV.	CASING ELEV BOTTOM	WELL ELEV BOT	DEPTH BELOW PDC BASE	END DEPTH Below PDC Base	STATIC WATER DEPTH	FIRST UNIT BELOW TILL
W00333 101459 104972 107733 107734 120028 120028 132996 132996 132996 132996 132996 132996 132996 132996 132996 132996 132996 140977 147031 147031 156957 156980 179203 192548 219251 226553 226555 226555 226555 226555 226555 226555 226555 226556 240797 401618 401641 409456 42109	Jordan Jordan	1963 1975 1977 1977 1977 1977 1977 1977 1977	106N 106N 106N 106N 106N 106N 106N 106N	88 99 108 99 108 99 108 108 108 108 108 108 108 108 108 108	<b>19 25 31 5 26 44 75 31 5 42 725 37 30 45 42 33 86 44 42 86 14 120 133 86 14 120 133 86 14 120 133 14 140 180 19 111 11</b>	NEWYING SOUTHERS IN S	292 343 343 293 337 293 337 286 362 337 286 362 337 286 362 337 286 362 323 325 325 325 326 309 321 358 326 300 302 324 539 302 324 539 302 325 325 302 325 302 325 325 302 325 325 325 325 325 325 325 325 325 32	312 300 388 340 380 340 456 380 320 418 380 320 411 411 411 411 425 411 411 425 411 425 411 425 411 425 411 425 411 425 411 425 411 425 411 425 400 367 601 370 352 400 360 360 360 380 380 380 380 380 380 380 38	1228 1183 1190 1218 1155 1168 1142 1155 1135 1165 1170 1170 1170 1180 1175 1185 1195 1185 1195 1185 1195 1185 11225 1136 1220 1175 1280 1175 1280 1175 1280 1175 1280 1175 1280 1175 1280 1175 1280 1175 1280 1175 1280 1290 1290 1290 1290 1290 1290 1290 129	996 840 847 885 818 8750 818 8750 818 8750 818 8750 818 8770 818 847 8480 851 847 9018 851 741 9008 851 741 9008 851 741 9008 851 840 840 855 855 855 855 840 855 840 847 840 847 840 847 840 847 840 847 847 847 847 847 847 847 847 847 847	916 783 802 875 828 775 828 6775 828 6775 828 6775 828 6775 828 6775 7790 7755 7790 7755 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 6775 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 828 7790 7755 7757 7757 7757 7757 7757 7757	<b>43</b> 24 533 57 41 22 6 313 17 19 63 20 19 19 27 46 30 -15 17 31 420 28 60 54 59 59	100 69 90 80 100 88 154 65 40 83 65 105 98 94 120 121 109 99 131 90 40 60 93 87 60 57 100 100 100	88 1400 260 258 2104 129 40 123 80 125 131 66 2158 268 2242 265 820 245 128 190 166 90 120 662 70	
W00060 W00135 W00285 W00334 W00345 W00385	PDC PDC PDC PDC PDC PDC PDC	<1935 <1950 <1935 <1935 <1935 <1935 <1935	106N 106N 106N 106N 106N 106N	9W 9W 9W 8W 8W 8W	10 10 24 19 7 20	NW SE SW NW SW		200 260 264 325 300 278	1150 1205 1205 1250 1160 1235		950 945 941 925 860 957				Prairie DC Prairie DC Prairie DC Prairie DC Prairie DC Prairie DC
317 393 107692 132668 140993 144674 144674 144674 219103 219103 219266 219246 219246 219246 219246 226529 226537 226540 226540	PDC PDC PDC PDC PDC PDC PDC PDC PDC PDC	<1935 <1935 1976 1977 1977 1977 1977 1977 1977 1973 1943 1974 1974 1974 1973 1974 1975 1964 1963	106N 106N 106N 106N 106N 106N 106N 106N	10W 9W 10W 10W 10W 9W 9W 10W 10W 10W 10W 10W 10W 10W 10W 10W 10	36 12 28 39 30 30 53 20 6 30 20 53 20 5 20 5	NN NEW SOLUTION NO STATE	137 140 323 259 142 261 309 112 36 282 106 239 118 79 334 354	270 167 200 475 330 323 354 128 110 360 203 288 414 401	1210 1205 1180 1330 1200 1320 1320 1160 1240 1130 1240 1130 125 1325 1325 1325	1068 1040 1007 941 1039 1011 1048 958 1024 958 1024 951 1057 1125 991 971	940 1038 980 855 870 971 966 1032 1050 866 850 790 982 917 911 924 1015			85 82 61 181 233 82 88 161 48 70 52 129 263 237 130	Prairie DC St.Peter St.Peter Galena St.Peter Shakopee Plattvle Galena St.Peter St.Peter St.Peter St.Peter St.Peter St.Peter St.Peter Shakopee Galena Plattvle

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\* all depth and elevation units are in feet

UNIQUE WELL #	Summ. Samp. date	field tempera	ture	fld. to alkalin mg/l Ca	otal nity nCO3	fld. pl std. ur	ł nits	redo: rela mV	x tive	conduc umho/ci	tivity m25	disso oxyge mg/l	olved en
		April	Summer	Ăpriľ	Summer	· April	Summer	April	Summer	April	Summer	April	Summer
W00333 101459 104972 107733 107734 120028 120034	**** * *	9.8 9.7 10 9.8 10.3 8.8 10	10.5 10.9 12.3 16.7 13.2 10.4	205 195 190 246 215 155	206 184 256 248 171 229	7.6 7.7 7.4 7.5 7.5 7.4	7.6 7.6 7.4 7.7 7.7	280 229 240 272 278 309 291	163 237 265 320 243 300	472 440 483 512 468 422 452	444 435 456 483 486 412 463	9.5 10.5 7.2 10.2 12.0 7.3	10.5 12.3 6.6 7.2 11.9 7.3
132995 132996 139564 140956 140977 147031 147093	** * *	10 9.3 9.5 8.6 8.3 9.7	11.2 10.4 11.8 11.4 11.7 11.9	255 195 168 220 160 175	198 173 224 160 178 159	7.65 7.65 7.6 7.6 7.3 7.5	7.5 7.8 7.5 7.6 7.6 7.7	68 254 172 200 179	7 227 164 170 194 212	409 416 485 439 445	404 375 445 417 433 399	3.8 3.4 5.2 0.4 11.3 9.2	4.2 6.1 0.5 11.7 8.8 8
150210 156957 156980 179203 192548 219156	** * *	10.9 9.3 9.1 8.6 9.2	10.7 10.5 10.8 10.3 9.4	162 167.5 240 197.5 153	180 213 200 150 241	7.9 7.5 7.3 7.5 7.4	7.7 7.5 7.6 7.6 7.4	270 246 271 180 130	237 242 183 194 237	397 434 546 471 466	423 514 445 437 649	7.3 8.0 5.6 1.8 10.8	8.6 7.9 1.7 9.4 12.6
219245 219251 226524 226533 226535 226548 226555	* *	9.4 7.6 9.6 10.9 10.2 9.6 9.3	10.1 10.9 9.8 16.1 10.4 10.1 11.2	225 225 195 226 235 238 210	228 237 211 213 240 247 212	7.6 7.5 7.5 7.4 7.5 7.3 7.5	7.4 7.5 7.2 7.4 7.5 7.4 7.6	154 266 270 298 11 269 194	150 279 316 245 -25 270 245	488 542 531 515 524 535 500	454 485 548 483 495 526 467	4.0 10.4 10.3 7.1 0.3 11.8 5.8	3.7 8.5 13.2 5.5 0.4 13 2.9
226556 240797 401603 401618 401641	*	9.9 9.4 9.8	13.6 10.1 10.1 11.1	178 165 223	180 206 191 233	7.6 7.4 7.5	7.7 7.4 7.4 7.4	251 281 168	239 282 309 210	345 338 607	408 519 393 570	9.6 9.9 4.5	9.2 8.5 9.4 2.4
409456 421099	*	9.5	11.2	233 160	186	7.75	7.3	250	190	374	368	8.0	10
W00060 W00135 W00285 W00334 W00345 W00385	*** *** ***	10.2 9.4 9.7	12.8 10.1	330 275 235	325 272	7.15 7.4 7.6	7.4 7.2 7.4 7.2 7.1 7.4	280 223 315	273 216	997 703 637	789 704 756 1164 900 850	7.0 7.7 10.3	8.1 6.9
317 393 107692 132668 140993	**	8.6 10.4 9.6 9.8	11.6 9.9 11.2 10	238 235 180 190	246 200 188 235	7.3 7.5 7.4 7.4	7.2 7.4 7.5	266 250 221 250	308 191 253 326	646 668 629 390	723 619 436 511	8.2 8.7 8.9 10.8	9.4 8.8 12.3 7.9
144674 144677 147008 219103 219161	*	9.9 9.6 9.3 11.6 9.8	10.4 9.7 10.6 15.2 10.1	153 265 285	153 317 216 250 294	7.6 7.1 7.75 7.5 7.1	7.7 6.9 7.4 7.5 7.1	193 300 239 319	158 234 314 323 237	443 723 544 534 821	420 1050 485 533 781	9.9 10.5 7.8 8.9 9.4	9.7 8.8 12.8 8.4 10.6
219167 219246 219247 220603 226526	* * **	9.2 9.4 8.9 8.6 7.4	14.1 11.8 10.4 10.8	179 253 200 180 185	190 283 207 203	7.5 7.3 7.4 7.7 7.3	7.6 7.2 7.7 7.4	260 246 189 200 171	23/ 223	506 690 447 485 646	484 672 445 408	12.4 9.8 7.6 0.6 7.0	7.8 10 6.3 6.1
226529 226537 226540 226541	**	9.4 8.7 9.3	10.5 11.9 12.5	265 283 270	230 276 345	7.2 7.1 7.4	7.3 6.9	270 253 268	294 230	620 910 686	618 978	9.2 11.3 13.0	10.2 10.8

Table 3 Field measured parameter results.

Key for summer sampling date

- No star August 8 or 9, 1991
  - \* June 26 or 27, 1991
  - \*\* No summer sampling
  - \*\*\* Number in summer column represents the average of sampling during 1988-1989.

Table 4	4	Concentrations	of	major	ions.

UNIQUE WELL #	QUE nitrate-k L∉ mg/l		chlo mg/	chloride mg/l		sulfate mg/1		magnesium mg/l		i un	sociuma mag/1		Potassiuma mg/1		T. as	alk. ÇaCO3
W00333 101459 104972 107733 107734 120028 120034	April 4.8 2.3 8 1.2 2.7 6.8 2	Summer 4.2 2.8 7.6 1.1 2.3 6.6 1.8	April 0.8 3.4 5.2 2.0	Summer 2.0 2.2 10.0 2.2 5.4 5.2 1.0	April 6.1 7.1 10.0 10.0	Summer 8.0 18.0 15.0 5.4 5.8 9.9 8.8	April : 28.4 27.0 18.7 25.5	Summer 24.5 21.8 19.9 28.8 28.8 18.7 26.4	April 61.3 60.2 52.9 57.2	Summer 53.2 56.0 64.0 60.0 64.0 52.0 56.0	April 2.9 3.2 1.8 2.3	Summer 3.0 1.9 4.3 2.7 3.2 1.7 2.1	April 0.5 0.4 0.6 0.6	Summer 1.3 0.7 0.5 <0.5 <0.5 0.6 0.6	Aprii 260 250 170 240	Summer 219 220 200 280 270 180
132995 132996 139564 140956 140977 147031 147093 150210	0.26 0.01 3.9 0.02 8.3 6.3	0.02 3.9 <.01 7.4 6.4 5.6	3.8 1.2 3.5 0.5 6.8	<.05 4.2 <0.5 6.5 7.2 3.2	34.9 17.0 11.0 15.0 11.0	17.0 11.0 15.0 9.9 14.0 12.0	25.0 19.6 25.3 15.8	20.4 19.7 26.4 16.1 17.3 16.1	65.4 51.5 59.6 58.1	52.0 52.0 60.0 60.0 64.0 56.0	2.7 1.4 1.5 2.9	1.7 1.3 1.4 2.7 3.2 2.2	1 0.9 0.9 0.8	0.5 0.6 0.7 0.8 0.5 0.6	200 240 170	210 190 250 170 200 180
1362957 156980 179203 192548 219156 219254 229251 226533 226535 226555 226555 226555 226555 226555 226555 226555 226555 226555 226555 226555 226555 240797 401603 409456 421099	4.4 4.4 2.5 11 0.01 3.9 6.3 0.01 3.9 6.3 0.01 3.2.5 1 2.7 2.8 2.2 3.2	4.7 6.7 311 10 0.03 5.6 5.501 3.56 3.501 3.6 3.6 3.6 3.4 3.2 9 4.5 2.9 4.5 2.2 3.2	3.2 5.8 2.8 13.0 1.2 9.2 5.0 2.0 6.0 7.0 3.9 1.2 8.7.0 2.8	$\begin{array}{c} \textbf{3.8} \\ \textbf{9.09} \\ \textbf{15.5} \\ \textbf{14.2} \\ \textbf{27.8} \\ \textbf{880} \\ \textbf{15.5} \\ \textbf{14.5} \\ \textbf{55.6} \\ \textbf{14.5} \\ \textbf{55.6} \\ \textbf{19.52} \\ \textbf{40.5} \\ $	15.0 18.0 18.0 10.0 15.0 22.0 16.0 26.0 15.0 15.0 15.0 45.0 45.0 12.0	$\begin{array}{c} 15.0\\ 14.0\\ 18.0\\ 8.8\\ 27\\ 14.0\\ 20.0\\ 27.0\\ 17.0\\ 22.0\\ 17.0\\ 12.0\\ 16.4\\ 52.0\\ 44.0\\ 9.1 \end{array}$	15.8 26.1 22.3 18.2 27.5 29.8 26.7 23.7 16.9 24.2 26.1	15.4 26.4 21.4 16.3 33.6 26.4 31.2 28.8 20.2 19.4 31.2 24.0 17.3 28.8 17.5 26.4 17.5	60.2 66.8 59.3 58.4 58.1 63.9 59.6 8.8 73.9 62.8 63.3 56.2 80.9 59.3 56.2 80.9 59.3	60.0 68.0 52.0 76.0 52.0 64.0 68.0 68.0 68.0 68.0 68.0 68.0 68.0 68	2.85 32.63 1.57968299 1.5.3 1.5.3 1.5.5	2.6 3.2.9 6.1.4 5.5.1 1.2.5 3.1.6 2.0 8.1 1.1 5.5.1 1.1 1.5 5.1.5 5.1.5	0.5 0.5 0.9 1.3 0.9 0.8 0.5 0.8 1.1 0.9 0.7 0.5 0.8 1.5 1.2	0.5 0.6 1.3 <0.5 0.7 0.8 0.8 0.7 0.8 0.7 0.7 <0.5 0.6 1.1 0.9 0.5	170 240 220 160 250 250 250 250 250 250 230 250 250 230 250 250 230 250 250 250 250 250 250 250 250 250 25	190 240 210 170 250 250 250 240 230 260 250 230 230 230 230 250 250 250
W00060 W00135 W00285 W00334 W00345 W00385 137 132668 140993 144674 144677 147008 219103 219167 219246 219247 229246 219247 226526 226529 226557 226541	18 5.9 8.8 19 13 18 4 9.2 10 1.9 2.1 13 8.4 5.9 1.6 0.46 15 1.3 14 7.2	17 4.9 11.7 28 26 17 12 16 4.1 3.4 5 22 3.8 21 23.8 21 2,6 7.2 3.2 0.27 3.2 1.3 24	36.0 21.0 11.0 24.0 7.0 40.0 14.0 24.0 3.2 2.8 30.0 56.0	45.0 16.0 35.0 58.0 43.0 32.0 33.0 21.0 4.5 14.0 81.0 4.5 7.8 35.0 14.0 20.0 7.0 1.8 18.0 13.0 35.0 18.0 13.0 35.0 18.0 19.0 18.0 18.0 19.0	24.0 15.0 11.0 23.0 17.0 22.0 14.0 28.0 14.0 12.0 12.0 12.0 12.0 35.0	73.0 65.0 26.0 51.0 41.0 43.0 24.0 15.0 9.5 10.0 29.0 12.0 17.0 20.0 11.0 31.0 11.0 32.0 60.0	30.6 23.2 18.9 37.8 17.2 35.3 24.5 19.3 23.5 22.2 25.9 24.8	60.0 40.8 39.1 60.0 53.3 45.8 36.0 23.0 14.5 16.1 50.4 13.6 24.0 20.4 24.0 26.4 28.8 22.8 33.6	83.4 78.3 53.9 80.1 88.4 97.3 58.0 102.5 54.9 56.8 80.6 127.6	120.0 88.0 93.6 137.6 110.8 104.4 82.8 76.0 66.6 44.0 108.0 64.0 108.0 60.0 92.0 60.0 60.0 92.0 140.0	16.9 7.4 3.4 6.8 3.0 15.7 3.4 8.8 1.5 6.6 22.1	9.9 4.6 7.0 21.0 19.0 9.4 9.0 7.5 2.2 3.4 27.0 2.0 2.4 27.0 2.8 14.0 3.3 7.2 2.1 1.4 8.3 9 22.0	17.7 3.6 0.8 4.2 1.0 5.0 1.2 1.8 1.1 0.9 5.0 4.0	$\begin{array}{c} 1.6 \\ < 0.5 \\ 0.6 \\ 1.0 \\ 3.0 \\ 1.5 \\ 1.1 \\ 3.5 \\ 0.7 \\ 0.8 \\ 0.7 \\ 0.8 \\ 0.7 \\ 0.8 \\ 1.0 \\ 1.8 \\ 1.0 \\ 1.8 \\ 0.8 \\ 0.9 \\ 5.6 \end{array}$	270 210 290 260 310 190 270 230 220 230 220 230	350 280 290 358 313 252 210 170 330 240 270 300 200 290 230 230 230 230 230

Table 5 Redox, D.O. tritium, nitrate, Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC) and silica concentrations.

UNIQUE WELL #	red AQUIFER mV		ox	D. 0x mg/1	ygen	Trit (TU	ium )	Nitrate-N mg/l		TOC mg/l		DOC mg/1		silica mg/l	
		Apr.	Summ.	Apr.	Summ.	Conc.	range	Apr.	Summ.	Apr.	Summi	.Apr.	Summ.	Apr.	Summ.
W00333 101459 104972 107733 107734 120028 120034 132995 132995 132996 139564 140956 140977 147031	JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN	286 229 240 272 278 309 291 68 254 172 200 179	163 237 265 320 243 300 7 227 164 170 194 212	11.2 9.5 10.5 10.2 12.0 7.3 5.8 3.4 5.2 0.4 11.3 9.2	10.5 12.3 6.6 7.2 11.9 7.3 4.2 6.1 0.5 11.7 8.8	40.0 <0.8 22.0 2.7 0.8 21.0 <0.8 28.0	+/-8.0 +/- 0.6 +/- 8.0 +/-0.8 +/- +/-8 +/- +/-8.0	4.8 2.3 8 5 1.2 2.7 6.8 0.26 0.01 3.9 0.02 8.3 6.3	2.8 7.6 1.1 2.3 6.6 1.8 0.02 3.9 <.01 7.4 6.4 5.6	8.0 14.0 7.7 11.0 1.0 3.1 8.7 7.5	0.0	5.5 6.8 1.0	13.0 8.3 3.7 8.7 7.7 10.0 10.0 8.7 14.0 8.3 6.5 8.7	8.7 8.5 5.2 5.3 5.2 5.1 5.5	11 7.2 13 0
150210 156957 156980 179203 192548	JORDAN JORDAN JORDAN JORDAN JORDAN	270 246 271 180	237 242 183 194	7.3 8.0 5.6 1.8 10.8	8.6 7.9 1.7 9.4	11.7 23.0	+/-1.0 +/- 8.0	4.8 4.4 2.5 11	4.7 6.7 3 11	2.9 2.9 3.8 7.1		2.4	7.2 10.0 6.0 2.5	5.8 8.0 5.5 6.0	18
219156 219245 219251 226524 226533 226535 226555 226555 240797 401603 401618 409456 421099	JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN JORDAN	154 266 270 298 11 269 194 251 281 168 193 250	237 150 279 316 245 -25 270 245 239 239 239 210 190 196	4.0 10.4 10.3 7.1 0.3 11.8 5.8 9.6 9.9 4.5 3.0 8.0	3.7 8.5 13.2 5.4 13 9.4 2.9 9.4 2.7 10	<0.8 27.0 0.8 15.0 10.4 1.8 0.9	+/-0.5 +/- 1.9 +/-0.5 +/-8.0 +/-8.0 +/-1.0 +/-0.6 +/-0.7	0.01 3.9 6.3 4.3 0.01 3.6 2.5 4.1 2.7 5.2 2.8 3.2	0.03 3.5 5.6 3.5 <.01 3.6 3.1 4.2 2.4 2.5 2.4 2.5 3.2	12.0 7.3 7.5 17.0 11.0 7.5 1.1 2.8 2.5 13.0 7.6 40.0		1.0 2.9	10.0 14.0 13.0 6.7 14.0 8.9 2.1 4.6 14 10.0 3.8 9.1 6.4	5.5 8.4 5.0 7.0 6.9 4.8 4.8	0
W00060 W00135 W00285 W00334 W00345	PDC PDC PDC PDC PDC PDC	280 223 315	273 216	7.0 7.7 10.3	8.1 6.9			18 5.9 8.8	17 4.9	1.0 1.6		1.0 1.0	19.0 15.0		
317 393 107692 132668 140993	PDC PDC PDC PDC PDC PDC	266 250 221 250	308 191 253 326	8.2 8.7 8.9 10.8	9.4 8.8 12.3 7.9	30.0	+/-	19 13 18 4	12 16 4.1 3.4	5.5 1.8		1.8	13.0	6.0 7.0	6.8
144674 144677 147008 219103 219161 219167 219246 219247 220603	PDC PDC PDC PDC PDC PDC PDC PDC PDC	193 300 239 319 260 246 189 200	158 234 314 323 237 237 223	9.9 10.5 7.8 8.9 9.4 12.4 9.8 7.6 0.6	9.7 8.8 12.8 8.4 10.6 7.8 10 6.3 6.1	33.0 40.0 8.2 1.6	+/-8.0 +/-8.0 +/- 0.8 +/-0.6	9.2 10 1.9 2.1 13 8.4 5.9 3 1.6 0.46	8.5 22 3.8 2 12 7.6 7.2 3.2 0.27	5.7 6.1 9.8 193.0 2.6 12.0 5.7	9.0	0.0	17.0 13.0 7.2 8.8 13.0 6.1 13.0	5.0 6.6 9.1 5.8 6.0 4.9 5.0	
226526 226529 226537 226540 226541	PDC PDC PDC PDC PDC	171 270 253 268	315 294 230	7.0 9.2 11.3 13.0	9.5 10.2 10.8			15 1.3 14 7.2	3.2 1.3 24	8.9 15.0			25.0	0.8 10.7	

# Figure 11

West-Central Winona County Ground Water Study Average Nitrate-N Concentrations (mg/l)




The difference in nitrate concentrations between the April and summer sampling events was less than 10 percent in just over half of the wells and was less than 20 percent in over three-fourths of all wells. Six wells had nitrate concentrations that varied by more than 20 percent between the two sampling events. Overall, there was no change in any one direction, with 15 wells having nitrate increases, 18 wells having nitrate decreases and eight wells with no change. One trend that was observed was that most of the Jordan wells in the northwestern corner of the study area that had nitrate over 1 mg/l showed an increase in nitrate from spring to summer.

The relationship of nitrate concentration to other parameter concentrations is shown in Figures 13 to 22. A direct relationship is observed between nitrate and chloride, sodium, calcium, and magnesium. An inverse relationship between nitrate and pH is also observed. Note, however, that while some relationships are observed in figures 13 to 22 by combining PDC and Jordan wells, there is no relationship when looking strictly at Jordan wells.

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#### Tritium (Residence Time)

Water from 20 wells in the study area was analyzed for tritium in 1990. Two other wells were sampled in 1988. Tritium is a radioactive isotope with a half life of 12.43 years which is produced naturally in the atmosphere at very low levels. The atmospheric concentration of tritium increased considerably during the mid to late 1950s due to nuclear weapons testing. Precipitation falling since 1954 has tritium levels reflective of the high atmospheric tritium. Therefore, tritium can be used as an indicator of water entering the soil since the mid 1950's. It is very difficult to determine the age of ground water based on tritium alone, other than knowing whether the water entered the ground prior to 1954, after 1954, or is a mixture of older and more recent ground water.

Since ground water systems are a mixture of water from different areas and times, tritium concentrations can, and often do, reflect a mixture of pre- and post-1954 precipitation. According to a system stated by Alexander and Alexander (1989), a water sample containing more than about 10 tritium units (TU) is water that mostly entered the ground since 1954. If the water sample contains less than about 1 TU, that water entered the ground prior to 1954. Water samples with tritium concentrations between one and ten TUs are either mixtures of recent and old waters or are of intermediate age.

Samples for tritium analyses were collected in 1,000 ml polyethylene bottles and shipped to the Environmental Isotope Laboratory of the University of Waterloo, Ontario, Canada. Tritium is reported in TUs (TUs = Tritium units = 1 atom of H per 10<sup>18</sup> atoms of H = about 3pCi/L). Two types of tritium analyses were conducted. Fourteen of the 22 wells were analyzed using the enriched tritium analysis, which has a detection limit of 0.8 TU. Eight additional wells were analyzed using another method which is much less accurate, providing a confidence interval of plus or minus 8 TUs. The wells chosen for the non-enriched tritium analysis were from wells suspected of having more recent water. The locations and tritium concentrations in the 22 wells analyzed for tritium are shown in Figure 23.

Sixteen Jordan well samples were analyzed for tritium in the study area. Results from the analyses are listed in Table 5 (page 23). The results show six Jordan wells with water predating 1954, four Jordan wells with a mix of older (pre-1954) and more recent waters, and seven Jordan wells that have mostly recent water (post-1954). One well had 15  $\pm$  8 TUs, which could be mixed or mostly recent.

# Figure 23

## West-Central Winona County Ground Water Study Tritium (TU)



Of the five Prairie du Chien well samples analyzed for tritium, three have recent water and two have mixed water. Three of the PDC wells were chosen for analysis based on their relatively low nitrate concentrations. Well #220603 had nitrate concentrations of 0.46 and 0.27 mg/l on the two sampling dates and a tritium concentration of 1.6 +/- 0.6, which is likely to be mostly pre-1954 water, perhaps mixed with some recent water.

Table 6 lists mean parameter concentrations for the pre-1954, post 1954 and mixed water. Mean nitrate, chloride, redox and dissolved oxygen were much higher in the more recently recharged water. Lower sodium concentrations were observed in older water. Mean sulfate, magnesium, calcium, potassium, bicarbonate and pH were very similar in the older vs. more recent water.

Table 12 Mean parameter concentrations of older, mixed, and recently recharged ground water for all wells sampled for tritium.

	# <u>Wells</u>	NO3-N Mg71 Mean	NO3-N mg/l Median	<u>C1</u> mg/ Mean	SO4 mg/l Mean	<u>Mg</u> mg/l Mean	Ca mg/l Mean	<u>Na</u> mg/l Mean	K mg/l Mean	HCO3 as <u>CaCo3</u> mg/1 <u>Mean</u>	Redox MV Mean	DO mg/l Mean	<u>pH</u> <u>Mean</u>
Older Water < 1 TU	6	0.9	<0.01	1.3	14.5	23.3	58.3	1.8	0.7	231	140	4.1	7.51
Mixed Water 1–11.7 Tl	J6	2.0	2.6	5.4	28.3	24.4	66.6	3.2	1.0	232	191	4.0	7.52
Recent Water > 20 TUs	9	6.5	6.4 1	0.8	14.2	22.3	55.9	3.8	0.8	216	240	9.1	7.54

Alexander and Alexander (1989) reported that in 31 samples throughout Minnesota containing less than 0.8 TU, the highest nitrate-N concentration was 0.11 mg/l. Most of the other 30 pre-1954 water samples had less than 0.02 mg/l nitrate-N. This suggests that either very little nitrate was entering ground water before the mid-1950's or that nitrate entering ground water before 1954 has since been lost through denitrification. Four of the five samples collected in this study containing < 0.8 TU had less than 0.01 mg/l nitrate. The fifth well (107733) had nitrate concentrations of 1.2 and 1.1 mg/l. This well consistently had between 0.65 and 1.1 mg/l in nine samples taken between 1978 and 1987. Another well (421099) sampled in this study area had 0.9 +/- 0.7 TUs and had 3.2 mg/l nitrate-N in both samples taken during 1990. This well had between 2.8 and 3.7 mg/l nitrate-N in six samples taken during 1988 and 1989.

Wells 107733 and 421099 had higher redox and dissolved oxygen and lower dissolved organic carbon than the four wells with nondetectable tritium. These three conditions suggest that there is less potential for denitrification in these two wells compared to the four wells with < 0.02 mg/l nitrate-N. Dissolved organic carbon, redox, and dissolved oxygen were measured again during  $292^{\circ} = 500^{\circ}$  ing. These results will be incorporated into future reports.

#### Other Parameters

#### Chloride

Chloride is a very soluble and highly mobile anion that is found naturally in ground water, but may also originate from human and animal waste, fertilizers (potassium chloride), salts, and industrial waste. The secondary drinking water standard for chloride is 250 mg/l. The maximum chloride concentration in study wells was 58 mg/l.

#### Table 7

#### Chloride (mg/l)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC	12	22.5	22.4	16.2	20	20.5	25.6	19.9	
Jordan	25	3.9	4.4	3.0	31	5.2	6.0	5.4	

The "natural" chloride concentration in the Prairie du Chien-Jordan formations is less than 10 mg/l and may be as low as 1-3 mg/l based on the large number of low chloride wells (see Figure 13 and Table 7). The Prairie du Chien wells generally had much higher chloride than Jordan wells. However, there were four PDC wells that had less than 10 mg/l Cl. A direct relationship was observed between nitrate and chloride (Figure 13). This is not surprising since nitrate originates from many of the same sources as chloride (fertilizers, human,



animal, and industrial waste). A direct relationship was also observed between sodium and chloride (Figure 24). This would suggest that the chloride is not only originating from sources such as fertilizers, human, animal, and industrial waste, but is also likely originating from road salt and water softener salt (via septic tanks).

#### Sodium

Sodium can be a principle cation in certain waters of western Minnesota, but was found at relatively low concentrations (< 25 mg/1) in the Prairie du Chien-Jordan water in Winona County. Sodium in ground water can result from dissolution of the minerals plagioclase feldspar, halite, nahcolite, nepheline and montmorillonite clays. Sodium can also originate from water softener salts, road salts, and industrial waste.

#### Table 8

#### Sodium (mg/l)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC	12	6.7	8.1	6.7	20	7.4	8.9	7.5	
Jordan	23	2.9	3.1	1.4	31	2.8	3.0	1.4	

Sodium, while low in water from both formations, is significantly higher in PDC wells. Background (natural) sodium concentrations are less than 5 mg/l. All wells with no tritium had sodium concentrations less than 3 mg/l. The direct relationship of sodium with both nitrate (Figure 17) and chloride (Figure 24) could suggest that either septic tank effluent is impacting ground water, the introduction of nitrate and chloride to ground water allows for greater dissolution of sodium containing minerals, or a combination of nonpoint sources and chemical processes.

#### Bicarbonate Alkalinity

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Bicarbonate is the principle anion in most of Minnesota's waters, including the PDC-Jordan aquifer. Bicarbonate will determine the capacity of a water to neutralize acid. In the upper portions of the soil zone, bacteria consume oxygen and organic carbon and produce carbon dioxide. This respiration will increase the partial pressure of carbon dioxide from an atmospheric level of 0.03 percent to a soil zone level greater than 1.0 percent. This carbon dioxide combines with water to form carbonic acid  $(H_2CO_3)$ . A percentage of this carbonic acid will dissociate into hydrogen ion (H+) and bicarbonate ion (HCO3-). The increases in dissolved hydrogen will slightly increase the acidity of the water, i.e., lower its pH.

Table 9

Laboratory Bicarbonate Alkalinity (mg/l as CaCO3)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC	12	245	244	46	19	290	279	61	
Jordan	23	240	220	32	31	230	222	36	

#### Table 10

Field Bicarbonate Alkalinity (mg/l as CaCO<sub>2</sub>)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC	18	237	233	49	18	240	246	53	
Jordan	29	205	200	31	30	211	206	30	

Field measured bicarbonate concentrations were usually lower than laboratory measured concentrations. Cation/Anion balance calculations indicated that the field measured bicarbonate concentrations were probably a little low. Bicarbonate was slightly lower in Jordan wells compared to PDC wells. An inverse relationship of alkalinity vs. nitrate was observed for Jordan wells, but not for PDC wells (Figure 15). An inverse relationship between pH and alkalinity was noticed (Figure 25). Bicarbonate was directly related to calcium and magnesium concentrations (Figures 26 and 27).

#### Calcium and Magnesium

Calcium is the most abundant cation in most of Minnesota's waters. While its sources are mostly natural (calcite, dolomite, and to a lesser extent, gypsum, plagioclase feldspar, aragonite, and other minerals), human activities that change the chemistry of the water can result in a greater dissolution of calcium bearing minerals. Calcium, along with magnesium concentrations, affect water hardness. Jordan waters contain lower calcium concentrations in general compared to PDC water. No relationship is observed between nitrate and calcium in Jordan wells; yet a rough direct relationship exists in PDC wells (Figure 18).

Table 1	.2
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Calcium (mg/l)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC Jordan	12 23	80.4 60.2	80.1 62.3	22.3 7.1	20 31	90 60.0	87.8 61.5	26.9 8.1	











Ta	bl	e 1	.3
			_

Magnesium (mg/l)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC	12	24.0	25.3	6.4	20	31.2	32.7	14.9	
Jordan	23	24.6	23.0	10.1	31	24.0	23.0	5.3	

Magnesium originates mostly from dissolution of the Magnesium bearing minerals, such as dolomite, olivine, pyroxene, amphibole, mica and limestone. Human activities that change the chemical make-up of water (increased Cl,  $NO_3$ ,  $HCO_3$  or changes in pH) can result in more dissolution of Magnesium.

The Magnesium to nitrate relationship is similar to the calcium to nitrate relationship -- there is no relationship in Jordan wells and PDC wells have a rough direct relationship (Figure 19). Carbonate minerals, particularly calcite (CaCO3) and dolomite (CaMgCO<sub>3</sub>)<sub>2</sub>) are abundant in many of the glacial deposits and in the bedrock Prairie du Chien Group. Carbon dioxide, in the form of carbonic acid, increases the water's ability to dissolve these carbonate minerals. A dissolution reaction for calcite (calcium carbonate) can be written as follows:

$$CaCO_3 + H_2O + CO2 = 2 HCO_3 - + Ca$$

This reaction puts calcium (Ca) and bicarbonate (HCO3-) into solution. In a situation where there is only a small finite amount of dissolved carbon dioxide, this reaction may consume the available carbon dioxide before much calcium carbonate can be dissolved. In this case, the system is closed to any additional carbon dioxide and the amount of carbon mineral dissolution is dependent on the original amount of carbon dioxide in the system.

In other instances, the system is open to a sufficiently large reservoir of carbon dioxide and the calcite dissolution reaction does not significantly deplete the concentration of carbon dioxide. In this situation, the water is able to dissolve a greater amount of calcite. Here, the amount of calcium and bicarbonate in the water is determined by the solubility of calcite. Once a certain amount of calcite has been dissolved, the water is not able to keep any additional calcium and bicarbonate in solution. This water is then said to be saturated with respect to calcite. Waters which contain lesser amounts of calcium and bicarbonate are undersaturated with respect to calcite. Waters which contain greater concentrations of calcium and bicarbonate are supersaturated with respect to calcite. These waters will, with time, lower their dissolved concentrations by crystallizing out solid calcite.

The water chemistries of the well samples suggest the presence of a calcite dissolution trend. Calcium concentration increases moderately with alkalinity (Figure 26). However, there is not exactly a one calcium to two bicarbonate ratio, which the above reaction would generate. This is a result of the dissolution of other minerals, particularly dolomite, into the ground water. Dolomite (CaMg(CO3)2) is chemically similar to calcite (CaCO3), except that half of the calcium in calcite is replaced with magnesium in dolomite. Dolomite will liberate calcium, magnesium and bicarbonate into solution in a one-to-one-to-four ratio, respectively. Magnesium concentration also moderately increases with field alkalinity (Figure 27). A direct relationship was observed between calcium and magnesium (Figure 29). Many dissolved ions have more than one potential mineral source. Geochemical models contain information on the concentration of ions in waters saturated with respect to a large number of minerals. One such model was utilized in this study. The results indicate that, within a small degree of uncertainty, all of the waters sampled were saturated with respect to or in equilibrium with calcite (calcium carbonate). While several of the wells were in equilibrium with respect to dolomite (calcium-magnesium carbonate), most wells were slightly to moderately undersaturated with dolomite. This can be attributed to the fact that dolomite dissolution is considerably more sluggish than calcite dissolution.

#### Sulfate

Sources of the relatively mobile ion sulfate can include industrial wastes, acid mine drainage, combustion of coal, smelting of sulfide ores, certain fertilizers, and natural dissolution of the minerals gypsum, pyrite, and anhydrite.

#### Table 11

#### Sulfate (mg/l)

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	<u>No</u> .	Median	Mean	St. Dev.	
PDC	12	17.0	19.3	7.2	20	25.0	28.8	19.6	
Jordan	25	15.0	17.5	10.4	31	15.0	16.2	10.1	

Sulfate concentrations in all wells were below the 250 mg/l secondary drinking water standard, with a maximum concentration of about 73 mg/l. The lack of a relationship between nitrate and sulfate (Figure 14), direct relationship between calcium and sulfate (Figure 28) and similarity of sulfate levels in the PDC and Jordan wells, all indicate that the sulfate is likely originating from natural resources (probably dissolution of the mineral gypsum). Four outlier wells are noticed in Figure 28 which have a higher sulfate concentration in proportion to calcium. An additional source of sulfate (#401678 and #409456) are located very close together and the two PDC wells with higher sulfate (W00135 and W00060) are also located close together. Therefore, there appears to be two areas of possible anthropogenic sulfate.

#### Potassium

Potassium is of little concern in ground water in Southeast Minnesota and is a very minor component of ground water in study wells. Common sources are from potassium bearing minerals such as potassium feldspar and mica and from fertilizers.

Potassium (mg/l)

	April					Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.		
PDC	12	2.7	3.9	4.7	18	1.4	1.6	1.4		
Jordan	23	0.8	0.8	0.3	31	0.7	0.7	0.2		

Potassium concentrations were less than 5 mg/l in all wells and were less than 1.4 mg/l in all Jordan wells (see Figure 16). The five wells standing out as having higher potassium are PDC wells with nitrate-N in excess of 10 mg/l. Potassium in these wells are likely from potassium fertilizer.

pН

The pH of a water is a measure of its acidity or basicity. Drinking water should have a pH greater than 6.5 and less than 8.5 (secondary drinking water standard). All water from wells in the study area had pH between 7.0 and 7.9 and most wells fell in the range of 7.2 to 7.7.

#### Table 15

pН

		Ap	ril		Summer				
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.	
PDC	20	7.4	7.39	0.2	22	7.4	7.34	0.22	
Jordan	30	7.5	7.52	0.14	31	7.5	7.52	0.14	

The lowest pH in a Jordan well was 7.3. All low pH wells (< 7.3) withdrew water from the PDC formation. An inverse relationship was observed between pH and nitrate and pH and alkalinity (Figures 20 and 25).

#### Dissolved Oxygen

The amount of dissolved oxygen in ground water can affect iron and nitrate concentrations in addition to other chemical parameters. Waters in more direct contact with air or more recently recharged will usually have higher dissolved oxygen (D.0.).

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Dissolved Oxygen (mg/l)

	April				Summer			
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.
PDC	20	9.1	8.9	2.6	18	9.1	9.1	1.8
Jordan	30	8.0	7.4	3.4	30	8.5	7.5	3.8

Most of the wells in the study area have well oxygenated water. The lower  $\mathbb{D}.0$ . waters are mostly waters that recharged before the mid 1950's (see section on tritium). All wells with nitrate-N greater than 5 mg/l also had D.O. greater than 6.5 (Figure 21).

#### Redox Potential

The redox potential is a numerical index of the intensity of oxidizing or reducing conditions within the aquifer. Positive potentials indicate a system that is relatively oxidizing. Redox potential is an important variable affecting the amount of dissolved iron and potential for denitrification within an aquifer.

#### Table 17

Redox Potential (MV)

	April				Summer			
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.
PDC	19	250	248	41	16	245	258	51
Jordan	29	250	223	, 70	30	237	217	77

#### Organic Carbon

Organic carbon is found naturally in waters from humic, fulvic, and hydrophilic acids, clay-humic-metal complexes, and bacteria. Organic carbon may also originate from hydrocarbons, pesticides, and other man-induced organics. Organic matter moving directly into ground water through sinkholes or fractures could be another source in southeastern Minnesota. The primary reason for analyzing water for organic carbon in this study was to determine the potential for denitrification, which is discussed in the following section of this report. Total organic carbon (unfiltered) was analyzed in the April samples and dissolved organic carbon (filtered) was analyzed for in the summer samples. Samples were field filtered using a 0.45 silver membrane filter for DOC analysis.

#### Table 18

	TOC mg/l (April)				DOC mg/l (Summer)			
	No.	Median	Mean	St. Dev.	No.	Median	Mean	St. Dev.
PDC	13	5.7	6.3	4.4	12	13.0	13.6	5.4
Jordan	24	7.5	8.6	7.9	28	8.7	8.4	3.3

Note the increase in organic carbon during the summer in the PDC wells. This could perhaps be due to recharge through sinkholes and fractures carrying organic matter into ground water.

#### Pesticides

Pesticides were not sampled for in many wells due to budgetary constraints and because pesticide information from 22 wells in the sampling area had been previously collected. The base neutral pesticide analysis, which includes 19 pesticides, was performed on water from six wells. The wells were chosen primarily to supplement pesticide-residence time relationships being measured in Jordan wells in other counties. The pesticide, nitrate and tritium results for the six wells are listed in Table 19.

<u>Unique Well #</u>	Pesticides Detected	<u>Nitrate-N Conc</u>	<u>Tritium (TU)</u>		
139564	None	3.9 mg/l	21 (recent)		
179203	None	2.7	11.7 (mixed)		
147031	None	6.4	28 (recent)		
107734	None	2.5	22 (recent)		
107733	None	1.2	< .8 (old)		
219247	1.7 ppb atrazine	2.4	8.2 (mixed)		

Table 19 Base neutral pesticide analysis results, shown along with nitrate-N and tritium.

\* The reporting limit for atrazine at the MDA laboratory was 0.05 ppb.

None of the five Jordan wells had any pesticides detected. The one PDC well (#219247) had 1.7 ppb atrazine. This well is located on a farm, where the farmer reportedly has not used atrazine in several years. Three Jordan wells with recent water (tritium greater than 20 TU) all had no pesticides detected.

#### DISCUSSION

#### Potential for Denitrification

With the exception of plant uptake of nitrogen from areas of high water table, the only known nitrogen loss mechanism from ground water is through denitrification. Denitrification, which is the reduction of nitrate or nitrite to gaseous nitrogen products by anaerobic bacteria, has been studied primarily in soils and waste treatment systems. Relatively few studies have examined denitrification occurring within aquifers and more research is needed to determine potential rates and controls on denitrification in hydrogeologic settings in Minnesota.

Conditions required for denitrification include a sufficiently warm water temperature (greater than 5 - 10°C), an anaerobic environment (indicated by a low dissolved oxygen and low redox potential), denitrifying bacteria, and an organic carbon source to serve as food for the bacteria. Denitrification will result in the release of methane gas and an increase in bicarbonate and calcium in the water (Eyboka, 1984; Trudell, et al. 1986). In a very reducing environment (redox potential < -200 mV at pH 7), nitrate can potentially reduce to ammonium (Howard, 1985).

Chemically the denitrification reaction can be expressed in the form:

$$5 \text{ CH}_20 + 4 \text{ NO}_3^- = 2 \text{ N}_2(g) + 5 \text{ HCO}_3^- + 2 \text{ H}_20$$

where  $CH_2O$  represents organic material.

Previous studies have shown through a variety of research techniques that denitrification can be responsible for substantial nitrogen removal in bedrock and sand and gravel aquifers in Canada, Germany, France, England, Iowa, Massachusetts and Delaware (Gillham and Cherry, 1978; Eyboka, 1984; Trudell, et al., 1986; Smith and Duff, 1988; Bottcher, 1990; Wilson et al., 1990; and Mariotti et al., 1988). However, not all aquifers studied showed evidence of denitrification (Fujikawa and Hendry, 1990; Howard, 1985). From the studies conducted, denitrification appeared to be limited mostly by an organic carbon source within the aquifer. From the literature, it appears that a dissolved organic carbon (DOC) concentration greater than about 10 mg/l and a redox less than about 200 mv are conditions where denitrification is most likely to occur.

Water from western Winona County wells were considered to have a high, medium, or low potential for denitrification based on the following criteria:

Denitrification Potential	Redox	Dissolved Oxygen	DOC
High	< 200 mv	< 4 mg/l	> 10 mg/l
Medium	< 300 mv	< 8 mg/l	5-10 mg/l
Low	(all	other wells)	_

Most of the Jordan wells and about one-half of the Prairie du Chien wells were analyzed for DOC. The potential for denitrification from all wells where DOC was analyzed is listed in Table 19. Table 19 Potential for Denitrification in Western Winona County Wells.

	# Wells High	<pre># Wells Medium</pre>	<pre># Wells Low</pre>	
Jordan	4	5	20	
PDC	1	3	7_	
Average NO <sub>2</sub> -N	0.08	5.5	6.5	

From the results, it appears that there are areas within the PDC-Jordan aquifer where denitrification is likely. The average nitrate-N concentration of the five high denitrification wells was 0.08 mg/l. These same wells also had a low tritium concentration (older water).

#### Water Quality Differences Between the Prairie du Chien and Jordan

As is discussed later in this report, there are a number of layers within the Prairie du Chien and Jordan Formations that can greatly influence the chemistry of water within these formations. Also, what one well driller may call the base of the Prairie du Chien, another well driller will call the top of the Jordan. Despite these complications, some general differences between water in a the PDC and Jordan were observed.

It is evident from Figures 13 to 22 that the range in concentrations for most parameters is much greater in the sampled PDC wells compared to Jordan wells. However, some of the PDC wells had water chemistries typical of Jordan water, and a few Jordan wells had water falling outside of the fairly tight cluster of Jordan points in the plots shown in figures 13 to 22. Data from one Jordan well plotted as an outlier in many of the plots. This well is one of two Jordan municipal wells in the city of Lewiston. Based on the water chemistry in this well, it is likely that water withdrawn from this well, which was constructed in 1945, is PDC water. High capacity pumpage, perhaps combined with a poor seal or lack of grout, could explain this condition. The other Lewiston Jordan well, constructed in 1951, has water chemistry more typical of other Jordan water in the area.

For most parameters, PDC water concentrations are generally higher than Jordan water concentrations. This difference is particularly evident with chloride, sodium, calcium, and bicarbonate. pH is the only measured parameter with generally lower values for PDC wells compared to Jordan wells. The mean and median concentrations of various measured parameters are listed in tables 7 to 18. Median dissolved oxygen concentrations are only slightly higher in PDC wells (9.1 and 8.3). However, while only one PDC well has dissolved oxygen less than 6 mg/l, eight Jordan wells have dissolved oxygen below 6 mg/l. Median potassium is similar in PDC and Jordan wells, with the exception of six PDC wells that stand out as having higher potassium.

While many wells in both formations have nitrate-N in the range of 1 to 7 mg/l, nitrate concentrations are generally higher in PDC wells than Jordan wells. Only two Jordan wells had nitrate in excess of 10 mg/l. One of the two was the Lewiston municipal well suspected of having a poor seal. The other Jordan well, domestic well #192548, had 11 mg/l. It was reported by the well owner of well #192548 that during well construction, it was difficult to pour in enough grout to seal the well. "Cement truck after cement truck" was brought in to seal the well. It is possible that a complete seal never was obtained. It is also possible that the Jordan aquifer near this well is more contaminated with nitrate, since a Jordan well across the street had a somewhat high nitrate concentration, averaging 6.5 mg/l. While several PDC wells had nitrate in excess of 10 mg/l, many of these wells are old with no associated well log to be found.

#### Well Age and Depth

#### Age of Well

Prior to 1974, there were no state requirements when drilling and constructing a well. As a result, some wells were 1) constructed near pollution sources, such as septic tanks and feedlots, 2) improperly grouted and sealed, allowing surface contaminants to readily move into the aquifer and move through natural confining layers down into deeper aquifers, 3) constructed in low lying areas at or below grade where surface water could runoff and directly enter the well, and 4) left improperly sealed. As a result of these practices, there is/was a greater potential for nitrate, bacteria, and other contaminants to move into aquifers and to greater depths within the aquifers.

During 1974, the Minnesota Department of Health enacted a Water Well Construction Code (chapter 4725) that required: licensing of well drillers, permits for new well construction, isolation distances, sealing of abandoned wells, specific standards for casing, grouting, sealing, completing, and capping wells, and water samples analyzed for nitrate and bacteria be taken from newly constructed wells.

Newly constructed wells must be located on a site which has good surface drainage, at a higher elevation than, and at a sufficient distance from cesspools, buried sewers, septic tanks, privies, barnyards and feedlots or other possible sources of contamination.

This study was not designed in order to make a statistical comparison of how the age of a well affects nitrate concentrations. However, it was obvious when looking at the data that the older Prairie du Chien wells had higher nitrate than newer Prairie du Chien wells. A comparison of the mean and median nitrate concentrations for various age wells are shown in Table 21.

From Table 21 there is very little difference in median nitrate concentrations between wells constructed from 1960 to 1974 and those constructed since 1974. Most of the pre-1960 Prairie du Chien wells in Table 21 were reportedly constructed before 1935. These wells had a higher mean and median nitrate concentration than more recently constructed wells. The two Jordan wells constructed before 1960 are the two Lewiston municipal wells sampled. Table 21

Prairie du Chien				Jordan			
	<u> </u>	Mean	Median	<u># Wells</u>	Mean	Median	
Date Construct	ed						
< 1960	8	18.0	17.0	2	8.1	8.1	
1960-74	10	7.1	5.0	9	3.2	3.5	
> 1974	6	12.3	6.3	22	4.0	3.1	

#### Well Depth and Cased Depth

The total well depth was not found to correlate with nitrate concentrations in Jordan wells (Figure 30). Often, the depth to which the well is cased is more important than the total well depth in affecting well water quality.

The shallower cased (generally older) PDC wells have a higher mean and median nitrate concentration than the PDC wells cased to at least 200 feet (Table 22). Jordan wells cased greater than 350 feet had generally lower nitrate concentrations than wells cased less than 350 feet (Table 22). However, from Figure 31, it can be seen that there is not a very close relationship (wide scatter) between depth of casing and nitrate-N concentrations.

Table 22 Mean and Median Nitrate-N concentrations for various categories of well casing depth.

	Prairie du Chien				
ased Depth (ft.) 200 (36-176) 200 (239-354) well log (older wells)	Number	Mean	Median		
< 200 (36-176)	9	9.5	8.0		
> 200 (239-354)	8	5.6	3.1		
No well log (older wells)	8	16.7	17.2		
	J	ordan Wel	ls		

13	3.9	3.9
9	4.5	4.6
9	2.8	1.5
	13 9 9	13 3.9 9 4.5 9 2.8





The depth cased did not appear to be a function of the year constructed. Based on well driller logs, a plot of nitrate concentration vs. depth cased below the PDC-Jordan contact was made (Figure 32). The depth to which the casing in Jordan wells penetrates below the PDC-Jordan contact varies from well to well, ranging between two and 63 feet. Two wells were not completely cased through the PDC and are represented as negative numbers on Figure 32. It would seem reasonable to see an inverse relationship in Figure 32. However, there does not appear to be any relationship. Since the contact between the PDC and Jordan is not abrupt and the 30 foot thick Coon Valley member between the two aquifers is called Jordan by some well drillers and PDC by others, relying on well driller logs alone was insufficient for examining this relationship. More detailed geologic information obtained with the Minnesota Geological Survey aided in better understanding the relationship between casing penetration and water quality. A discussion of this is included in the following section of the report.



#### Geologic Factors Influencing Water Quality

The PDC-Jordan aquifer is likely being recharged from vertical percolation throughout much of the aquifer's extent in the project area. As illustrated in Figure 9, water in the PDC-Jordan moves in the general direction from the South west to the North and Northeast. From the wells sampled, there were no apparent patterns or evident trends as water moved downgradient. Well age, cased depth, overlying bedrock and position of the open borehole in relation to the bedrock stratigraphy tended to overshadow water chemistry trends related to distance from potentiometric highs.

The Decorah, Platteville, Glenwood and perhaps basal St. Peter Formations all contain shale or siltstone units that may impede the downward migration of water. These younger bedrock formations overly the PDC-Jordan aquifer in the southwestern part of the project area, and therefore, greater protection of the aquifer would be expected in this area. Of five PDC wells sampled in this protected region, four of these wells had nitrate-N concentrations 1 to 4 mg/l. These nitrate concentrations are lower than most other PDC wells sampled. The presence of any nitrate in these wells may be due to water flowing back underneath the shale from the north. Potentiometric levels are highest in the area around the fringes of the shale formations just south and east of St. Charles (see Figure 9). This suggests that focused recharge from water flowing off of the shale units is moving down into the PDC-Jordan in this region. From the potentiometric high, the water table drops off approximately 30 feet per mile to the north and east and about five feet per mile to the south and west. Therefore, ground water is likely to be moving much faster to the north and Yet some slower movement of water (probably containing nitrate) back east. under the shale is likely.

The other PDC well under the large area of younger bedrock south of St. Charles had nitrate concentrations of 14 and 24 mg/l. Great temporal variability in a number of parameters in this relatively old well (1963 construction) suggest that water is moving quite rapidly from the upper aquifer or soil surface down to the PDC. The conduit for this water is likely to be a poor seal around the well, but could also be a natural fracture system. The one Jordan well sampled in the "protected" area had no detectable nitrate or tritium.

The PDC well with the lowest nitrate concentration (averaging 0.36 mg/l) is located just across the Winona County border into Olmsted county (#220603). This well is located on the edge of an area covered by the Decorah, Platteville, and Glenwood formations and is likely protected by these units.

The Minnesota Geological Survey obtained downhole geophysical logs in three existing study wells during April 1991. Two of the logged wells were located 0.6 miles apart and had greatly differing chemistries. Well #219245 had 0.03 mg/l nitrate-N, contained no tritium and had a low redox and dissolved oxygen. Well #156980 had over 6 mg/l nitrate-N and higher redox and dissolved oxygen. Geophysical logging data showed that well #156980 was only cased into the upper Coon Valley Formation and was open between elevations 735 and 835 ft. Well #219245 was cased through the Coon Valley and through the lower permeability Sunset Mb of the Jordan. This well was open in the lower portion of the Jordan Formation between elevations 745 and 780. From this information, the lower Jordan appears much less sensitive than wells cased only into the Coon Valley. The three geophysical logs taken in April 1991 supplemented six previously obtained gamma logs in the area (Figure 33). A north-south stratigraphic cross section through St. Charles and an east-west cross section were developed from the nine geophysical logs and well logs and are shown along with nitrate and tritium results in figures 34-37. From these figures, it appears that most of the wells cased to the lower portion of the Jordan have older water and low nitrate. One possible explanation for this is the presence of laterally discontinuous but commonly present layers of very fine-grained well-cemented Sunset Point Mb. Wells cased to the upper Jordan have much more variable nitrate and several wells have mixed age water. The Coon Valley Mb may be retarding vertical movement of ground water in some areas. Wells cased into the PDC also have variable nitrate. No relationship is evident between depth cased into the PDC and nitrate concentrations in PDC wells.

### Figure 33 Location of Gamma Logged Wells and Transect Lines for Cross Sections Shown in Figures 34 - 37





Figure 34 Stratigraphic cross-section(west-east) shown with nitrate-N concentrations.



Figure 35 Stratigraphic cross-section (west-east) shown with Tritium concentrations





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Figure 37 Stratigraphic cross-section (north-south) with Tritium concentrations.

#### Sensitivity Ranking

The Minnesota Department of Natural Resources (MDNR) coordinated the development of a level 1 sensitivity map based on criteria and guidelines for assessing geologic sensitivity in Minnesota. A level 1 sensitivity map is based on the permeability of the parent materials from which soils have formed. From this assessment, most of the area project area was classified as having high to very high sensitivity. Only very small areas were deemed medium or low sensitivity based on the parent materials. Since elevated nitrate and tritium were found throughout the project area, this area does indeed appear to be sensitive to ground water contamination.

There were, however, several wells with very low tritium and nitrate throughout the project area. From well logs alone these wells did not appear to be in a confined aquifer. However, from a more detailed geologic analysis, including geophysical logging of several area wells, the presence of semi-confining layers was discovered. Therefore, well logs alone may not be adequate to estimate the sensitivity of deeper aquifers. Future work will involve creating a level 2 and level 3 sensitivity assessment and comparing the results to water quality data.

In the Winona County Geologic Atlas, Kanivetsky (1984) described and rated the susceptibility of the ground water system to pollution. By combining information and other maps in the county atlas, Kanivetsky developed a susceptibility map. The mapped susceptibility for the west-central Winona County study area is shown in Figure 38. Current and potential development of Karst was an important factor used in evaluating susceptibility. The presence of confining bedrock and till deposits were also important considerations in the development of the map. Several areas of till exist that are more than 10 feet thick, which would protect the underlying aquifer. However, the lateral extent of these till deposits is not believed to be great enough to provide more than localized protection. The susceptibility map (Figure 38) was created using similar criteria as a level 2 sensitivity assessment in the MDNR guidelines for assessing geologic sensitivity.

The region of highest susceptibility is an area of gently rolling terrain where infiltrating precipitation and meltwater percolates through a relatively thin mantle of soil and glacial deposits into karsted rocks of the Prairie du Chien group. This region has a high potential for sinkhole development. The moderate to high susceptibility rated area in west-central Winona County is also in an area of ridgetops with soils overlying the Prairie du Chien. However, the potential for Karst development is diminished in this area largely because of a lower water table. Areas where the Glenwood Formation overlies the St. Peter Sandstone and Prairie du Chien were rated moderate susceptibility. An exception to this is where isolated mesas are also capped by the Platteville Formation.

Nitrate and chloride results were compared for the three susceptibility zones in the project area (Tables 23 and 24). Mean and median nitrate and chloride concentrations in PDC wells were two to four times higher in high rated areas compared to moderate sensitivity areas. Mean and median nitrate was 2 mg/l higher (nearly doubled) in high sensitivity Jordan wells compared to moderate-high sensitivity Jordan wells. Only one Jordan well was located in the moderate area and this well had very low nitrate and chloride. Chloride was only slightly higher in high rated Jordan wells compared to the moderate-high area. While nitrate, and perhaps chloride appear to be related to the sensitivity within the study area, the relationship between residence times and sensitivity of discernible.



Figure 38 Susceptibility of the Ground Water System to Pollution

Table 23	Nitrate	-N concentrations	from wells	located i	n various	susceptibility
	areas.	The susceptibili	ty rankings	are from	Kanivetsky	y (1984).

	Moderate		Moderate to High		High	
	Susceptibility		Susceptibility		Susceptibility	
	Jordan	PDC	Jordan	PDC	Jordan	PDC
# of wells	1	5	14	3	16	15
Median NO <sub>3</sub> -N	0	2.9	2.8	6.6	4.8	12.5
Mean NO <sub>3</sub> -N	0	5.7	3.1	4.7	5.3	11.9
St. Dev.	0	7.4	2.4	3.8	2.8	7.1

Table 24 Chloride concentrations from wells located in various susceptibility areas. The susceptibility rankings are from Kanivetsky (1984).

	Moderate Susceptibility		Moderate to High Susceptibility		High Susceptibility	
	Jordan	PDC	Jordan	PDC	Jordan	PDC
<pre># of wells</pre>	1	4	14	2	16	16
Median NO <sub>2</sub> -N	2.1	10	4.2	12.1	4.8	32
Mean NO <sub>2</sub> -N	2.1	17.5	4.5	12.1	6.8	29.0
St. Dev.	0	18.7	2.8		6.3	15.9

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## CONCLUSIONS

A summary of the study and study results is provided in the Executive Summary. Some of the conclusions drawn from the study are listed below.

- Great lateral and vertical variability in water quality and residence times exists in the Prairie du Chien-Jordan aquifer in west-central Winona County.
- Many, but not all, Prairie du Chien (PDC) wells that are not overlain by lower permeability units show evidence of being sensitive to surficial contamination. Overlying shale tends to reduce the sensitivity of PDC and Jordan wells.
- All but four Jordan wells were impacted by nitrate. However, good water quality can be obtained throughout most of the Jordan Formation. Only two Jordan wells had nitrate at or above the drinking water standard, one of which was an old municipal well. It is recommended that new wells in the area be cased at least 30 to 55 feet into the Jordan, where possible.
- Since the Jordan Formation is divided into several geozones by lower permeability units, significant differences in water chemistry exist vertically within the Jordan. The lower part of the Jordan, especially where the Sunset Mb is present, is much less sensitive to surficial contamination compared to the PDC and upper Jordan.
- Vertical and lateral variability in water quality and residence times may only be understood when detailed geologic information is available. Relying on well driller's logs alone is insufficient for accurately defining geologic sensitivity in this region. Level 2 and level 3 assessments (MDNR guidelines) should be a minimum for much of southeastern Minnesota.
- Dissolved solids concentrations are generally lower in Jordan wells than PDC wells. Water from both formations has low chloride, sulfate, and total dissolved solids compared to secondary drinking water standards and many other Minnesota aquifers.
- Denitrification is likely to be causing a reduction in nitrate in parts of the PDC-Jordan aquifer. Due to the likelihood of denitrification in the deeper part of the Jordan Formation, and the relatively low residence times of water in the PDC and much of the upper Jordan, the nitrate situation could significantly improve in the PDC-Jordan (Winona Co.) within one generation following reductions in nitrate loading into the aquifer.
- Nitrate concentrations from this study correspond fairly well with 1984 Minnesota Geological Survey determined geologic sensitivity. Geologic sensitivity assessments utilizing detailed geologic information appear to be a reasonable means of prioritizing where to implement certain Best Management Practices.

## FUTURE/ONGOING WORK

Funding from the Legislative Commission on Minnesota Resources allowed sampling of the first two rounds of data from which this report is based. The U.S. Environmental Protection Agency provided funding for a third round of sampling, which was completed in April 1991. All laboratory results from the 1991 collected samples should be returned by September 1991. The third round of sampling included additional wells for tritium, carbon 14 for low tritium wells, nitrogen isotopes and dissolved organic carbon for most wells, nitrate, ammonium, and other major cations and anions. Results from this third round of sampling will enable us to better understand 1) the residence times of water in this area, 2) the relationship between residence times to water quality, 3) whether denitrification is occurring within the aquifers, and 4) the temporal variability of water quality and chemistry.

Further work is also planned by MDNR to characterize the geologic sensitivity (Level 2 and Level 3 assessment) based on the Minnesota Department of Natural Resources sensitivity guidelines and criteria. The resulting sensitivity rankings will be compared to water quality and residence time results from all three sampling rounds.

## REFERENCES

- Alexander, Scott C. and E. Calvin Alexander. 1989. Residence Times in Minnesota Ground Waters. Journal of the Minnesota Academy of Science. Volume 55, Number 1, pp 48-52.
- Austin, G.S. 1972. Paleozoic Lithostratigraphy of Southeastern Minnesota, in Sims P.K. and Morey G.B. eds. Geology of Minnesota: A centennial volume. Minnesota Geological Survey, pp 459-471.
- Bottcher, J., O. Strebel, Susanne Voerkelius and H.L. Schmidt. 1990. Using Isotope Fractionation of Nitrate-Nitrogen and Nitrate-Oxygen for Evaluation of Microbial Denitrification in a Sandy Aquifer. J. Hydrol., Volume 114, pp 413-424.
- Davis, R.A. 1966. Revision of Lower Ordinance Stratigraphy in the Upper Mississippi Valley, Journal of Geology, Volume 74, Number 3, pp 361-365.
- Drever. 1972. The Geochemistry of Natural Waters, Prentice Hall, Inc., Englewood Cliffs. New Jersey.
- Egboka, B.C.E. 1984. Nitrate Contamination of Shallow Groundwaters in Ontario, Canada. The Science of the Total Environment, Volume 35, pp 53-70.
- Gillham, R.W. and J.A. Cherry. 1977/1978. Field Evidence of Denitrification in Shallow Groundwater Flow Systems. Water Poll. Res. Canada, Volume 13, pp 53-71.
- Hobbs, H. 1984. Surficial geology in <u>Geologic Atlas for Winona County</u>, <u>Atlas</u> <u>C-2</u> edited by N.H. Balaban and B.M. Olsen, Minnesota Geological Survey, <u>University of Minnesota</u>, St. Paul.
- Howard, K.W.F. 1985. Denitrification in a Major Limestone Aquifer. J. Hydrol., Volume 76, pp 265-280.
- Kanivetsky, R. 1984. Bedrock Hydrogeology in <u>Geologic Atlas for Winona County;</u> <u>Atlas C-2</u>, edited by N.H. Balaban and B.M. Olsen, Minnesota Geological Survey, University of Minnesota, St. Paul.
- Kanivetsky, R. 1984. Susceptibility of the ground water system to pollution in <u>Geologic Atlas for Winona County</u>, edited by N.H. Balaban and B.M. Olsen, Minnesota Geological Survey, University of Minnesota, St. Paul
- Mariotti, Andre, Alain Landreau and Beatrice Simon. 1988. 15N Isotope Biogeochemistry and Natural Denitrification Process in Groundwater: Application to the Chalk Aquifer of Northern France. Geochimica et Cosmochimica Acta., Volume 52, pp 1869-1878.
- Mossler, J.H. and Book P.R. 1984. Bedrock Geology in <u>Geologic Atlas for Winona</u> <u>County; Atlas C-2</u>, edited by N.H. Balaban and B.M. Olsen, Minnesota Geological Survey, University of Minnesota, St. Paul.

- Odom, E. and Ostrom, M. 1978. Lithostratigraphy, Petrology and Sedimentology of Late Cambian - Early Ordivician Rocks near Madison, Wisconsin: Wisconsin Geological and Natural History Survey Fieldtrip Guidebook Number 3, pp 23-45.
- Setterholm, D. 1991. Personal communication, Bedrock Geology of the Garvin Brook area.
- Smith, Richard L. and John H. Duff. 1988. Denitrification in a Sand and Gravel Aquifer. Applied and Environmental Microbiology, Volume 54, No. 5, pp 1071-1078.
- Wall, David B., Susan A. McGuire, and Joseph A. Magner. 1989. Water Quality Monitoring and Assessment in the Garvin Brook Rural Clean Water Project Area. Minnesota Pollution Control Agency, Division of Water Quality.
- Wall, David B., Susan A. McGuire, and Joseph A. Magner. 1990. Nitrate and Pesticide Contamination of Ground Water in the Garvin Brook Area of Southeastern Minnesota. Minnesota Pollution Control Agency, Division of Water Quality. Presented at the Agricultural Impacts on Ground Water Quality Conference sponsored by NWWA, Kansas City, MO. February 1990.
- Webers, G.F. 1972. Paleoecology of the Cambrian and Ordovician strata of Minnesota, in Sims P.K. and Morey G.B. eds. Geology of Minnesota: A Centennial volume: Minnesota Geological Survey pp 474-484.
- Wilson, G.B., J.N. Andrews and A.H. Bath. 1990. Dissolved Gas Evidence for Denitrification in the Lincolnshire Limestone Groundwaters, Eastern England. J. Hydrol., Volume 113, pp 51-60.