

Ground Water Quality in Cottage Grove, Minnesota

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Executive Summary

Elevated concentrations of nitrate occur throughout much of the Prairie du Chien and Jordan aquifers in Cottage Grove, Minnesota. We conducted a study in Cottage Grove to assess ground water quality, identify factors that contribute to ground water contamination, identify factors that affect the fate of chemicals in ground water, determine if there are trends in water quality, identify research needs, and recommend management strategies to minimize ground water contamination.

In summer, 1999, we sampled 74 private domestic wells for major ions, trace inorganics, agricultural herbicides, volatile organic compounds (VOCs), and field parameters. Most of the wells were completed in the Prairie du Chien and Jordan aquifers, which provide drinking water for most of the residents in Cottage Grove. We also sampled three temporary wells that were screened at the water table. Our sample design was hampered by an inadequate number of wells completed in sewered residential areas and by limitations to drilling temporary wells. Consequently our results are skewed towards sampling in the eastern half of the study area and from wells completed in deeper portions of the aquifers.

Nitrate was the contaminant of greatest concern in ground water. The median nitrate concentration was 6.1 mg/l in the Prairie du Chien aquifer and 5.4 mg/l in the Jordan aquifer. Twelve wells exceeded the drinking water criteria of 10 mg/l. There were no differences in nitrate concentration between the surficial sand and gravel (Quaternary) aquifer, the Prairie du Chien aquifer, the Jordan aquifer, and the Franconia aquifer. There were no differences in nitrate concentrations between wells drilled in agricultural, unsewered residential, and sewered residential areas. There was no effect of well depth, depth to water, depth to bedrock, or presence of confining geologic deposits on the distribution of nitrate in ground water. Nitrate concentrations were strongly correlated with herbicide concentrations, indicating that agriculture is the probable source for much of the nitrate. We were unable to identify trends in nitrate concentrations. The Quaternary, Prairie du Chien, and Jordan aquifers are well mixed and vulnerable to contamination with nitrate and herbicides throughout their vertical extent. There are portions of the Franconia that are not vulnerable to nitrate contamination, although the

median tritium concentration in the Franconia was 10.9 tritium units. Low nitrate vulnerability in the Franconia aquifer is related to the presence of nitrate-reducing conditions.

Herbicides and herbicide degradates were found in 68% of the sampled wells. Degradates accounted for 95% of the total herbicide mass. Alachlor ESA (sulfonic acid), alachlor OA (oxanilic acid), metolochlor ESA, metolochlor OA, atrazine, and deethylatrazine were the most common herbicides found in ground water. The distribution of herbicides was similar to the distribution for nitrate, with herbicides being found in samples containing dissolved oxygen.

VOCs were detected in only two wells, at concentrations far below drinking water standards. Concentrations of other chemicals were below drinking water standards, except iron, which exceeded the Secondary Maximum Contaminant Level in nine wells.

Additional ground water studies should focus on identifying recharge and chemical leaching patterns, monitoring trends in water quality, and utilizing existing models to predict water quality in response to changes in land use. Specific recommendations include the following.

1. Calibrate existing ground water models using age-dating and geochemical results. Utilize the model in conjunction with historic nitrate concentrations to determine if there are trends in nitrate concentrations.
2. Add a solute transport component to existing models to track the fate of nitrate and herbicides in ground water.
3. Utilize existing models to predict ground water quality in response to changes in land use.
4. Install four monitoring wells in the upper 10 feet of the Quaternary aquifer for purposes of monitoring trends in water quality. Three wells should be completed in areas where agricultural land use will change to unsewered residential, sewer residential, and commercial/industrial land use. The fourth well should be completed in an area that will remain in agricultural land use indefinitely. Wells should be equipped with continuous water level recorders to provide information on recharge. Wells should be sampled quarterly for nitrate and annually for major ions, herbicides,

and oxidation-reduction parameters (dissolved iron, nitrate, dissolved oxygen, and oxidation-reduction potential) for a period of five years. Sampling should then occur indefinitely on an annual basis for the full parameter list.

5. Establish a trend-monitoring network using domestic wells that were sampled during this study. This network includes about 25 wells that are completed at a variety of depths in the Prairie du Chien and Jordan aquifers.
6. Conduct additional sampling for Volatile Organic Compounds in sewer residential areas.

1. Introduction

In 1996, we began a study in St. Cloud, Minnesota, to determine the effects of land use on ground water quality (Minnesota Pollution Control Agency, 1998a; 1999a). Our data indicate that human activity impacts ground water quality. Concentrations of many inorganic and organic chemicals are higher under all urban and rural land uses compared to undeveloped land uses. The primary chemicals of concern are nitrate in irrigated agricultural areas and unsewered residential areas, volatile organic compounds (VOCs) in sewered areas, and herbicides in agricultural areas. Our results are corroborated by other researchers (Lucey and Goolsby, 1993; Burkhart and Kolpin, 1993; Keeney and DeLuca, 1993; Bauder et al., 1993; Cain et. al, 1989; Geron et al., 1993; Eckhardt and Stackelberg, 1995; Haycock and Pinay, 1993; Anderson, 1993).

Ground water in St. Cloud occurs in sand and gravel deposits. Although land use impacts are evident in shallow ground water, they do not extend deeply into the aquifer. We wanted to conduct a study in a different physical setting to determine how our results compare with those from St. Cloud.

We chose Cottage Grove for a second study to determine land use impacts to ground water. Agriculture is the principal land use, but urbanization has occurred in the past 20 years. The primary aquifers underlying the study area occur in Paleozoic bedrock, and they are considered vulnerable to contamination from activities at the land surface (Minnesota Geological Survey, 1990).

We conducted a study in 1999 to determine water quality in ground water underlying Cottage Grove. Our objectives were to determine

1. if the aquifer is impacted by human activity;
2. how deep land use effects extend into aquifers;
3. what factors affect the distribution of chemicals in the aquifers underlying Cottage Grove;
4. if there are trends in ground water quality;
5. if there are additional research needs; and
6. appropriate management strategies to minimize ground water contamination.

2. Methods and Materials

2.1. Physical Setting

Cottage Grove encompasses about 30 mi² near the southeastern edge of the Twin Cities Metropolitan Area (Figure 1). The population of Cottage Grove is approximately 30000. The area has experienced rapid growth and changes in land use within the past 20 years, but the area is primarily agricultural.

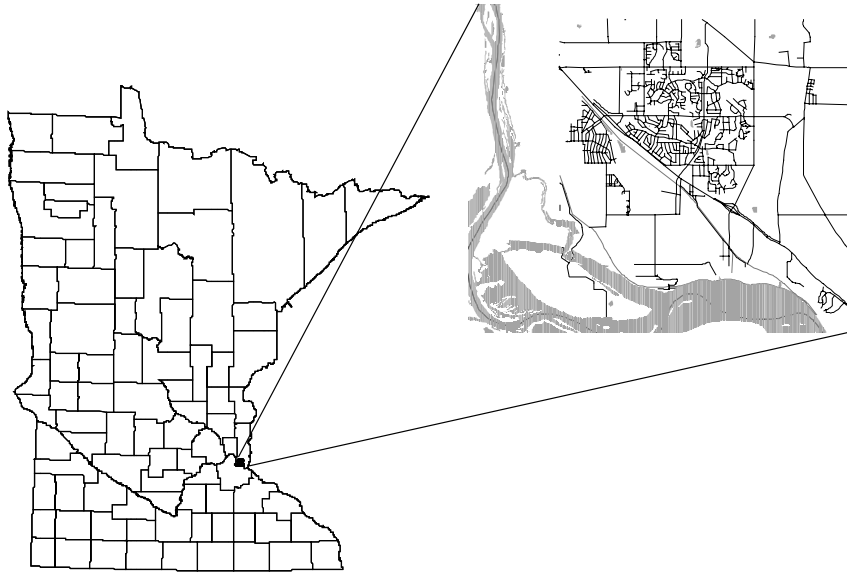


Figure 1: Location of study area.

Surficial geology consists of Superior lobe outwash of the Cromwell Formation over the northeastern half of the study area and terrace deposits over the southwestern half (Minnesota Geological Survey, 1990). Outwash deposits consist of sand, loamy sand, and gravel, cobbly in places, and covered by 3 to 6 feet of loess. Terrace deposits consist of coarse sand and gravelly sand. Loamy sand deposits, up to 15 or more feet in thickness, cover the terrace deposits. Bedrock units of Early Paleozoic Age underlie the glacial deposits. Depth to bedrock varies from 0 to over 180 feet, but is less than 90 feet across most of the study area (Figure 2). Bedrock crops out along the Mississippi River. The Prairie du Chien Group is the bedrock unit closest to the land surface across most of the study area. It consists primarily of dolostone, although there are thin beds of shale

and chert. The Prairie du Chien is the most important aquifer within the study area. The Jordan sandstone underlies the Prairie du Chien except near the Mississippi River, where it crops out. The Jordan Sandstone is a coarse-grained, friable, quartzose sandstone. It is an important aquifer in the study area. The Prairie du Chien and Jordan aquifers are often treated as a single aquifer based on similarities in head measurements in the two aquifers. There is evidence that these aquifers may act independently, however, both hydraulically (Streitz, personal communication) and geochemically (MPCA, 1998b). In the northern third of the study area, the Platteville Formation, Glenwood Formation, and St. Peter Sandstone overlie the Prairie du Chien Group. The Platteville is a fine-grained dolostone, the Glenwood is a sandy shale, and the St. Peter is a medium-grained sandstone, although the lower portion of the St. Peter consists of mudstone, siltstone, and shale intermingled with sandstone. The Glenwood and lower St. Peter formations act as confining layers for the Prairie du Chien aquifer. Tills serve as local confining layers within the unconsolidated deposits, but they are discontinuous. Figure 3 illustrates ground water flow in the Prairie du Chien and Jordan aquifers. These are treated as a single aquifer in Figure 3.



Figure 2: Depth to bedrock, in feet.



Figure 3: Ground water flow within the Prairie du Chien-Jordan aquifer. Contour intervals are 15 meters or 47.4 feet.

The northern and eastern portions of the area are covered by soils of the Antigo-Chetek-Mahtomedi association. These are nearly level to steep, well drained, and excessively drained, medium to coarse textured soils occurring on outwash plains. The southern portion of the study area consists of soils from the Sparta-Dickman-Hubbard association and from the Copaston-Sparta association. These are level to moderately steep, well drained and excessively drained, medium and coarse textured soils. The Sparta-Dickman-Hubbard association occurs on outwash plains and upland terraces, while the Copaston-Sparta association occurs on lowland terraces. The Waukegan-Baytown-Ripon, Ostrander-Baytown, Ripon, Antigo-Comstock, and Santiago-Kingsley associations cover small areas of the study. These soils predominantly occur on undulating uplands and are medium to coarse textured and poorly to well drained. In heavily industrialized, commercial, and some residential areas, the upper 5 to 10 feet of soil may consist of fill (United States Department of Agriculture - Washington County Soil Survey). Average annual precipitation is 28 inches, with about 18 inches falling between April and September.

2.2. Land Use

Figure 4 illustrates land use in 1957, 1970, 1980, and 1990. The increase in residential land use between 1957 and 1990 is evident. About 71 percent of Cottage

Grove is still classified as agricultural, however (Table 1). Residential areas account for about 11 percent of total land use. Commercial and industrial areas account for less than two percent of all land use. Figure 4 does not accurately show all residential areas in Cottage Grove, since several small developments occur throughout the area. Single-family homes, typically on larger lots (2 or more acres), dominate these developments. These developments are common in the southern part of Cottage Grove, particularly along the Mississippi River. The population of Cottage Grove has increased steadily from about 13000 in 1970 to nearly 31000 in 1997 (Figure 5).

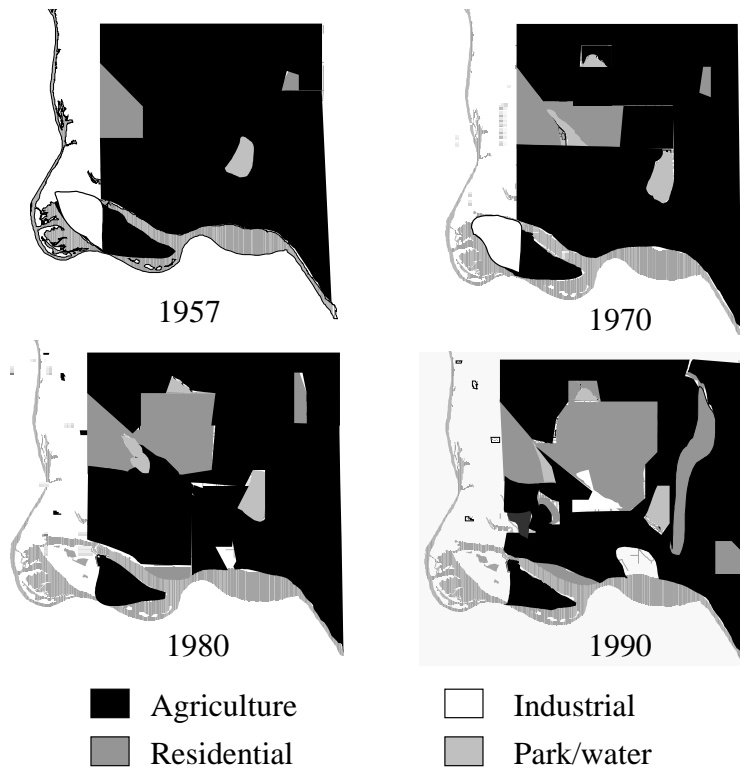


Figure 4: Land use in Cottage Grove in 1957, 1970, 1980, and 1990.

Land Use	Percentage of Total Use
Agriculture	71.4
Single family	10.4
Water	8.7
Parks	4.1
Industrial	1.3
Transportation	1.1
Other Public land	1.1
Farmsteads	0.8
Commercial	0.6
Multi-family	0.4

Table 1: Distribution of land use in Cottage Grove.

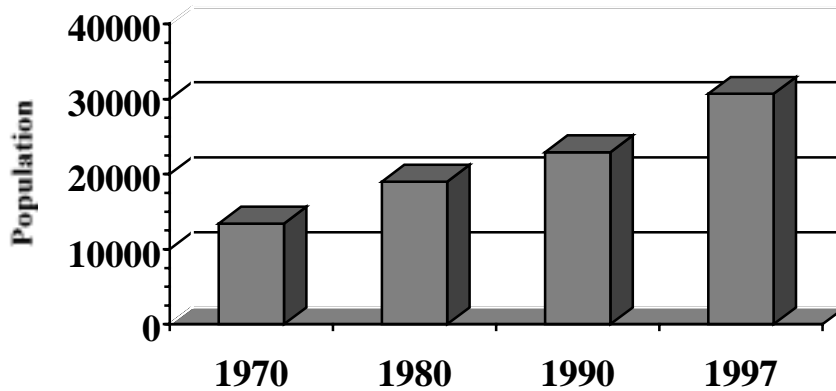


Figure 5: Population of Cottage Grove from 1970 to 1997.

2.3. Site Selection

We used the County Well Index (CWI)(Wahl and Tipping, 1991) to identify domestic wells for sampling. Selected wells encompass a range of depths and provide a distribution across the study area. There are fewer domestic wells in the urban areas because municipal supplies service these areas. Figure 6 illustrates locations of the 74 sampled domestic wells. Table 2 summarizes the distribution of wells.

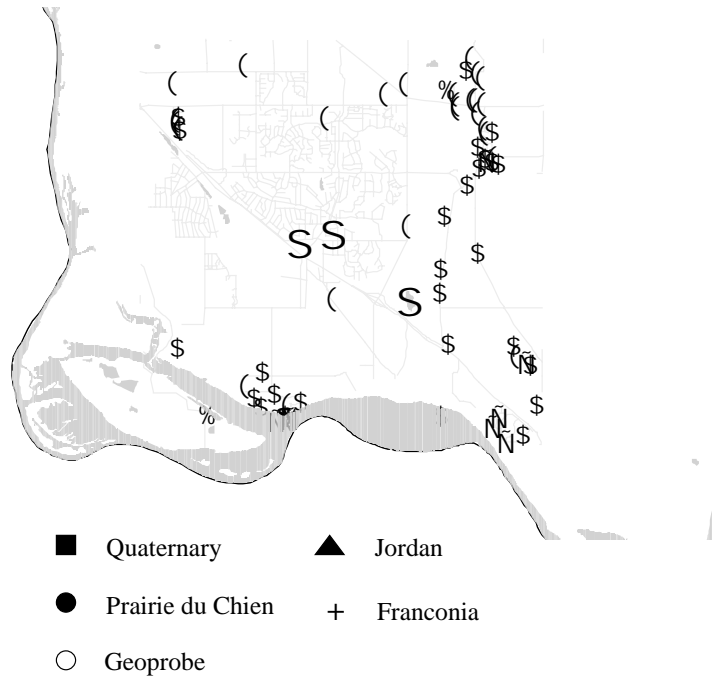


Figure 6: Location of sampled wells.

Well Type	Number sampled	Median well depth (ft)	Median depth to water (ft)	Median age of well (yrs)
Temporary wells				
Sand and gravel	3	26	23	-
Domestic wells				
Sand and gravel	4	107	43	17
Prairie du Chien	27	147	115	16
Jordan	28	189	120	16
Franconia	8	222	99	15
Unknown or multiple	7	150	-	41

Table 2: Summary information for sampled domestic and temporary wells.

In addition to the domestic wells, we installed three temporary wells using push probe drilling (Figure 6). 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. Drilling methods are described in MPCA (1998a).

2.4. Sample Collection

Sampling occurred between June and September of 1999. Sample collection for temporary wells consisted of pumping each well using a peristaltic pump. For domestic wells, we used an outdoor spigot that bypassed any type of water treatment system. A YSI 600XL multi-parameter water quality monitor provided continuous measurements of dissolved oxygen, oxidation-reduction potential, pH, temperature, and specific conductance. Stabilization criteria were 0.1 pH unit, 10 percent for specific conductance, and 0.1 °C for three consecutive readings. Samples for laboratory analysis included major cations and anions, some trace inorganic chemicals, total organic carbon, total Kjeldahl nitrogen (TKN), Volatile Organic Carbons (VOCs), and herbicides. Sample collection included 200 ml clear HDPE Level II bottle with 5 ml of nitric acid preservative for cations, 200 ml clear HDPE bottle with 5 ml sulfuric acid preservative for anions, 500 ml plastic bottle with no preservative for ammonia and TKN, a 20 ml glass vial with 8 drops of phosphoric acid preservative for organic carbon, a 40 ml, clear glass vial with 2 drops of hydrochloric acid preservative for VOCs, and 50 ml bottles for herbicides. Organic carbon samples and cation samples for temporary wells were filtered using a 0.45 micron in-line filter. All samples were placed into coolers with ice until delivered to the laboratory for analysis. Laboratory methods included inductively coupled plasma/atomic emission spectrometry for cations, cadmium reduction for nitrate, ion chromatography for sulfate and chloride, field titration for alkalinity, a Dohrman carbon analyzer for total organic carbon, digestion and colorimetric analysis for total Kjeldahl nitrogen (TKN), colorimetric analysis for ammonia-nitrogen, purge and trap (MDA Method 465A) for VOCs, and GS/MS for herbicides (Kalkhoff et al., 1998). Appendix I summarizes reporting limits and analysis methods.

We took field duplicates at a rate of ten percent. Laboratory duplicates were analyzed at a rate of ten percent. Concentrations for all duplicates were within ten percent of the primary samples. Acid blanks showed no detectable chemical. Laboratory spikes were within acceptable limits. Reporting limits and laboratory Quality Assurance/Quality Control are discussed in MPCA (1996).

2.5. Data Analysis

Statistical methods included the Kruskal-Wallis and Mann-Whitney tests for group comparisons. We performed correlation analysis using the Spearman rho method and simple linear regression. Data analysis methods are described in MPCA (1998c).

3. Results

Results are presented separately for inorganic and organic chemicals.

3.1. Inorganic Chemicals

Although we collected information for a large number of inorganic chemicals, nitrate was the anthropogenic chemical of greatest concern. We therefore divided the discussion into a general summary of results and a discussion on the distribution of nitrate.

3.1.1. General Results

Table 3 shows a comparison of chemical concentrations between different aquifers. Water quality of the Prairie du Chien and Jordan aquifers was similar, except for concentrations of calcium, potassium, sodium, and bicarbonate, which were higher in the Prairie du Chien aquifer. Concentrations of chemicals did not differ between surficial sand and gravel aquifers and the Prairie du Chien aquifer. Ground water in the sand and gravel aquifer, Prairie du Chien aquifer, and Jordan aquifer contain oxygen and have similar geochemistry. The Franconia aquifer, which includes wells completed in the St. Lawrence Formation, had water quality that differed from the Prairie du Chien aquifer in oxidation-reduction chemistry. Eh and concentrations of dissolved oxygen were significantly lower in the Franconia aquifer, and iron and manganese concentrations were higher. Nitrate-reducing conditions were evident in the Franconia aquifer, but nitrate concentrations were statistically equal between the Franconia, St. Lawrence, and Prairie du Chien aquifers. There was, however, a tendency for lower nitrate concentrations in the Franconia aquifer, and, given a larger sample size, we might have observed differences in concentrations of nitrate between the Franconia aquifer and the other aquifers.

Parameter	Surficial Sand	Prairie du Chien	Jordan	Franconia
Physical				
Depth	84 c	179 b	218 a	200 a
Depth to bedrock	-	58	36	160
Depth to water	20 b	110 a	124 a	30 ab
Chemical				
Alkalinity	217	223	196	222
Aluminum	< 0.049	< 0.049	< 0.049	< 0.049
Ammonia	0.18	0.030	0.030	0.045
Boron	0.024	0.018	0.014	0.018
Cadmium	< 0.0019	< 0.0019	< 0.0019	< 0.0019
Calcium	62	71	55	60
Chloride	10.0	14.1	8.9	2.3
Chromium	< 0.0034	< 0.0034	< 0.0034	< 0.0034
Copper	< 0.0055	< 0.0055	< 0.0055	< 0.0055
Dissolved oxygen	6.37 bc	8.50 ab	10.11 a	1.10 c
Eh	314 a	316 a	294 a	141 b
Fluoride	0.12	0.13	0.13	0.15
Iron	0.0071 b	< 0.0034 b	< 0.0034 b	0.38 a
Lead	< 0.024	< 0.024	< 0.024	< 0.024
Magnesium	23	26	24	26
Manganese	0.023 b	< 0.00070b	< 0.00070b	0.032 a
Nickel	< 0.0061	< 0.0061	< 0.0061	< 0.0061
Nitrate	4.0	6.1	5.4	3.6
pH	7.15	7.42	7.40	7.42
Potassium	1.3	1.1	0.93	1.0
Sodium	3.3	4.0	3.0	3.2
Specific conductance	794	779	523	456
Sulfate	7.2	7.1	7.9	7.1
Temperature	11.7 a	9.8 b	10.1 ab	10.1 a
Total organic carbon	< 0.50	< 0.50	< 0.50	< 0.50
Total phosphorus	< 0.020	0.02	< 0.020	< 0.020
Tritium	10.1	12.2	11.7	10.9
Zinc	0.0085	0.043	0.042	0.019

Table 3: Median concentrations of chemicals in the different sampled aquifers. Depths are in feet and concentrations are in mg/l, except for pH, Eh (mV), specific conductance (umhos/cm), tritium (tritium units), and temperature (°C). Different letters within a row indicate concentrations that differed at a significance level of 0.05.

Table 4 illustrates median values for physical and chemical parameters, by land use. Because only one sample was collected from an undeveloped area (a temporary well completed in a regional park), statistical comparisons were not possible with that land use. Concentrations of bicarbonate (alkalinity), calcium, chloride, potassium, and sodium were higher under sewered residential areas compared to unsewered residential and agricultural land uses. Concentrations of all other inorganic chemicals were statistically equal. Well depth and depth to water were greatest under sewered residential land use, but there was no effect of well depth or depth to water on the distribution of any chemical.

Data in Table 4 should be viewed with caution. Most of the data are from domestic wells screened below the water table. The median depth below the water table was 74 feet, with only two wells being screened in the top 20 feet of an aquifer. We do not have sufficient data near the water table to measure land use impacts at the top of the aquifer, where we would expect land use impacts to be greatest.

The coefficient of variation (CV) and the 95th percentile provide an indication of the distribution in chemical concentrations. Most importantly, these measurements provide an indication of the tendency for high concentrations, because it is high concentrations that we are typically most concerned with. For example, if we sampled five wells and determined concentrations of 0, 0, 10, 500, and 500, the median is 10. There is a tendency, however, for very low and very high concentrations in this data.

Table 5 illustrates upper 95th percentile concentrations and CVs for sampled parameters. The CV, equal to the standard deviation divided by the mean, provides a measure of the variability in the data. Values exceeding about 1 indicate there is large variability in the data, typically associated with a few high concentrations. There were relatively few parameters having high CV. Iron, manganese, and ammonia concentrations had high CVs under all three land uses. These parameters are all sensitive to oxidation-reduction (redox) conditions, and the CVs indicate a tendency for low concentrations of these chemicals under aerobic conditions and high concentrations under anaerobic conditions.

Parameter	Agricultural	Sewered	Unsewered	Undeveloped ¹
Physical parameters				
Depth	200 b	271 a	180 b	10
Depth to bedrock	60	55	38	-
Depth to water	110 b	168 a	100 b	7
Chemical parameters				
Alkalinity	206 b	242 a	199 b	-
Aluminum	< 0.049	< 0.049	< 0.049	< 0.049
Ammonia	0.030	0.050	0.040	0.070
Boron	0.0139	0.0222	0.0149	0.0237
Cadmium	< 0.0019	< 0.0019	< 0.0019	< 0.0019
Calcium	63 b	79 a	57 b	25
Chloride	10.0 b	21.6 a	5.8 b	20.3
Chromium	< 0.0034	< 0.0034	< 0.0034	< 0.0034
Copper	< 0.0055	< 0.0055	< 0.0055	< 0.0055
Dissolved oxygen	8.33	7.61	10.6	4.6
Eh	300	295	284	330
Fluoride	0.12	0.13	0.14	0.050
Iron	< 0.0034	< 0.0034	< 0.0034	0.0071
Lead	< 0.024	< 0.024	< 0.024	< 0.024
Magnesium	25 b	27 a	24 b	8.3
Manganese	< 0.00070	< 0.00070	< 0.00070	0.061
Nickel	< 0.0061	< 0.0061	< 0.0061	< 0.0061
Nitrate	5.8	4.7	4.4	1.2
pH	7.43	7.37	7.46	6.60
Potassium	1.06 b	1.75 a	0.87 b	3.23
Sodium	3.3 b	8.0 a	3.2 b	15.1
Specific conductance	634	787	495	287
Sulfate	7.60	8.37	6.96	5.14
Temperature	10.0	10.1	10.0	14
Total organic carbon	< 0.50	0.50	< 0.50	< 0.50
Total phosphorus	< 0.020	0.020	< 0.020	< 0.020
Tritium	12.2	9.5	11.4	-
Zinc	0.039	0.046	0.043	0.044

¹ Statistical comparisons were not possible due to inadequate sample size.

Table 4: Median concentrations of chemicals, by land use. Depths are in feet and concentrations are in mg/l, except for pH, Eh (mV), specific conductance (umhos/cm), tritium (tritium units), and temperature (°C). Different letters within a row indicate concentrations that differed at a significance level of 0.05.

Parameter	Agricultural			Sewered			Unsewered		
	N	95th percentile	CV	N	95th percentile	CV	N	95th percentile	CV
Physical parameters									
Depth	19	320	0.28	8	395	0.48	29	320	0.30
Depth to bedrock	15	130	0.64	7	115	0.60	24	103	0.68
Depth to water	19	218	0.35	8	174	0.36	29	183	0.40
Chemical Parameters									
Aluminum	19	< 0.049	0.00	8	< 0.049	0.00	29	< 0.049	0.00
Alkalinity	15	264	0.13	8	278	0.10	21	241	0.13
Ammonia	19	0.79	1.96	9	0.51	1.50	29	2.35	2.21
Boron	19	0.022	0.36	8	0.071	0.76	29	0.037	0.48
Calcium	19	94	0.29	8	103	0.18	29	96	0.31
Cadmium	19	< 0.0019	0.00	8	< 0.0019	0.00	29	< 0.0019	0.00
Chloride	19	33	0.79	9	129	1.12	29	60	1.10
Chromium	19	< 0.0034	0.00	8	< 0.0034	0.00	29	< 0.0034	0.00
Copper	19	< 0.0055	0.01	8	< 0.0055	0.00	29	< 0.0055	0.00
Dissolved oxygen	14	12	0.47	8	8.0	0.29	21	103	1.32
Dissolved organic carbon	17	3.4	1.16	8	0.80	0.26	25	7.6	2.07
Eh	14	371	0.27	8	404	0.33	21	394	0.83
Fluoride	9	0.16	0.19	6	0.20	0.25	17	0.19	0.26
Iron	19	0.36	2.55	8	0.28	2.54	29	0.56	2.36
Potassium	19	1.8	0.37	8	5.3	0.63	29	2.9	0.64
Magnesium	19	29	0.21	8	34	0.10	29	30	0.21
Manganese	19	0.032	1.54	8	0.026	2.26	29	0.051	2.13
Sodium	19	12	0.67	8	60	1.39	29	16	0.81
Nickel	19	0.025	0.63	8	0.0061	0.00	29	0.014	0.47
Nitrate	18	9.3	0.67	8	9.7	0.56	26	19	0.85
Phosphorus	19	0.099	0.66	8	0.048	0.40	29	0.048	0.34
Lead	19	< 0.024	0.00	8	< 0.024	0.00	29	< 0.024	0.00
Phosphorus	14	7.6	0.03	8	7.5	0.01	21	7.7	0.03
Specific conductance	14	1290	0.37	8	1340	0.58	21	1024	0.32
Sulfate	19	18	0.50	9	12	0.20	29	13	0.29
Temperature	14	10.6	0.03	8	14.1	0.14	21	11.1	0.06
Total organic carbon	17	1.6	0.64	8	0.70	0.21	25	0.67	0.19
Tritium	13	33	0.57	6	16	0.55	18	20	0.47
Zinc	19	0.15	0.76	8	0.19	0.81	29	0.39	1.51

Table 5: Upper 95th percentile concentrations and Coefficients of Variation (CV) for sampled parameters. Depths are in feet and concentrations are in mg/l, except for pH, Eh (mV), specific conductance (umhos/cm), tritium (tritium units), and temperature (°C).

Chloride concentrations varied widely under urban land use, reflecting multiple inputs from road salt, septic systems, and leaking underground sewer lines. Concentrations of dissolved organic carbon varied widely under agricultural and unsewered land uses, possibly reflecting inputs of organic matter associated with manure application or septic systems.

Percentiles are used to estimate the percent of samples that are equal to or less than a certain value. The 95th percentile concentrations of nitrate, ammonia, and dissolved organic carbon are much higher under unsewered residential areas than under agricultural and sewered land use. This may be related to the formation of septic plumes under unsewered areas. Samples collected from areas between plumes will have relatively low concentrations of chemicals, while samples taken from plumes will have high concentrations. Percentile concentrations for sodium and chloride are higher under sewered residential areas than under other land uses, probably due to use of road salt.

Concentrations of all chemicals were below drinking water criteria, with the exception of iron in nine samples and nitrate in 12 samples. The drinking water criteria for iron (0.300 mg/l) is not health based, but is instead based on the likelihood that iron will stain plumbing fixtures. The maximum iron concentration was 0.793 mg/l. Five of the nine samples that exceeded 0.300 mg/l were completed in the Franconia and St. Lawrence aquifers.

3.1.2. Nitrate

The distribution of nitrate in ground water in Cottage Grove is difficult to explain with existing information. Six factors confound our understanding of nitrate in ground water. First, there appears to be extensive mixing within the ground water system. This is evidenced by the presence of detectable tritium at depths of more than 200 feet. Second, fractured flow occurs in the Prairie du Chien aquifer. This makes it difficult to determine where the water in a particular sample originated, and it confounds our understanding of travel times. Third, extensive land use changes over the past 20 years make it difficult to associate water quality with a particular land use. Fourth, we were unable to collect a sufficient number of samples at the water table to determine how land

use correlates with nitrate concentrations in the upper part of the ground water system. Fifth, we do not have a good understanding of the unsaturated zone, particularly rates and patterns of recharge and chemical leaching to ground water. Sixth, we collected only a small number of samples from the portions of Cottage Grove that are serviced by municipal sewers, thus limiting our ability to map the distribution of nitrate in these areas.

There were twelve exceedances of the Health Risk Limit (HRL) of 10 mg/l. The HRL is the drinking water criteria for nitrate. The HRL represents the concentration below which no adverse health impacts are anticipated for a 70 kg person consuming 2 liters of water over a lifetime, but for nitrate, the health endpoint is the cardiovascular/blood system for infants. Seven of the twelve exceedances of the HRL were under unsewered land use, four were under agriculture, and one was under sewered residential land use. It must be remembered, however, that water quality in the sampled wells probably does not reflect overlying land use due to aquifer mixing and changes in land use over the past 20 years. There were six exceedances in the Jordan aquifer (21 percent of sampled wells), three in the Prairie du Chien (11 percent), two in the sand and gravel aquifer (50 percent), and one in a well screened across the Prairie du Chien and Jordan aquifers.

Figure 7 illustrates the distribution of nitrate in nitrate-vulnerable wells in the study area (see discussion in Section 3.1.2.1 for definition of nitrate-vulnerable wells). Consideration of just wells vulnerable to contamination allows us to reduce the confounding effects of different aquifers. We found that within nitrate-vulnerable wells there were no differences in nitrate concentrations between aquifers (Table 3). The contours in Figure 7 are based on samples we collected as part of this study (see Figure 6). Consequently, the contours in the west-central part of Cottage Grove are questionable because of limited sampling points. This is the area where municipal sewers exist. The maximum contour used in developing Figure 7 was 10 mg/l, since that is the drinking water criteria. Consequently, areas where nitrate concentrations are more than 12.5 mg/l (the next highest contour interval) are not shown. Nitrate concentrations are generally greater than 5.0 mg/l across the study area. About 41 percent of the study area falls within areas where the median concentration is greater than 7.5 mg/l. Approximately 17

percent of the study area occurs within locations where the median concentration exceeds 10 mg/l. The highest concentrations are located in the south and central parts of the study area. Since we had a good sampling density in these areas, the percentages provided above are considered reasonably accurate. We found no correlation between nitrate concentration and the concentration of any other sampled parameter, with the exception of chloride and herbicides. Chloride concentrations were highest in wells having high concentrations of nitrate. There was no correlation between the distribution of nitrate and physical factors such as well depth, depth to water, depth to bedrock, and the formation comprising the uppermost bedrock unit.



Figure 7: Distribution of nitrate in nitrate-vulnerable wells sampled for this study. All aquifers are considered together. Contours show concentrations in mg/l. A nitrate-vulnerable well is defined as having an Eh greater than 250 mV, a dissolved oxygen concentration greater than 1.0 mg/l, and an iron concentration less than 0.1 mg/l (MPCA, 1999a). Nitrate introduced to these wells will not be denitrified because of the presence of oxidizing conditions in the water.

If we include data from public supply wells, the distribution of nitrate appears to change somewhat (Figure 8). The median concentration of nitrate in 42 public supply wells was 1.5 mg/l, with a maximum concentration of 8.5 mg/l. Furthermore, concentrations were less than 1 mg/l in most of the wells located in areas serviced by municipal sewers. About 15.5 percent of the study area has nitrate concentrations

exceeding 10 mg/l, compared to about 17 percent when public supply wells are not considered. The highest nitrate concentrations occur in the eastern half of the study area, where agriculture exists and where a buried bedrock valley may have an impact on water quality (see discussion in Section 3.1.2.4).

Although utilizing the public supply wells seem to fill in data gaps in the portions of the study area served by municipal sewers, there are problems with using these data. The aquifers in which these wells are completed are often unknown, or the well may be completed across multiple aquifers. There is no additional water quality information for these wells, including information on oxidation-reduction conditions in the wells. There is no age-dating information for the wells. Finally, in some cases, water is blended from more than one well.



Figure 8: Distribution of nitrate in private (circles) and public (squares) supply wells. Contours show concentrations in mg/l, with a contour interval of 2.5 mg/l. The hachured contours enclose areas where concentrations exceed 10 mg/l.

We attempted to describe the distribution of nitrate in ground water by examining effects of aquifer geochemistry, historic concentrations in domestic wells, relationships

between water quality and changes in land use, and effects of physical factors, such as recharge and ground water flow. These are discussed below.

3.1.2.1. Aquifer Geochemistry

Table 6 summarizes data for wells with nitrate concentrations of less than 1 mg/l, 1 to 5 mg/l, 5 to 10 mg/l, and more than 10 mg/l. There were significant differences between these groups for each of the parameters shown in Table 6. Wells with low nitrate concentration had more reducing conditions than wells with elevated concentrations. Consequently, we divided the data into wells that were vulnerable to nitrate contamination and those that were not vulnerable. Wells that were vulnerable to nitrate contamination had an Eh greater than 250 mV, a dissolved oxygen concentration greater than 1.0 mg/l, and an iron concentration less than 0.1 mg/l (MPCA, 1999a). Nitrate introduced to these wells will not be denitrified because of the presence of oxidizing conditions in the water.

Interestingly, the median tritium concentration of 12.2 TUs in nitrate-vulnerable wells does not differ from the median of 12.5 TUs in wells that have nitrate-reducing conditions. These results indicate the presence of nitrate-reducing areas in the ground water system, even in areas where relatively young water is present. Figure 9 indicates that nitrate-reducing conditions occur in some wells in the southeastern corner of the study area, and possibly in the north-central part of the study area. The correlation between the nitrate concentration in a well and the presence of nitrate-vulnerable conditions is apparent in Figure 9. The occurrence of nitrate-reducing conditions in the southeastern part of the study area may be a function of ground water discharging up through the Franconia formation into the Jordan and Prairie du Chien aquifers or increasingly reducing conditions as ground water moves down-gradient. Water within the Franconia is reducing with respect to nitrate. Clays within the unsaturated zone appear to have little impact on the presence of nitrate-reducing conditions in ground water. Either the clays are discontinuous, recharge occurs in areas where clays are not present, or clays are fractured. This is in contrast to the results of Walsh et al. (1993), who observed a median nitrate concentration of 0.6 mg/l in Paleozoic aquifers of Southeast Minnesota for

wells that had more than 10 feet of clay in their geologic profile. The areas they studied were located south of Washington County, where tills may be more continuous and hence protective of bedrock aquifers.

We did not look at the effect of different till units on nitrate occurrence. Recent work on the distribution of tills in the study area, completed by the Minnesota Geological Survey, may prove useful for understanding the presence of nitrate-reducing conditions in ground water.

Parameter	Nitrate concentration (mg/l)			
	< 1	1-5	5-10	> 10
No. samples	23	16	24	12
Physical parameters				
Depth to bedrock	20	54	58	75
Sand thickness	24	54	70	69
Well depth	260	170	220	174
Chemical parameters				
Alkalinity	190	221	229	199
Calcium	53	59	71	75
Chloride	2.2	5.5	13	20
Dissolved organic carbon	< 0.50	0.50	0.50	0.50
Dissolved oxygen	2.2	8.8	9.7	13.6
Eh	201	330	316	301
Iron	0.17	< 0.0030	< 0.0030	< 0.0030
Manganese	0.024	< 0.00060	< 0.00060	< 0.00060
Phosphorus	< 0.020	< 0.020	< 0.020	0.022
Sodium	2.8	3.3	4.6	4.7
Specific conductance	466	562	818	621
Sulfate	9.1	6.3	6.9	8.0
Total organic carbon	< 0.50	< 0.50	0.50	< 0.50

Table 6: Summary of water quality in samples with different nitrate concentrations. Depths are in feet and concentrations are in mg/l, except for pH, Eh (mV), specific conductance (umhos/cm), tritium (tritium units), and temperature (°C).



Figure 9: Location of nitrate-vulnerable samples (circles) and samples in which nitrate-reducing conditions were observed (triangles). Contours show concentrations of nitrate, in mg/l.

The Quaternary aquifer is mapped as highly sensitive to ground water pollution across the entire study area, while the Prairie du Chien and Jordan aquifers are mapped as being sensitive or highly sensitive, depending on the presence of the St. Peter or Platteville formations (Minnesota Geological Survey, 1990). Our data indicate that this assessment is accurate for most of the study area. These three aquifers are not only vulnerable in the upper portions of the aquifer, but throughout their entire vertical thickness. There are insufficient sources of food for reduction of nitrate (carbon and reduced sulfur), and nitrate introduced to these aquifers will persist for long periods. Dilution appears to be the only mechanism for attenuation of nitrate throughout much of these aquifers, but dilution will be ineffective if nitrate concentrations in recharge water are equal to or higher than concentrations in ground water.

3.1.2.2. Comparison with Historic Data

It would be useful to know if nitrate concentrations are increasing or decreasing with time. Unfortunately, nitrate data has not been collected for purposes of trend analysis. One-time sampling for nitrate has occurred in domestic wells since about 1980. This data base does not contain information on other chemical parameters, so nitrate-vulnerable wells cannot be identified. Figure 10 illustrates the distribution of nitrate in samples collected since 1980. We determined no trend in nitrate concentration for the Prairie du Chien, Jordan, or Franconia aquifers (Figure 11).

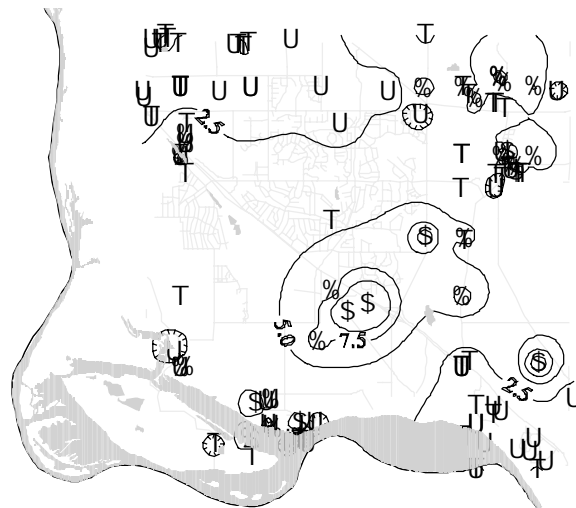


Figure 10: Historic concentrations of nitrate in Cottage Grove. Contours show concentrations of nitrate in mg/l.

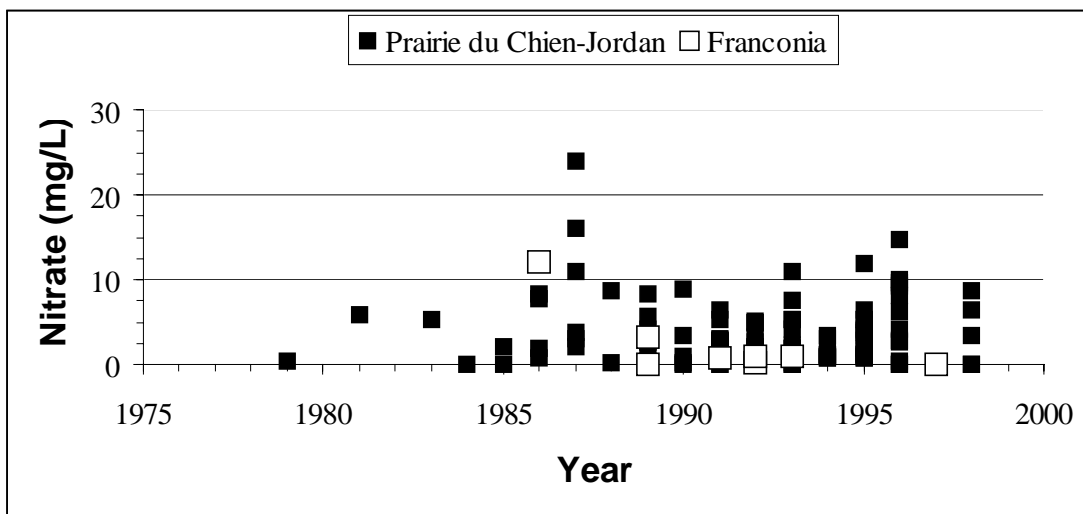


Figure 11: Distribution of nitrate over time in the Prairie du Chien-Jordan and Franconia aquifers.

We separated the wells based on geographic location to determine if there were trends in nitrate concentration in any portion of Cottage Grove. There was no trend for wells located in the southern, northern, western, or eastern halves of the study area.

For the historic data for Cottage Grove, we performed a sign test to determine if there was any correlation between nitrate concentrations and precipitation (Figure 12). We first calculated the median nitrate concentration and median precipitation for their respective periods of record. Then, for each year, we assigned a “+” if the median concentration in that year was greater than the overall median concentration. We made the same calculation for precipitation. We then compared signs. Of the 17 years in which we had adequate information to conduct the analysis, signs were opposite in 12 of the years. This means that when precipitation is above normal, nitrate concentrations in ground water are below the overall median, and vice versa. In the remaining five years, nitrate concentrations were positively correlated with precipitation. For these five years, there was no tendency for drier or wetter periods preceding the year in which positive correlations might occur. There was no correlation between nitrate concentration and annual precipitation ($R^2 = 0.135$). Thus, precipitation alone is not a good indicator of nitrate concentrations, but the tendency for higher or lower nitrate concentrations in a given year appears to be a function of precipitation. The lower nitrate concentrations evident in wet years may be due to dilution with recharge water. Unfortunately, we have insufficient information to know whether recharge and precipitation are positively correlated (see discussion in Section 3.1.2.4). We observed no correlation between nitrate concentration and month of sampling.

We conducted trend analysis on 21 public supply wells in Cottage Grove. Water quality samples have been collected in each of these wells since at least 1994, although only two wells had data preceding 1991. Table 7 summarizes results for trend analysis in each well. Twelve wells had no trend in nitrate concentration, one well had a downward trend, and eight wells had upward trends. The median increase in concentration in the wells with upward trends was 0.33 mg/l/year. Most of the wells with upward trends were located in the southeast and southwest part of the study area, while most wells with no trend were located in the central part of the study area. These results should be viewed

with caution, since there was no attempt to account for seasonality or differences in time of sampling or sampling methods. When we pooled all data (266 samples from 24 sites), we found evidence for a weak upward trend ($p = 0.085$) of 0.17 mg/l/year.

Site	Trend	Slope (mg/l/year)
5	No	-
6	No	-
7	No	-
8	No	-
13	No	-
14	No	-
19	No	-
22	No	-
23	No	-
27	No	-
30	No	-
41	No	-
25	No	-
31	No	-
34	No	-
35	No	-
36	No	-
39	No	-
43	No	-
12	Down	0.02
32	Up	0.10
10	Up	0.12
9	Up	0.12
29	Up	0.22
11	Up	0.23
42	Up	0.25
38	Up	0.25
26	Up	0.27
28	Up	0.38
33	Up	0.52
24	Up	0.70
40	Up	0.88

Table 7: Trend analysis for public supply wells in Cottage Grove.

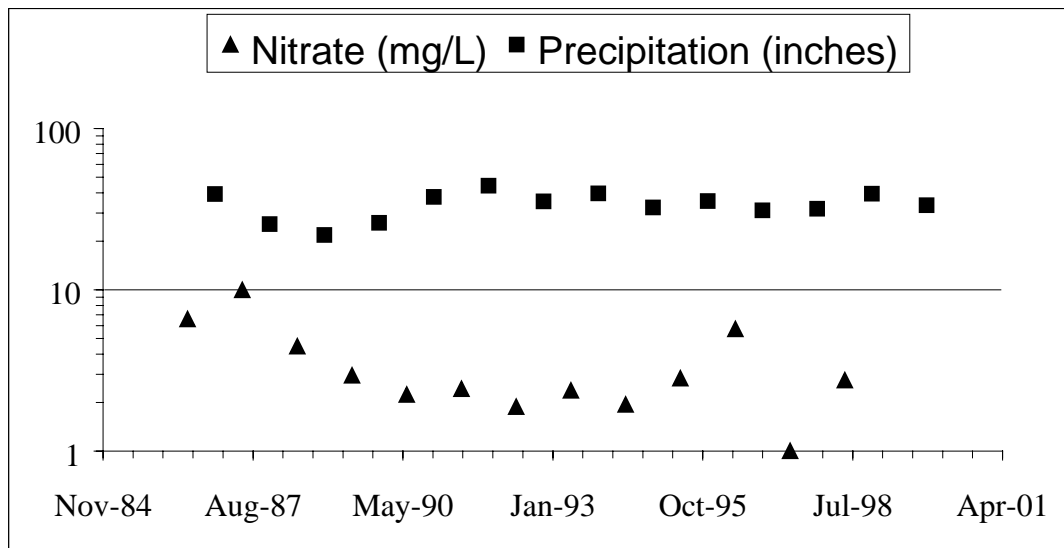


Figure 12: Concentration of nitrate and amount of precipitation between 1985 and 1999. Data are from the Washington County database.

3.1.2.3. Correlation with the distribution of herbicides

The distribution of herbicides in ground water provides valuable information about the distribution of nitrate. We observed a strong positive correlation between nitrate concentrations and the distribution of herbicides. In wells with detectable herbicide, the median nitrate concentration was 6.7 mg/l, compared to a median concentration of less than 0.5 mg/l in wells with no detectable herbicide. The cumulative concentration of herbicides in a well increased as the nitrate concentration increased ($p = 5.69 \times 10^{-10}$; $R^2 = 0.439$; Figure 13). The slope for this relationship was 1.36 mg-nitrate/l per 1 ug-herbicide/l.

Our data are in agreement with results presented by Walsh et al. (1993), who sampled for atrazine, deethylatrazine, deisopropylatrazine, alachlor, and the alachlor degradates 2, 6-diethylalanine and demethoxymethyl alachlor. Using their data, we calculated a slope of 4.8 mg-nitrate/l per 1 ug-herbicide/l for 31 wells sampled in the Prairie du Chien and Jordan aquifers of Southeast Minnesota ($p = 0.00077$; $R^2 = 0.328$). Median nitrate concentration in the 20 wells with detectable herbicide was 5.9 mg/l, compared to less than 0.4 mg/l in the wells with no detectable herbicide.

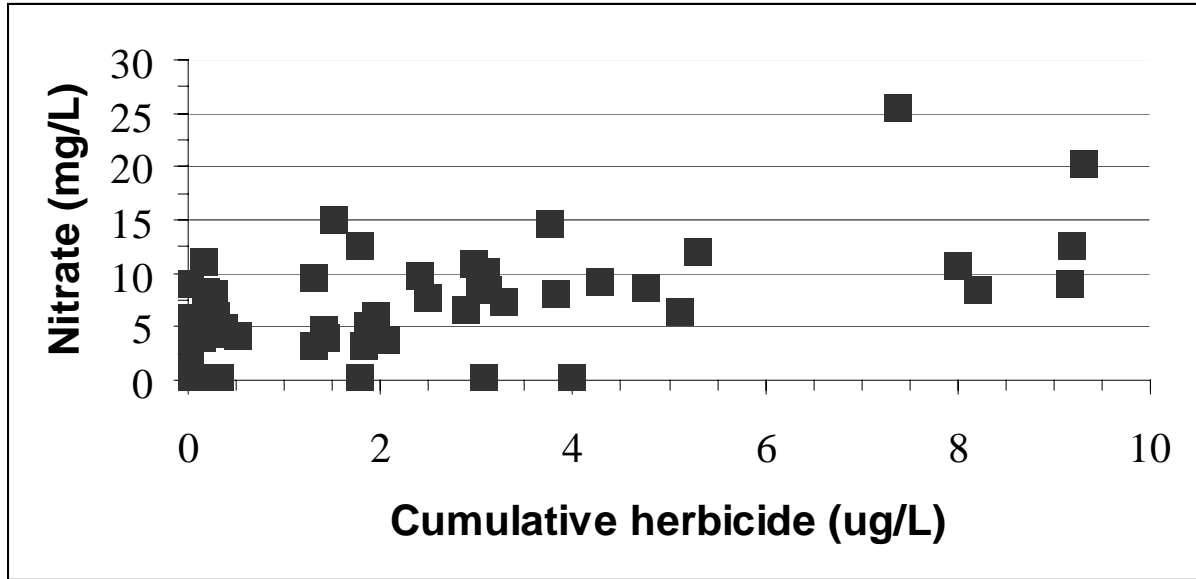


Figure 13: Nitrate in a well as a function of cumulative concentration of herbicide.

The herbicides sampled in our study and the study of Walsh et al. (1993) are associated with agricultural use. We therefore assume that much of the nitrate in sampled wells originated from agricultural land use. The correlation coefficients for the nitrate-herbicide relationship were relatively low, however, and the distribution of herbicide in ground water only partly accounts for the distribution of nitrate. There is additional discussion of herbicides in Section 2.

Considering the relationship between the amount of nitrate and herbicide found in ground water samples, we conclude that many of the processes affecting the distribution of nitrate in ground water also affect the distribution of herbicide. These would include recharge, ground water flow, and geochemical factors. We compared concentrations of nitrate in wells containing different combinations of herbicides and degradates. Median concentrations of nitrates did not differ significantly between wells containing different herbicides ($p = 0.668$). The type of herbicide found in a well was not correlated with the concentration of nitrate. Use of metolochlor has increased over the past ten years, while use of alachlor has decreased. The lack of significant difference for nitrate concentrations in wells with alachlor and metolochlor provides further evidence for a lack of trend in nitrate concentrations.

3.1.2.4. Effects of Physical Factors

An important hindrance to understanding the distribution of nitrate in ground water is the lack of information on quantities and patterns of recharge and chemical leaching. A recharge value of 5.12 inches per year was used for the Cottage Grove area in the County's Multilayer Analytical Element Flow model for ground water. This value was obtained from a water balance model and is assumed to represent ground water baseflow. A uniform recharge rate across the study area is unlikely, however. First, considerable topographic relief probably leads to focused recharge within the study area. Second, depth to bedrock varies, and recharge may consequently be more rapid in some areas than in others. Third, at least three different tills have been identified in the unsaturated zone, and these vary widely in their conductive properties.

There is limited information on recharge rates and patterns of recharge. There are no Department of Natural Resources observation wells within the study area. We examined data from several observation wells in northern Dakota County and eastern Ramsey County that are located within 10 miles of the study area. The data, summarized in Table 8, indicate there is considerable variability in recharge rates, with median annual recharge varying from 3.39 to 18.3 inches. Wells with higher recharge rates may be influenced by infiltration from losing streams and rivers. Recharge rates were calculated as the difference in maximum and minimum water levels during a year, assuming a porosity of 0.25 for the aquifer material. Water levels generally increase in response to precipitation, but the relationship was not strong and was not significant at the 0.05 level. Monthly water levels in individual wells showed the same result – generally positive correlations with precipitation but not significant at the 0.05 level. There was no effect of either well depth or depth to water on recharge (Figure 14).¹

¹ We performed two statistical tests for correlation between recharge and precipitation. The first was a Spearman rank test in which we correlated annual recharge, in inches, with annual precipitation, also in

Well	Period of record	Median depth to water (ft)	Well Depth (ft.)	Annual recharge (in)	Correlated with precipitation
19015	1973-present	173.7	189	4.82	Yes
19066	1985-1996	3.3	89	3.39	No
19067	1985-present	21.7	29.5	7.68	No
19068	1985-1993	21.0	74.1	6.40	No
19070	1991-present	3.9	42.4	11.28	No
19071	1991-present	44.9	59	18.30	No
62039	1982-present	7.6	46	3.54	No

Table 8: Characteristics of observation wells located within 10 miles of the study area.

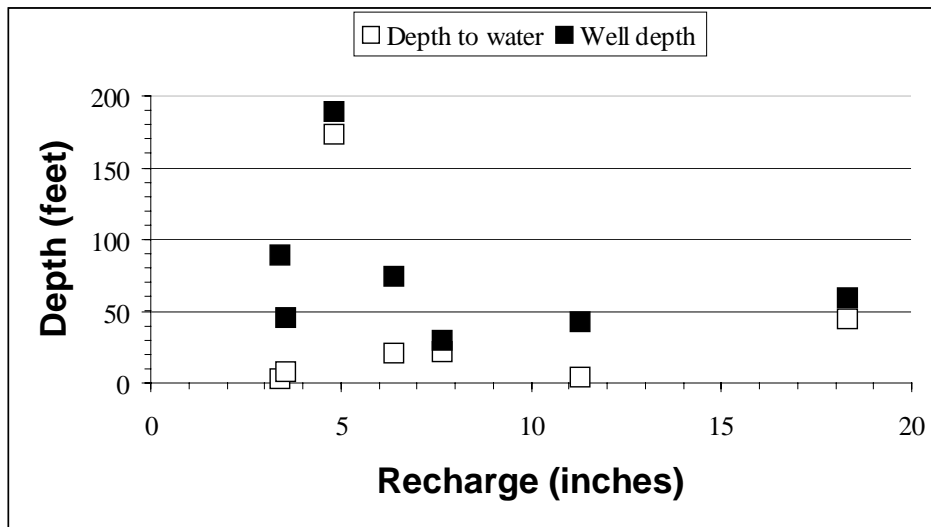


Figure 14: Median annual recharge in observation wells as a function of well depth and depth to water.

Ground water flow within the Prairie du Chien and Jordan aquifers is generally to the south, toward the Mississippi River (see Figure 3). A ground water divide passes through the study area, roughly corresponding with the St. Croix and Mississippi River watershed boundaries. The Prairie du Chien aquifer is confined in the northern third of the study area. A water table system occurs across the western and southern part of the study area. A buried bedrock channel runs north to south near the eastern edge of the study area. Sand deposits may be more than 100 feet thick in this area, and the buried channel dissects each of the major bedrock aquifers. It is considered an area that is highly

inches. The second test was a sign test comparing whether annual recharge was above normal compared to the same measurement for precipitation.

vulnerable to contamination, while the confined portions of the Prairie du Chien aquifer are considered less vulnerable (Minnesota Geological Survey, 1990).

A detailed discussion of the relationship between water quality and the hydrogeologic system is beyond the scope of this report. The water quality information, particularly the distribution of nitrate and herbicides, do not correlate well with the hydrogeologic information. We observed no correlations between water quality and well depth, depth to water, depth to bedrock, and thickness of sand or clay units. We observed no difference in water quality from unconfined and confined portions of the Prairie du Chien aquifer. We observed no significant differences in water quality between areas near the buried bedrock valley and other parts of the study area.

The lack of correlations are primarily due to two factors. First, the primary source of nitrate in ground water appears to be agriculture. Since many of the residential areas were in agricultural production less than 20 years ago, and since nitrate is stable in oxidized ground water, the water quality we measured may actually reflect inputs from many years ago. The lack of data for the shallow ground water system further confounds our understanding of the relationship between nitrate concentrations and hydrology. The effect of land use is probably the most critical factor affecting nitrate concentrations in ground water. While it is true that recharge will probably be greatest near the buried bedrock valley, the effect of this will primarily be on the percentage of the underlying aquifers that are affected. In any agricultural area where recharge occurs, nitrate concentrations are likely to be elevated, including areas away from the bedrock valley. This is why it is critical to identify recharge areas and correlate these with nitrogen inputs (i.e. land use). Second, the hydrogeology of the area is complex. Fractured flow, coupled with geochemical conditions that are conducive to persistence of agricultural chemicals, ensure that nitrates penetrate deeply into the aquifers. This makes it difficult to understand where water originated and how long it took water to get to a certain location.

Tritium is a tool we can use for estimating the relative age of ground water. Peak concentrations of tritium in precipitation occurred in the 1960's. Concentrations in precipitation have declined since then. In Minnesota, data collected monthly since April 1996 show mean and median values of 11 TU with minimums around 5 TU and

maximums around 23 TU (Walsh, personal communication). The half life of tritium is 12.43 years. Consequently, as water proceeds along a flow path, tritium concentrations decrease because of radioactive decay. Since we know when the peak in tritium concentration occurred and we know the decay rate for tritium, the vertical distribution of tritium can sometimes provide information on age of ground water within an aquifer. If nitrate concentrations change with tritium concentrations, this provides evidence that nitrate concentrations are changing with time.

Figures 15 and 16 illustrate the distribution of tritium and nitrate as a function of depth in the Prairie du Chien and Jordan aquifers. Although tritium and nitrate concentrations appear to decrease with depth in the Prairie du Chien aquifer, there were no significant correlations with depth. Tritium and nitrate concentrations remain relatively constant with depth in the Jordan aquifer. Walsh (1992) speculated that the Jordan aquifer was relatively homogenous and well mixed. If this is the case, then we cannot expect to find a relationship between nitrate concentration and age.

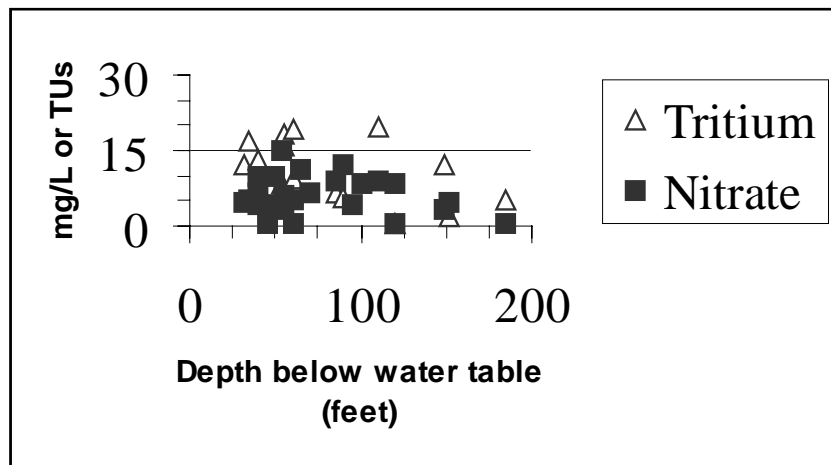


Figure 15: Distribution of tritium and nitrate as a function of depth in the Prairie du Chien aquifer.

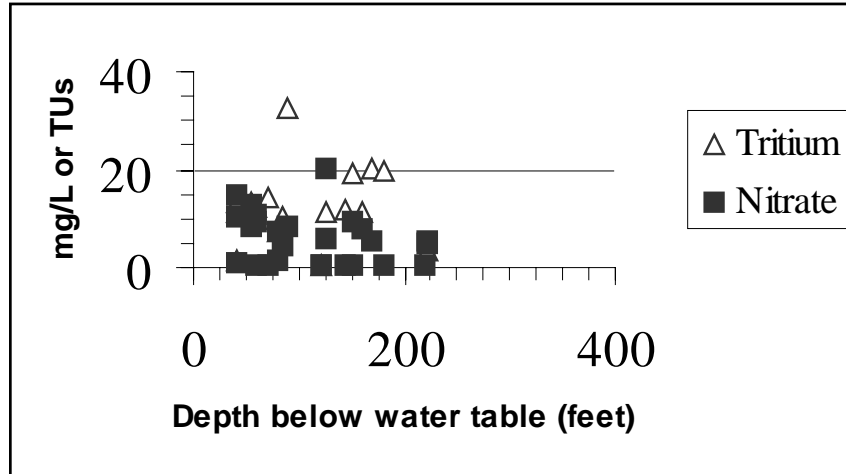


Figure 16: Distribution of tritium and nitrate as a function of depth in the Jordan aquifer.

If we divide the data for nitrate-vulnerable wells into four groups based on nitrate concentration (less than 1 mg/l, 1 to 5 mg/l, 5 to 10 mg/l, and more than 10 mg/l), we find a pattern to the distribution of tritium (Figure 17). One explanation for the pattern is that water increases in age as we proceed from low to high nitrate concentrations, as evidenced by the increase in tritium concentrations. Tritium concentrations decrease for the high nitrate group (more than 10 mg/l). Water in this group may thus be older than 1960. Peak concentrations of tritium, reflective of the early 1960's, would thus be represented by the 5 to 10 mg/l nitrate group. This model indicates a decreasing trend in nitrate concentration, but the model can only be verified with age dating. For example, water in the wells with concentrations greater than 10 mg/l may also be young, since the tritium concentration in these wells was 6.6, which is reasonably close to the value of 10 or 11 found in rain water.

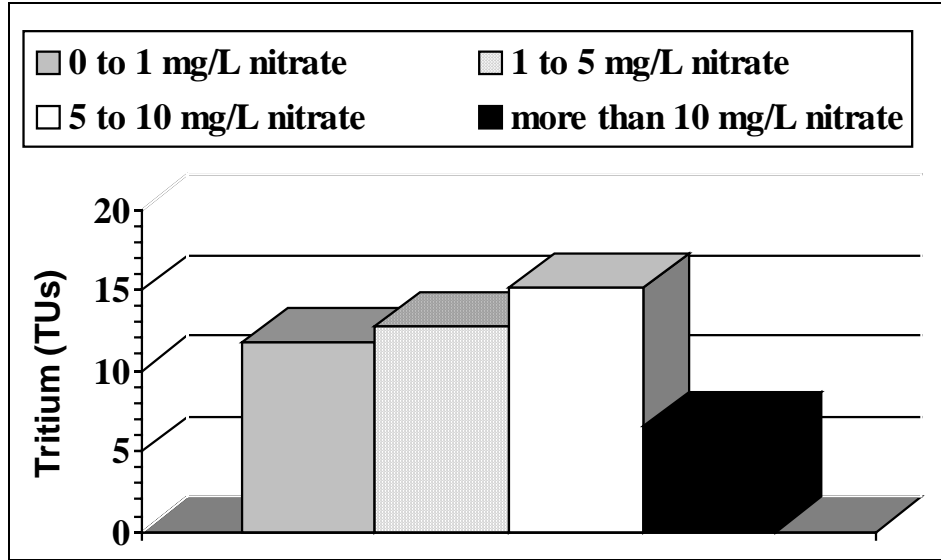


Figure 17: Distribution of tritium in wells having different concentrations of nitrate.

We looked at tritium and nitrate concentrations for two well nests, illustrated in Figure 18. The wells in each nest comprise a variety of depths below the water table, although most samples are less than 100 feet deep. No trends were observed for either nitrate or tritium in either well nest. The results again reflect a high degree of aquifer mixing or nitrate inputs that have been constant over time.

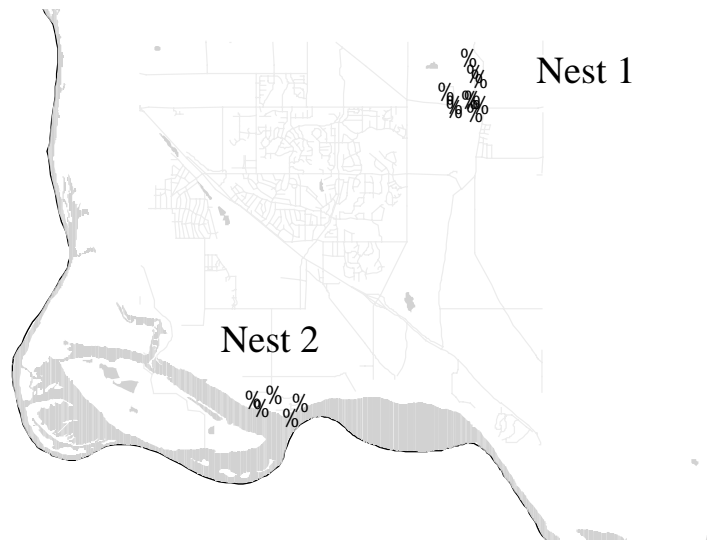


Figure 18: Location of well nests where tritium and nitrate were analyzed.

3.2. Organic Chemicals

3.2.1. Volatile Organic Compounds (VOCs)

VOCs were detected in only two samples. In each sample, dichlorodifluoromethane was the chemical detected. Concentrations were 0.0012 and 0.0008 mg/l. The drinking water criteria for dichlorodifluoromethane is 1 mg/l. Both wells were completed in the Jordan aquifer and occur near the city of Old Cottage Grove, although both wells were classified as being agricultural. Tritium concentrations in the two wells were 19.3 and 32.3 TUs. These are among the highest tritium concentrations observed in the study. Both wells had detectable herbicide concentrations and nitrate concentrations greater than 9 mg/l. Dichlorodifluoromethane, also known as Freon 12, is associated with the use of aerosols, refrigerants, etc. It is commonly found in ground water that is less than 50 years old. The two wells containing dichlorodifluoromethane were located close to the buried bedrock valley, which is likely to be an area of focused recharge.

3.2.2. Herbicides

Herbicides or herbicide breakdown products (degradates) were detected in 53 of 78 sampled domestic wells (68%)(Table 9). Herbicides were not sampled in the three samples from temporary wells. The parent herbicides alachlor [(2-chloro-N-(2,6-diethylphenyl)-N-methoxymethyl)acetamide] and metolochlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl)acetamide] were detected on four occasions, while there were 120 detections of their degradates alachlor ESA [2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid], alachlor OA [2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid], metolochlor ESA [2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid], metolochlor OA [2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid]). Degradates accounted for 95 percent of the total mass detected. Atrazine [(6-chloro-N-ethyl-N'-(1-methylethyl-1,3,5-triazine-2,4-diamine))] was detected in 25 samples and atrazine degradates deethylatrazine [(6-chloro-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine)] and deisopropylatrazine [(6-chloro-N-ethyl)-1,3,5-triazine-2,4-diamine] were detected in 28 samples. There is currently no identified toxic endpoint for

the herbicide degradates. Atrazine concentrations are below drinking water criteria, even when endpoints for the parent chemicals are used for the degradates. If the same toxic endpoint is used for alachlor and its degradates, the drinking water criteria of 4 ug/l was exceeded in five samples.

	Number	Overall Median ¹	Median ²	Maximum	HRL	MCL	Endpoint
		ug/l					
Total wells sampled	78	-	-	-	-	-	-
No. wells herbicide detected	53	-	-	-	-	-	-
No. wells herbicide not detected	25	-	-	-	-	-	-
No. wells multiple herbicides detected	41	-	-	-	-	-	-
Alachlor	2	< 0.20	1.62	3.18	4	2	cancer
Alachlor ESA	40	0.20	1.31	7.54	-	-	-
Alachlor oxanilic acid	27	< 0.20	0.76	2.23	-	-	-
Atrazine	25	< 0.20	0.08	0.86	20	3	cancer
Deethylatrazine	27	< 0.20	0.09	0.31	-	-	-
Deisopropylatrazine	1	< 0.20	0.09	0.09	-	-	-
Metolochlor	2	< 0.20	0.06	0.06	100	-	reproductive
Metolochlor ESA	29	< 0.20	0.50	1.7	-	-	-
Metolochlor Oxanilic Acid	24	< 0.20	0.41	6.91	-	-	-

¹ Median concentration for all sampled wells

² Median concentration in wells where herbicide was detected.

Table 9: Summary for herbicide data.

The results are similar to those of Kalkhoff et al. (1998), who sampled 88 municipal wells in Iowa. They found degradates in almost 75 percent of the sampled wells. Degradates accounted for over 95 percent of the mass of herbicide detected. In a similar study, Kolpin et al. (1997) found herbicides or degradates in 81.8 percent of wells sampled in bedrock wells from karst areas.

Median concentrations of sampled chemicals are compared in Table 10 for wells that had a detectable herbicide and wells that had no detectable herbicide. Differences between the two groups are striking. Eh and concentrations of chloride, nitrate, and dissolved oxygen are much higher and concentrations of iron and manganese are lower in

Parameter	Wells with herbicide detected	Wells with no herbicide detected
Alkalinity	220	193
Aluminum	< 0.050	< 0.050
Boron	0.016	0.015
Cadmium	< 0.002	< 0.002
Calcium	70	50
Chloride	11.5	1.7
Chromium	< 0.004	< 0.004
Copper	< 0.0055	< 0.0055
Depth	180	240
Depth to bedrock	58	36
Depth to water	110	130
Dissolved organic carbon	0.50	< 0.50
Dissolved Oxygen	8.9	2.2
Eh	311	161
Fluoride	0.13	0.14
Iron	< 0.0034	0.058
Lead	< 0.024	< 0.024
Magnesium	26	23
Manganese	< 0.0007	0.0249
Nickel	< 0.00061	0.006
Nitrate	7.5	< 0.50
pH	7.42	7.44
Phosphorus	< 0.030	< 0.030
Potassium	1.11	0.86
Sodium	3.77	2.80
Specific conductance	644	457
Temperature	10.0	10.0
Total organic carbon	< 0.50	< 0.50
Tritium	11.7	12.2
Zinc	0.046	0.030

Table 10: Concentrations of different chemicals in wells with detectable herbicide and wells with no detectable herbicide. Concentrations are in mg/l, except pH, Eh (mV), specific conductance (umhos/cm), tritium (tritium units), and temperature (°C).

wells containing a detectable herbicide. The same geochemistry that supports the presence of nitrate supports the presence of herbicides. This relationship was discussed

in Section 3.1.2.3. Tritium concentrations were equal between the two groups (wells with or without detectable herbicide), indicating the age of ground water in the two groups is similar. Consequently, geochemistry exerts a major control on the stability of herbicides in ground water. Depth to water, depth to bedrock, well depth, and concentrations of other inorganic constituents did not differ between the two groups.

Stamper et al. (1997) studied the degradation of chloroacetanilide herbicides by aerobic and anaerobic microbial cultures. They were unable to isolate cultures capable of degrading the parent compound with the exception of sulfate-reducing bacteria. Their data confirm the persistence of chloroacetanilide herbicides and their degradation products in aerobic ground water.

The presence of these herbicide degradates has increasingly been documented in ground waters and surface waters of the Midwestern United States (Kolpin et al., 1997; Kalkhoff et al., 1998; Kolpin et al., 1998; Thurman et al., 1994). This is partly due to improved laboratory methods for detecting these compounds. Unfortunately, there is limited information regarding the fate of these degradates in the environment and even less information to determine trends in concentration and frequency of detection. The chloroacetanilide compounds, alachlor and metolochlor, have relatively short half-lives in soil. Their degradation products, the ESA and OA compounds, are much more persistent and are highly mobile. Atrazine is more persistent in soil and is therefore more likely to be found in ground water than the parent chloroacetanilide herbicides.

Figure 19 illustrates the distribution of herbicide and herbicide degradates in Cottage Grove. There was no correlation with land use, and herbicides were detected in urban areas. Since these herbicides are assumed to be from agricultural use, the herbicides detected in urban areas indicate that water under these areas does not fully reflect impacts from urban land use.

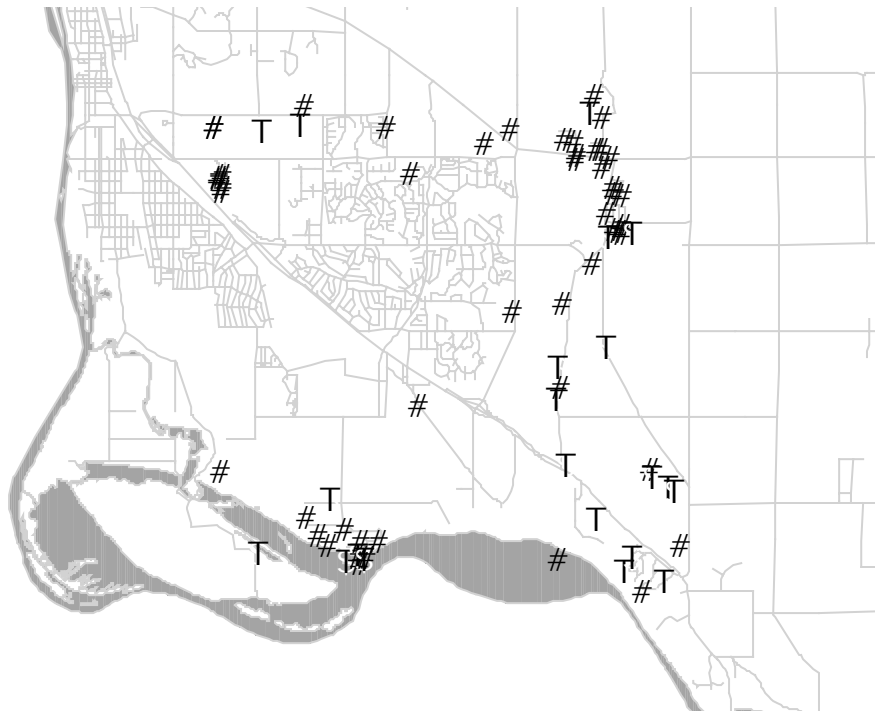


Figure 19: Location of herbicide detections (solid circles) and non-detections (open triangles).

Kolpin et al. (1997) observed positive correlations between the occurrence of degradates and dissolved oxygen concentration and an inverse relationship with well depth. The authors speculate these relationships were indicators of the age of ground water. Our data indicate that geochemistry is also a controlling factor on the occurrence of herbicides and their degradates in ground water. Field and Thurman (1996) identified a pathway by which parent chloroacetanilide herbicides are transformed to ethanesulfonic acid and oxanilic acid degradates in the presence of oxygen. The authors indicate the formation of these degradates is unlikely under anaerobic conditions. They also indicate that the degradates, which are ionized at pH values typically observed in ground water, are mobile and persistent in aqueous systems. The occurrence of herbicide degradates in oxygenated ground water in Cottage Grove is consistent with this research. The importance of geochemistry is exemplified in two St. Lawrence aquifer wells where herbicide was not detected. Tritium concentrations in these wells were 14.4 and 14.1, indicating post-1953 water. The Eh in these wells was 98 and 133 mV.

Ratios of the various degradates to each other and to parent compound can be used to identify the mechanism by which chemicals are reaching ground water (Philips et al., 1999; Graham et al., 1999). Because of the prevalence of degradates for the chloroacetanilide herbicides, the parent compound is likely being degraded in soil. This is further supported by the high ratios for ESA to OA (SAO ratio), since the ESA compound is favored in soil (Table 11). Figure 20 indicates that SAO ratios are lowest in the residential areas of the study area, while ratios are highest in agricultural areas. A variety of ratios were observed in the southern part of the study area, where land use is mixed.

Chemical	Ratio ESA to OA		
	Graham et al. (1999)	Phillips et al. (1999)	Our data
Alachlor	0.15	-	2.88
Metolochlor	0.53	3	1.05

Table 11: Ratios of ESA to OA degradation products for alachlor and metolochlor.

Another tool for identifying herbicide transport processes is the ratio of deethylatrazine to atrazine (DAR). Deethylatrazine is more mobile than atrazine and typically leaches through soil and into ground water. Thurman et al. (1998) observed that the DAR ratio in soil water increased from about 0.14 shortly after application of atrazine to more than 1.0 at 140 days after application. The DAR ratio increased to more than 5 in deep lysimeter samples after 140 days. Low DAR ratios are evidence of rapid transport mechanisms. Figure 21 indicates that the DAR ratio decreases steadily from the residential areas in the western part of Cottage Grove to the agricultural areas in the east. Rapid leaching of agricultural chemicals through the vadose zone may be occurring in the eastern part of the study area. This may be attributable to both the continued use of herbicides in these areas and to the presence of the buried bedrock valley, which is an area of focused recharge.

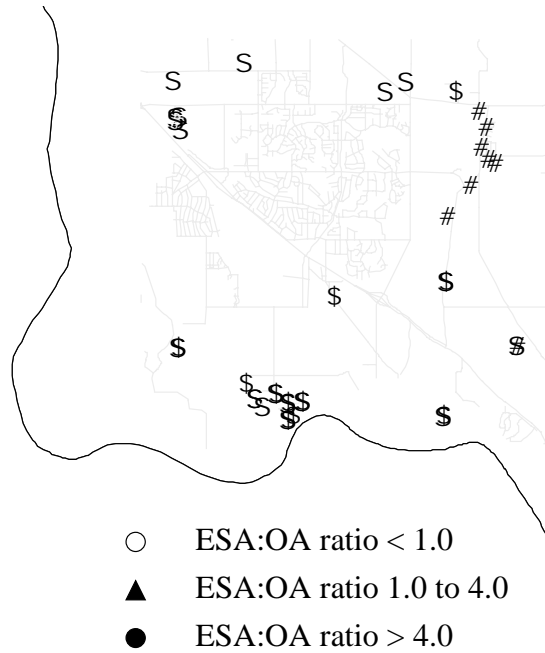


Figure 20: Ratios of ESA to OA degradates for the chloroacetanilide herbicides.

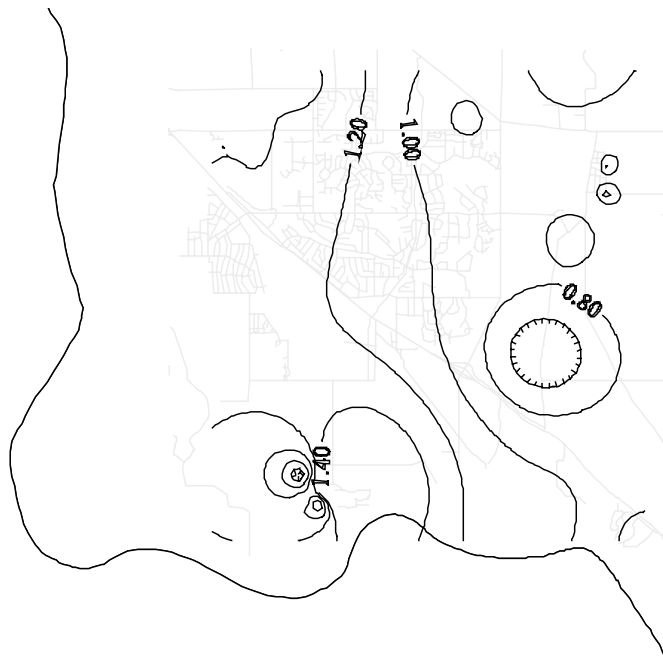


Figure 21: Deethylatrazine to atrazine ratio across the study area.

The Prairie du Chien aquifer appears particularly sensitive to contamination with herbicides, with all but one of the 27 sampled wells having at least one herbicide or

degradate detected (Table 12). The Jordan and surficial sand and gravel aquifers are also sensitive. Considering the Jordan aquifer, there was no correlation between occurrence of herbicides or degradates and well depth, depth to bedrock, and the aquifer being confined or unconfined. Redox chemistry was the primary factor affecting the presence of a herbicide or degradate in samples from the Jordan aquifer.

Aquifer	Wells sampled	Wells with detectable herbicide
Surficial sand and gravel	4	3
Prairie du Chien	27	26
Jordan	28	16
St. Lawrence	4	1
Franconia	4	2
Undefined	11	3

Table 12: Distribution of herbicides and degradates by aquifer.

4. Cumulative and Comparative Risk

Ground water represents one pathway by which people or ecological receptors (such as fish and mammals) may be exposed to chemicals. Other pathways include inhalation of vapors and dust in air, contact with soil and sediments, and contact with surface water. An assessment of overall environmental quality in a particular area, such as Cottage Grove, would incorporate exposure from each of these pathways.

The Minnesota Pollution Control Agency (PCA) is attempting to implement a multimedia approach to assessing environmental quality, with the objective of identifying environmental priorities. Two concepts that are part of this approach are cumulative risk and comparative risk. We define the cumulative risk to an individual (human or ecological) as the sum of risks of different stressors (e.g. chemicals) from different exposure pathways. If we add the risks from each pathway, or media, we can identify the total risk and determine the source of greatest risk. This priority setting is a form of comparative risk, that is, comparing the risk from different sources within and between different media. We can also use this information to target areas where risk is greatest and prevent activities that further increase risk.

It is beyond the scope of this paper to present a comprehensive assessment of cumulative and comparative risk in Cottage Grove. Environmental data has not been collected for purposes of conducting a multimedia analysis. Consequently, we have data from individual sites where air, soil, or ground water monitoring has occurred, but this information, in its current form, cannot be used in conjunction with our ground water information to conduct a comprehensive environmental assessment for Cottage Grove. For example, Figure 22 illustrates locations of sites found in the PCA's Master Entity System. These are sites currently being monitored or investigated by the PCA. Soil and ground water information likely exists at each of these sites. Figure 22 also illustrates two surface water monitoring locations. In addition, there may be air monitoring at some of the larger industrial sites in Cottage Grove. Unfortunately, this information has not been compiled in a format that is useful for assessing the overall environmental quality in Cottage Grove.

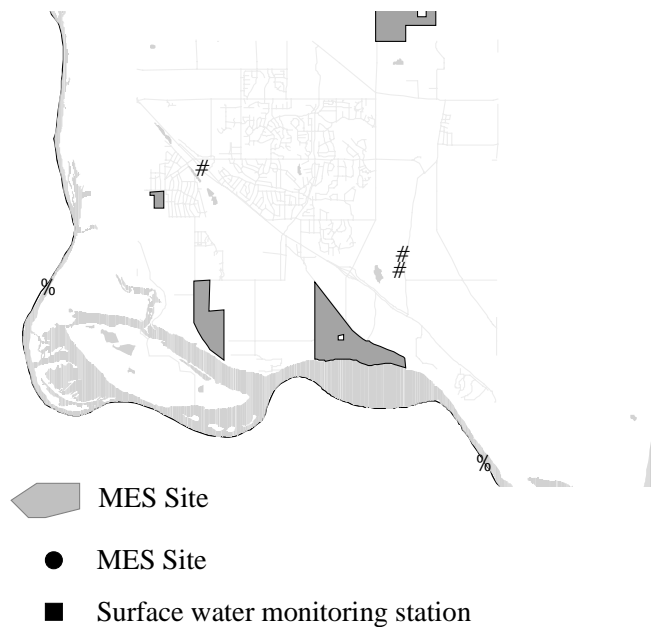


Figure 22: Location of MES and surface water monitoring sites in Cottage Grove.

We can, however, present our information in a manner that is useable for risk assessors who may conduct analyses that are more comprehensive in the future. One tool

that risk assessors use is to calculate cumulative risk for a particular health endpoint. An example of a health endpoint is cancer. Risk assessors use criteria such as Health Risk Limits (HRLs) for ground water and Health Risk Values (HRVs) for air. The risk associated with exposure to an individual chemical is given by dividing the concentration by the risk criteria. Different chemicals may have the same endpoint. We can calculate the exposure risk for a certain endpoint for each media, then add up the risks for that endpoint. For example, consider nitrate and atrazine, both of which affect the cardiovascular/blood system. The ground water criteria are 10 mg/l for nitrate and 0.003 mg/l for atrazine. If the concentrations in a well are 5 mg/l of nitrate and 0.001 mg/l of atrazine, the calculated risk values are $5/10$ or 0.50 for nitrate and $1/3$ or 0.33 for atrazine. The cumulative risk for the cardiovascular/blood endpoint is $(0.50 + 0.33)$ or 0.83. A value less than 1.0 is considered to represent a “safe” condition. As mentioned earlier, however, ground water is only one exposure pathway. If another chemical affects the cardiovascular/blood system and people are exposed to the chemical from air or soil, the added risk of this exposure must be added to the exposure from ground water.

The primary objective of this cumulative analysis is to identify areas where exposure exceeds the acceptable risk and to identify areas that might be susceptible to increased exposure risk. For example, an area with a cumulative risk value of 0.10 is much less susceptible than an area where the risk value is 0.90. It would be wise to minimize additional exposure burden in the more susceptible area. For example, certain types of development may be undesirable in these susceptible areas.

Figure 23 illustrates risk values for the cardiovascular/blood endpoint. Nitrate, atrazine, atrazine degradates, and zinc contribute to this value. Nitrate is the most important chemical contributing to this endpoint, but contributions from atrazine or atrazine degradates are significant in the northeastern and southern parts of the study area. The risk value exceeds 0.8 over much of the central part of the study area. These are areas where additional burdens for the cardiovascular/blood endpoint will potentially have the greatest impact. Table 13 contains a list of some chemicals that have this endpoint. The table lists industrial or agricultural activities that may introduce these

chemicals into the environment. These additional chemicals may be monitored in areas where the existing ground water risk value exceeds or is close to 1.0.

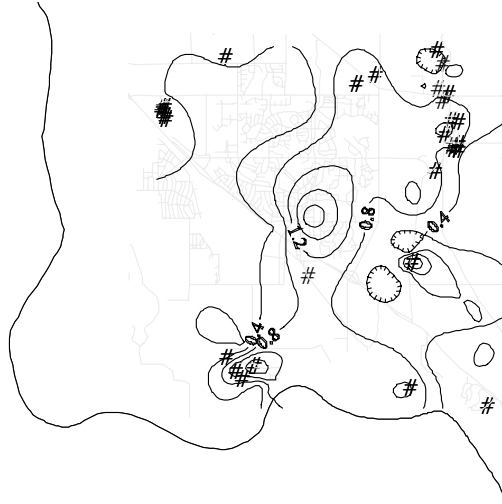


Figure 23: Cumulative ground water risk values for the cardiovascular/blood system. Circles represent locations where atrazine or atrazine degradates were detected.

Chemical	Common uses
Acetochlor	Herbicide
Acetonitrile	Polymer production, coatings, metallurgy
2,4-D	Herbicide
cis-1,2-Dichloroethene	Solvent, plastics, dye extraction, medicine, perfumes, lacquers
2,4-Dimethylphenol	Pharmaceuticals, plastics, solvent, dyes, insecticides, additive to fuel oils
EPTC	Herbicide
Linuron	Herbicide
Methyl Parathion	Insecticide
Fluorene	Resins, tars, dyes, insecticides
Trifluralin	Herbicide

Table 13: Chemicals that have the cardiovascular/blood system as their endpoint.

There were no other endpoints for which the risk value exceeded 0.1. There are some isolated areas where concentrations of alachlor and alachlor degradates are relatively high. One of the limitations of this approach to assessing multimedia impacts is that we do not have risk criteria for many chemicals. These include the herbicide degradates. Although the endpoint for alachlor is cancer, it is widely believed that the

degradation products of the chloroacetanilide herbicides are much less toxic than the parent herbicide. Nevertheless, we do not have toxicological information for the degradates, and the widespread occurrence of these chemicals is sufficient justification for obtaining this information.

An additional concern of high nitrate concentrations in ground water is the potential impact to surface water. Surface water monitoring locations exist on the Mississippi River at Grey Cloud Island and Hastings. Concentrations of (nitrate+nitrite) increased over the period 1985 to 1996 (Figure 24). Although ground water is likely to have a small effect on nitrate concentrations in the river, any effect it has will be negative.

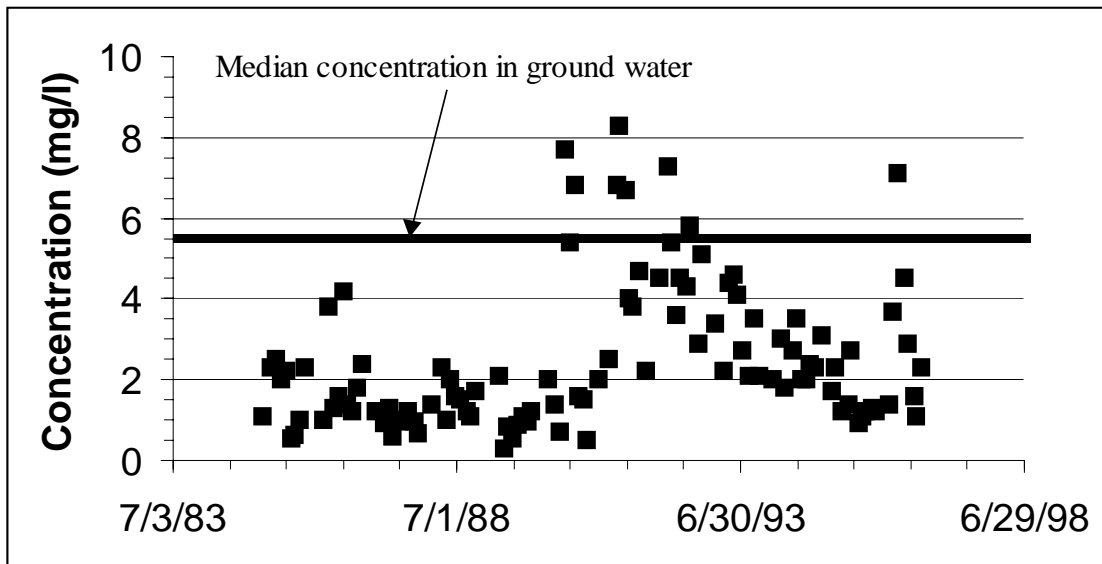


Figure 24: Nitrate concentrations at Grey Cloud Island, 1985 to 1996.

5. Management Strategies

Washington County has an approved local water plan, is in the process of adopting a Groundwater Protection Plan, and has a ground water component in the County Comprehensive Plan. Elevated concentrations of nitrate in ground water under Cottage Grove are widely acknowledged by state and local officials. Several management strategies have been identified and developed to alleviate the nitrate problem in Cottage Grove. Several objectives for better understanding the extent and causes of nitrate contamination were identified in the recent Clean Water Partnership Agreement.

Some of these strategies and objectives are likely to be successful, while others are not. Some of these strategies and objectives are discussed below.

1. *Refine the County's Multi Layer Analytical Element Method ground water flow model.* Further modeling should focus on three objectives. First, existing age-dating and geochemical results should be used to calibrate the model's estimates of time of travel for selected flow paths. This information can then be used to evaluate trends in nitrate concentrations, and will provide a tool for predicting water quality. The second objective should be to incorporate contaminant transport into the existing model. This is not required if it can be demonstrated that contaminants are not attenuated within the aquifer, but existing data suggests there is some attenuation, particularly in the Franconia aquifer. Third, the model should be used to predict water quality following changes in land use. Since a generalized land use plan exists for the County, anticipated land use changes would serve as model inputs.
2. *Conduct water table monitoring.* One of the stated goals for water table monitoring is to act as an early warning system for identifying trends in nitrate concentrations. A second objective is to monitor changes in water quality in response to land use, changes in land use, or implementation of Best Management Practices. Three wells are proposed. A monitoring network, particularly one consisting of three wells, is unlikely to achieve the intended objectives. We do not fully understand recharge to the aquifer system, and there are insufficient data from the upper portion of the water table aquifer to demonstrate that water quality in shallow ground water is correlated with the overlying land use. Installing temporary wells proved difficult because of the geologic material and depth to water. Since there are large differences in nitrogen inputs between different land uses, the monitoring wells should be installed in general land use areas and used for monitoring trends. Ideally, the wells would be installed prior to changes in land use. Four proposed locations are shown in Figure 25. Well 1 is located in an area currently used for agriculture. The projected land use is unsewered residential. Well 2 is currently in an area with mixed land use. The projected land use is sewer residential. Well 3 is located in an area that is expected to remain in agriculture. Well 4 is currently in an agricultural area that is expected to

transition to commercial/industrial land use. If only three wells can be installed, Wells 1, 2, and 3 should be selected. All wells are located at the down-gradient edge of the predicted land use. The water table is mapped as occurring in sand and gravel deposits at each of these locations (Minnesota Geological Survey, 1990).

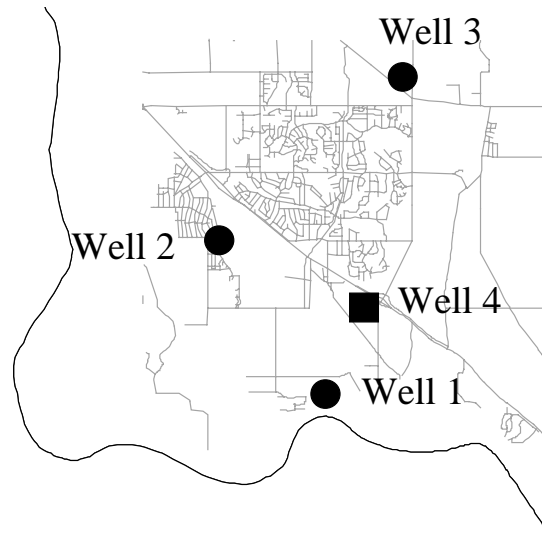


Figure 25: Recommended locations of water table monitoring wells.

All wells should be equipped with continuous water level recorders for purposes of quantifying recharge. Water quality sampling would occur quarterly, with annual sampling for major ions. Sampling includes measurement of field parameters, particularly dissolved oxygen and oxidation-reduction potential.

If a monitoring network is established to correlate changes in water quality with land use, a minimum of ten wells will be required. Prior to installation of these wells, recharge should be quantified across the study area so that wells can be located in areas where water quality is likely to reflect overlying land use. Monitoring wells should be equipped with continuous water level recorders to quantify recharge and the pattern of recharge.

3. *Map and summarize the occurrence of nitrate contamination with ground water flow information.* Information for completing this has largely been obtained. The extent of contamination in the study area can adequately be described with existing

information, with the possible exception of areas serviced by municipal sewers. Using the model to help understand the distribution of nitrate in ground water may not be the most efficient use of the model, since aquifers are well mixed, recharge is poorly understood, and because land use, and consequently nitrogen inputs, are changing.

4. *Quantify potential sources of nitrate contamination.* The strong correlation between nitrate and herbicides provides sufficient evidence that agriculture is the primary source of nitrogen in ground water. In this report, however, we did not consider how agricultural practices within the study area have changed, nor did we differentiate between different types of agriculture (row crop with commercial fertilizer, row crop with commercial and manure fertilizer, irrigated versus nonirrigated agriculture). These would be part of the effort to quantify on-farm management practices. Conversion of agricultural land to developments with individual sewage treatment systems on small lots (less than acre) may not diminish inputs of nitrogen to ground water (MPCA, 2000).
5. *Perform ground water quality tests at selected sites and monitor for trends.* Much of the Prairie du Chien and Jordan aquifers are vulnerable to nitrate contamination, but there appear to be areas that are not sensitive. This sensitivity is based on geochemical data that show nitrate will be reduced in portions of the aquifers. The ground water flow model may be useful for identifying these areas. The existing domestic well network can be utilized to establish a trend monitoring network. This network includes wells with differing concentrations of nitrate and screened at different depths in the Quaternary, Prairie du Chien, and Jordan aquifers. Figure 26 illustrates an example of such a network. This network includes a range of wells screened in different aquifers and at different depths. Sampling in these wells would be conducted quarterly for an indefinite period of time. Measurements at each well include dissolved oxygen, oxidation-reduction potential, nitrate, and reduced iron. Each of these can be measured with field kits, although there are limitations to use of these kits (see MPCA, 1999b).



Figure 26: Potential trend monitoring network for Cottage Grove. Prairie du Chien wells are indicated by triangles, Jordan wells by squares, and Quaternary wells by open circles.

6. *Various land uses are examined for their potential impact to ground water and management strategies are included with these discussions.*
 - Animal waste management: Data from our study of manure storage structures (unpublished) indicate these structures have a minimal effect on nitrogen loading to ground water, particularly if the storage structures are properly built. Unlined basins can result in significant inputs of organic nitrogen and ammonia to ground water. These in turn may be converted to nitrate. Identifying these facilities should rate as a higher priority than locating new facilities, unless new facilities are proposed in karst areas.
 - Individual sewage treatment systems (septic systems): Our data indicate that nitrate concentrations under unsewered communities with lot sizes of 0.5 to 1.0 acre will be 4 to 7 mg/l. Up to 20 percent of shallow ground water can exceed the drinking water criteria under these conditions. Construction and maintenance of the septic systems has little effect on nitrogen loading to ground water. Lot size and age of development are the most important factors affecting nitrate concentration. Modeling can be used as an effective tool for predicting nitrate concentrations under unsewered communities. Experimental systems should

focus on removing nitrogen as it passes beneath the soil treatment system. These systems may be effective in Cottage Grove, since there is adequate unsaturated zone thickness to implement a denitrifying system beneath the soil treatment zone, although the cost may be prohibitive.

- Agriculture: Agriculture introduces the greatest quantity of nitrogen to ground water. Annual fertilizer use should be determined to identify potential correlations between fertilizer use and nitrate concentrations in trend monitoring wells.

7. *Develop a program to ensure immediate and coordinated remediation efforts upon discovery of contamination.* Remediation of nitrate-contaminated ground water is difficult and expensive in the hydrogeologic setting found in Cottage Grove. New technologies designed to create denitrifying conditions, such as injection of hydrogen gas, are promising but unproven. Prevention is the most effective way of controlling nitrate concentrations in ground water.

8. *Sampling for other chemicals.* Our study was limited both in the range of chemicals that we sampled and in our distribution of sampling points. We make the following recommendations based on our existing data.

- Conduct additional sampling for VOCs in shallow ground water under industrial and sewer residential areas.
- As part of the trend monitoring network, sample for agricultural herbicides and their degradates annually in late spring.

6. Summary

An area covering approximately 17 percent of Cottage Grove has nitrate concentrations exceeding the drinking water criteria in the Quaternary, Prairie du Chien, and Jordan aquifers. Nitrate is primarily associated with agricultural activity. Nitrate is persistent in oxidized ground water, and because water in the aquifers is well mixed, nitrate penetrates to depths of more than 200 feet. There were no apparent trends in nitrate concentration. Continued urban development is likely to lead to decreasing

concentrations, unless this development consists of unsewered communities with lot sizes less than one acre.

Herbicides were detected in 68 percent of sampled wells. Herbicide degradates accounted for 95 percent of the detected herbicide mass. Concentrations of herbicide and nitrate were positively correlated. Factors that affect the distribution of nitrate are therefore likely to affect herbicides. There is no historic information for herbicides in ground water.

Volatile organic compounds were detected in two samples at concentrations below drinking water standards. Sampling for VOCs, however, largely occurred in areas where we would not expect to find these chemicals. There were no health concerns associated with other chemicals in ground water, although our sample parameter list was limited.

Additional ground water research should focus on identifying patterns of recharge and chemical leaching to ground water, further calibration of the ground water flow model, and using the model to predict water quality under projected land use scenarios. Monitoring should focus on trend monitoring of shallow ground water in areas where land use will change in the next ten years, and on trend monitoring in deeper wells to measure long-term changes in nitrate concentrations. Nitrate and herbicides are the chemicals of greatest concern based on existing data. Further sampling for VOCs should occur in shallow ground water under industrial and sewer residential areas.

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Appendix I – Reporting Limits And Laboratory Methods

Chemical	Reporting Limit	Laboratory Method
Inorganics		
Alkalinity	1 mg/l	Titration
Aluminum	0.049 mg/l	ICP
Ammonia	0.020 mg/l	Colorometric
Boron	0.13 mg/l	ICP
Cadmium	0.0019 mg/l	ICP
Calcium	0.055 mg/l	ICP
Chloride	0.10 mg/l	Ion Chromatography
Chromium	0.0034 mg/l	ICP
Copper	0.0055mg/l	ICP
Dissolved organic carbon	0.50 mg/l	Dohrman carbon analyzer
Dissolved oxygen	0.010 mg/l	Field meter
Eh	1 mV	Field meter
Fluoride	0.20 mg/l	Ion Chromatography
Iron	0.0034 mg/l	ICP
Lead	0.024 mg/l	ICP
Magnesium	0.020 mg/l	ICP
Manganese	0.00070 mg/l	ICP
Nickel	0.0061 mg/l	ICP
Nitrate	0.020 mg/l	Cadmium reduction
pH	0.1 pH unit	Field meter
Phosphorus	0.030 mg/l	ICP
Potassium	0.118 mg/l	ICP
Sodium	0.060 mg/l	ICP
Specific conductance	0.1 mmho/cm	Field meter
Sulfate	0.10 mg/l	Ion chromatography
Temperature	0.1 °C	Field meter
Total organic carbon	0.5 mg/l	Dohrman carbon analyzer
Total phosphorus	0.020 mg/l	ICP
Tritium (enriched)	0.8 tritium units	Liquid scintillation
Zinc	0.0027 mg/l	ICP
Herbicides		
Acetochlor	0.05	GC/MS
Acetochlor ESA	0.20 ug/l	HPLC
Acetochlor OA	0.20 ug/l	HPLC
Alachlor	0.05 ug/l	GC/MS
Alachlor ESA	0.20 ug/l	HPLC
Alachlor OA	0.20 ug/l	HPLC
Ametryn	0.05 ug/l	GC/MS
Atrazine	0.05 ug/l	GC/MS
Cyanazine	0.05 ug/l	GC/MS

Appendix I – Reporting Limits And Laboratory Methods Cont.

Chemical	Reporting Limit	Laboratory Method
Inorganics		
Cyanazine-amide	0.05 ug/l	GC/MS
Deethylatrazine	0.05 ug/l	GC/MS
Deisopropylatrazine	0.05 ug/l	GC/MS
Hydroxy-atrazine	0.20 ug/l	HPLC
Metolochlor	0.05 ug/l	GC/MS
Metolochlor ESA	0.20 ug/l	HPLC
Metolochlor OA	0.20 ug/l	HPLC
Metribuzin	0.05 ug/l	GC/MS
Prometon	0.05 ug/l	GC/MS
Prometryn	0.05 ug/l	GC/MS
Propachlor	0.05 ug/l	GC/MS
Propazine	0.05 ug/l	GC/MS
Simazine	0.05 ug/l	GC/MS
Terbutryn	0.05 ug/l	GC/MS
Volatile Organic Compounds		
1,1-Dichloroethane	0.2 ug/l	MDH 465A
1,1-Dichloroethene	0.5 ug/l	MDH 465A
1,1-Dichloropropene	0.2 ug/l	MDH 465A
1,1,1-Trichloroethane	0.2 ug/l	MDH 465A
1,1,1,2-Tetrachloroethane	0.2 ug/l	MDH 465A
1,1,2-Trichloroethane	0.2 ug/l	MDH 465A
1,1,2,2-Tetrachloroethane	0.2 ug/l	MDH 465A
1,1,2-Trichlorotrifluoroethane	0.2 ug/l	MDH 465A
1,2-Dichlorobenzene	0.2 ug/l	MDH 465A
1,2-Dichloroethane	0.2 ug/l	MDH 465A
1,2-Dichloropropane	0.5 ug/l	MDH 465A
1,2,3-Trichlorobenzene	0.5 ug/l	MDH 465A
1,2,3-Trichloropropane	0.5 ug/l	MDH 465A
1,2,4-Trichlorobenzene	0.5 ug/l	MDH 465A
1,2,4-Trimethylbenzene	0.5 ug/l	MDH 465A
1,3-Dichlorobenzene	0.2 ug/l	MDH 465A
1,3-Dichloropropane	0.2 ug/l	MDH 465A
1,3,5-Trimethylbenzene	0.5 ug/l	MDH 465A
1,4-Dichlorobenzene	0.2 ug/l	MDH 465A
2,2-Dichloropropane	0.5 ug/l	MDH 465A
2-Chlorotoluene	0.5 ug/l	MDH 465A
4-Chlorotoluene	0.5 ug/l	MDH 465A
Acetone	20 ug/l	MDH 465A
Allyl Chloride	0.5 ug/l	MDH 465A
Bromochloromethane	0.5 ug/l	MDH 465A

Appendix I – Reporting Limits And Laboratory Methods Cont.

Chemical	Reporting Limit	Laboratory Method
Inorganics		
Bromodichloromethane	0.2 ug/l	MDH 465A
Benzene	0.2 ug/l	MDH 465A
Bromobenzene	0.2 ug/l	MDH 465A
Bromoform	0.5 ug/l	MDH 465A
Bromomethane	0.5 ug/l	MDH 465A
cis-1,2-Dichloroethene	0.2 ug/l	MDH 465A
cis-1,3-Dichloropropene	0.2 ug/l	MDH 465A
Carbon tetrachloride	0.2 ug/l	MDH 465A
Chlorodibromomethane	0.5 ug/l	MDH 465A
Chlorobenzene	0.2 ug/l	MDH 465A
Chloroethane	0.5 ug/l	MDH 465A
Chloroform	0.1 ug/l	MDH 465A
Chloromethane	0.5 ug/l	MDH 465A
1,2-Dibromo-3-chloropropane	0.5 ug/l	MDH 465A
Dibromomethane	0.5 ug/l	MDH 465A
Dichlorodifluoromethane	0.5 ug/l	MDH 465A
Dichlorofluoromethane	0.5 ug/l	MDH 465A
1,2-Dibromomethane	0.5 ug/l	MDH 465A
Ethylbenzene	0.2 ug/l	MDH 465A
Ethyl ether	2 ug/l	MDH 465A
Hexachlorobutadiene	0.5 ug/l	MDH 465A
Isopropylbenzene	0.5 ug/l	MDH 465A
Methylene chloride	0.5 ug/l	MDH 465A
Methyl ethyl ketone	10 ug/l	MDH 465A
Methyl isobutyl ketone	5 ug/l	MDH 465A
Methyl tert butyl ether	2 ug/l	MDH 465A
n-Butylbenzene	0.5 ug/l	MDH 465A
Naphthalene	0.5 ug/l	MDH 465A
n-Propylbenzene	0.5 ug/l	MDH 465A
o-Xylene	0.2 ug/l	MDH 465A
p- and m-Xylene	0.2 ug/l	MDH 465A
p-Isopropyltoluene	0.5 ug/l	MDH 465A
sec-Butylbenzene	0.5 ug/l	MDH 465A
Styrene	0.5 ug/l	MDH 465A
tert-Butylbenzene	0.5 ug/l	MDH 465A
trans-1,2-Dichloroethene	0.1 ug/l	MDH 465A
trans-1,3-Dichloropropene	0.2 ug/l	MDH 465A
Trichloroethene	0.1 ug/l	MDH 465A
Trichlorofluoromethane	0.5 ug/l	MDH 465A
Tetrachloroethene	0.2 ug/l	MDH 465A

Appendix I – Reporting Limits And Laboratory Methods Cont.

Chemical	Reporting Limit	Laboratory Method
Inorganics		
Tetrahydrofuran	10 ug/l	MDH 465A
Toluene	0.2 ug/l	MDH 465A
Vinyl chloride	0.5 ug/l	MDH 465A