



# Water Quality in the Upper Fifteen Feet of a Shallow Sand Aquifer

IN A VARIABLE LAND USE SETTING

ST. CLOUD AREA, MINNESOTA



Minnesota Pollution Control Agency

# **Water Quality in the Upper Fifteen Feet of a Shallow Sand Aquifer in a Variable Land Use Setting**

**December, 1998**

## **Published by**

Minnesota Pollution Control Agency  
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Environmental Monitoring and Analysis  
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### **Executive Summary**

In fall, 1996, the Minnesota Pollution Control Agency (MPCA) Ground Water Monitoring and Assessment Program (GWMAP) began a study of the effects of land use on ground water quality near St. Cloud. St. Cloud is a metropolitan area of approximately 100000 in east-central Minnesota and is undergoing rapid urbanization, accompanied by gradual shifts in agriculture. A shallow sand and gravel aquifer underlies the study area. Results for 1997 from a monitoring network consisting of 46 surface and ground water sampling points suggests ground water quality is strongly affected by land use.

To enhance information gathered from the monitoring network, a geoprobe study was conducted in spring, 1998. Potential sampling locations, spaced at one mile intervals, were identified using GIS coverages for land use and ground water flow. Sites were chosen if the land use was consistent 1000 feet in the up-gradient direction of ground water flow and if the site could be accessed. Thirty-seven sampling points were selected in eight land uses : nonirrigated corn, soybeans, and alfalfa; irrigated agriculture; sewered and unsewered residential development; commercial/industrial; and undeveloped land. At each sampling point, a geoprobe was advanced to the water table and a sample collected at the top of the aquifer. At 13 and 10 sites, respectively, samples were also collected at 7.5 and 15 feet below the water table. Sample parameters included major cations and anions, some trace inorganics, dissolved and total organic carbon, ammonia-nitrogen, total Kjeldahl nitrogen, volatile organic compounds (VOCs) in urban areas, pesticides in agricultural areas, and field parameters (pH, temperature, specific conductance, oxidation-reduction potential, alkalinity, dissolved oxygen, chloride, sulfate, dissolved iron, and nitrate-nitrogen).

Concentrations of many inorganic chemicals were greater under all land uses compared to undeveloped land. Nitrate concentrations were greatest and exceeded the drinking criteria of 10000 ug/L under all agricultural land and were close to the drinking criteria under unsewered development. Concentrations of many trace inorganics were greatest in sewered residential and commercial/industrial areas, but generally at concentrations well below drinking criteria. VOCs were detected in 80 percent of the samples, although no sample exceeded the drinking criteria. Toluene, xylene, 1,1,2,2-



tetrachloroethene, and ethylbenzene accounted for most of the VOC detections. Pesticides were detected in only one sample, but pesticide sampling from the monitoring network during the same time period indicates that pesticide metabolites, which were not analyzed in geoprobe samples, occur more frequently than the parent compound.

Associations between land use and ground water quality extended to the 7.5 foot depth for calcium, chloride, dissolved oxygen, and to the 15 foot depth for chloride and calcium. The relationships for chloride and calcium indicate some mixing is occurring within the upper 15 feet of the aquifer. Associations between land use and nitrate concentrations extended to the 7.5 foot depth if the aquifer remained aerobic, but not if conditions were conducive to denitrification. There was no association between land use and nitrate concentrations at the 15 foot depth, suggesting nitrate has been completely denitrified in the upper portion of the aquifer. Sodium and barium, which differed in concentration between different land uses, showed no association with depth, probably due to adsorption within the aquifer.

Significant changes in geochemistry were observed in the upper 15 feet of the aquifer. Eh and concentrations of dissolved oxygen decreased with depth, while concentrations of iron and manganese increased. Concentrations of dissolved oxygen increased at the water table and at the 7.5 and 15 foot depths during the period of recharge due to inputs of oxygen-rich water. Concentrations of total organic carbon increased with depth. If soil is the source of carbon to the aquifer, the increase in carbon concentrations with depth indicates microbial activity is potentially very important to water quality in the upper portion of the aquifer. Since some aquifer mixing is occurring in the upper 15 feet of the aquifer, the observed oxidation-reduction profile indicates that recharge alone is not a good indicator of chemical fate within the aquifer.

The current monitoring network is adequate for assessing land use effects. Pooling data from the geoprobe and monitoring wells did not significantly change the overall coefficients of variation for the data. Concentrations of most oxidation-reduction parameters, including iron, manganese, nitrate, dissolved oxygen, total organic carbon, and Eh, differed between samples collected from the monitoring network and samples collected with the geoprobe. The primary reason for this was increased concentrations of

suspended material in the geoprobe samples. Concentrations of some trace inorganics were lower in the geoprobe samples, because trace inorganics are at their lowest concentration during spring.

Geoprobe samples are adequate for assessing shallow ground water quality but should not be combined with data from monitoring networks. Data from geoprobe samples are weakened by temporal effects and sample quality, particularly suspended sediments. Geoprobe sampling, however, is an effective tool for conducting initial screening of water quality in an area because it can be used at a variety of depths and at much lower cost than installing permanent wells.

Additional data collected during the geoprobe study will be used to calibrate models for the study area. This data includes information on geology of the unsaturated zone, aquifer attenuation properties, and potential chemical sources. This will help resource managers predict aquifer impacts from changes in land use.

## **Introduction**

Land use has significant impacts on ground water quality. Typical observed changes include increased nitrate concentrations and detection of pesticides in agricultural areas (Lucey and Goolsby, 1993; Burkhart and Kolpin, 1993; Anderson, 1993; Keeney and DeLuca, 1993; Bauder et al., 1993; Cain et. al, 1989), increased nitrate concentrations and pesticide detections in residential areas (Anderson, 1993; Geron et al., 1993; Eckhardt and Stackelberg, 1995), and increased nitrate concentrations and volatile organic compound (VOC) detections in commercial and industrial areas (Eckhardt and Stackelberg, 1995) compared to undeveloped land use settings (Haycock and Pinay, 1993; Anderson, 1993). Increased concentrations of major ions, lower concentrations of dissolved oxygen, changes in oxidation-reduction conditions, and presence of minor constituents (e.g. trace metals, boron) are also often observed in developed land use settings compared to undeveloped settings. Factors within individual land use settings also affect chemistry of ground water, including the type, extent, and age of sewerage and turfgrass management practices in residential areas (Yates, 1985; Flipse et. al, 1984; Gold et. al, 1990; Moosburner and Wood, 1980; Katz et. al, 1980), types of industries in commercial-industrial settings (Burkhart and Kolpin, 1993), cropping practices in agricultural areas (Keeney and DeLuca, 1993; Randall and Iragavarapu, 1995; Jemison and Fox, 1993; Giebnik, 1997; Kitchen et. al, 1997), and extent of irrigation or watering in agricultural and residential areas (Morton et. al, 1988; Petrovic, 1990; Geron et. al, 1993; Hamilton and Helsel, 1995). The effect of human activity on ground water chemistry is likely to be greatest in vulnerable hydrogeologic settings, such as karst bedrock aquifers or shallow, surficial sand and gravel aquifers.

The Anoka Sand Plain Aquifer is a large surficial aquifer in east-central Minnesota consisting predominantly of outwash sand and gravel. These are covered in places by Mississippi River Valley train deposits, which tend to be somewhat coarser than the outwash materials. Depth to water is typically less than 25 feet and the vadose zone consists primarily of coarse-textured materials. The aquifer is therefore vulnerable to pollution from chemicals which may leach through the vadose zone. The hydrology and geology of the Anoka Sand Plain has been described in numerous reports (Anderson,

1993; Helgeson and Lindholm, 1977; Lindholm, 1980; Ericson et. al., 1974; Helgeson et al., 1975; Minnesota Geological Survey, 1989; Minnesota Geological Survey, 1995).

The Minnesota Pollution Control Agency (MPCA) Ground Water Monitoring and Assessment Program (GWMAP) is studying the relationship between land use and ground water quality in the vicinity of St. Cloud. Results from quarterly sampling in 1997 indicate a strong relationship between land use and water quality in the upper portion of the surficial sand and gravel aquifer (MPCA, 1998a). Data from the monitoring network in 1997 show that although there are strong correlations between water quality and land use in the upper portion of the surficial aquifer, there appears to be no relationship between land use and ground water quality in deeper portions of the aquifer. Water quality in the upper portion of the surficial aquifer differs from deeper portions of the aquifer, particularly for the oxidation-reduction parameters (dissolved oxygen, Eh, reduced iron, reduced manganese).

A study was conducted in spring of 1998 to determine water quality and characterize geochemistry in the upper fifteen feet of the sand and gravel aquifer underlying St. Cloud. The objectives of this study were to:

1. determine if there are differences in water quality under different land uses;
2. determine the depth to which correlations exist between water quality and land use;
3. determine if differences exist between the geoprobe and monitoring well data and determine if the monitoring well network is sufficient to achieve intended objectives.

## **1. Methods and Materials**

The land use study is located near St. Cloud in east-central Minnesota (Figure 1). St. Cloud is a metropolitan area with a population of approximately 100000. It has experienced rapid growth and changes in land use within the past 10 years. A permanent monitoring network was established in 1996 and 1997 and is illustrated in Figure 2 (MPCA, 1998a). Quarterly sampling of this network will continue through the year 2001. Field sampling and data analysis protocol are described in MPCA (1996) and MPCA (1998b), respectively.

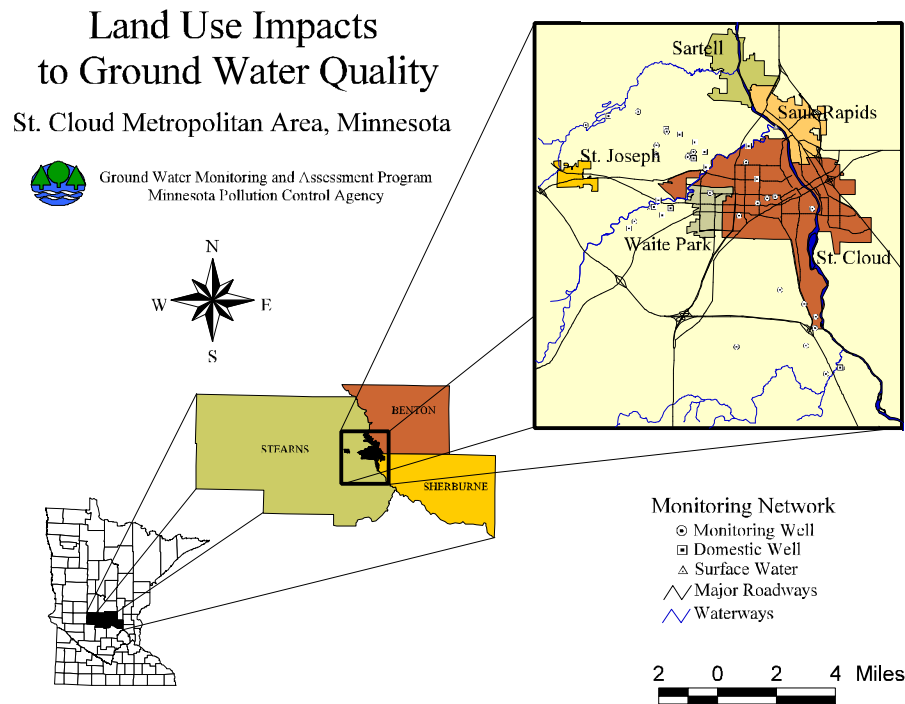


Figure 1 : Location of study area.

### 1.1. Sample Collection and Analysis

A geoprobe study was conducted in spring of 1998 to supplement information collected from the permanent monitoring network. Geographic Information System (GIS) coverages were developed to determine potential sampling locations. The coverages included a 7 mile by 5 mile grid with one mile grid node spacings, United States Geological Survey digital orthophotos (used to evaluate land use at each grid node), and ground water flow maps generated from 1997 data. The following land use categories were established:

1. Nonirrigated agriculture - corn
2. Nonirrigated agriculture - soybeans
3. Nonirrigated agriculture - alfalfa
4. Irrigated agriculture
5. Residential sewered
6. Residential unsewered
7. Commercial/industrial
8. Undeveloped

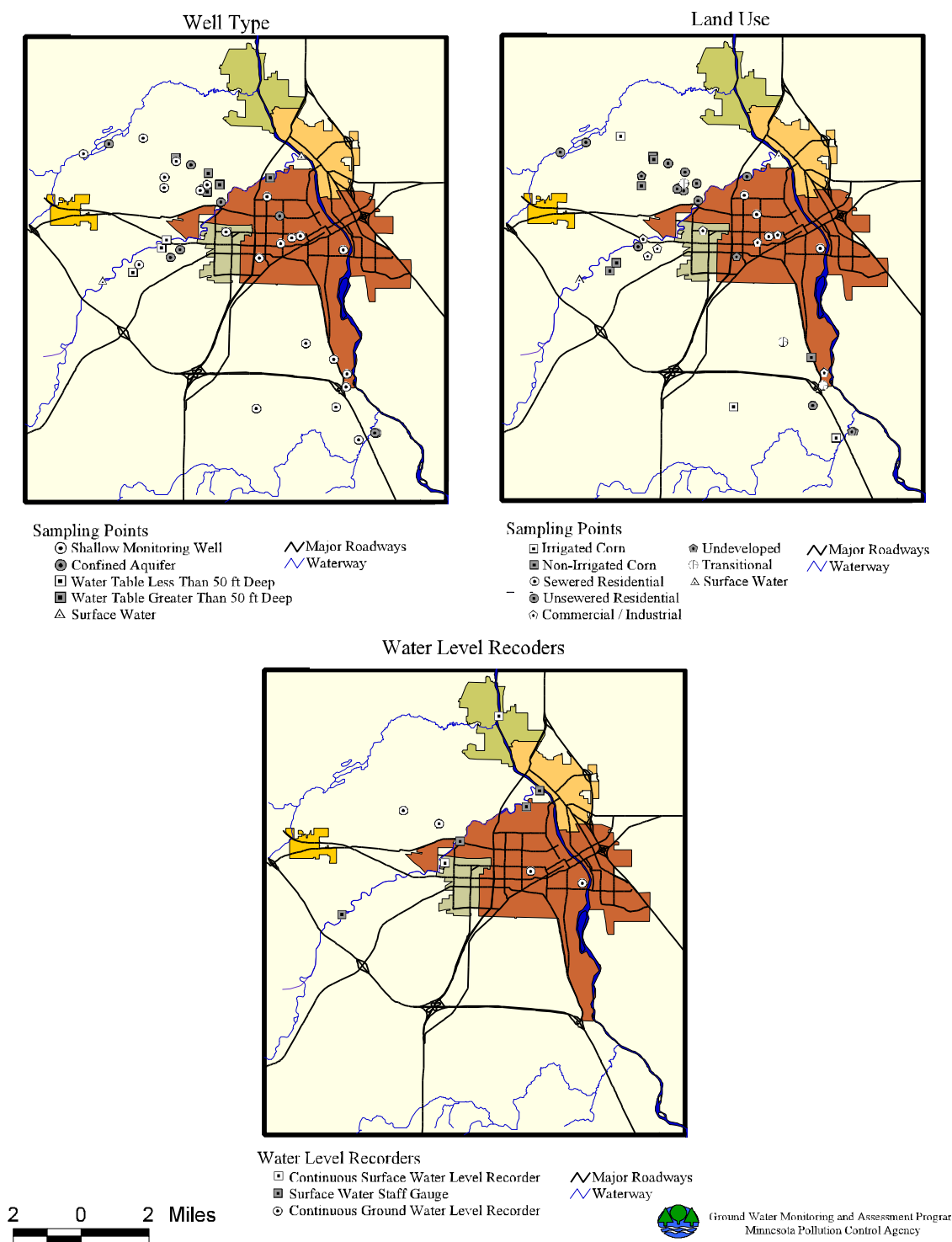


Figure 2: Location of monitoring points, including wells, surface water sampling points, and continuous recorders.

Land use at each grid location was field verified and sites were selected for sampling if land use was uniform 1000 feet in an upgradient ground water flow direction. Undeveloped land consisted of one site which was formerly agriculture but has been abandoned for several years, two sites located in wooded areas, one private park adjacent to the Sauk River, and one site with mixed woodland and grassland. Sample locations are illustrated in Figure 3. The final distribution of sites is summarized in Table 1.

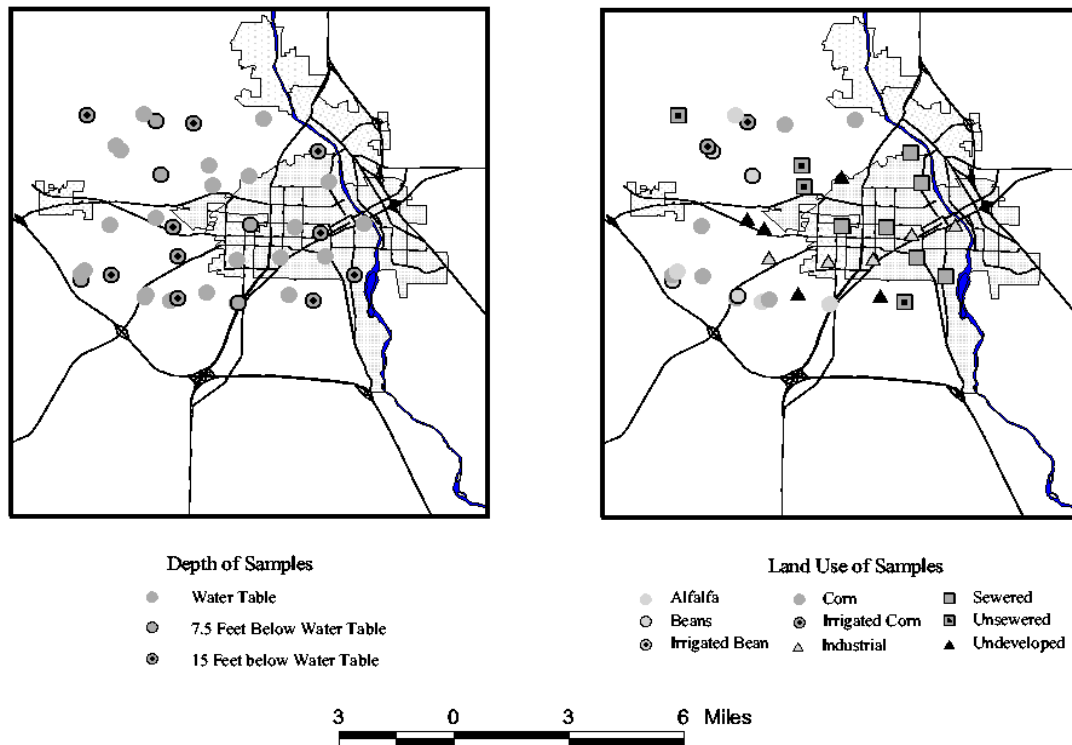


Figure 3 : Grid and sampling locations for the geoprobe study.

Thirty-seven geoprobe samples were collected between March and early June, 1998. At each site, continuous split spoon samples for textural analysis were collected to the water table. Five-foot screens (0.010 slot, threaded PVC) were installed across the water table and samples were pumped using a peristaltic pump until sample turbidity became uniform. Dissolved oxygen, oxidation-reduction potential, pH, temperature, and specific conductance were measured using a YSI 600XL multi-parameter water quality monitor.<sup>1</sup> Alkalinity, nitrate-nitrogen, chloride, and sulfate were measured in the field

<sup>1</sup> Mention of a particular product does not represent endorsement of or preference for that product.

using commercially available field test kits. Laboratory analysis included major cations and anions, dissolved and total organic carbon, ammonia-nitrogen, and total Kjeldahl nitrogen. Samples for VOC analysis were collected in urban and undeveloped areas. Pesticide samples were collected in agricultural areas. A summary of laboratory methods and reporting limits is provided in Appendix A.

Land use	Water Table	7.5 feet	15 feet
nonirrigated corn	7	3	3
nonirrigated soybean	3	2	0
nonirrigated alfalfa	4	1	0
irrigated	3	0	0
sewered residential	6	3	2
unsewered residential	4	1	2
commercial/industrial	5	2	2
undeveloped	5	1	1
<b>Total</b>	<b>37</b>	<b>13</b>	<b>10</b>

Table 1 : Number of samples collected by land use and geoprobe depth.

At approximately one-third of the sampling locations, additional samples were collected at 7.5 and 15 foot depths below the water table. Two-foot well screens (0.010 slot, threaded PVC) were installed at each depth. Sampling procedures were similar to the water table samples, but did not include VOCs or pesticides. At six locations, aquifer sediment samples were collected for laboratory analysis of cation exchange capacity, organic carbon, and calcium carbonate. Results of textural analysis and analysis of aquifer attenuation properties will be discussed in subsequent reports on hydrologic modeling for the study.

## 1.2. Data Analysis

Chemical concentrations at the water table were compared between the eight land uses. The null hypothesis was that concentrations did not differ between land uses. The Kruskal-Wallis test was used at a significance level of 0.05. One advantage of this nonparametric test over parametric methods is lower sensitivity to the small sample sizes comprising this study. It was not possible to compare land uses at the deeper depths due to insufficient sample size. Chemical concentrations were compared between the three



well depths using the Kruskal-Wallis test at a significance level of 0.05. Median concentrations of each chemical at the water table were compared between monitoring wells and geoprobe samples for each land use using the Mann-Whitney test at a significance level of 0.05. Correlation tests were conducted between chemical concentration and the oxidation-reduction parameters (oxidation-reduction potential, dissolved iron, dissolved manganese, nitrate, and dissolved oxygen), well depth, geographic location (Universal Trans Mercator coordinate), and date of sampling. The Spearmann rho test was used for correlation analysis at a significance level of 0.05. Coefficients of variation for each chemical were calculated for geoprobe samples, by land use and overall, and compared to coefficients of variation for the monitoring wells as a means of evaluating the suitability of the monitoring network for evaluating land use impacts.

## **2. Results and Discussion**

Results are divided into inorganic chemicals, volatile organic compounds (VOCs), and pesticides.

### **2.1. Inorganic Chemicals**

Factors considered in evaluating the distribution of inorganic chemicals in ground water were land use, well depth, and spatial and temporal effects. These are discussed separately below.

#### **2.1.1. Land Use Effects at the Water Table**

Land use comparisons were conducted for water table samples only, since sample size was insufficient for comparisons at the deeper depths. Median concentrations of each chemical at the water table are illustrated by land use in Table 2. Considering all land uses simultaneously, there were significant ( $p < 0.05$ ) differences in concentrations of barium, calcium, chloride, dissolved oxygen, lead, nitrate-nitrogen, sodium, and zinc between land uses. Differences in median concentration between land uses are indicated in Table 2 by different letters within a row.

Median concentrations of barium were greatest in commercial (86 ug/L) and sewer residential (80ug/L) areas. Concentrations were statistically equal in the remaining land uses (17 to 58ug/L), although the lowest concentrations were in the undeveloped land use (17ug/L). Independent t-tests indicate barium concentrations are lower under undeveloped land use compared to other land uses. Barium concentrations were well below the drinking water criteria (HRL) of 2000ug/L. Barium is a common trace metal found in lubricants. For example, barium is found at relatively high concentrations (up to 620 mg/kg) in soils at automobile salvage yards (MPCA, 1995), with the greatest concentrations being associated with high concentrations of diesel range organic chemicals (e.g. oil).

Calcium concentrations were greatest in irrigated (104810ug/L) and commercial areas (101510 ug/L), with the lowest concentrations in undeveloped areas (51132ug/L). The reasons for the elevated concentrations in the irrigated and commercial areas are difficult to explain, since calcium is most likely being leached through the unsaturated zone. Two independent processes may be responsible for the elevated calcium concentrations. Increased leaching may be occurring in irrigated areas (MPCA, 1998a), while there may be industrial sources of calcium (alloys, use as a reducing agent) in the commercial areas. There is no drinking water criteria for calcium.

Median chloride concentrations were greatest in unsewered residential areas (90445 ug/L) and lowest in undeveloped areas (780ug/L). There was considerable variability between land uses in chloride concentrations. Concentrations in all land uses were more than an order of magnitude greater than concentrations in undeveloped areas.

Parameter	Nonirrigated Corn	Nonirrigated soybeans	Nonirrigated alfalfa	Irrigated agriculture	Unsewered residential	Sewered residential	Commercial industrial	Undeveloped
Alkalinity	235000	241000	274000	181500	264667	305333	337333	248500
Aluminum	< 49.9	< 49.9	< 49.9	< 49.9	< 49.9	< 49.9	< 49.9	< 49.9
Ammonia-nitrogen	80	80	70	260	55	80	140	170
Arsenic	< 10.4	12	< 10.4	< 10.4	13	14	16	< 10.4
Barium	58 bc	53 ab	47 ab	57 abc	39 ab	80 bc	86 c	17 a
Beryllium	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron	40	62	27	23	36	33	55	16
Cadmium	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8
Calcium	94239 abc	99229 abc	94950 abc	104810 c	77422 ab	96186 abc	101510 bc	51132 a
Chloride	26250 abc	14110 ab	15815 abc	33090 bcd	90445 d	76390 bcd	61670 cd	780 a
Chromium	7.2	8.2	7.4	5.5	5.8	9	7.4	5.5

Parameter	Nonirrigated Corn	Nonirrigated soybeans	Nonirrigated alfalfa	Irrigated agriculture	Unsewered residential	Sewered residential	Commercial industrial	Undeveloped
Cobalt	3.3	6.0	2.6	3.9	5.3	3.7	2.0	2.0
Copper	< 5.4	9.5	< 5.4	6.6	< 5.4	7.2	< 5.4	< 5.4
Depth to water	9.5 abc	6.5 ab	9.6 ab	15.6 bc	18.7 c	13.7 abc	11.9 bc	6.0 a
Dissolved carbon	2400	2700	1950	2200	1550	2050	2100	2900
Dissolved oxygen	8780 abc	9090 bc	6880 abc	11335 c	9165 bc	2600 ab	1030 a	5690 ab
Eh	310	356	329	343	259	334	187	282
Fluoride	320	370	435	190	240	370	610	240
Iron	13	15	55	3.7	36	49	19	34
Lead	< 24.5 a	< 24.5 ab	< 24.5 a	< 24.5 a	< 24.4 a	25 b	< 24.5 a	< 24.5 a
Lithium	< 4.4	< 4.4	< 4.4	< 4.4	< 4.4	< 4.4	< 4.4	< 4.4
Magnesium	27585	29007	29684	27432	24877	28415	27067	18026
Manganese	49	30	83	129	258	210	785	130
Molybdenum	< 4.1	< 4.1	< 4.1	< 4.1	4.5	< 4.1	< 4.1	< 4.1
Nickel	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0	< 6.0
Nitrate-nitrogen	19060 cd	26500 cd	12330 bc	30550 d	8375 bc	310 a	4810 ab	120 a
pH	7.43	7.53	7.48	7.54	7.51	7.34	7.28	7.67
Phosphorus	16	21	31	118	45	31	46	29
Potassium	1746	1968	1162	2216	2377	2386	2448	535
Rubidium	< 337.5	< 337.5	< 337.5	< 337.5	< 337.5	< 337.5	< 337.5	< 337.5
Silica	7300	7651	8736	7249	8706	8528	7494	8371
Sodium	5173 ab	6847 abc	5941 a	12598 abcd	60675 d	31287 bcd	27416 cd	3611 a
Specific conductance	598	638	570	1221	669	760	936	333
Strontium	105	127	88	104	76	113	132	53
Sulfate	7129	6417	7097	10766	8262	11379	8023	2551
Sulfur	6900	6210	6705	11420	8190	11160	8130	2580
Temperature	6.59	5.03	6.72	9.43	9.54	8.16	9.17	6.59
Titanium	< 3.4	< 3.4	< 3.4	< 3.4	< 3.4	< 3.4	< 3.4	< 3.4
Total Kjeldahl nitrogen	190	200	230	190	310	225	200	680
Total organic carbon	3300	5500	2000		1150	2000	2200	4800
Vanadium	5.2	5.7	4.5	< 4.7	< 4.7	6.6	4.9	< 4.7
Well depth	12.1	8.5	13.3	18.3	23.3	15.6	17.0	10.2
Zinc	5.2 ab	4.3 a	2.9 a	12 bc	6.0 bc	9.3 c	16 c	3.1 a

Table 2 : Median concentrations of chemicals for different land uses. Different letters within a row indicate significant differences in concentration ( $p < 0.05$ ). All concentrations are ug/L, except depth to water and well depth (feet), specific conductance (umhos/cm), Eh (mV), temperature ( $^{\circ}$ C), and pH.

Chloride may have many anthropogenic sources, including road salts, human or animal waste, and fertilizer. The results suggest that contributions from human waste may be significant in unsewered areas. The median concentrations were well below the Secondary Maximum Contaminant Level (SMCL) of 250000ug/L.

The greatest concentrations of dissolved oxygen were under irrigated (11335 ug/L), unsewered (9165 ug/L), nonirrigated corn (8780 ug/L), and nonirrigated soybeans (9090 ug/L). These are land uses in which recharge is high compared to most other land uses (MPCA, 1998a). The areas with the lowest recharge rates are sewer and commercial, and concentrations of dissolved oxygen were lowest in these areas (2600 and 1030 ug/L, respectively). Dissolved oxygen is not a drinking water concern, but is an indicator of physical processes such as recharge.

Lead was detected in only four samples, but three of these were in sewer residential areas (the other was under nonirrigated soybeans). Median concentrations were 25 ug/L in sewer residential areas and below the reporting limit of 24.5 ug/L in the remaining land uses. This reporting limit is not sufficient to assess impacts to drinking water receptors, since the drinking water criteria (action level at tap) is 15 ug/L.

Concentrations of nitrate-nitrogen were greatest under irrigated agriculture (30550 ug/L), nonirrigated soybean (26500 ug/L), and nonirrigated corn (19060 ug/L). Concentrations were above or near the HRL of 10000 ug/L under alfalfa (12330) and sewer residential (8375 ug/L). The primary sources of nitrogen will be fertilizer, including animal waste applied to agricultural fields, and human waste from septic systems. The data appear to break into three groups - low nitrate concentrations in undeveloped and sewer areas, intermediate concentrations under sewer areas and alfalfa, and high concentrations under irrigated and row crop agriculture.

Sodium concentrations were greatest under sewer residential areas (60675 ug/L), but concentrations were also high under sewer (31287 ug/L) and commercial land (27416 ug/L). Concentrations were low under nonirrigated agriculture (< 7000 ug/L) and undeveloped land (3611 ug/L). These results suggest road salt and human waste may be significant contributors to sodium concentrations in ground water. There is no drinking water criteria for sodium.

Zinc concentrations were greatest under commercial (16 ug/L), sewer residential (9.3 ug/L), irrigated (12 ug/L), and sewer (6.0 ug/L) land. Concentrations were lowest under nonirrigated agriculture (< 5.2 ug/L) and undeveloped (3.1 ug/L) areas. Zinc has many potential anthropogenic sources. Some of the more mobile forms may be

associated with automotive use, since zinc will occur in oil, radiator, and lubricating fluids. Median zinc concentrations for all land uses were well below the drinking water criteria (HRL) of 2000 ug/L.

Specific comparisons between different land uses are of interest. These are summarized below.

#### ***Undeveloped versus remaining land***

Variability in the data associated with simultaneously comparing eight different land uses masks the relationship between human activity and ground water quality. Concentrations of chemicals at the water table were compared between undeveloped land and all remaining land uses combined. Specific conductance and concentrations of arsenic, barium, boron, chloride, calcium, chromium, magnesium, nitrate, potassium, sodium, strontium, vanadium, and zinc were lower under undeveloped land compared to other land uses. Results are summarized in Table 3.

#### ***Agricultural versus urban land***

The three nonirrigated land uses were combined with the irrigated land use and compared to urban land, which included unsewered, sewer, and residential land. Concentrations of sodium, zinc, chloride, and alkalinity were greater under urban land, while nitrate concentrations were greater under agricultural land. Results are summarized in Table 4.

#### ***Sewered versus unsewered residential land***

Sewered and unsewered residential land uses were compared. The only chemical which differed in concentration between the two land uses was nitrate. The median concentration of nitrate in unsewered areas was 8375 ug/L, compared to a median concentration of 310 ug/L in sewer areas.

Parameter	Undeveloped land use	All other land uses
Arsenic	< 10.4	12
Boron	16	34
Barium	17	56
Calcium	51132	94175
Chloride	780	34820
Chromium	5.5	7.3
Potassium	535	1974
Magnesium	18026	27525
Sodium	3611	12709
Nitrate-nitrogen	120	7010
Strontium	53	112
Specific Conductance	333	604
Zinc	3.1	6.0
Vanadium	< 4.7	4.9

Table 3 : Median concentrations for chemicals which differed in concentration between undeveloped land and all remaining land uses. Concentrations are  $\mu\text{g/L}$ , except specific conductance ( $\mu\text{mhos/cm}$ ).

Parameter	Urban land use	Agricultural land use
Alkalinity	277000	238833
Chloride	65380	26250
Sodium	29701	6847
Nitrate	3380	20500
Zinc	9.4	5.2

Table 4 : Median concentrations for chemicals which differed in concentration between urban and agricultural land. Concentrations are  $\mu\text{g/L}$ .

### ***Residential versus commercial land***

Sewered residential and commercial/industrial areas were compared. There were no statistically significant differences in concentration of any parameter between the two land uses.

### ***Nonirrigated versus irrigated agricultural land***

The three nonirrigated agricultural land uses were combined and compared with irrigated agriculture. Concentrations of zinc, nitrate, and dissolved oxygen were significantly greater under irrigated agriculture compared to nonirrigated agriculture. Results are summarized in Table 5.

Parameter	Nonirrigated agriculture	Irrigated agriculture
Dissolved oxygen	8025	11335
Nitrate	19425	30550
Zinc	4.7	12

Table 5 : Median concentrations for chemicals which differed in concentration between irrigated and nonirrigated agriculture. Concentrations are ug/L.

### ***Different crop comparisons in nonirrigated agriculture land***

The three nonirrigated agricultural land uses were compared. The only chemical in which concentrations differed was manganese, which was greater under alfalfa (83 ug/L) than under soybeans (30 ug/L), with concentrations under corn being intermediate (49 ug/L).

#### **2.1.2. Land Use Effects at the 7.5 and 15 Foot Depths**

There were an insufficient number of samples to make comparisons of chemical concentrations between different land uses at the 7.5 and 15 foot depths. Data from individual wells can be used to determine if land use effects extend deeper into the aquifer. Assuming the concentration of a chemical at the water table is impacted by land use, a correlation between concentrations at the water table and at a deeper depth suggests the effects of land use extend deeper into the aquifer. Correlations are valid only for chemicals in which there were significant differences in concentration between land uses (see Table 2), for geoprobe nests (which provide a depth profile at a specific location), and for chemicals which do not naturally increase in concentration with depth. For example, zinc is not a valid parameter for correlation analysis, since it increases naturally in concentration with depth.

Regression analysis was performed using each well nest as an individual data point. The regression model was (concentration at 7.5 or 15 feet) =  $a + b \times (\text{concentration at the water table})$ , where  $a$  and  $b$  are the slope and intercept, respectively, and the null hypothesis was that there was no correlation between concentrations at the water table and deeper depths. Parameters for analysis included barium, calcium, chloride, sodium, dissolved oxygen, and nitrate. Results of the regression analysis are summarized in Table 6. Chloride, which is assumed to represent a conservative tracer in ground water, showed correlations in concentrations at the water table and at both the 7.5 and 15 foot depths. Some mixing is occurring within the upper 15 feet of the aquifer. A similar relationship was observed for calcium, which may also behave fairly conservatively in the aquifer. Results for nitrate at the 7.5 foot depth were dependent on aquifer geochemistry. If the aquifer was aerobic ( $E_h > 300$  mV), there was a significant relationship between nitrate at 7.5 feet and at the water table. In anaerobic samples, there was no correlation, presumably because all nitrate had undergone denitrification. There was no relationship for nitrate at the 15 foot depth, indicating denitrification is complete within the upper 15 feet of the aquifer. The results for dissolved oxygen support this, with a strong relationship between oxygen concentrations at the water table and 7.5 foot depth, but no relationship at the 15 foot depth. No depth relationships were evident for barium and sodium, both of which are highly adsorbed.

Parameter	p-values	
	7.5 foot depth	15 foot depth
Barium	0.063	0.13
Calcium	0.00029	0.003
Chloride	0.0083	0.017
Dissolved Oxygen	0.0035	0.87
Sodium	0.16	0.49
Nitrate <sub>aerobic</sub>	0.0000011	0.49
Nitrate <sub>anaerobic</sub>	0.074	0.49

<sup>1</sup> Insufficient sample size

Table 6 : Summary of regression analysis for the model : (chemical concentration at 7.5 or 15 foot depth) =  $a + b \times (\text{concentration at the water table})$ , where  $a$  and  $b$  are the intercept and slope, respectively.



### 2.1.3. Depth Effects

Concentrations of different chemicals were compared for the three sampled depths (0, 7.5, and 15 feet below the water table). Median concentrations for all sampled parameters are illustrated in Table 7. Concentrations which differed between depths ( $p < 0.05$ ) are indicated with different letters. Concentrations of dissolved oxygen and nitrate were greater at the water table while concentrations of iron, manganese, total organic carbon, dissolved organic carbon, ammonia, and total Kjeldahl nitrogen were greater at the deeper depths. The differences in concentration of these chemicals is primarily related to changes in geochemical conditions within the aquifer, since some aquifer mixing appeared to be occurring within the upper 15 feet. Eh decreased with depth from 308 mV at the water table to 300 and 287 mV at depths of 7.5 and 15 feet, respectively. These differences were not statistically significant, but the range of 287 to 308 mV for Eh is close to the oxidation-reduction potential at which denitrification will occur.

The data in Table 7 indicate geochemistry changes with depth. Regression analysis was performed with depth below the water table as the independent variable and Eh, dissolved oxygen, nitrate, reduced iron, and reduced manganese as dependent variables. The analysis was performed using just the geoprobe data and also using the monitoring and geoprobe data combined. Results are summarized in Table 8. Correlation coefficients were low ( $< 0.20$ ) for these regressions due to large variability in concentrations between different land uses. The results differ using just geoprobe data and using monitoring well plus geoprobe data. The regressions were generally stronger for all data combined, except for dissolved oxygen. Oxidation-reduction conditions within the upper 15 feet of the aquifer are variable and influenced by factors such as recharge and inputs of organic carbon into the aquifer. Pooling regression results from individual wells did not improve the results of the regression analysis. No regressions were significant for nitrate. This is expected because concentrations of nitrate are affected by inputs at the land surface and nitrate will not be utilized by microbes until oxygen is consumed, which means concentrations in the aerobic zone remain relatively constant. This was illustrated in Table 6, in which nitrate concentrations appeared to change very rapidly between 7.5 and 15 feet.

Parameter	0 Feet	7.5 Feet	15 Feet
Aluminum	< 49.9	< 49.9	< 49.9
Ammonia-Nitrogen	80 a	135 b	280 b
Arsenic	10	11	11
Barium	55	75	63
Beryllium	< 0.2	< 0.2	< 0.2
Boron	29	33	44
Cadmium	< 1.8	< 1.8	< 1.8
Calcium	90194	86737	102160
Chloride	32330	21770	29820
Chromium	7.0	7.8	7.8
Cobalt	3.4	2.5	3
Copper	< 5.4	< 5.4	< 5.4
Dissolved organic carbon	2200 a	2400 a	4000 b
Dissolved Oxygen	6320 b	4600 ab	1760 a
Eh	308	300	287
Fluoride	290	360	350
Iron	28 a	69 b	260 b
Lead	< 24.5	< 24.5	< 24.5
Lithium	< 4.4	< 4.4	< 4.4
Magnesium	27432	27027	26982
Manganese	75 a	225 a	477 b
Molybdenum	< 4.1	< 4.1	< 4.1
Nickel	< 6.0	< 6.0	< 6.0
Nitrate-Nitrogen	5640 b	450 a	45 a
pH	7.45	7.51	7.42
Phosphorus	30	44	43
Potassium	1746	2283	2268
Rubidium	< 337.7	< 337.7	< 337.7
Silica	7651	8338	7546
Sodium	10302	8361	12287
Specific Conductance	601	533	611
Strontium	104	123	123
Sulfate-Sulfur	8130	10345	10175
Sulfur	8023	10404	10238
Temperature	7.38	7.68	8.31
Titanium	< 3.4	< 3.4	< 3.4
Total Kjeldahl Nitrogen	250 a	490 ab	965 b
Total Organic Carbon	2300 a	3100 a	7800 b
Vanadium	< 4.7	< 4.7	< 4.7
Zinc	5.7	4.3	5.8

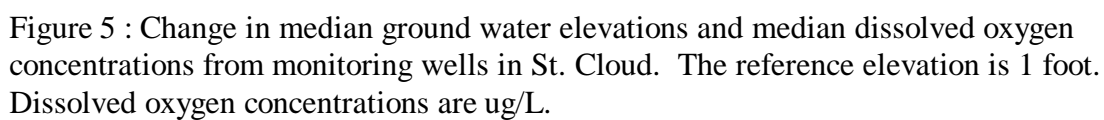
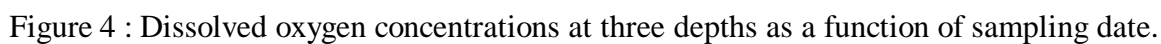
Table 7 : Median concentrations of chemicals at three depths relative to the water table. Concentrations are ug/L, except temperature (°C), pH, specific conductance (umhos/cm), and Eh (mV). Different letters within a row indicate significant differences in concentrations at the 0.05 level.

Parameter	Significance of regression	Intercept	Slope
<i>Geoprobe samples</i>			
Eh	0.77	-	-
Nitrate	0.12	-	-
Dissolved Oxygen	0.0045	7836	- 0.431 ug/L/ft
Reduced Iron	0.068	56.4	103 ug/L/ft
Reduced Manganese	0.027	110	34 ug/L/ft
<i>Geoprobe and monitoring wells</i>			
Eh	0.000027	324 mV	-1.7 mV/ft
Nitrate	0.85	-	-
Dissolved Oxygen	0.0094	4238 ug/L	- 28.3 ug/L/ft
Reduced Iron	0.000039	199 ug/L	13.9 ug/L/ft
Reduced Manganese	0.043	173 ug/L	1.7 ug/L/ft

Table 8 : Results of analysis for the regression : parameter concentration = a +b\*depth, where a and b are the intercept and slope, respectively.

Geochemical conditions in the upper portion of the aquifer are influenced by recharge. Recharge introduces oxygen-rich water to the aquifer. Dissolved oxygen concentrations at depths of 0, 7.5, and 15 feet below the water table are shown in Figure 4 as a function of date of sampling. Dissolved oxygen increased at all three depths during the period of sampling, but the effect was less noticeable with increasing depth. Eh at the water table increased by approximately 1.6 mV per day during the sampling period but did not change at the deeper depths. Concentrations of nitrate, iron, manganese, ammonia, and organic nitrogen were unaffected by sampling date.

Median elevations of the water table (referenced to a 1 foot depth) from the 23 monitoring wells are illustrated in Figure 5 during the period of geoprobe sampling. Recharge occurred primarily in April in response to snowmelt, with a median recharge of approximately 14 inches, assuming an aquifer porosity of 0.30 cm<sup>3</sup>/cm<sup>3</sup>. Dissolved oxygen concentrations at the water table increased rapidly during the period of recharge.



#### **2.1.4. Spatial and Temporal Effects**

Spatial or temporal trends potentially confound the data because they mask land use effects. Geoprobe samples were spaced a minimum of 1000 feet apart. Concentrations are thus assumed to represent the overlying land use. Serial effects were minimized by collecting a single sample from each site and collecting all samples over as short a time frame as possible. Concentrations of chloride and sodium increased from west to east, while nitrate and dissolved oxygen concentrations decreased. The density of roads increases from west to east. Thus, the distribution of chloride and sodium is likely related to use of road salts. The distribution of nitrate is associated with the location of unsewered areas and agriculture, both of which occur near the western outskirts of St. Cloud. Changes in concentrations of dissolved oxygen are likely due to recharge, which decreases from west to east due to increasing extent of pavement.

Specific conductance, pH, and concentrations of calcium, magnesium, nitrate, total organic carbon, and dissolved oxygen at the water table increased from south to north. These results are likely due to irrigated agriculture, which increases to the north, and to use of manure on irrigated fields. Recharge under irrigated fields is much greater than under nonirrigated fields, resulting in greater quantities of dissolved oxygen, magnesium, and calcium in leachate. Nitrogen fertilizer applications on irrigated soils are typically greater than those on nonirrigated fields. Use of manure on irrigated soil creates the potential for greater quantities of organic carbon to be leached to the aquifer.

Concentrations of nitrate, Eh, and dissolved oxygen increased at the water table during the sampling period, while concentrations of boron, barium, fluoride, and nickel decreased. These results are related to recharge, which introduces oxygen-rich water to the aquifer and dilutes the concentration of many trace inorganic chemicals in ground water. The effect on trace inorganics was observed in the monitoring wells in 1997, with most trace inorganic chemicals having showing the lowest concentrations in spring.

#### **2.2. Volatile Organic Compounds (VOCs)**

VOCs were sampled at seventeen locations : 4 in commercial areas, 3 in undeveloped areas, 7 in sewer areas, and 3 in unsewered areas. The number of

detections in commercial, undeveloped, sewer, and unsewered areas was 4, 1, 6, and 2, respectively. More than one VOC was detected at 5 sites. A total of 23 chemicals were detected. The breakdown of chemicals is illustrated in Table 9. Locations of detections are illustrated in Figure 6. There were no exceedances of drinking criteria.

Toluene, xylene, and ethylbenzene were the most commonly detected VOCs. It is unclear if these detections represent natural or anthropogenic sources. These chemicals are constituents of gasoline and fuel oils. The increased frequency of detection in commercial and sewer areas suggests an influence of human activity. Two of the three tetrachloroethylene detections, the chloromethane detection, and the dichlorodifluoromethane detection were in commercial areas. The third tetrachloroethylene detection, although in an area now considered to be undeveloped, probably reflects a commercial/industrial source, based on historical information for the site. All the VOCs detected are mobile in soil and ground water and poorly adsorbed by geologic material. The results indicate widespread occurrence of low level concentrations of VOCs in shallow ground water beneath commercial/industrial areas and in residential and commercial/industrial areas.

Chemical	Number of detections	Concentration range (ug/L)
Toluene	10	0.1 to 0.7
Xylene	3	0.3 to 0.4
1,1,2,2-Tetrachloroethene	3	0.2
Ethylbenzene	2	0.2
Benzene	1	0.3
Chloromethane	1	32
Dichlorodifluoromethane	1	2.7
n-propylbenzene	1	0.5
Naphthalene	1	0.5

Table 9 : Summary of VOC detections.

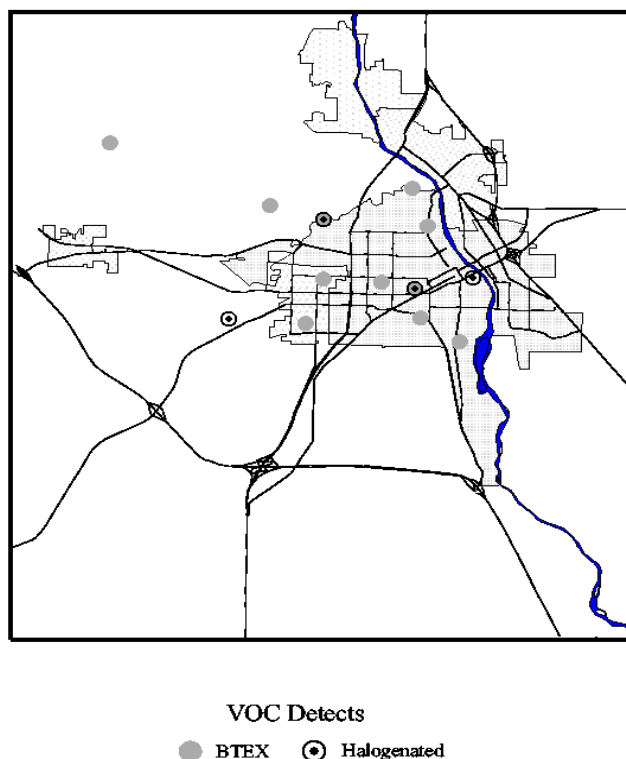


Figure 6 : Location of VOC detections. BTEX includes benzene, toluene, ethylbenzene, xylene and substituted benzenes.

### 2.3. Pesticides

List 1 herbicides (e.g. atrazine, alachlor, etc.), which are most widely used on agricultural crops, were sampled at 17 agricultural sites and the five undeveloped sites. There was only one detection, of cyanazine at 7.6 ug/L, beneath a corn field. List 2 herbicides (e.g. 2,4-D, dicamba), which are widely used in residential areas, were sampled at three residential sites. No pesticides were detected at these three sites. The lack of detections may be related to the time of sampling, which was pre-planting for most of the agricultural fields and prior to typical application times for turfgrass chemicals. The data are not consistent with results from the first and second quarter sampling events from the St. Cloud monitoring network, in which seven and eight wells showed herbicide detections, respectively. Of the 62 compounds detected during the quarterly events, 49 were metabolites of parent compound. Lower reporting limits were used for the quarterly

data, and only 2 of the 10 detections of atrazine for the quarterly sampling would have been detected at the reporting limit used for the geoprobe samples (0.5 ug/L). Additional data is needed for geoprobe samples at low reporting limits, including herbicide metabolites, before conclusions can be drawn regarding the relationship between land use and pesticides in ground water.

### **3. Comparisons with Monitoring Well Data**

An important objective of the geoprobe work was to compare results with the monitoring network and determine if there was greater variability in either the geoprobe or the monitoring data. This information can be used to assess the validity of the monitoring network for assessing differences in ground water quality between land uses and for detecting trends in water quality. The analysis was completed only for the major cations and anions, trace metals analyzed using ICP, total organic carbon, ammonia-nitrogen, total Kjeldahl nitrogen, and field parameters. Several trace inorganics could not be compared because of differences in laboratory analysis methods.

Comparisons of median concentrations between geoprobe and monitoring well samples are illustrated by land use in Tables 10 through 12. Within nonirrigated agriculture, median concentrations of boron, fluoride, iron, magnesium, manganese, nitrate, and silica were greater in the geoprobe samples, while concentrations of phosphorus and zinc were lower. Overall, the standard deviation in chemical concentrations was 17 percent greater in the monitoring wells than in geoprobe samples. Use of just nonirrigated corn data for the geoprobe samples improved the comparisons (monitoring wells were drilled in corn fields), but large differences were still evident for iron, manganese, and the nitrogen species. An important factor affecting water quality results for the geoprobe samples was suspended sediment concentration. Although samples were filtered in the field, the concentration of suspended sediment was greater in geoprobe samples than those from monitoring wells, based on visual observations. Comparisons of median concentrations of geoprobe data with monitoring well data under



Parameter	Nonirrigated Agriculture Monitoring Wells	Geoprobe	Irrigated Agriculture Monitoring Wells	Geoprobe
Alkalinity	202000	250000	259000	181500
Ammonia-nitrogen	65	80	70	260
Barium	63	55	90	57
Boron	13*	37	34	23
Calcium	75651	96734	106859	104810
Chloride	10955	17045	41315	33090
Copper	< 5.4	< 5.4	9.5	6.6
Eh	375	324	396	343
Fluoride	100*	320	100	190
Iron	3.1*	24	5.1	3.7
Lithium	< 4.4	< 4.4	< 4.4	< 4.4
Magnesium	22148*	28541	28080	27432
Manganese	2.9*	54	1.8*	129
Molybdenum	< 4.1	< 4.1	< 4.1	< 4.1
Nickel	< 6.0	< 6.0	< 6.0	< 6.0
Nitrate-nitrogen	3145*	19425	18860*	30550
pH	7.40	7.48	7.13*	7.54
Phosphorus	41*	25	36	118
Potassium	2015	1729	1385	2216
Rubidium	< 337.7	< 337.7	< 337.7	< 337.7
Silica	6274*	7760	10195*	7249
Sodium	5198	6369	8303	12598
Specific conductance	504	594	751	1221
Strontium	82	110	136	104
Sulfate	17970	19797	24225	34260
Sulfur	6654	6799	8167	10766
Temperature	10.90*	6.05	9.62	9.43
Total Kjeldahl nitrogen	325	195	100*	190
Total Organic carbon	3450	2650	1200	-
Vanadium	< 4.7	< 4.7	8	< 4.6
Zinc	10*	4.7	10	12

Table 10 : Median values for water quality parameters for nonirrigated and irrigated agriculture. Concentrations are ug/L except for pH, temperature (°C), Eh (mV), and specific conductance (umhos/cm). An \* indicates significant differences (p < 0.05) between geoprobe and monitoring well samples.

Parameter	Unsewered		Sewered	
	Monitoring Wells	Geoprobe	Monitoring Wells	Geoprobe
Alkalinity	224335	264667	266670	305333
Ammonia-nitrogen	50	55	95	80
Barium	49	39	73	80
Boron	44	36	37	33
Calcium	68837	77422	104010	96186
Chloride	60010	90445	74365	76390
Copper	5.7*	5.0	5.7	7.2
Eh	259	259	372	334
Fluoride	100	240	100	370
Iron	3.0*	36	9.1	49
Lithium	< 4.4	< 4.4	5.1	< 4.4
Magnesium	18905	24877	28625	28415
Manganese	0.40*	258	23	210
Molybdenum	< 4.1	< 4.1	< 4.1	< 4.1
Nickel	< 6.0	< 6.0	< 6.0	< 6.0
Nitrate-nitrogen	6080	8375	2225	310
pH	7.40	7.51	7.14	7.34
Phosphorus	24	45	31	31
Potassium	933*	2377	2682	2386
Rubidium	< 337.7	< 337.7	< 337.7	< 337.7
Silica	8829	8706	8963	8528
Sodium	29195	60675	12918	31287
Specific conductance	646	669	773	760
Strontium	79	76	127	113
Sulfate	16560	24570	50550	33480
Sulfur	5625	8262	17399	11379
Temperature	10.14	9.54	10.85	8.16
Total Kjeldahl nitrogen	100*	310	100	225
Total Organic carbon	1400	1150	1850	2000
Vanadium	< 4.7	< 4.7	6.2	6.6
Zinc	7	6.0	13	9.3

Table 11 : Median values for water quality parameters for unsewered and sewer land. Concentrations are ug/L except for pH, temperature (°C), Eh (mV), and specific conductance (umhos/cm). An \* indicates significant differences (p < 0.05) between geoprobe and monitoring well samples.

Parameter	Commercial/Industrial		Undeveloped	
	Monitoring Wells	Geoprobe	Monitoring Wells	Geoprobe
Alkalinity	303667	337333	233168	248500
Ammonia-nitrogen	100	140	50	170
Barium	206	86	27	17
Boron	59	55	13	16
Calcium	125155	101510	66659	51132
Chloride	65270	61670	1925	780
Copper	7.7*	5.0	7.2*	5.0
Eh	355	232	318	282
Fluoride	150*	610	100	240
Iron	7.8	19	14	34
Lithium	< 4.4	< 4.4	< 4.4	< 4.4
Magnesium	30106	27067	24264	18026
Manganese	32	785	1.2	130
Molybdenum	< 4.1	< 4.1	< 4.1	< 4.1
Nickel	< 6.0	< 6.0	< 6.0	< 6.0
Nitrate-nitrogen	1365	4810	820*	120
pH	6.92	7.28	7.35	7.67
Phosphorus	41	46	22	29
Potassium	3324	2448	1114	535
Rubidium	< 337.7	< 337.7	< 337.7	< 337.7
Silica	9085	7494	7291	8371
Sodium	17172	27416	9088	3611
Specific conductance	939	936	418	333
Strontium	174	132	69	53
Sulfate	37635	24390	9090	7740
Sulfur	13181	8023	3463	2551
Temperature	10.30	9.17	9.05	6.59
Total Kjeldahl nitrogen	160	200	100*	680
Total Organic carbon	2100	2200	1350*	4800
Vanadium	7.1	4.9	5.2*	< 4.7
Zinc	14	15.9	8.6*	3.1

Table 12 : Median values for water quality parameters for commercial/industrial and undeveloped land. Concentrations are ug/L except for pH, temperature (°C), Eh (mV), and specific conductance (umhos/cm). An \* indicates significant differences (p < 0.05) between geoprobe and monitoring well samples.

irrigated agriculture show that pH and concentrations of manganese, total Kjeldahl nitrogen, and nitrate-nitrogen were greater in the geoprobe samples compared to samples from the monitoring wells, while concentrations of silica were lower. Overall, the standard deviation in measured chemical concentrations was 6 percent greater in geoprobe samples than in monitoring well samples.

For unsewered residential land uses, concentrations of iron, manganese, potassium, and total Kjeldahl nitrogen were greater in geoprobe samples whereas copper concentrations were lower. Overall, standard deviations were two percent greater in monitoring well data compared to geoprobe samples. Only nitrate concentrations differed between geoprobe and monitoring well samples for sewer residential, with concentrations being greater in the monitoring wells.

For commercial/industrial land uses, median concentrations of fluoride were greater in geoprobe samples than in monitoring wells, while concentrations of copper were less. Overall, standard deviations were two percent greater in geoprobe samples than in monitoring wells. For undeveloped land, median concentrations of total Kjeldahl nitrogen and total organic carbon were greater in geoprobe samples than monitoring well samples, while concentrations of vanadium, zinc, copper, and nitrate were lower.

Comparisons of the standard deviation of overall median and mean concentrations are illustrated in Table 13. Medians and means differ significantly, as would be expected since concentrations vary widely. The greatest variability occurred for irrigated land use, primarily because of large variability in concentrations of nitrate, alkalinity, calcium, and sulfate. These are chemicals which are readily leached, and recharge was greater under irrigated agriculture than under other land uses (MPCA, 1998a). The variability in concentrations of nitrate, magnesium, phosphorus, potassium, sulfate, copper, and total Kjeldahl nitrogen were greatest under irrigated agriculture, while variability in iron, manganese, and sodium was low compared to other land uses. This reflects the impact of recharge and fertilizer use in irrigated agriculture. Variability in concentration was less for the nonirrigated data compared to the irrigated data. Nitrate and potassium showed the greatest variability, probably reflecting fertilizer use. The variability within sewer and unsewered land use data was low. An exception was chloride, reflecting inputs from road

salt and possibly human waste. The chemicals with the greatest variability within commercial areas were barium, boron, chloride, manganese, nickel, copper, and zinc. Except for chloride, which reflects inputs from road salt, the remaining chemicals are trace elements which may have a variety of industrial sources, including automobile fluids such as oil and radiator fluid. Samples collected from undeveloped land had a large number of chemicals with low and high variability in concentration. There was large variability in concentrations of total Kjeldahl nitrogen, total organic carbon, silica, magnesium, iron, alkalinity, pH, ammonia, and calcium. These are chemicals with few human inputs and the results reflect variability in natural leaching concentrations under different undeveloped land uses. Chemicals with low variability were those in which there can be significant human inputs, including nitrate, chloride, boron, phosphorus, and potassium.

	Nonirrigated	Irrigated	Unsewered	Sewered	Commercial	Undeveloped
Median	93	107	130	133	125	195
Mean	5925	15483	6174	8247	6471	8751

Table 13 : Median and mean overall standard deviations in chemical concentration, by land use.

Comparisons of overall medians and coefficients of variation between geoprobe and monitoring well samples are illustrated in Table 14. Overall, concentrations and variability in concentrations tended to be greater in geoprobe samples (about 10 percent overall). This may partly be related to greater concentrations of suspended material and organic carbon in the geoprobe samples. Another factor was the difference in median Eh, which was 352 mV in the monitoring wells and 302 mV in the geoprobe samples. A third factor was season of sampling. This was most important for some of the trace chemicals, including barium, boron, copper, manganese, nickel, and zinc. These are chemicals for which significantly lower concentrations have been observed in spring sampling from the monitoring wells. The greatest differences in median concentration were for the nitrogen species, iron, and manganese, all of which had higher concentrations in the geoprobe samples. Variability in data from geoprobe samples was large for these parameters.

Parameter	Medians		Coefficient of Variation			
	Monitoring	Geoprobe	Monitoring	Geoprobe	Overall	RPD
<b>Chemicals in which geoprobe and monitoring well medians did not differ</b>						
Alkalinity	259333	259667	0.30	0.28	0.29	-1.77
Barium	68	55	0.86	0.67	0.77	-5.06
Boron	32	29	1.22	1.00	1.11	-4.46
Calcium	97914	90194	0.31	0.59	0.44	18.20
Chloride	45020	32330	0.91	3.59	2.03	38.20
Copper	5.8	5	1.09	0.64	0.88	-10.51
Fluoride	100	290	2.05	0.93	1.22	-25.46
Magnesium	26424	27432	0.30	0.50	0.40	14.56
pH	7.18	7.45	0.05	0.07	0.06	9.01
Phosphorus	33	30	2.33	1.67	2.02	-7.30
Potassium	2220	1746	1.03	1.72	1.34	12.88
Silica	8328	7651	0.23	0.32	0.27	8.55
Sodium	12583	10302	2.12	4.80	3.33	22.11
Specific Conductance	692	601	0.38	0.53	0.45	7.88
Strontium	122	104	0.60	1.40	0.97	23.65
Sulfate-S	8731	8023	1.15	1.47	1.30	6.30
Sulfur	26100	24390	0.40	0.53	0.46	7.02
Temperature	10.1	7.38	0.31	0.35	0.33	2.92
Vanadium	5.7	< 4.7	0.53	-	0.76	18.37
Zinc	10.2	5.7	0.84	1.09	0.93	4.94
<b>Chemicals in which geoprobe and monitoring well medians differed</b>						
Ammonia-N	70	80	0.71	1.59	1.18	24.59
Dissolved Oxygen	6520	6320	0.56	0.52	0.85	20.6
Eh	352	302	0.38	0.33	0.36	-3.47
Iron	5.7	28	9.30	27.11	24.09	44.31
Manganese	4.3	75	51.16	3.59	6.17	-78.49
Nitrate-N	2490	5640	3.08	5.31	4.63	20.06
Total Kjeldahl Nitrogen	100	225	4.95	30.64	22.74	64.25
Total Organic Carbon	1900	2300	0.98	1.70	1.38	16.82

Table 14 : Comparison of overall median concentrations and coefficients of variation between monitoring wells andgeoprobe samples.

Data from the monitoring network can be evaluated to determine if three wells are suitable for evaluating water quality effects from land use and trends in water quality associated with land use. Comparisons were made of coefficients of variability for

geoprobe samples, monitoring well samples, and all samples combined. The data are separated into those in which median concentrations did not differ between geoprobe and monitoring samples and those for which medians differed. If three wells were not adequate for assessing land use, coefficients of variation should decrease by adding additional samples. The Relative Percent Difference (RPD) is an indication of the differences in coefficients of variation, with negative values indicating decreasing variability as the number of samples increased. The results indicate increasing coefficients of variation for 15 chemical parameters and just 8 for decreasing coefficients of variation. Overall, median coefficients of variation increased by 2.8 percent when adding the geoprobe samples to the data. For the oxidation-reduction parameters, the results were more striking, with coefficients of variation increasing by 19.5 percent when the geoprobe samples were added to the data. Water quality information collected with a geoprobe should be viewed with some caution for the oxidation-reduction chemicals, since these appear to be highly affected by the quality of sample collected with the geoprobe.

It is difficult to evaluate the existing monitoring network even when data from the geoprobe sites is pooled with the monitoring data, primarily because of the small sample sizes and differences in the quality of sample collected using the two methods. The monitoring network appears to be adequate for representing differences in ground water quality under different land uses, but the monitoring network does not appear to be optimum. Consequently, caution should be exercised when attempting to quantify concentrations of chemicals under different land uses.

#### 4. Conclusions and Recommendations

1. Ground water quality at the water table was strongly correlated with land use.
2. Concentrations of chloride at the 7.5 and 15 foot depths were correlated with concentrations at the water table, suggesting some aquifer mixing was occurring. However, correlations between land use and ground water quality for other chemicals were limited to the upper few feet of the aquifer. Attenuation by either adsorption (cations) or denitrification (nitrate) appears to be the major chemical sink within the upper portion of the aquifer.
3. Changes in oxidation-reduction status of the upper 15 feet of the aquifer were observed during the period of recharge, primarily as a result of introduction of oxygenated water to the aquifer. These changes became less noticeable with depth below the water table.
4. The primary chemical of concern from a potential health standpoint was nitrate, which was close to or exceeded the drinking water criteria under irrigated agriculture, nonirrigated soybeans, nonirrigated corn, nonirrigated alfalfa, and unsewered land.
5. VOCs were widely distributed in the upper portion of the aquifer under urban land settings, although at concentrations below drinking water criteria. Toluene, xylene, 1,1,2,2-tetrachloroethylene, and ethylbenzene were found in 10, 3, 3, and 2 samples respectively. Benzene, chloromethane, dichlorodifluoromethane, n-propylbenzene, and naphthalene were each found in one sample.
6. Pesticides were detected in only one of 22 samples (cyanazine at a concentration of 7.6 ug/L), but the low frequency of detection may be due to reporting limits that were too high, a lack of sampling for metabolites, and sampling at a time of year when pesticide concentrations are likely to be low. The geoprobe results do not correlate with the monitoring well data, in which 62 chemicals, including 31 metabolites, were detected in 15 wells during March and May sampling events.
7. Geoprobe samples had significantly different concentrations of many oxidation-reduction parameters compared to monitoring wells, including greater concentrations of iron, manganese, total organic carbon, ammonia, and organic nitrogen, and lower concentrations of dissolved oxygen, nitrate, and lower Eh. Differences in these chemicals were related to the greater concentration of suspended material in the geoprobe samples.

Geoprobe samples also had lower concentrations of many trace inorganic chemicals, but this was related to sampling during the period of recharge, which tends to dilute the concentration of these chemicals in ground water.



8. Coefficients of variation for most chemicals within a particular land use did not differ significantly between monitoring wells and all data (monitoring wells plus geoprobe samples). Coefficients of variation for the oxidation-reduction-related parameters (dissolved iron and manganese, dissolved oxygen, Eh, nitrate, and total organic carbon) were much greater in the geoprobe samples because of greater concentrations of suspended material compared to the monitoring wells. The monitoring well network appears adequate for assessing land use effects on ground water quality but may not be adequate for understanding processes affecting the distribution of chemicals in the aquifer.

The following recommendations are made based on results of the geoprobe study.

1. Geoprobe samples provide information about water quality but should not be combined with information collected from other sampling methods (e.g. monitoring wells). Geoprobe samples should be filtered for turbidity and filtering may be required for all parameters when ground water is turbid.
2. The current St. Cloud monitoring network should be maintained.
3. Chemical parameters affected by oxidation-reduction conditions should be sampled more frequently in monitoring wells during periods of recharge. This requires collecting water level information from continuous water level recorders on a weekly basis in spring following snowmelt and during periods of prolonged, heavy precipitation.
4. Information from the geoprobe study should be used to calibrate the ground water model for the study area. Geologic layers can be developed using textural information in conjunction with information from the County Well Index (Wahl and Tipping, 1991). Water quality information can be used to calibrate the three-dimensional distributions of nitrate and chloride within the aquifer. Aquifer attenuation properties can be incorporated into the model using chemical information from aquifer samples collected during the study. The model will help ground water managers estimate impacts from different land uses and trends in water quality following land use changes, and in determining which parameters (e.g. aquifer conductance, chemical input, recharge) have the greatest effect on ground water quality.

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### Appendix A - Analytical Methods and Reporting Limits

Parameter	Method	Reporting Limit ug/L
Aluminum	ICP	49.9
Arsenic	ICP	10.4
Barium	ICP	1.0
Beryllium	ICP	0.20
Boron	ICP	6.5
Cadmium	ICP	1.8
Calcium	ICP	5.0
Chromium	ICP	3.1
Cobalt	ICP	2.9
Copper	ICP	5.4
Iron	ICP	3.1
Lead	ICP	24.5
Lithium	ICP	4.4
Magnesium	ICP	20
Manganese	ICP	0.9
Molybdenum	ICP	4.1
Nickel	ICP	6.0
Phosphorus	ICP	14.0
Potassium	ICP	100
Rubidium	ICP	337.5
Silica	ICP	20
Sodium	ICP	60
Sulfur	ICP	20
Titanium	ICP	3.4
Vanadium	ICP	4.7
Zinc	ICP	1.7
Chloride	Ion chromatography	100
Fluoride	Ion chromatography	200
Sulfate	Ion chromatography	100
Dissolved Oxygen	Field meter	10
Alkalinity	Titration	1000
Oxidation-reduction potential	Field meter	1 mV
pH	Field meter	0.01 pH unit
Temperature	Field meter	0.01 °C
<b>Volatile organic compounds</b>		
1,1-Dichloroethane	MDH 465A	0.2
1,1-Dichloroethene	MDH 465A	0.5
1,1-Dichloropropene	MDH 465A	0.2
1,1,1-Trichloroethane	MDH 465A	0.2

Parameter	Method	Reporting Limit ug/L
1,1,1,2-Tetrachloroethane	MDH 465A	0.2
1,1,2-Trichloroethane	MDH 465A	0.2
1,1,2,2-Tetrachloroethane	MDH 465A	0.2
1,1,2-Trichlorotrifluoroethane	MDH 465A	0.2
1,2-Dichlorobenzene	MDH 465A	0.2
1,2-Dichloroethane	MDH 465A	0.2
1,2-Dichloropropane	MDH 465A	0.2
1,2,3-Trichlorobenzene	MDH 465A	0.5
1,2,3-Trichloropropane	MDH 465A	0.5
1,2,4-Trichlorobenzene	MDH 465A	0.5
1,2,4-Trimethylbenzene	MDH 465A	0.5
1,3-Dichlorobenzene	MDH 465A	0.2
1,3-Dichloropropane	MDH 465A	0.2
1,3,5-Trimethylbenzene	MDH 465A	0.5
1,4-Dichlorobenzene	MDH 465A	0.2
2,2-Dichloropropane	MDH 465A	0.5
2-Chlorotoluene	MDH 465A	0.5
4-Chlorotoluene	MDH 465A	0.5
Acetone	MDH 465A	20
Allyl chloride	MDH 465A	0.5
Bromochloromethane	MDH 465A	0.5
Bromodichloromethane	MDH 465A	0.2
Benzene	MDH 465A	0.2
Bromobenzene	MDH 465A	0.2
Bromoform	MDH 465A	0.5
Bromomethane	MDH 465A	0.5
cis-1,2-Dichloroethene	MDH 465A	0.2
cis-1,3-Dichloropropene	MDH 465A	0.2
Carbon tetrachloride	MDH 465A	0.2
Chlorodibromomethane	MDH 465A	0.5
Chlorobenzene	MDH 465A	0.2
Chloroethane	MDH 465A	0.5
Chloroform	MDH 465A	0.1
Chloromethane	MDH 465A	0.5
1,2-Dibromo-3-chloropropane	MDH 465A	0.5
Dibromomethane	MDH 465A	0.5
Dichlorodifluoromethane	MDH 465A	0.5
Dichlorofluoromethane	MDH 465A	0.5
1,2-Dibromoethane	MDH 465A	0.5
Ethylbenzene	MDH 465A	0.2
Parameter	Method	Reporting Limit

		ug/L
Ethyl ether	MDH 465A	2
Hexachlorobutadiene	MDH 465A	0.5
Isopropylbenzene	MDH 465A	0.5
Methylene chloride	MDH 465A	0.5
Methyl ethyl ketone	MDH 465A	10
Methyl isobutyl ketone	MDH 465A	5
Methyl tertiary butyl ether	MDH 465A	2
n-Butylbenzene	MDH 465A	0.5
Naphthalene	MDH 465A	0.5
n-Propylbenzene	MDH 465A	0.5
o-Xylene	MDH 465A	0.2
p&m-Xylene	MDH 465A	0.2
p-Isopropyltoluene	MDH 465A	0.5
sec-Butylbenzene	MDH 465A	0.5
Styrene	MDH 465A	0.5
tert-Butylbenzene	MDH 465A	0.5
trans-1,2-Dichloroethene	MDH 465A	0.1
trans-1,3-Dichloropropene	MDH 465A	0.2
Trichloroethene	MDH 465A	0.1
Trichlorofluoromethane	MDH 465A	0.5
Tetrachloroethene	MDH 465A	0.2
Tetrahydrofuran	MDH 465A	10
Toluene	MDH 465A	0.2
Vinyl chloride	MDH 465A	0.5
Total organic carbon	Dohrman carbon analyzer	100
Specific conductance	Field meter	0.1 mmho/cm
Nitrate-nitrogen	Cadmium reduction	100
Kjeldahl-nitrogen	Digestion/colorimetric	200
<b>Herbicides</b>		
Acetochlor	EPA 507	0.03
Alachlor	EPA 507	0.15
Atrazine	EPA 507	0.10
Desethylatrazine	EPA 507	0.050
Deisopropylatrazine	EPA 507	0.050
Chlorpyrifos	EPA 507	0.05
Chlorthalonil	EPA 507	0.08
Cyanazine	EPA 507	0.20
Diazinon	EPA 507	0.04
Dimethoate	EPA 507	0.10
EPTC	EPA 507	0.11
<b>Parameter</b>	<b>Method</b>	<b>Reporting Limit ug/L</b>

Fonofos	EPA 507	0.05
Malathion	EPA 507	0.10
Metolachlor	EPA 507	0.09
Metribuzin	EPA 507	0.10
Methyl parathion	EPA 507	0.04
Pendimethalin	EPA 507	0.10
Phorate	EPA 507	0.07
Terbufos	EPA 507	0.10
Trifluralin	EPA 507	0.03
2,4-D	EPA 515.1	0.20
Dicamba	EPA 515.1	0.20
Dichlorprop	EPA 515.1	0.20
MCPA	EPA 515.1	0.20
MCPP	EPA 515.1	0.20
Triclopyr	EPA 515.1	0.20