# Cottage Grove Area Nitrate Study Report October 2003

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This report presents the results of the Cottage Grove Area Nitrate Study (CGANS) that was conducted for Washington County (County) for the purposes of: (1) determining the general location and types of sources responsible for the nitrate detected in groundwater and (2) Identifying zones of denitrification to determine if there are areas in the Jordan Sandstone in the Cottage Grove vicinity that are more suitable for water supply than others. This study is a more detailed follow-up to a 1999 study performed by the Minnesota Pollution Control Agency in southern Washington County which found elevated levels of nitrate in several wells. Nitrate concentrations were strongly correlated with herbicide concentrations, indicating that much of the nitrate is agriculturally derived.

Nitrate  $(NO_3)$  is a ubiquitous, naturally occurring constituent in groundwater but it also is derived from man-made sources; especially as fertilizer applications. Nitrate has a drinking water standard of 10 mg/L. At low exposure levels, nitrate can cause methemoglobinemia - a toxic effect in which hemoglobin is oxidized, causing oxygen levels in the blood to dwindle. Infants up to 3 months are most susceptible to methemoglobinemia, which manifests itself as cellular anoxia, causing "blue baby syndrome". Nitrate can persist for long periods of time in groundwater and can travel great distances without concentrations being substantially effected.

Because nitrate is ubiquitous and both naturally and artificially occurring, an interdisciplinary approach was used in this study. Groundwater samples were collected and analyzed for nitrate. Nitrogen isotopes were evaluated to determine if a source type of nitrate could be discerned. Groundwater flow modeling was used to estimate the flow paths of groundwater throughout the study area and to identify recharge areas for various points of interest. The study focused on the major geologic units that provide potable groundwater in southern Washington County – the Prairie du Chien Group (a dolomite) and the Jordan Sandstone.

Based on the results of this study, the following are concluded regarding the presence of nitrate in groundwater in the Cottage Grove area of Washington County:

 Nitrate in the Prairie du Chien Group appears to correlate with agricultural land use in areas sampled where the Prairie du Chien Group is the uppermost bedrock. Based on this evaluation, the groundwater in the uppermost bedrock appears to be highly susceptible to nitrate contamination where it underlies agricultural land.

- 2. Higher concentrations of nitrate were also detected in both the Prairie du Chien and Jordan aquifers in the area just west of East Cottage Grove where ponds and wetlands on top of the bedrock valley are fed by run-off from agricultural land.
- 3. A number of faults, generally trending southwest to northeast were discovered during the course of this study with the assistance of Charles Regan of the Minnesota Pollution Control Agency and Robert Tipping and John Mossler of the Minnesota Geological Survey. The displacement on some of these faults exceeds 100 feet, causing portions of the Jordan Sandstone to abut against the permeable Shakopee Dolomite of the Prairie du Chien Group. A north-south trending buried bedrock valley in the eastern part of Cottage Grove may have been formed where these faults intersect and zones of weakness in the rock had formed.
- 4. The nitrate present in groundwater in the Jordan Sandstone appears to correlate with these faults – particularly a fault in eastern Cottage Grove, just west of the buried bedrock valley. The Jordan Sandstone is the uppermost bedrock unit along the axis of the buried bedrock valley and is susceptible to nitrate contaminated water that infiltrates through the unconsolidated material of the bedrock valley. The fault zones appear to be areas of higher horizontal and vertical permeability, which may be responsible for relatively rapid migration of nitrate-containing groundwater southward, along the fault zones and downward into the Jordan Sandstone.
- 5. The Prairie du Chien is the uppermost bedrock across the southeastern portion of the study area and the topography promotes flow of surface water run-off to the St. Croix and Mississippi Rivers. The groundwater in the Jordan Sandstone in the southeastern portion of the study area was found to be low in nitrate most likely do to denitrifying condition<sup>1</sup> in the aquifer in this area. Therefore, in this area the Jordan Sandstone appears to be protected from the nitrate contamination even though the land use across this entire southeastern area is agricultural and faulting is prevalent.

The transition from mostly agricultural to mostly single -family residential land use over the next 20 years may result in a reduction in nitrate concentrations, as nitrate from fertilizer use is reduced in the area and drainage over the buried bedrock valley and faulted areas becomes somewhat more

<sup>&</sup>lt;sup>1</sup> The reduction of nitrates or nitrites, commonly by bacteria, that results in the release of nitrogen.

controlled. Neverthe less, locating municipal water supply wells in the areas near the fault (particularly the fault in eastern Cottage Grove) should be avoided in order to lessen the chance of pulling higher nitrate concentration groundwater from the fault zone into the wells' capture zones. A map that provides some general guidance on well siting is one product of this study.

Based on the conclusion of this study, it is recommended that: (1) nitrate levels in water from ponds and wetlands along the trend of the buried bedrock valley and fault zone should be evaluated to verify the role of infiltration over the bedrock valley on groundwater nitrate contamination and to evaluate surface-water management and passive surface-water treatment options for reducing of the nitrate load to the Prairie du Chien-Jordan aquifer; (2) groundwater from the Prairie du Chien Group and the Jordan Sandstone in the eastern study area should be evaluated for additional chemical parameters and stable nitrogen isotope to determine the source of contamination in the eastern region of the study area that cannot be explained by infiltration of nitrate contaminated water to the uppermost bedrock; (3) farming practices across the study area should be examined to determine if a correlation exists between farming practices (e.g., form of nitrogen applied or application rate) and the lower nitrate concentrations in the Jordan Sandstone in the southeastern region of the study area, and (4) municipal well siting near the faults should be avoided, where possible, to reduce the chances of elevated nitrate levels in the wells. This report has been prepared to document the results of Cottage Grove Area Nitrate Study (CGANS) that was conducted for Washington County (County). The work was performed in accordance with the Sampling and Analysis Plan (SAP) (Barr, October 2002). The objectives of this study were to:

- Perform a nitrate source evaluation to determine the types of sources responsible for the nitrate detected in groundwater samples from the Cottage Grove area and
- Identify zones of denitrification to determine if there are areas in the Jordan Sandstone in the Cottage Grove vicinity that are more suitable for water supply than others, based on geochemical characteristics that promote denitrification.

Nitrate (NO<sub>3</sub>) is a ubiquitous, naturally occurring constituent in groundwater. Anthropogenic uses of nitrate (or compounds that can produce nitrate) are also common, especially as fertilizer applications. Nitrate is also a pollutant with a Maximum Contaminant Limit (MCL) drinking water standard in the U.S. of 10 mg/L (NO<sub>3</sub> as N). The toxicity of elevated levels of nitrate in drinking water includes vasodilatory/cardiovascular effects at high doses and methemoglobinemia at low doses. Methemoglobinemia is an effect in which hemoglobin is oxidized, causing oxygen levels in the blood to dwindle. Infants up to 3 months are most susceptible to nitrate-induced methemoglobinemia, which manifests itself as cellular anoxia, causing the baby to run "blue" (hence, the term "blue baby syndrome").

Nitrate is not substantially attenuated by sorption or precipitation processes at the concentrations typically encountered in groundwater. Nitrate, however, is a part of the nitrogen cycle and is subject to oxidation-reduction process, leading to the process of denitrification or reduction to nitrite. Nitrate can persist for long periods of time in groundwater and can travel great distances without concentrations being substantially effected.

Because nitrate is ubiquitous and both naturally and artificially occurring, an interdisciplinary approach was used to meet the study objectives. Groundwater samples were collected and analyzed for nitrate. Nitrogen isotopes were evaluated to determine if source or use of nitrate could be discerned. Groundwater flow modeling was used to estimate the flow paths of groundwater throughout the study area and to identify recharge areas for various points of interest. This report summarizes the results of these activities.

# 1.1 Scope of Work

The following tasks were completed as part of the Cottage Grove Area Nitrate Study during 2002 and 2003:

- Relevant hydrogeologic, water quality, and land use information were compiled into a readily accessible form so that it could be analyzed and used to aid in this study.
- Data and information from existing groundwater flow models were combined into a new groundwater flow model specific to this project and study area. The model was calibrated to groundwater level data.
- Potential source areas of nitrate were determined preliminarily using backward particle tracking techniques with the calibrated groundwater model. This preliminary source area evaluation aided in the selection of sample collection locations.
- We assisted the County in the collection of water samples for nitrate analyses. Samples were measured for field parameters at the time of collection and selected samples were further analyzed for additional parameters, including stable nitrogen isotopes.
- Additional particle tracking was performed using the groundwater flow model to further identify the sources of nitrate in groundwater and delineate recharge areas for portions of the aquifers in southern Washington County.
- With the assistance of the Minnesota Pollution Control Agency (MPCA) and the Minnesota Geological Survey (MGS), a number of north-south trending faults were identified. The groundwater model was modified to include this new information and particle tracking was performed to evaluate the effects of the faults, which were found to be significant.
- We developed recommendations to the County for ways to better understand the groundwater nitrate contamination in the area.

# 1.2 Background

In 1999, the Minnesota Pollution Control Agency (MPCA) performed a study of groundwater contamination in the Cottage Grove area (MPCA, 2000). The MPCA study found median nitrate concentrations in the Prairie du Chien-Jordan aquifer system of between about 5 and 6 mg/L. Twelve of the 74 private wells that they sampled had nitrate concentrations that exceeded the 10 mg/L

drinking water standard. Nitrate concentrations were strongly correlated with herbicide concentrations, indicating that much of the nitrate is agriculturally derived. Nitrate concentrations were statistically similar in the unconsolidated surficial aquifer, the Prairie du Chien Group and the Jordan Sandstone.

During August 2002, Washington County conducted a walk-in "nitrate clinic" where residence brought in samples of their tap water for analysis of nitrate levels. Numerous samples analyzed had nitrate concentrations that exceeded the 10 mg/L drinking water standard. Barr Engineering Co. was not involved in the collection of this data. However, this data, along with results from the MPCA's study, were used throughout the course of the CGANS.

# 1.3 Report Organization

This report is organized into five sections including this introduction. Section 2 summarizes the investigation methods, Section 3 summarizes the groundwater sampling results, Section 4 presents the nitrate source evaluation, and Section 5 provides the study conclusions and recommendations to the County.

This section describes the methods that were used in this study to evaluate the extent and sources of nitrate in the Cottage Grove area of southern Washington County. The methods included the development and use of a groundwater flow modeland chemical analyses of water samples.

### 2.1 Groundwater Modeling

Groundwater flow modeling was performed to aid in the investigation of the source and the distribution of groundwater with nitrate in southern Washington County. Groundwater modeling was performed in three phases: in phase one, preliminary particle tracking was used to help identify flow paths to aid in further data collection; in phase two, (discussed in Section 4.1) recharge areas were delineated for various locations in the study area. After discovery of fault systems in southern Washington County, a third phase of groundwater modeling and particle tracking was performed to evaluate the effects of the faults on groundwater flow and the distribution of nitrate in groundwater.

### 2.1.1 Initial Model Development and Calibration

Groundwater flow modeling for the Cottage Grove Area Nitrate Study was performed using the U.S. Geological Survey's three-dimensional, finite-difference groundwater flow code, MODFLOW (McDonald and Harbaugh, 1984). A six-layer model, encompassing the southern two-thirds of Washington County was constructed. The six-layer model simulated the various aquifers and confining units from the surficial glacial drift, downward through the combined Franconia Formation-Ironton Sandstone-Galesville Sandstone aquifer. A combination of previous ly developed groundwater models and other relevant data was used in the construction of this new model.

The groundwater model was calibrated to observed groundwater levels (heads) through a trial-anderror process, where aquifer parameters were manually varied until there was an acceptable match between observed heads and simulated heads. Hydraulic conductivity values for the model layers were varied within a range of expectable values during the calibration process. Ultimately, an acceptable set of parameter values was found that provided a good match between observed heads and simulated heads. A more detailed discussion of model construction and calibration can be found in Appendix C.

#### 2.1.2 Preliminary Source Area Evaluation

The particle tracking code MODPATH (Pollock, 1994) was used in conjunction with the groundwater flow model to determine the capture zones<sup>2</sup> and source areas (i.e. locations of recharge at the ground surface) of groundwater within the study area. MODPATH uses the output files from the MODFLOW simulations to compute three-dimensional flow paths by tracking particles throughout the model domain until they reach a boundary or enter an internal source or sink.<sup>3</sup> Particles for backward tracing were started around wells that had known elevated nitrate as measured during the walk-in "nitrate clinic" and the MPCA study. The particles were tracked backwards in time to determine the capture zone for each well. The results of this phase of groundwater modeling were used to aid in identifying additional wells that should be sampled.

### 2.2 Groundwater Sampling Activities

The field investigation was conducted in accordance with the Sampling and Analysis Plan (SAP) (Barr, 2002). Over a seven-week period, MPCA staff, with periodic assistance from County staff, collected groundwater samples from 49 private wells and 10 municipal wells. The locations of these sampled wells are shown on Figure 1.

Water samples from private wells were collected from outside taps located on each of the 49 private properties. At well location site numbers 19 and 53, MPCA and County staff collected a second sample from the inside faucet tap at the owner's request. Ten Cottage Grove municipal water supply wells were sampled from taps located inside the wellhouses. Before sampling, wells were allowed to purge for a period of 10 to 20 minutes or until the stabilization criteria were met. Stabilization criteria refer to geochemical parameters that were measured at frequent intervals during the purging of the wells to determine when stagnant water had been evacuated from the well and formation water was forthcoming. The stabilization criteria for dissolved oxygen, oxidation-reduction potential, pH, temperature and conductivity of +/- 5% were met. In increments of 5 minutes, stabilization parameters were measured and, once stabilization was achieved, samples were collected for field and/or laboratory analysis. All stabilization data was documented on the field data sheets and are included in Appendix A.

<sup>&</sup>lt;sup>2</sup> A capture zone is the area where a pumping well receives its groundwater.

<sup>&</sup>lt;sup>3</sup> A source is a feature that puts water into the groundwater system and a sink is a feature that takes water out. An example of a source is rainfall that percolates to the water table. An example of a sink is a well. P:\23\82\366\Nitrate Study Report\nitrate report sep 2003 draft.doc8

All wells, including wells at locations identified in the SAP for nitrate source evaluation and wells at locations identified as being in a denitrifying zone (or any alternates), were analyzed for nitrate both in the field and at the Minnesota Department of Health (MDH) laboratory. Samples that met three of four geochemical screening criteria were submitted for additional analysis of sulfate, sulfide and chemical oxygen demand as specified in the SAP. A total of 8 wells were analyzed for the additional analyses referenced above. The geochemical screening criteria are as follows:

- DO <5.0 mg/L,
- ORP <50 mV,
- Ferrous Iron >0.5 mg/L,
- Nitrate <1 mg/L

Based on field analysis results, eleven denitrifying zone wells were submitted to the laboratory for nitrogen isotope analysis. All analytical results are presented in Table 1.

Split samples and field duplicate samples were collected to monitor the representativeness of the field (and laboratory) procedures. A total of nine field duplicates and laboratory-split samples were collected and analyzed over the study period.

# 2.3 Field Analyses

Groundwater samples were collected and analyzed for nitrate and ferrous iron using the HACH field test kit methods as specified in the Sampling and Analysis Plan (SAP) that was developed for this project. It should be noted that the determination of nitrate in the field uses a reagent that reduces nitrates to nitrites for measurement. Effectively, this is a nitrate+nitrite analyses, however since no nitrite source or nitrite supporting conditions were expected or encountered, these results primarily represent nitrate concentrations in the wells. Each home owner was given documentation of their field nitrate results using the form from the SAP.

Dissolved oxygen, conductivity, pH, oxidation-reduction potential, and temperature were also measured in the field, as specified in the SAP. Calibration of field instrumentation was performed daily and the calibration was found to be acceptable. With the exception of battery replacement, no difficulties were reported with the field instrumentation. All field data are documented on the field sheets provided in Appendix A.

# 2.4 Laboratory Analyses

Groundwater samples were analyzed for nitrate+nitrite nitrogen using EPA Method 353.2 by the MDH laboratory and by Braun Intertec laboratories. As stated above, this analysis is primarily a measure of nitrate concentrations in the wells. Nine field duplicate samples were analyzed for nitrate by the MDH laboratory. The field duplicate results show acceptable reproducibility and are presented on Table 2. Nine laboratory-split samples were analyzed by Braun Intertec using the same EPA method. The laboratory-split sample results show acceptable reproducibility and are presented on Table 3. Laboratory reports are included in Appendix B.

Nitrogen isotope analyses were performed by the Illinois Geological Survey laboratory under subcontract with Isotech Laboratories, as specified in the SAP. Samples collected from well locations 35 and 18 were submitted but had insufficient nitrate concentrations to complete the isotope analysis. The nitrogen isotope analysis results are also presented in Table 1.

The results of the groundwater sampling are presented in this section for the sampling events performed in 2002.

### 3.1 Groundwater Sample Analyses Results

Table 1 presents the analytical results for the groundwater samples collected during this study. Field analyses of nitrate-nitrogen were performed to provide real-time data for evaluating further laboratory analysis, to estimate a current concentration for possible nitrogen isotope analysis, and to provide data to the homeowners. Results of the field nitrate results were compared to the laboratory results by evaluating the relative percent difference (RPD) between the duplicate pair where both data points were positive (above detection). In general, an RPD of 30% or lower is considered good reproducibility. In this study, roughly 37% of the RPDs were approximately 30% or less. However, because the overall concentrations of nitrate were low and the colormetric method result was variable, these RPDs do not necessarily represent poor data quality.

Approximately 80% of the laboratory nitrate results were greater than the associated field results by approximately +/- 20%, showing an overall bias low in the field instrument readings. Field nitratenitrogen results from well location numbers 1, 2, 4, 7, 20, 25, 37, 41, 42, 49 and 71 had concentrations below the 10 mg/L MCL. However, the associated laboratory results for these samples had concentrations of nitrate-nitrogen greater than the 10 mg/L MCL. Alternately, field nitrate-nitrogen results from well location numbers 3 and 23 had concentrations above the 10 mg/L MCL but associated laboratory results showed concentrations below the 10 mg/L MCL. Because each property owner was given documentation of their field nitrate result, follow-up transmittal of the final laboratory results by the County may be warranted.

### 3.2 Quality Control Review

Samples collected in support of this study were analyzed by the Minnesota Department of Health, Illinois Geologic Survey Laboratory, and Braun Intertec, Inc. following the protocols and requirements from the SAP (Barr, October 2002). The data quality evaluation involved a review of the aspects of sample collection and field and laboratory analytical performance based on EPA National Function Guidelines for data review. The sampling procedures specified in the SAP were P:\23\82\366\Nitrate Study Report\nitrate report sep 2003 draft.doc11 performed by the MPCA and Washington County personnel. Field data sheets and summary information are provided in Attachment A.

#### **Holding Times**

All samples submitted to the laboratories met EPA or method recommended holding times. Due to field instrument problems, pH could not be measured within the recommended holding time for samples collected on November 13, 2002. The associated data have been qualified with an "h" in the summary table.

#### **Duplicate and Split Analyses**

Field duplicate and laboratory split samples were collected and analyzed to evaluate the precision of the analytical measurements. Precision was evaluated by calculating the relative percent difference (RPD) between the two measurements where both data points had positive results. All field duplicate and laboratory split results displayed acceptable levels of precision. Field duplicate and laboratory split sample results are provided in Tables 2 and 3, respectively.

#### **Field Analyses**

Field calibrations were performed at the appropriate frequency and displayed acceptable results as documented in Appendix A. Overall, the field nitrate results appear to be biased low as compared to the laborator y analysis. High RPDs are expected when results are at or near the detection limit and do not always indicate poor precision. However, due to the nature of colormetric analyses such as these, higher variability is expected as there is more inherent susceptibility to very slight interferences such as the amount of suspended solids, etc. While RPD results were higher than expected, no system errors were discovered.

#### **Blank Analyses**

Field blanks were not collected for this project. Laboratory blank samples were not reported from the Minnesota Department of Health; however, verbal confirmation was obtained from the MDH that stated that there were no positive concentrations measured in the laboratory method blanks at the method reporting limit. No positive concentrations were present in the laboratory method blanks analyzed by Braun during the performance of the split analysis.

#### **QA/QC Review Conclusions**

The QA/QC review indicates that field sampling procedures were appropriate, did not introduce contamination, and did not adversely affect sample representativeness. All analytical data were reviewed and determined useable as presented in the data summary table.

As part of the evaluation of the groundwater nitrate contamination in the Cottage Grove area, groundwater chemistry, geochemistry, structural geology, groundwater modeling, and nitrate fate and transport were used to identify potential locations and sources of the nitrate in the groundwater. Samples were collected from 60 existing wells in the Cottage Grove area and analyzed for dissolved oxygen (DO), oxidation-reduction potential (ORP), and nitrate. Samples evaluated in the field as anoxic (i.e., DO<0.5 mg/L; ORP<50 mV; ferrous iron>0.5 mg/L) were also analyzed for sulfate, sulfide, and chemical oxygen demand (COD). Twelve samples were selected from wells across the study area and from both the Prairie du Chien Group and the Jordan Sandstone<sup>4</sup> for stable nitrogen isotope analysis. Results of all groundwater analysis are presented in Table 1.

The analytical results were evaluated to identify groundwater nitrate plumes in both the Prairie du Chien Group and Jordan Sandstone, sources of the nitrate contamination, areas within the geologic units with nitrate concentrations greater than 1 mg/L, and conditions that support denitrification (i.e., biological conversion of nitrate to nitrogen gas). The groundwater flow model was then used to identify areas that are the likely infiltration zones where nitrate-contaminated water entered the aquifer and to evaluate the effect of fault systems on nitrate distribution. In addition, the groundwater flow model was used to identify the recharge zones for the groundwater on the southeastern end of the County that appear to not be adversely affected by nitrate contamination.

## 4.1 Faulting in Southern Washington County

A significant outcome of this study was the discovery of a series of approximately north-south trending faults in southern Washington County. The discovery came about through the observations of Charles Regan of the MPCA during review of draft reports for this study. Regan noted that some wells in relatively close proximity to one another displayed elevation differences in the top of the

<sup>&</sup>lt;sup>4</sup> The Prairie du Chien Group (dolomite) and the Jordan Sandstone together make up the Prairie du Chien-Jordan aquifer. Locally, these two geologic units can act as two separate aquifers that are hydraulically connected through leakage. On a more regional basis, the differentiation between these two units may not be as important.

Jordan Sandstone of several tens of feet. The gridded unit elevation data provided to Barr by the Minnesota Geological Survey (MGS) is based on these data and therefore, the model had accounted for these elevation variations, but it did so as a continuous smooth surface. Regan hypothesized that instead of an undulating surface, the differences in elevation of the top of the Jordan Sandstone reflected faulting.

The information regarding bedrock elevations was brought to the attention of the MGS. Robert Tipping and John Mossler of MGS evaluated the County Well Index (CWI) data and Dr. Mossler developed a draft map (Mossler, 2003) of faults in southern Washington County. The faults identified by the MGS are shown on Figure 2. The relative displacement of the faults is also shown.

Faulting appears to be concentrated primarily in the eastern half of southern Washington County, with fault orientation north-south to northeast-southwest. The western half of southern Washington County (Cottage Grove area) appears to be relatively absent of faulting and the strata are nearly flat-lying. Fault displacement is generally about 50 to 75 feet, except along the St. Croix River where a displacement of 175 feet is indicated. Dr. Mossler (personal communication) has hypothesized that there are likely a series of "step" faults that cause the larger displacements, rather than one large fault but that data density is insufficient to characterize this. Strata are generally believed to be flat lying – i.e. the structural displacement is due to faulting rather than folding. Some of these faults extend south, underneath the Mississippi River into Dakota County.

Barr has taken the liberty of developing two cross sections through the faults in order to illustrate the relative stratigraphic orientations. The locations of the cross sections are shown on Figure 3. Cross-Section A-A' is on Figure 4 and Cross-Section B-B' is on Figure 5. Mossler's map and CWI well log data were used together to construct these cross sections. In the eastern most part of the cross sections, dipping strata are shown in order to provide continuity with the elevation data in CWI – these dips are likely not present but instead, probably indicate several closely spaced faults that well data do not allow to be delineated. According to Mossler (personal communication) it is best to assume that these faults are near-vertical normal faults.

Faulting may extend up through the Afton Anticline area, north of study area for this project (Mossler, personal communication). Additional work would be needed to evaluate the nature of faulting in that area and is beyond the scope of this study.

# 4.2 Recharge Area Delineations

The groundwater flow model was used to delineate recharge areas for wells located in the study area with the intention of being able to identify spatial trends in the recharge areas for wells with similar chemical compositions. In addition, the groundwater flow model was used to identify approximate areas of recharge for the major aquifers in the study area and evaluate the effects of faulting.

In the western and central portion of the study area, high nitrate concentrations were measured in both the Jordan Sandstone and the Prairie du Chien Group. Wells in this area include: 16, 42, 37, 34, 63, and 2 (numbers correspond to site ID numbers listed in Table 1 and shown on Figure 1). In the eastern portion of the study area, low nitrate levels were measured in the Jordan Sandstone and analytical data suggests denitrifying conditions exist in a portion of the Jordan Sandstone in this area. Wells in this area include: 64, 67, 68, 75, and 77 (numbers correspond to site ID numbers listed in Table 1 and shown on Figure 1).

Recharge areas and relative groundwater travel times for the various wells listed above were delineated using the groundwater flow model in conjunction with the particle tracking code MODPATH. For this study, particles were placed at the various locations of interest in the model and tracked backwards in time to their point of recharge. Information provided in the well construction reports was used to vertically place the particles in the model corresponding to the portion of the aquifer to which the wells are open.

The results of the groundwater particle tracking and delineation of recharge areas are presented here under two conditions: (1) without consideration of faulting and (2) with consideration of faulting. The reason for presenting it this way is that even though there are lines of evidence to suggest that the faults play a role in the movement of nitrate-contaminated groundwater, the effects of the faulting are not necessarily definitive and are subject to some speculation. In other words, we know there are faults and it does appear that the faults affect the distribution of nitrate in groundwater *but* we are not certain how the faults behave hydraulically.

### 4.2.1 Recharge Areas, Assuming No Effects of Faulting

This section describes delineated recharge areas for individual wells with high nitrate concentrations, assuming that the faulting plays no significant role.

Delineated recharge areas for the individual wells with high nitrate concentrations are shown on Figure 6. The recharge areas are divided into two zones based on time of travel, either less than or

greater than 60 years. Only wells 63 and 34 receive water older than 60 years. Wells in the eastern portion of the aquifer receive water that recharges relatively close to each well, while wells in the central and western portion of the aquifer receive water that recharges a greater distance from each well. Figure 7 shows the recharge areas and the subcropping bedrock units. The recharge areas for the wells in the western and central portion of the study area intersect the buried bedrock valley that runs through the central portion of southern Washington County. Faulting is not considered in this part of the analyses.

The groundwater flow model was also used to delineate the recharge areas for *all* wells completed in the Jordan Sandstone and Prairie du Chien Group within the study area. Particles were started in the model at various locations and depths throughout the study area and tracked backwards in time to their recharge area. These recharge areas were then compiled to form a broad area of recharge for the southern portion of each aquifer. These recharge area delineations are intended only to provide information on the possible recharge areas for wells in southern Washington County and are not intended to indicate the recharge zone for the entire Prairie du Chien or Jordan aquifer.

Figures 8 and 9 show the recharge areas for the Prairie du Chien Group and the Jordan Sandstone in southern Washington County, respectively (assuming no effects of faulting) overlying current land use. In general, the recharge area of the Jordan Sandstone is further from sources of discharge, such as the Mississippi and St Croix Rivers than is the recharge area for the Prairie du Chien Group. In addition, the recharge area for the Jordan Sandstone extends further north than the recharge area for the Prairie du Chien Group. Figures 10 and 11 show the recharge zones overlying the planned future land use (Metropolitan Council Regional Planned Land Use – Twin Cities Metropolitan Area, 2002) for the area. Currently, the majority of the recharge areas are vacant or used for agriculture, with a portion of the recharge area in the west having single-family residences. The planned land use for 2020 shows a decrease in agricultural land in the recharge areas and an increase in rural and single family residential land.

#### 4.2.2 Potential Effects of Faulting on Flow Paths to Wells

#### 4.2.2.1 Possible Hydraulic Effects of Faults

Faults can affect groundwater flow in two basic ways: (1) they can act as barriers that hinder groundwater flow or (2) they can be zones of preferentially high groundwater flow velocities and rates. In other parts of the country, were faulting is more common, faults have been observed to behave in either manner – as barriers or as conduits. In Minnesota, we have much less experience

assessing the role of faulting in the Prairie du Chien-Jordan aquifer on flow – therefore, both conditions need to be considered.

A fault can act as a barrier or less permeable zone if the fault zone is : (1) filled with fine-grained material such as fine fault gouge, or (2) displacement along the fault results in a normally high transmissivity zone (e.g., Shakopee Formation of the Prairie du Chien Group or the Jordan Sandstone) abutting against a lower permeable zone (e.g., the Oneota Dolomite of the Prairie du Chien Group or the St. Lawrence Formation). Fine, low-permeability material in the fault zone would not only act as a hindrance to horizontal groundwater flow but also hinder vertical flow between hydrostratigraphic units. A barrier effect caused by displacement, however, could limit horizontal flow but the fault zone may still have high vertical permeability, allowing rapid leakage between hydrostratigraphic units.

In southern Washington County, the faults are generally oriented north-south, roughly parallel to the regional groundwater flow direction. If the faults are acting as barriers to flow, they would not have much of an observable effect on regional groundwater flow because their alignment is parallel to flow. High rates of pumping adjacent to the faults would be required to discern a barrier effect.

A fault can act as a conduit (i.e. a zone of much higher permeability and groundwater flow velocities) if the fault zone becomes a feature of high secondary permeability. Secondary permeability differs from primary or matrix permeability in that it forms separate from the intergrannular or bedding plane porosity of the geologic unit. Faulting and jointing are common examples of the formation of secondary permeability features. In carbonate rocks, such as the Prairie du Chien Group, jointing and faulting can be further enhanced by dissolution (Runkel, et al., 2003). As a conduit, a fault represents a linear zone for rapid horizontal flow along the axis of the zone and rapid vertical movement and or equilibration of heads vertically between hydrostratigraphic units and across regional aquitards.

It is uncommon for joint features in the Prairie du Chien Group and Jordan Sandstone to display finegrained fill material. In general, joints and faults are open or contain rock fragments that are similar to gravel. The tendency is for these zones to be further enlarged by dissolution of the carbonate rock (Runkel et al., 2003).

In this study, the faults were modeled both ways because there is no verdict as to which way these types of faults behave. More study would be needed in the immediate vicinity of the faults, such as pumping tests very close to the faults and borehole investigation of the fault zones, to determine the hydraulic characteristics of the faults. In the absence of these types of data, we felt it prudent to

analyze the faults both ways, as either barriers or conduits. However, as the modeling results presented in this report demonstrate, treating the faults as zones of higher permeability and preferential flow seems in best agreement with observations.

#### 4.2.2.2 Modifications to Groundwater Model to Simulate Faults

In order to accurately simulate the faults in the groundwater model, some additional modification was required. First, the finite-difference grid was further discritized (i.e. refined) in the area surrounding the faults, with a longitudinal spacing of 135 meters and a latitudinal spacing of 155 meters. This refinement was done in order to make the fault zones as thin as possible and accommodate the displacement across faults. After re-discretization, the faults were incorporated as zones of differing hydraulic conductivity, based on the locations provided by MGS.

The base elevations of the individual layers were already quite accurate because they were assigned on the basis of grids developed by the MGS from CWI data. Fault block elevations provided by the MGS (Mossler, 2003) could not be accommodated everywhere due to model stability problems associated with the drying out of cells. This problem is solvable but is beyond the scope and needs of this project.

When simulating the fault zones as high hydraulic conductivity features, a hydraulic conductivity (K) value of 100 m/day was used. When simulating the fault cones as low K features, a K value of 0.01 m/day was used. These values were constrained by the stability of the modelbut they reflect significant contrast compared to the surrounding rock. Isotropic conditions within the faults were assumed (that is, horizontal and vertical hydraulic conductivities were equal).

Although the model was not recalibrated after the inclusion of the fault zones, the resulting calibration statistics, absolute residual mean (ARM) and root mean squared error (RMSE), associated with each of these simulations (base, high K faults, and low K faults) were calculated as a means to compare the models. These statistics are as follows:

	Layer	ARM	RMSE
	1	6.44	9.89
lse	2	4.63	6.40
$C_2$ B <sup>2</sup>	3	4.96	6.25
	4	5.46	7.20
	1	6.08	8.75
v K ults	2	4.36	6.13
Lov Fai	3	4.70	5.93
	4	6.24	6.73
	1	6.51	10.11
h F ults	2	4.63	6.41
Hig Faı	3	5.01	6.29
I	4	5.59	7.32

As this table illustrates, the addition of the faults did not significantly affect the calibration statistics. However, it should be kept in mind that the statistics include targets located throughout the model domain; many are some distance from the faults.

#### 4.2.2.3 Recharge Areas Assuming Faults

The simulated groundwater flow paths, assuming the faults act as higher permeability zones, are shown on Figure 12. The simulation results showing groundwater flow paths to the selected wells with the faults functioning as lower permeability barriers to groundwater flow (both laterally and vertically) are shown on Figure 13.

At first glance and comparing to the recharge areas without faults, the three simulations do not appear much different. This apparent lack of difference is because the hydraulic parameters of the non-faulted units are identical in each simulation and much of the groundwater flow is through the unfaulted zones. There are, however, some important differences:

- In the case where the faults are assumed to be low-permeability features, flow paths are "deflected" around the faults. An example of this deflection is in the eastern part of the study area in Figure 13, where an "S-shape" to the flow paths is exhibited. The other differences, compared to the recharge zones without faulting, are minor.
- In the case where the faults are assumed to be higher-permeability features (Figure 12), there are more differences from the no-faulting simulation. Flow paths extend much farther to the north (upgradient), due most likely to the rapid travel of groundwater within the fault zones. Flow paths to wells tend to be somewhat narrower, more elongated, and tend to be confined

or otherwise directed along the fault zones. Most importantly, perhaps, is that groundwater is predicted to move rapidly downward from the water table, through the fault zones, and into the Jordan Sandstone. This would suggest that the faults (as higher permeability zones) allow for more rapid movement of water from near ground surface to deeper aquifer units.

### 4.3 Evaluation of Nitrate Plumes

Samples of water were drawn from municipal and private wells throughout the study area. Wells in the study area included wells screened in either in the Prairie du Chien Group or in the Jordan Sandstone. Each water sample was analyzed for nitrate. The nitrate results are presented in Table 1. The nitrate results and iso-concentration<sup>5</sup> contours are plotted on Figure 14 for the Prairie du Chien Group and on Figure 15 for the Jordan Sandstone. Data from the Minnesota Pollution Control Agency study, "Groundwater Quality in Cottage Grove, Minnesota," (June 2000) were also used to develop the iso-concentration contours shown on Figures 14 and 15.

### 4.3.1 Prairie du Chien Group

All groundwater samples were analyzed for dissolved oxygen (DO), oxidation-reduction potential (ORP), and dissolved iron. These results are presented in Table 1. These data indicate that the groundwater in the Prairie du Chien Group is highly aerobic. No attenuation of nitrate through denitrification is expected in the Prairie du Chien Group in this area because of these aerobic conditions.

All wells analyzed *as part of this study* in the Prairie du Chien Group had a nitrate-nitrogen concentration in excess of 5 mg/L. Several samples had nitrate-nitrogen concentration in excess of 10 mg/L. The groundwater flow model was used to evaluate the infiltration area for well 2, which is screened in the Praire du Chien Group (Figure 3).<sup>6</sup> Figure 6 shows that infiltration of water that reaches well 2 takes place within less than <sup>1</sup>/<sub>2</sub> mile from the well. This is consistent with the fact that the Praire du Chien Group is the uppermost bedrock in the vicinity of well 2. With the exception of well 9, all other wells sampled as part of this study that are screened in the Prairie du Chien Group are in an area where the Prairie du Chien Group is the uppermost bedrock.

<sup>&</sup>lt;sup>5</sup> lines connecting equal concentration

<sup>&</sup>lt;sup>6</sup> Wells are referenced by their study site identification number presented in Table 1.

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The groundwater in the uppermost bedrock is most likely to be directly affected by the quality of the infiltrating water. Therefore, nitrate contamination in the Prairie du Chien Group is likely a result of land use increasing the nitrate concentration in the infiltrating water. Though no samples were collected in the Praire du Chien Group in the southeastern part of the study area, measurable nitrate concentrations in the Prairie du Chien Group are likely in this area because it is the uppermost bedrock and the land use in this region is almost entirely agricultural.

#### 4.3.2 Jordan Sandstone

Table 1 presents the nitrate analytical results for samples collected in wells screened in the Jordan Sandstone. Figure 15 shows the nitrate iso-concentration curves for nitrate-nitrogen in the Jordan aquifer. The Jordan aquifer appears to have three separate nitrate plumes in the study area. The first and largest plume is in the south-central region of the study area. The second plume is in eastern region of the study area. The third plume is associated with well 43 in the southeastern region of the study area.

The groundwater model was used to evaluate the groundwater flow paths for specific Jordan wells. The modeled flow paths (without faulting) are presented on Figure 16, superimposed over the nitrate concentrations in the Jordan Sandstone. The modeling shows that impacted wells in the south-central nitrate plume within the Jordan Sandstone have flow paths from the phreatic surface to the well that intersect a north-south trending buried bedrock valley in this area. Both the modeled flow paths for selected Jordan wells and the south-central plume may correlate with the bedrock valley that runs north and south in this area.

The burie d bedrock valley is an area where the bedrock was eroded away down to the Jordan aquifer and then was filled in with a more permeable material. The bedrock valley represents an area where infiltrating water could percolate down into the Jordan Sandstone faster than in other portions of the study area where infiltrating water must travel through the Prairie du Chien Group and other bedrock units. A topographic depression correlates with the buried bedrock valley. In this topographically lower area, surface runoff collects in several ponds and wetlands. The collection of water in this topographic depression is significant because it overlays the buried bedrock valley. Therefore, the bedrock valley is an important geologic and topographic feature that likely provides a higher permeability soil profile for surface water to collect and infiltrate to the deeper bedrock units such as the Jordan Sandstone. The nitrate concentrations in the Jordan Sandstone are superimposed on the groundwater flow paths assuming the faults are low-permeability zones (Figure 17) and high permeability zones (Figure 18). It appears that the nitrate plume in south central Washington County is closely correlated with the trend of the fault – perhaps more so than the buried bedrock valley. The data, combined with the groundwater modeling, suggest that nitrate-containing groundwater infiltrates in the upgradient areas of the fault, preferentially migrates downgradient along the fault zone, and migrates downward along the fault zone into the Jordan Sandstone.

The eastern nitrate plume in the Jordan Sandstone appears to emanate from the vicinity of well 71. Groundwater flow in this area of the Jordan Sandstone is to the east, toward the St Croix River. No significant geologic features appear to correlate with this nitrate plume, other than a fault zone, which may allow for rapid downward migration of surface-originated nitrate groundwater into the Jordan Sandstone. Wells 73 and 76 are downgradient of well 71. The higher nitrate concentrations in wells 73 and 76 are likely a result of nitrates from the area around well 71 migrating downgradient.

This study did not include additional wells screened in the Jordan aquifer in the vicinity of well 43. Therefore, the extent of the higher nitrate concentrations in this area is unknown.

The southeastern quadrant of the study area contains wells 64, 67, 74, 75, and 77 that are screened in the Jordan Sandstone. Groundwater samples from these wells had nitrate-nitrogen concentrations less than 1 mg/L (Table 1). Groundwater flow modeling results show that the infiltration zones for these wells do not intersect the bedrock valley or the fault zone along the axis of the higher nitrate concentrations. Groundwater extracted from these wells infiltrated through the unconsolidated soils and the Praire du Chien Group. The topography of this region of the study area is quite hilly. Surface water flows to various streams and then to either the St. Croix or Mississippi Rivers. There are no large localized depressions in this region for surface run-off to collect and infiltrate. The groundwater quality data, the geology, and the surface topography of this area suggest that it may continue to remain unimpacted by nitrate contamination from agricultural land use.

The geochemistry within the nitrate plumes shows that the groundwater is highly aerobic. No denitrification is expected in the Jordan Sandstone nitrate plumes. Geochemical results for samples from several wells that are not in the nitrate plumes and do not have elevated nitrate concentrations (i.e., wells 18, 35, 64, 68, 69, and 77) showed anoxic conditions that would likely support denitrification.

### 4.4 Stable Nitrogen Isotope Evaluation

#### 4.4.1 Background

Nitrogen occurs naturally in two stable isotopes, nitrogen 14 (7 protons - 7 neutrons; <sup>14</sup>N) and nitrogen 15 (7 protons and 8 neutrons; <sup>15</sup>N). Nitrogen gas in the atmosphere is 99.632% <sup>14</sup>N and 0.368% <sup>15</sup>N. Air is used as the standard for evaluating the relative percentage of <sup>14</sup>N and <sup>15</sup>N in a sample containing nitrogen compounds. The relative amount of <sup>15</sup>N in a nitrogen-containing compound is expressed in terms of the nitrogen isotope ratio del value ( $\delta$ ) in parts per thousand (ppt) as defined in the following equation (Wolterink, 1979; Green, 1998).

$$d^{15}N = \frac{\frac{\frac{15}{14}N}{N}(\text{sample}) - \frac{\frac{15}{14}N}{\frac{14}{14}N}(\text{air})}{\frac{\frac{15}{14}N}{14}} \times 1000$$

Based on this equation, the  $\delta^{15}N$  value for air is zero. In the environment,  $\delta^{15}N$  values can range from -20 to +20. A  $\delta^{15}N$  value of -20 is a sample with nitrogen depleted in <sup>15</sup>N where as a  $\delta^{15}N$  value of +20 is enriched in <sup>15</sup>N (Wolterink, 1979; Green, 1998).

Various types of physical, chemical and biological processes on nitrogen compounds can cause the  $\delta^{15}$ N to increase or decrease based on the relative rate of reaction for <sup>14</sup>N versus <sup>15</sup>N (Wolterink, 1979; Green, 1998; Fahlman, 2001; Averena, 1993). For example, since <sup>14</sup>N is lighter than <sup>15</sup>N, <sup>14</sup>N ammonia will volatilize at a faster rate than <sup>15</sup>N ammonia at the same temperature. The  $\delta^{15}$ N for ammonia in solution will increase if volatilization is occurring (Wolterink, 1979; Green, 1998; Fahlman, 2001; Averena, 1993). Biologically catalyzed reactions, such as nitrification (i.e., ammonia oxidation to nitrate) will have a higher reaction rate for <sup>14</sup>N than for <sup>15</sup>N. Once again, nitrification will increase the  $\delta^{15}$ N for the ammonia (Wolterink, 1979; Green, 1998; Fahlman, 2001; Averena, 1993). The nitrate produced, though, will have a lower  $\delta^{15}$ N (i.e., lower than the ammonia source) initially that will increase as the reaction continues. This is because <sup>14</sup>N nitrate is produced at a faster rate than <sup>15</sup>N nitrate. In addition, denitrification (i.e., conversion of nitrate to nitrogen gas) is a biologically catalyzed reaction rate for <sup>14</sup>N than for <sup>15</sup>N. If denitrification is taking place, the  $\delta^{15}$ N for the nitrate will increase (Wolterink, 1979; Green, 1998; Fahlman, 2001; Averena, 1993).

Based on the above information, the  $\delta^{15}$ N of nitrate contamination found in groundwater will be strongly affected by both the source of the nitrate (i.e., chemically or biologically produced) and by whether or not denitrification is taking place in the aquifer.

Several studies reviewed the  $\delta^{15}$ N values for specific sources of nitrate in groundwater from varying geographic locations (Wolterink, 1979; Green, 1998; Fahlman, 2001; Averena, 1993). The sources include nitrate from fertilizer, from the breakdown of plant matter in topsoil, septic field leachate, manure lagoon leachate, and sewage pipe leakage. The published reports support that nitrate from fertilizer has a  $\delta^{15}$ N value of -5 to +3. Nitrate from topsoil has a  $\delta^{15}$ N value from +2 to +8. Nitrate from manure lagoons/septage/sewage has a  $\delta^{15}$ N from +10 to +20 (Green, 1998; Fahlman, 2001; Averena, 1993).

Based on the reactions that affect  $\delta^{15}N$  in the environment, these ranges are good indications of the nitrate source when the  $\delta^{15}N$  is statistically in the range, the aquifer is aerobic, and the dissolved organic carbon in the groundwater is low (Green, 1998; Fahlman, 2001; Averena, 1993). Under these conditions, little or no denitrification is taking place and these published ranges can be used for identification. If the groundwater has low dissolved oxygen and organic carbon is available to support microbial reactions, denitrification may be taking place and the  $\delta^{15}N$  will be increased. Under these conditions, false identification of the actual nitrate source can result. Therefore, use of the  $\delta^{15}N$  value alone as a method for nitrate source identification is not recommended.  $\delta^{15}N$  can be used in conjunction with an evaluation of the nitrate plume and redox conditions in the aquifer in order to evaluate whether denitrification is taking place.

### 4.4.2. Source Type Evaluation

As stated above, twelve groundwater samples from study wells were analyzed for stable nitrogen isotopes. The samples were analyzed by Isotech Laboratories, Inc. of Champaign, Illinois. The  $\delta^{15}N$  results ranged from -5.2 to 5.4 per mil. All  $\delta^{15}N$  results have a 95% confidence interval of  $\pm 0.34$  per mil. The results are presented in the Table 1.

Taking into account the 95% confidence interval for the  $\delta^{15}$ N results, five samples (wells 20, 34, 37, 42, and 63) are statistically less than 2.0 per mil and therefore were from wells where the nitrate in the groundwater originated from commercial fertilizers. Three additional samples were within the 95% confidence interval of 2.0 per mil (wells 2, 9, and 16). These wells should be considered as possibly being impacted by commercial fertilizers. The results from the remaining four samples were between 4 and 6 per mil. In this range, a specific nitrate source type cannot be identified. P:\23\82\366\Nitrate Study Report\nitrate report sep 2003 draft.doc25

It should be noted that no  $\delta^{15}$ N results were in excess of 10 per mil thus eliminating septic tanks, manure holding ponds, and sewage lagoons as potential sources of groundwater nitrate contamination.

#### 4.4.2.1 Nitrate in the Prairie du Chien Group

Five groundwater samples that were analyzed for  $\delta^{15}$ N were collected from wells in the Prairie du Chien Group (i.e., wells 2, 3, 9, 17, and 20). As presented above, samples from three wells (i.e., wells 2, 3, and 20) are in an area where the Prairie du Chien Group is the uppermost bedrock and thus very susceptible to nitrate contamination from land use via surface infiltration. The sample from well 20 had a  $\delta^{15}$ N of –2.0 per mil. This clearly shows that the nitrate contamination in the groundwater in the vicinity of well 20 is impacted by commercial fertilizers. As presented above, the groundwater flow model suggests that infiltration zones for wells screened in the Prairie du Chien Group are relatively close to the wells (i.e., within a mile). Therefore, agricultural land use in the vicinity of well 20 is likely the source of the nitrate contamination at this well.

The groundwater sample from well 2 had a  $\delta^{15}$ N result of 1.7 per mil. The result is within the 95% confidence limit of 2 per mil. Therefore, the nitrate in the groundwater at well 2 cannot be definitively linked to commercial fertilizers. Based on the infiltration zone for well 2 (Figure 2), the fact that the Prairie du Chien Group is the uppermost bedrock, and the land use within the infiltration zone (i.e., agricultural), the  $\delta^{15}$ N result does not preclude commercial fertilizer as the nitrate source. Under the circumstances, commercial fertilizers are a likely suspect as the nitrate source for groundwater in the vicinity of well 2.

The groundwater sample from well 9 had a  $\delta^{15}$ N of 2.0 per mil. As discussed above, this value does not definitively identify the nitrate source as commercial fertilizer, though commercial fertilizer is a likely suspect. The Prairie du Chien Group is not the uppermost bedrock in the area of well 9 but the groundwater modeling showed that the infiltration zone for this well likely intersects the buried bedrock valley and the fault zone. Therefore, it appears that the likely source of the nitrate in the groundwater at well 9 is infiltration in the bedrock valley of stormwater run-off as discussed above, and preferential groundwater flow along the fault zone toward the Mississippi River. The  $\delta^{15}$ N results support this hypothesis of stormwater run-off from agricultural land leading to the infiltration of nitrates to the groundwater.

The groundwater sample from well 17 had a  $\delta^{15}$ N of 4.5 per mil. This result does not identify any particular source of the nitrate. The groundwater flow modeling showed that the infiltration zone for P:\23\82\366\Nitrate Study Report\nitrate report sep 2003 draft.doc?6

well 17 is in an area east of the well where the Prairie du Chien Group is the uppermost bedrock and that well 17 does not appear to be directly impacted by infiltration in the bedrock valley.

The groundwater sample from well 3 had a  $\delta^{15}$ N of 4.2 per mil. This result does not identify any particular source of the nitrate. The well is located on the eastern edge of the bedrock valley. The groundwater flow modeling predicts that the infiltration zone intersects the bedrock valley. Therefore, well 3 is likely impacted by infiltration of stormwater run-off in the bedrock valley.

#### 4.4.2.2 Nitrate in the Jordan Sandstone

Seven of the groundwater samples analyzed for stable nitrogen isotopes were collected in wells completed in the Jordan Sandstone (i.e. wells 13, 16, 34, 37, 42, 51, and 63). Four of the samples analyzed had  $\delta^{15}$ N less than 1.7 per mil (i.e., 2.0 per mil – 95% confidence interval), clearly indicating that the source of the nitrate in these samples is commercial fertilizers. These samples were collected from wells 34, 37, 42, and 63. Groundwater flow modeling showed that the infiltration zones for all of these wells intersected the bedrock valley and the fault zone. As discussed above, the bedrock valley is a likely source of infiltration of stormwater run-off from agricultural land. These results support the hypothesis that commercial fertilizers are collected in ponds and wetlands above the bedrock valley and then infiltrate to the Jordan Sandstone along the fault zone, leading to groundwater nitrate contamination in this hydrostratigraphic unit.

The groundwater sample from well 16 has a  $\delta^{15}$ N of 1.8 per mil. This result is within the 95% confidence interval of the top of the range indicating commercial fertilizer. The source of the nitrate in samples collected from well 16 cannot be definitively identified but commercial fertilizer is a potential source. Groundwater flow modeling also predicts that the infiltration zone for well 16 likely intersects the buried bedrock valley and the fault zone. Therefore, well 16 is likely impacted by infiltration in the buried bedrock valley.

The groundwater sample from well 51 had a  $\delta^{15}$ N of 4.5 per mil. This result is greater than 2.0 per mil so no source can be identified using stable nitrogen isotopes. Groundwater flow modeling predicts that the infiltration zone for well 15 intersects the buried bedrock valley. The groundwater at well 51 is likely impacted by the infiltration in the bedrock valley even though the stable nitrogen isotope data does not directly indicate commercial fertilizers. As mentioned above, denitrification (i.e., biological conversion of nitrate to nitrogen gas) will cause the  $\delta^{15}$ N value for nitrate in groundwater to increase. Geochemistry results within the south-central Jordan Sandstone nitrate plume show aerobic conditions that do not support denitrification in the aquifer. If surface water infiltration in the buried bedrock valley occurs in ponds and/or wetlands, sediments could provide the necessary conditions for denitrification leading to higher  $\delta^{15}N$  values measured in the groundwater.

The groundwater sample from well 13 had a  $\delta^{15}$ N of 5.4 per mil. No definitive identification of the nitrate source can be made based on this result. Well 13 is located on the eastern edge of the bedrock valley. Therefore, well 13 may be impacted by infiltration from the bedrock or from areas east of the bedrock valley where the Prairie du Chien Group is the uppermost bedrock.

# **5.0 Conclusions and Management Recommendations**

# 5.1 Conclusions

Based on the results of this study, the following are concluded regarding the presence of nitrate in groundwater in the Cottage Grove area of Washington County:

- <u>Nitrate in the Prairie du Chien Group appears to correlate with agricultural land use in areas</u> <u>sampled where the Prairie du Chien Group is the uppermost bedrock</u>. Limited stable nitrogen isotope analysis supports that some of the nitrate in the Prairie du Chien Group originated from commercial fertilizers. Based on this evaluation, the groundwater in the uppermost bedrock appears to be highly susceptible to nitrate contamination where it underlies agricultural land.
- Higher concentrations of nitrate were also detected in the area just west of East Cottage Grove where ponds and wetlands on top of the bedrock valley are fed by run-off from agricultural land. Infiltration of stormwater run-off into the bedrock valley appears to be another likely route for nitrate contamination of the Prairie du Chien Group with fault zones contributing to preferential flow.
- 3. <u>The nitrate present in groundwater in the Jordan Sandstone appears to correlate with the a northeast-trending fault zone</u>. The Jordan Sandstone is the uppermost bedrock unit along the axis of the buried bedrock valley. More importantly, however, the fault zone provides a mechanism for "young" groundwater entering the Prairie du Chien Group to migrate vertically into the Jordan Sandstone. Therefore, the Jordan Sandstone is susceptible to nitrate contaminated water that infiltrates through the unconsolidated material of the bedrock valley and through fault zones. Stable nitrogen isotope analysis supports the hypothesis that some of the nitrate in the Jordan Sandstone originated as commercial fertilizer.
- 4. <u>The Prairie du Chien is the uppermost bedrock across the southeastern portion of the study area and the topography promotes flow of surface water run-off to the St. Croix and Mississippi Rivers</u>. The groundwater in the Jordan Sandstone in the southeastern portion of the study area was found to be low in nitrate. Therefore, in this area the Jordan Sandstone

appears to be protected from the nitrate contamination even though the land use across this entire southeastern area is agricultural.

It should be noted that the groundwater in the Jordan in the vicinity of well 71 and downgradient to the St. Croix River is impacted by nitrate. The source of this nitrate is not known though the limited data in this area suggests that the nitrate source is in the vicinity of well 71 and is localized.

The most significant finding of this study is that the fault zones appear to act as higher zones of hydraulic conductivity in which groundwater containing nitrate can migrate relatively quickly from the ground surface, down into the Jordan Sandstone, and downgradient along the fault zone toward discharge at the Mississippi River. Identifying fault zones may be key to understanding the susceptibility of the Jordan Sandstone (and other units) to nitrate contamination in other parts of Washington County and elsewhere.

The transition from mostly agricultural to mostly single -family residential land use over the next 20 years may result in a reduction in nitrate concentrations, as nitrate from fertilizer use is reduced in the area and drainage over the buried bedrock valley becomes somewhat more controlled.

### 5.2 Recommendations and Management Strategies

Based on the conclusion of this study the following additional actions are recommended.

- 1. Analyze water from ponds and wetlands along the trend of the buried bedrock valley for nitrate. Also, sample water infiltrating in the buried bedrock valley in the area of the ponds and wetlands and analyze for nitrate. These additional analyses may aid in the evaluation of infiltration over the bedrock valley as a major nitrate source. Verification of the role of infiltration over the bedrock valley on groundwater nitrate contamination would allow the evaluation of surface-water management and passive surface-water treatment options for reducing of the nitrate load to the Prairie du Chien-Jordan aquifer.
- 2. Analyze the groundwater from the Prairie du Chien Group and the Jordan Sandstone in the vicinity of well 71 for additional chemical parameters and stable nitrogen isotopes. These additional analyses may aid in determining the source of contamination in the eastern region of the study area that cannot be explained using the current conceptual model for nitrate contamination in the study area (i.e., infiltration of nitrate contaminated water to the uppermost bedrock).

- 3. Re-evaluate the stratigraphic -structural conditions in other parts of the County. This study strongly suggests that the faulting can have a significant influence on the vertical and lateral migration of nitrate-containing groundwater. Deeper aquifer units that typically would be considered to be of low vulnerability may become contaminated because of rapid downward migration through fault zones. Faulting does not seem to be prevalent in the southwestern part of the County but it dominates the geology in the southeastern part. Areas northeast of this study area likely also contain faulting features that could contribute to rapid movement of surface contaminants down into deeper units.
- 4. At some point the County should seek an opportunity to conduct aquifer (pumping) tests near a known fault area in order to verify the hydraulic conditions in the faults and to better understand how pumping might draw water from the fault zones into wells.
- 5. Evaluate farming practices across the study area to determine if a correlation exists between farming practices (e.g., form of nitrogen applied or application rate) and the lower nitrate concentrations in the Jordan Sandstone in the southeastern region of the study area.

It seems prudent to consider the presence of the western fault zone, along which the nitrate contamination in the Jordan Sandstone appears to follow, in future well siting. This study did not attempt to determine how close to the fault zones a typical municipal well would need to be before groundwater would be drawn from the fault into the well. However, based on the particle tracking for the existing wells, a map was developed that provides some general guidelines on future siting of high-capacity wells (Figure 19). This management map should be used as a general guideline with the understanding that local conditions may be better or worse (in terms of potential nitrate contamination) for a future well. Site-specific assessments should always be done that take into account pumping rates of the wells.

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**Tables** 

## (concentrations in mg/L, unless noted otherwise)

Location	104137	104137	104208	104289	104297	106258	107308	110401	112269	121063	122028	123530	133461	13346IT	133499	145823
Site ID number	77	77	6	68	1	ո	2	42	3	4	4	48	16	16	9	5
Danie	11/19/2002	11/19/2002	11/13/2002	1141/2002	11/3/2002	11/4/2002	11/4/2002	11/13/2002	11/3/2002	11/19/2002	11/3/2002	11/8/2002	11/4/2002	11/4/2002	11/8/2002	10/28/2002
Ոս																
Chemical Oxygen Demand	<50		-	<30	-	-		-	-	-	-		-	-	-	-
Dischel wygen	0.56		1.59	0.82	10.24	9.78	9.07	6.43	10.18	1.11	9.04	10.20	8.62	-	6.89	8.21
Ninogen Boiope N15, per mil	-		-	-	-	-	1.7	-13	42	-	-		18	-	45	-
Nimogen Niirate	<0.05	<0.02	56	<0.05	17	92	ឋ	14	87	10	11	86	20	В	ឋ	22
Ninogen Nitrate (field)	12		3.8	20	10.00	43	80	6.6	11.7	3.8	57	63	105	-	11.1	150
Sullfate	20		-	28	-	-		-	-	-	-		-	-	-	-
Sulfide total	<0.10		<b>`</b> -	⊲0.10	-	–		-	-	-	-		–	-	-	-
pH, standard units	822		699	-	723	7.18	6.73	7.59	670	7.67	690	7.16h	6.84	-	7.09h	6.46
Redox (oxidation potential), mV	-943		-	-119	339.8	230.4	281.0	299.7	365.0	139.7	434.2	2039	2459	-	2982	268.1
Speaific Canduatance umhos@ 25oC	417		–	4D	616	524	655	670	877	576	918	രി	690	-	659	720
Temperature, degrees C	91		98	10.0	10.7	123	10.7	12.1	103	12.7	11.1	98	98	-	125	11.8
hun, Ferrus, FE II	093		<0.03	1.17	<0.03	0.06	<0.03	<0.03	004	0.40	0S	0.08	0.15	-	0.04	003

 Not analyzed
EPA sample extraction or analysis holding time was exceeded.

## (concentrations in mg/L, unless noted otherwise)

Location	162915	162946	170795	179806	185257	185279	185753	185780	185997	186338	194068	194154	2464	402556	406236	412480
Site ID number	78	75	50	79	76	7	17	n	-40	в	64	19	20	23	25	14
Danie	12.6/2002	11/8/2002	11/11/2002	1143/2002	11/19/2002	11/11/2002	11/3/2002	11/19/2002	1141/2002	11/19/2002	11.8/2002	11/11/2002	11.8/2002	11/8/2002	10/28/2002	11/19/2002
Ու																
Chemical Oxygen Demand	-		-	-	-	-		-	-	-	<30		-	-	-	-
Dissolved oy gen	8.88	927	5.58	999	8.66	999	1098	1.03	831	721	0.13	5.43	7.41	10.87	5.62	10.37
Ninogen Koiope N15, per mil	-		-	-	-	-	45	-	-	5.4	-	-13	-2.0	-	-	-
Nintrogen Nitrate	90	0.52	1.7	20	8.7	Б	56	0.82	51	5.1	⊴0.05	85	12	89	12	95
Ninogen Nitrate (field)	35	12	5.1	28	29	46	53	32	59	4.7	07	7.4	95	10.0	3.0	56
Sulfate	-		-	-	-	-		-	-	-	24		-	-	-	-
Sullidetotal	-		-	-	-	-		-	-	-	⊲0.10		-	-	-	-
pH, standard units	7.16		7.70 h	837	8.01	7.46h	6.80	7.68	7 <i>5</i> 7h	7.70	-	730h	694h	7.26h	732	7.89
Redox (oxidation potential), mV	252.2	345.4	147.1	337.1	165.1	138.7	3195	1135	1395	75.6	13	1319	137	233.0	270.2	1239
Specific Canduatance umhos@ 25oC	620	313	368	490	<b>56</b> 3	720	854	446	<b>4</b> 33	454	412	745	912	580	704	556
Temperature, degrees C	94	105	115	97	105	10.0	10.0	96	10.7	92	10.1	10.7	99	109	14.4	10.2
Inn, Ferrus, FE II	0.08	<0.03	0.04	⊲0.03	<0.03	<0.03	<0.03	0.03	⊲0.03	0.05	12	<0.03	0.04	⊲0.03	<0.03	0.03

Not malyzed
h EPA sample extraction or malysis holding time was exceeded.

## (concentrations in mg/L, unless noted otherwise)

Location	426921	42 <i>6</i> 921T	426924	426965	427043	427053	435099	447211	471485	480313	481262	506666	511729	526317	544354	544434
Site ID rumber	53	53	52	43	9	67	71	4	45	3	31	34	22	37	74	69
Dade	11/4/2002	11/4/2002	11/4/2002	11432002	11/3/2002	11.8/2002	11/8/2002	11.8/2002	11/8/2002	11/11/2002	11/13/2002	11/4/2002	12.6/2002	1028/2002	11/11/2002	11/13/2002
Ոպ																
Chemical Oxygen Demand	-		-	-	-	-		-	-	-	-		-	-	-	<5.0
Nischel oygen	10.68		9.72	898	4.77	0.75	8.18	7.60	646	821	4.45	537	2.66	679	10.10	0.16
Ninogen Koiope N15, per mil	-		-	-	20	-		-	-	-	-	-52	-	13	-	-
Ninogen Ninate	В	14	ឋ	61	63	0.17	12	В	81	49	82	19	58	Б	3.4	038
Ninogen Nitrate (field)	113		102	65	62	16	79	93	80	38	82	3.1	45	45	3.6	14
Sullfate	-		-	-	-	-		-	-	-	-		-	-	-	25
Sulfide total	-		-	-	-	-		-	-	-	-		-	-	-	⊲0.10
pH, standard units	6.52		7.15	7.42	7.61	-		7.16 h	721h	-	723	732	755	732	-	7.63
Redox (oxidation potential), mV	2359		214.8	273.6	347.0	108.1	264.5	266.6	2725	1793	349.2	2323	205.2	271.1	1219	18
Specific Conductance umhos@ 25oC	611		722	602	554	431	476	626	24	486	611	437	545	62	440	487
Temperature, degrees C	103		118	10.8	10.6	96	139	B6	119	11.0	95	9.1	128	113	123	11.7
Inn, Fermus, FE II	0.06		<0.03	⊲0.03	<0.03	0.06	0.04	<0.03	⊲0.03	<0.03	<b>0</b> ß	<0.03	0.20	009	<0.03	036

Notanalyzed.
h EPA sample extraction or analysis holding time was exceeded.

## (concentrations in mg/L, unless noted otherwise)

Location	561807	564098	577046	582011	CG1	CG-10	CG-2	CG3	CG-4	CG5	CG6	CG-7	CG8	CG-9
Site ID roumber	35	38	36	46	55	18	56	57	58	59	60	a	62	6
Date	10/29/2002	11.8/2002	1149/2002	11/11/2002	12.6/2002	12/6/2002	12.6/2002	12/6/2002	126/2002	12.6/2002	12/6/2002	12.6/2002	12/6/2002	126/2002
Ոպր														
Chemical Oxygen Demand	<5.0	-	<0	-	-	<50	-	<5.0	-	-		-	-	-
Dissolved oxygen	033	832	0.55	10.27	220	0.17	122	038	5.60	223	4.65	5.20	218	5.15
Nitrogen Isotope N15, permil		-	-	-	-		-	-	-	-		-	-	05
Nitrogen Nitrade	0.05	38	⊴0.05	89	0 <i>5</i> 1	<0.05	10	⊴0.05	0.15	⊴0.05	0.65	2.4	13	20
Nitrogen Nitrate (field)	09	65	08	52	16	0.6	10	00	0.01	10	2.6	28	12	4.7
Suitfate	21	-	11	-	-	46	-	46	-	-		-	-	-
Suifile total	<0.10	–	⊲0.10	-	–	<0.10	-	<0.10	–	-		-	-	-
pH, standard units	7.46	725h	8.17	7.49h	7.09	7.02	722	733	7.45	751	6.70	7.47	722	722
Redox (milation potential), mV	-37.7	251.2	1205	168.6	1123	29.4	1169	812	2043	180.6	210.4	201.1	230.7	2163
Specific Canductance umhos@ 25oC	471	416	440	545	600	516	576	250	575	636	587	556	ഖ	578
Temperature degrees C	115	150	19.4	10.0	10.0	92	10.0	9.4	12.1	12.4	8.0	93	9.7	103
Iran, Ferrous, FEII	0.09	<0.03	⊴0.03	0.05	<0.03	0.72	<0.03	<b>⊲</b> 0.03	<0.03	<b>⊲</b> 03	023	0.05	003	<0.03

Not analyzed.
EPAs ample extraction or analysis

holdingtine was exceeded.

## Table 2 Cottage Grove Nitrate Study Field Duplicate Results

## (concentrations in mg/L)

Location	104137	104137	RPD	162915	162915	RPD	185257	185257	RPD
Date	11/19/2002	11/19/2002	2/19/2003	12/6/2002	12/6/2002	2/19/2003	11/19/2002	11/19/2002	2/19/2003
Dup		DUP			DUP			DUP	
Nitrogen Nitrale	⊲0.05	⊲0.05		9.0	9.0	0	8.7	88	1.1
Nitrogen Nitrate (field)	-	–		3.5	<b> _</b>		29	_	

Location	194154	194154	RPD	412480	412480	RPD	48 126 2	48 126 2	RPD
Date	11/11/2002	11/11/2002	2/19/2003	11/19/2002	11/19/2002	2/19/2003	11/13/2002	11/13/2002	2/19/2003
Dup		DUP			DUP			DUP	
Nitrogen Nitrate	85	86	12	9.5	9.4	1.1	82	79	3.7
Nitrogen Nitrate (field)	7.4	_		5.6	_		82	—	

Location	CG-10	CG-10	RPD	CG-7	CG-7	RPD	CG-8	CG-8	RPD
Date	12/6/2002	12/6/2002	2/19/2003	12/6/2002	12/6/2002	2/19/2003	12/6/2002	12/6/2002	2/19/2003
Dup		DUP			DUP			DUP	
Nitrogen Nitrate	⊲0.05	⊲0.05		2.4	2.3	4.3	13	13	0
Nitrogen Nitrate (field)	0.6	-		2.8	-		12	–	

## Table 3 Cottage Grove Nitrate Study Laboratory-Split Sample Results

## (concentrations in mg/L)

Location Date Lob	104137 11/19/2002 MDH	104137 11/19/2002 BR AUN	RPD 2/19/2003	162915 12/6/2002 MDH	162915 12/6/2002 BR AUN	RPD 2/19/2003	185257 11/19/2002 MDH	185257 11/19/2002 BR AUN	RPD 2/19/2003
Dup	1911211	DIGOIN			DIVIDIO			DIGAUIT	
Nitrozen Nitrate	<0.05	<0.02		9.0	92	2.2	8.7	90	3.4

Location	402556	402556	RPD	412480	412480	RPD	48 1262	48 1262	RPD
Date	11/8/2002	11/8/2002	2/19/2003	11/19/2002	11/19/2002	2/19/2003	11/13/2002	11/13/2002	2/19/2003
Lab	MDH	BRAUN		MDH	BRAUN		MDH	BRAUN	
Dup									
Nitrogen Nitrate	89	9.1	22	9.5	10	5.1	82	86	48

Location	CG-10	CG-10	RPD	CG-7	CG-7	RPD	CG-8	CG-8	RPD
Date	12/6/2002	12/6/2002	2/19/2003	12/6/2002	12/6/2002	2/19/2003	12/6/2002	12/6/2002	2/19/2003
Lab	MDH	BRAUN		MDH	BRAUN		MDH	BRAUN	
Dup									
Nitrogen Nitrate	<0.05	<0.02		2.4	22	8.7	13	1.1	17

Figures







Fault Traces (from MGS)



Figure 2

LOCATION OF FAULT TRACES AND ELEVATION OF FAULT BLOCKS (AFTER MOSSLER, 2003) Cottage Grove Area Nitrate Study Cottage Grove, MN







Indicates Relative Movement Along Fault

NOTES: 1. Fault Locations Provided by Minnesota Geological Survey 2. Fault Orientations are Assumed to be Vertical or Nearly So 3. Well Logs Obtained from Minnesota Geological Survey's County Well Index





1	ST		
		1000	
		900	
		800	
		700	
		600	Ē

— 500

— 400











Cottage Grove, MN



, cdp, Fri Oct 03 15:53:16 2003 Barr: Arcview 3.1, OPT2643, I:\Projects\2382\366\Gis\Project\nitrate\_modeling.apr, Layout: skf-jordan recharge -fuure landuse.

2000 Meters 1000 0 1000

Cottage Grove Area Nitrate Study Cottage Grove, MN











Figure 13

SIMULATED GROUNDWATER FLOW TRACES WITH FAULTS SIMULATED AS LOW CONDUCTIVITY ZONES Cottage Grove Area Nitrate Study Cottage Grove, MN



- with MPCA data and BEDROCK, cdp, Fri Oct 03 16:07:21 2003 Barr. Arcview 3.1, OPT2643, I:/Projects/23/82/366/Modeling/updated\_project.apr, Layout: skf-cpdc nitrate -









Barr: Arcview 3.1,OPT2643, I:\Projects\23.82\366\Modeling\updated\_project.apr, Layout: Map of Guidelines, cdp, Fri Oct 03 15:58:38 2003



Favorable: areas with (1) low nitrate, (2) absence of faulting, and (3) denitrifying conditions



Figure 19

MAP OF FAVORABLE AREAS FOR HIGH CAPACITY WELLS IN THE JORDAN SANDSTONE Cottage Grove Area Nitrate Study Cottage Grove, MN

Appendix C

# Groundwater Flow Model Development and Calibration Cottage Grove Area Nitrate Study

Groundwater flow modeling for the Cottage Grove Area Nitrate Study was performed using the three-dimensional, finite-difference groundwater flow model, MODFLOW (McDonald and Harbaugh, 1984). Development of the model is described below.

# **Original Base Model**

The MODFLOW model used in this study was based on a previous model, the Scott-Dakota Counties Groundwater Flow Model (Barr, 1999), prepared for the Minnesota Department of Health. Although that model focused on Scott and Dakota Counties it also simulated flow in Washington and Ramsey Counties and portions of Hennepin and Anoka Counties. The Scott-Dakota Counties model used four layers to simulate the Upper Glacial Drift Aquifer, the Lower Glacial Drift and St. Peter Sandstone aquifer, the Prairie du Chien Group aquifer and the Jordan Sandstone aquifer. The model was developed using the Department of Defense's Groundwater Modeling System (GMS) Version 3.0-beta (BYU, 1996).

## **Model Modifications**

Modifications were made to the Scott-Dakota Counties Groundwater Flow Model so that it would be better suited for the modeling objectives of the Cottage Grove Area Nitrate Study. The following modifications were made:

- The Scott-Dakota Counties model was imported into Groundwater Vistas (GWV) Version 3.25 (Rumbaugh and Rumbaugh, 2001). This was done because it was determined that GWV was better suited for the type of work that was to be completed as part of this study. GWV is more versatile than GMS in terms of getting data into and out of the model. This versatility allows GWV to be used in conjunction with other applications such as Surfer (Golden Software, Inc., 2002) and ArcView (ESRI, 1998). The ability to interface with other applications was important for the Cottage Grove Area Nitrate Study.
- 2. A telescopic mesh refinement (TMR) was performed to focus the model on the area bounded by the Mississippi River on the west and the St. Croix River on the

east. This allowed for model grid refinement (compared to the original Scott-Dakota Counties model) in the Cottage Grove area. It was assumed that the Mississippi and St. Croix Rivers form hydraulic boundaries. The new model area has a uniform grid spacing of 271 m in the x-direction (NW-SE) and 311 m in the y-direction (NE-SW). Figure 1 shows the model area before and after the TMR was performed.

- 3. Model layer elevations in the area of interest (i.e., southern Washington County) were updated to better reflect changes in the bedrock topography. The original Scott-Dakota Counties model used a series of polygons to define the layer elevations, which resulted in a stair-step effect for the layer boundaries. The new model needed more precise layer elevations in order for particle tracking to realistically simulate groundwater flow paths. This was of particular importance in the area of the buried bedrock valley that runs south through the southern part of Washington County. Figure 2 shows the bottom elevations in Layer 1 for both the Scott-Dakota Counties model and the Cottage Grove Area Nitrate Study model. Bedrock surfaces were defined using the Minnesota Geological Survey's ArcView coverages of bedrock topography for the Seven County Metro Area (Mossler and Tipping, 2000).
- 4. Hydraulic conductivity zones in the area of interest were redefined in order to better match the local scale geology as depicted in the Minnesota Geological Survey's ArcView coverage of bedrock geology for the seven county metro area (Mossler and Tipping, 2000). Figures 3-6 show the hydraulic conductivity zones in the Scott-Dakota Counties model and the Cottage Grove Area Nitrate Study model for each layer. Figure 7 shows the hydraulic conductivity zones in Layers 5 and 6 of the Cottage Grove Area Nitrate Study model. As described below, Layers 5 and 6 were added to the TMR.
- Constant head and river cells used to simulate surface water features were updated to reflect more precise locations and water levels based on the Minnesota Department of Natural Resources' (DNR) lake and stream shapefiles

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(<u>http://deli.dnr.state.mn.us/</u>) and U.S. Geological Survey 7.5 minute topographic maps.

- 6. Two new model layers were added to simulate the St. Lawrence Formation aquitard and the combined Franconia Formation-Ironton Sandstone-Galesville Sandstone aquifer. These layers were given constant thicknesses consistent with the values reported in the MPCA Metropolitan Groundwater Model Information Data Base (http://www.pca.state.mn.us/water/groundwater/huc/index.html).
- Pumping rates for wells in the area of interest (southern Washington County) were updated using the most recent data reported in the SWUDs database (http://files.dnr.state.mn.us/waters/watermgmt\_section/appropriations/idxloc.pdf).

# Model Calibration

# Calibration Approach and Parameters

The MODFLOW model was calibrated to observed groundwater levels (heads) through a trial-and-error process in which aquifer parameters were manually varied until there was an acceptable match between observed heads and simulated heads. Because the Cottage Grove Area Nitrate Study model is a modified version of a previously calibrated model, a rigorous automated calibration was not considered necessary.

Horizontal and vertical hydraulic conductivity for each of the model layers was varied during calibration. In addition, recharge zone boundaries were modified slightly in order to prevent the mounding of water in eastern Washington County.

The head calibration dataset used in the Scott-Dakota Counties model calibration was used to calibrate Layers 1-4 of this model. This dataset was originally provided by the MPCA Metro Model group

(http://www.pca.state.mn.us/water/groundwater/metromodel.html#filesmaps) and was derived from the Minnesota Geological Survey's County Well Index (CWI) in a process that removed outlying targets (see ftp://files.pca.state.mn.us/pub/water/mm/readme1.txt). All targets located within the model area were used for this calibration; however, some targets completed in the unconsolidated aquifer were modified so that they would be in the correct model layer. This resulted in a total of 150, 709, 548, and 127 head targets in Layers 1, 2, 3, and 4 respectively. In order to constrain the aquifer parameters in Layers 5 and 6, additional water level data from the CWI were used as calibration targets in these layers (<u>http://www.geo.umn.edu/mgs/cwi.html</u>). A total of 13 head measurements in Layer 5 and 26 head measurements in Layer 6 were used. These targets are considered less reliable because they have not been screened to remove outliers. Figure 8 shows the locations of all head targets used during calibration.

## Calibration Requirements and Calibration Results

No formal calibration requirements were stipulated for the Cottage Grove Area Nitrate Study model. However, it is helpful to have some way to measure the model's goodness of fit to measured heads. A commonly used calibration requirement is that the root mean squared error (RMSE) of 90% of the head calibration points fall within 15% of the total head change for each layer (e.g. Barr, 1999). The RMSE differs for each model layer because the total head change across the model domain differs from layer to layer. Because there are so few calibration targets in Layers 5 and 6, and those targets that are present are less reliable than the other head targets because they have not been screened for outliers, only Layers 1-4 were examined using this calibration approach. The target RMSE value that must be attained under this approach for each of the four model layers is shown in Table 1.

Model Layer	Maximum Head	Minimum Head	Total Head Change Obs.	15% of Head Change
1	291.1	246.3	44.8	6.7
2	294.7	202.7	92.0	13.8
3	294.1	203.9	90.2	13.5
4	287.4	196.0	91.4	13.7

**Table 1**. Target RMSE values shown as "15% Head Change" for each model layer. Maximum and minimum observed heads and the total head change observed in the calibration dataset for each layer are also shown. All values are in meters.

Table 2 shows calibration statistics for the final Cottage Grove Area Nitrate study model and compares them to the statistics for the Scott-Dakota Counties model in the current study area. The Cottage Grove Area Nitrate Study model well exceeds the calibration criteria, particularity in Layers 2-4 where the majority of targets are located. The new model is also an improvement over the original Scott-Dakota Counties model. The residual mean for all calibration target locations was –1.1 meters and the absolute residual mean was 5.4 meters. Figure 9 shows a plot of residuals (observed head minus simulated head) versus observed heads for each of the model layers.

except where otherwise noted.							
			Cottage Grove Area Nitrate Study Model				
	15 % of	SDC Model		% of Observations			
Model	Observed	RMSE of	RMSE of	whose RMSE			
Layer	Head Change	90% targets	90 % targets	was ≤ Target RMSE			
1	6.7	5.9	5.2	96.6%			
2	13.8	6.1	4.1	100%			
3	13.5	10.5	4.8	100%			
4	13.7	9.7	5.5	100%			

**Table 2.** Calibration results for the Cottage Grove Area Nitrate Study model and the Scott-Dakota Counties (SDC) model. Calibration results were calculated using the same set of targets for both models. Values are in meters except where otherwise noted.

Figure 10 shows the spatial distribution of head residuals. For most of the model area, there does not seem to be a bias in residuals. In southern Washington County, there does seem to be a slight positive bias with observed heads tending to be larger than simulated heads. Because these targets are in the vicinity of the Cottage Grove municipal wells, it is possible that the targets are not representative of heads under the current pumping conditions, but reflect the heads at a time when there was less pumping. There is also a positive bias in western Ramsey County. However, since this area is far from the area of interest, it was not a focus of model calibration.

## Model Recalibration

Data collected during the final round of well sampling indicated that the model was underestimating water levels in the southwest portion of the county. It was believed that these low heads might affect the delineation of recharge areas. In order to fix this potential problem, recharge in the model was redistributed so that there was a zone of higher recharge in the southern portion of the county. This improved heads in the study area without adversely affecting model calibration. In addition, it was determined that the bottom elevation of model layer 4 was too high in this same area. Elevations were lowered to better match data from the CWI database. The resulting calibration statistics are shown below.

Model Layer	Old RMSE of 90 % targets	New RMSE of 90 % targets	% of Observations whose RMSE was ≤ Target RMSE
1	5.2	5.1	95.3%
2	4.1	4.1	100%
3	4.8	4.5	100%
4	5.5	5.5	100%

## References

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**Figure 1.** Areas modeled by the Scott-Dakota Counties model and the new model used in the Cottage Grove Area Nitrate Study.




1 0 1 2 3 4 Miles





**Figure 3.** Layer 1 hydraulic conductivity zones in the Scott-Dakota Counties model (A) and the Cottage Grove Area Nitrate Study model (B).



**Figure 4.** Layer 2 hydraulic conductivity zones in the Scott-Dakota Counties model (A) and the Cottage Grove Area Nitrate Study model (B).







**Figure 6.** Layer 4 hydraulic conductivity zones in the Scott-Dakota Counties model (A) and the Cottage Grove Area Nitrate Study model (B).



Figure 7. Hydraulic conductivity zones in Layers 5 (A) and 6 (B) of the Cottage Grove Area Nitrate Study model.



**Figure 8.** Location of head targets used during model calibration. Targets are colored based on the layer that they are in.







**Figure 9.** Plots of observed heads verses residuals for Layers 1-3 of the Cottage Grove Area Nitrate Study model. Target RMSE values are shown by the red lines.







**Figure 9.** Plots of observed heads verses residuals for Layers 4-6 of the Cottage Grove Area Nitrate Study model. Target RMSE values are shown by the red lines.



Figure 10a. Head residuals in Layer 1. A positive residual indicates an observed head that is larger than the simulated head.



Figure 10b. Head residuals in Layer 2. A positive residual indicates an observed head that is larger than the simulated head.



Figure 10c. Head residuals in Layer 3. A positive residual indicates an observed head that is larger than the simulated head.



Figure 10d. Head residuals in Layer 4. A positive residual indicates an observed head that is larger than the simulated head.



Figure 10e. Head residuals in Layers 5 and 6. A positive residual indicates an observed head that is larger than the simulated head.