

**Effects of Land Use on Ground Water Quality, St.  
Cloud Area, Minnesota – Short Report**

**June, 2001**

**Published by**

**Minnesota Pollution Control Agency**

**Prepared by**

**Ground Water Monitoring and Assessment Program**

## **Table of Contents**

List of Figures

List of Tables

Executive Summary

1. Materials and Methods
2. Results and Discussion
  - 2.1. Hydrology
  - 2.2. Water Quality
    - 2.2.1. Nitrate
    - 2.2.2. Chloride
    - 2.2.3. Volatile Organic Compounds
    - 2.2.4. Pesticides
    - 2.2.5. Polynuclear Aromatic Hydrocarbons
3. Future of the Project

References

### **List of Figures**

1. Location of study area.
2. Location of monitoring points, including wells, surface water sampling points, and continuous recorders.
3. 1997 Precipitation and water elevations (inches) in wells containing continuous recorders. Water levels are referenced to the lowest observed elevation during 1997.
4. 1998 Precipitation and water elevations (inches) in wells containing continuous recorders. Water levels are referenced to the lowest observed elevation during 1997.
5. 1999 Precipitation and water elevations (inches) in wells containing continuous recorders. Water levels are referenced to the lowest observed elevation during 1997.
6. Tritium concentrations as a function of depth in domestic wells.
7. Nitrate concentrations in private wells as a function of well depth.

### **List of Tables**

1. Sampling parameters for the monitoring network.
2. Mean recharge (inches) in monitoring wells, by land use.
3. Comparison of recharge calculated using continuous recorder with recharge calculated using water elevations.
4. Median chemical concentrations for different land uses. Concentrations are in ug/L, except specific conductance (umhos/cm), temperature (°C), pH, and Eh (mV). Different letters within a row indicate concentrations that differ at a 0.05 significance level.
5. Ratios of median chemical concentration to drinking water criteria for six land uses.
6. Median chloride concentrations, by land use, in monitoring wells and surface water. Different letters within a column indicate concentrations that differed at a significance level of 0.05.
7. Summary of VOC detections, by chemical.
8. Summary of VOC detections, by land use.
9. Number of detections and cumulative mass detected for different chemicals between 1998 and 2000.

## **Executive Summary**

A ground water study began in fall of 1996 to assess impacts of land use on ground water quality. The study area, located near St. Cloud, Minnesota, is experiencing rapid urbanization. A shallow sand and gravel aquifer underlies the area. The aquifer is sensitive to changes in land use. A sampling network across an approximately 30 square-mile area included 23 monitoring wells screened at the water table, 17 to 21 domestic wells screened at various depths in the aquifer, 2 surface water sampling locations, 4 continuous water level recorders in monitoring wells, 3 well nests, 2 surface water gauging stations, and a weather station. Quarterly sampling, conducted between 1997 and 2000, included major cations and anions, trace inorganics, volatile organic compounds (VOCs), herbicides, field parameters, total and dissolved organic carbon, total dissolved and suspended solids, ammonia, organic nitrogen, and water level measurements. Additionally, samples for tritium, polynuclear aromatic hydrocarbons (PAHs), total coliform bacteria, fecal coliform bacteria, and perchlorate were collected on one occasion during the study.

Recharge (measured with water levels in monitoring wells) averaged 3.42 inches between 1997 and 2000. Recharge ranged from 7.86 inches in 1998 to 0.88 inches in 1999. The strongest correlation for recharge was with cumulative precipitation between December and March. Water levels in continuous recorders illustrated the importance of wet periods prior to occurrence of recharge. These wet periods led to soil wetting and allowed subsequent precipitation to percolate to ground water. Recharge measured with water level recorders was greater than recharge measured with water levels in monitoring wells, because small recharge events and summer recharge were accounted for by the recorders. Recharge was greatest in undeveloped and agricultural areas and least in urban areas. Tritium data indicated the presence of age stratification in the aquifer. Water at about 100 feet appeared to originate around 1960.

Water quality differences were evident between different land uses. Concentrations of most trace elements and major ions were highest under urban land use compared to agricultural and undeveloped land use. The primary exception was nitrate, which was highest under irrigated agricultural land use. VOCs were commonly found under commercial/industrial areas, with chloroform, trichloroethylene, and

tetrachloroethylene being the most commonly detected VOCs. Degradates of the herbicides atrazine, alachlor, metolochlor, and acetochlor, were commonly found under agricultural land use. PAHs were detected in only one monitoring well. Perchlorate was not detected in any sample. Coliform bacteria were detected in 8 of 17 monitoring wells and 2 of 21 domestic wells, with the highest concentrations occurring under nonsewered residential land use. E. coli bacteria were not detected.

There were significant differences in water quality with depth. These were largely related to decreasing Eh with depth in the aquifer. Consequently, concentrations of iron, arsenic, ammonia, and manganese increased with depth, while concentrations of dissolved oxygen and nitrate decreased with depth.

The primary chemicals of concern, from a human health or environmental perspective, were nitrate, chloride, VOCs, and herbicides. Nitrate concentrations exceeded the drinking water criteria of 10000 ug/L in 38 of 41 samples under irrigated agriculture (median = 16010 ug/L). The median nitrate concentration was 6740 ug/L under nonsewered residential land use, with 9 of 37 samples exceeding the drinking water criteria. The median concentration was 4190 ug/L under nonirrigated agriculture, with 10 of 39 samples exceeding the drinking water criteria. There were no exceedances under undeveloped (median = 500 ug/L) or sewer residential (median = 2350 ug/L) land use, while 3 of 55 samples exceeded the criteria under commercial/industrial (median = 2000 ug/L) land use and 6 of 45 samples exceeded the criteria under transitional (median = 4190 ug/L) land use.

Chloride concentrations were higher under all land uses compared to undeveloped land use (median = 3015 ug/L). Median concentrations under other land uses were 82695 ug/L for nonsewered residential, 78775 ug/L for sewer residential, 59020 ug/L for commercial/industrial, 40920 for irrigated agricultural, 16525 ug/L for nonirrigated agricultural, and 13900 ug/L for transitional land use. Thus, chloride concentrations were highest in urban land use settings.

There were a total of 63 VOCs detected in commercial/industrial wells from 1997 to 2000, compared to 40 detections in transitional areas, 32 detections in sewer residential areas, and less than 5 detections in each of the remaining land uses. Chloroform was detected on 42 occasions, tetrachloroethylene on 36 occasions,

trichloroethylene on 23 occasions, toluene on 11 occasions, and numerous other chemicals, primarily chlorinated hydrocarbons, on less than 10 occasions each. Drinking water criteria were exceeded on five occasions.

Agricultural herbicides were widely detected in monitoring wells in agricultural areas, domestic wells in agricultural areas, and in surface water. Herbicide degradates accounted for over 90 percent of the detections and total herbicide mass detected in water samples. The primary chemicals of concern were degradates of alachlor, metolochlor, atrazine, and acetochlor. These chemicals do not have established drinking water criteria, so we cannot estimate potential health effects for humans. Prometon was detected on nine occasions, primarily in areas where this chemical was likely to be applied for weed control in road right-of-ways.

Domestic wells, in general, appeared protected from contamination at concentrations exceeding drinking water criteria. Only one well had nitrate concentrations exceeding the drinking water criteria. VOCs were detected on 8 occasions in domestic wells, but never at concentrations exceeding drinking water criteria. Nine of 20 domestic wells had a detectable concentration of a herbicide degradate. Concentrations were lower than concentrations detected in monitoring wells.

With just four years of data, it is difficult to evaluate trends in chemical concentrations. Seven wells showed decreasing trends in nitrate concentration, compared to 4 wells with an increasing trend and 33 wells with no trend. Increasing trends in chloride concentration were observed in five wells, with a decreasing trend in one well and no trend in 38 wells. No trends were observed in concentrations of VOCs or herbicides.

The future of the land use study is uncertain. Many of the original objectives, such as predictive modeling for different land use scenarios, expansion of the transitional well network, and sampling for new chemicals, are unlikely to be accomplished. If monitoring continues, it will include annual sampling in spring (following recharge) for the major ions, some trace elements, VOCs, and some general chemicals.

The Minnesota Pollution Control Agency (MPCA) Ground Water Monitoring and Assessment Program (GWMAP) began a study in 1996 to determine the effects of land use on ground water quality. The study area is located on the Anoka Sand Plain, near St. Cloud. The objectives of the study were to:

1. determine if water quality differs beneath different land uses;
2. evaluate overall water quality and risk to ground water receptors in a variable and changing land use setting;
3. evaluate seasonal and annual variability in water quality beneath several land uses; and
4. determine trends in water quality in areas where land use changes.

Information gained from this study may help predict and manage land use impacts on ground water quality in similar hydrologic settings. Results for 1997, 1998, and 1999 are found in MPCA (1998a), MPCA (1999), and MPCA (2000).

This report summarizes results of field activities for the first four years of this study (1997 through 2000). MPCA (2001) presents a detailed discussion of results, methods, materials, data analysis methods, and quality assurance analysis, as well as a detailed description of the study area.

## **1. Materials and Methods**

Specific details for establishment of the monitoring network are described in MPCA (1998a). Field sampling protocol used by GWMAP are described in MPCA (1996). Data analysis protocol utilized by GWMAP are described in MPCA (1998b). This section describes the monitoring network, sample design, sample collection, and data analysis.

The study area, illustrated in Figure 1, is located near St. Cloud, Minnesota, and lies on the west side of the Mississippi River. The St. Cloud area has a population of approximately 100000 and is undergoing rapid urbanization. St. Cloud is located in southeastern Stearns County. The study area, which encompasses approximately 30 square miles, was chosen because the area has shallow sand aquifers that are sensitive to contamination, a large quantity of data has been gathered for this area, a variety of land uses exist near St. Cloud, significant land use changes have occurred over the past several



years and are likely to continue in the near future, and because the information gathered from this study can be used for land use interpretations in similar hydrologic settings.

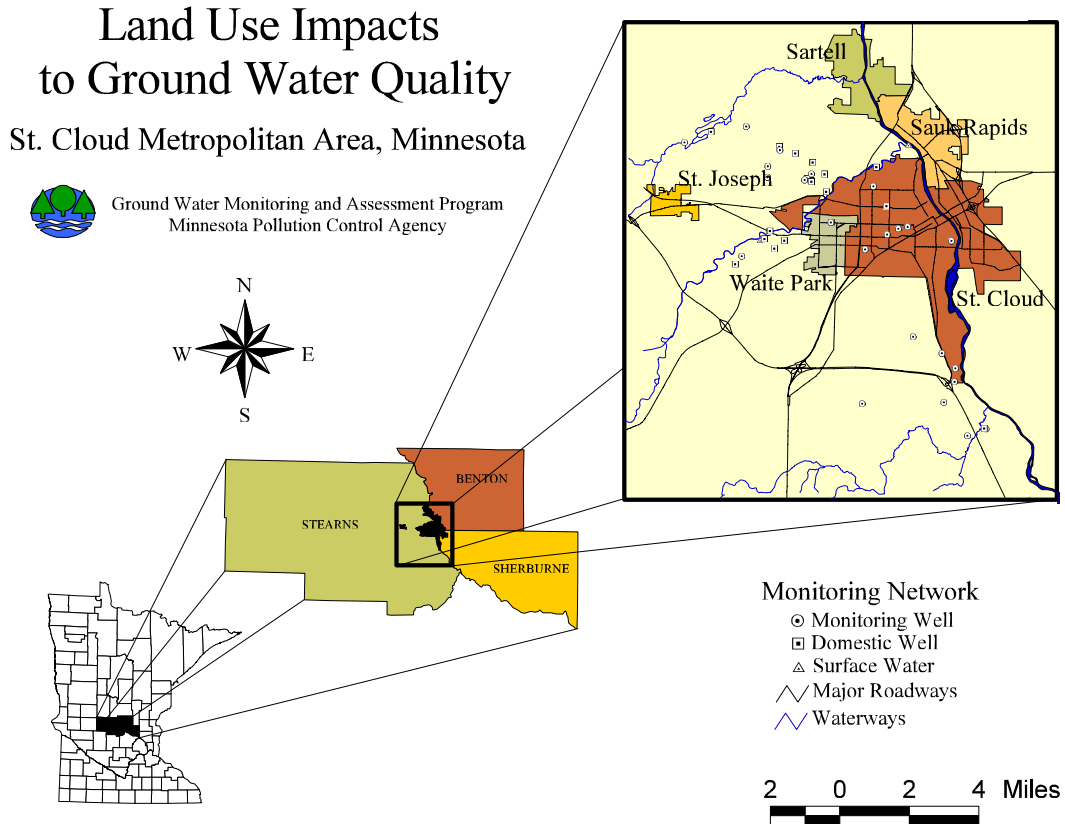


Figure 1 : Location of study area.

A ground water monitoring network was established in autumn, 1996. Twenty-three monitoring wells (MW) were completed at the water table, with three or more wells were completed in each of the following land uses:

1. non-irrigated agriculture, primarily corn;
2. irrigated agriculture, primarily corn;
3. nonsewered residential;
4. sewered residential;
5. commercial and industrial;
6. undeveloped; and
7. transitional.

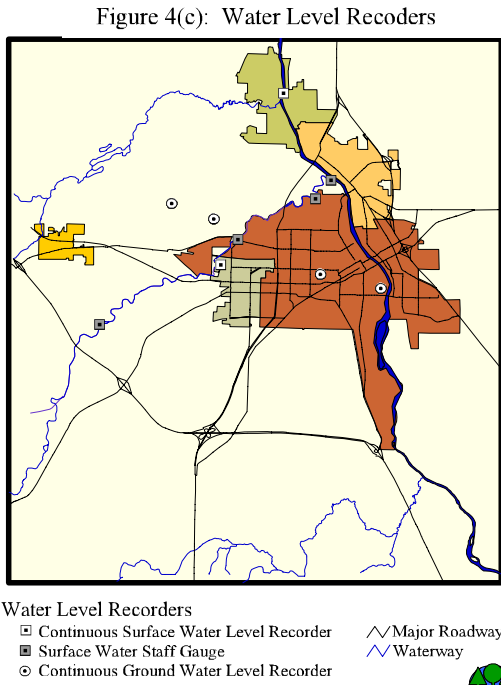
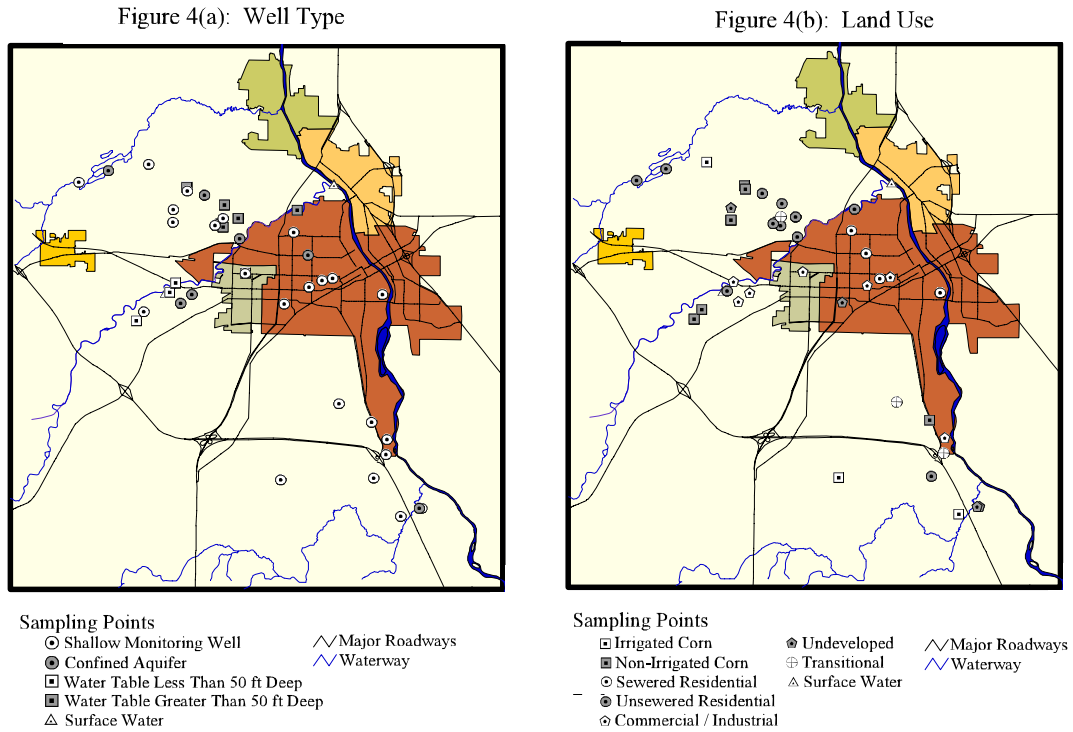
At the time of drilling, land use was uniform 500 or more feet in the assumed up-gradient flow direction. Monitoring wells completed in transitional land uses were areas where land use changed between 1996 and 2000.

The initial monitoring network included 21 domestic wells completed deeper in the aquifer or in the buried aquifer. Five of these wells were considered shallow water-table wells less than fifty feet deep. Three of these five wells comprise well nests with a monitoring well. Seven of the 21 deeper wells were water table wells which are greater than 50 feet deep. The remaining nine wells were completed in the buried, confined portion of the aquifer. Two surface water-sampling points were located on the Sauk River. One of these was at the up-gradient edge of the monitoring network and the second was located at a point where the Sauk River enters the Mississippi River. At the end of the 2000 sampling year, 17 domestic wells remained in the network.

Continuous water level recorders were installed in four of the monitoring wells screened at the water table. Recorders were operated between 1997 and 1999. One United States Geological Survey (USGS) continuous recording station is maintained on the Sauk River. Two additional gauging stations are maintained within the study area on the Mississippi River. The complete monitoring network is illustrated in Figure 2.

Water level measurements from the monitoring wells occurred during each sampling quarter (winter – early March, spring – late April to early May, summer late August to early September, fall – late October to early November). Water elevations from continuous recorders installed in four wells were determined to the nearest 0.1 foot at fifteen-minute intervals for 1998 and 24-hour intervals for 1999.

All wells and two surface water locations were sampled quarterly between 1997 and 2000. Sampling dates were typically March 1 to 12, April 26 to May 30, August 2 to September 2, and October 25 to November 5. For a particular sampling event, all samples were collected within a five-day period. Sampling parameters, including both field and laboratory parameters, are summarized in Table 1. In addition to the chemicals listed in Table 1, we collected samples for tritium during spring, 1997, polynuclear aromatic hydrocarbons (PAHs) in winter, 1999, and perchlorate in spring, 2001.



2 0 2 Miles

Ground Water Monitoring and Assessment Program  
Minnesota Pollution Control Agency

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

**Field**

Laboratory Analysis	Measurements
NO <sub>3</sub> , total organic carbon, Br, F, Cl, SO <sub>4</sub> , Ca <sup>1</sup> , Mg, Na, K, Fe, Al, Mn, Si, Sr, Zn, Cu, Ni, Cd, Ba, Be, Cd, Co, Li, Rb, V, As, B, Pb, Ti, Mo, Ag, Cr <sub>total</sub> , NH <sub>4</sub> , total Kjeldahl nitrogen, total phosphorus, total sulfur, total suspended solids, total dissolved solids, alkalinity, conductivity, volatile organic compounds, and herbicides <sup>2</sup>	Dissolved oxygen, pH, oxidation-reduction potential, alkalinity, electrical conductivity

<sup>1</sup> For monitoring wells, cation samples are filtered with a 0.45 um filter

<sup>2</sup> Herbicides include atrazine, cyanazine, alachlor, acetochlor, metolochlor, and degradates for agricultural settings and Minnesota Department of Agriculture List 2 for urban settings

Table 1 : Sampling parameters for the monitoring network.

We generated water table elevation maps for each sampling quarter using Surfer. We calculated annual recharge (inches) for each monitoring well by subtracting the water elevation measured in March from the post-recharge (after May 1) maximum water elevation and multiplying by 0.25 (assumed to be the porosity of the aquifer material). Procedures for conducting analysis of water quality data are described in MPCA (1998b). We used the Kruskal-Wallis test for conducting group tests and the Spearman rho method for conducting correlation analysis.

## 2. Results and Discussion

### 2.1. Hydrology

Table 2 summarizes recharge from water level measurements in monitoring wells. Recharge was very small in 1999 and 2000. The mean recharge of 3.42 inches over the four sampling years is less than the long-term average of 5.61 inches calculated from observation wells in Stearns County (DNR Observation Well Network). Recharge appeared to be larger in agricultural and undeveloped areas compared to urban landscapes.

Recharge was strongly correlated with total precipitation for the months of December through March ( $R^2 = 0.927$ ). We observed that recharge in 1997 occurred in summer only after significant precipitation lead to soil wetting. The same phenomenon appears to apply to spring recharge. Snowmelt plays an important role in wetting the soil. April and May precipitation then recharges ground water because the soil is saturated.

Land Use	1997	1998	1999	2000	Overall
Nonirrigated	7.20	9.04	1.49	1.20	4.73
Irrigated	5.40	9.55	1.21	0.56	4.18
Sewered	2.50	10.43	0.54	0.75	3.56
Nonsewered	4.50	6.25	0.99	0.00	2.94
Commercial	4.20	9.80	1.20	1.40	4.15
Undeveloped	4.80	10.6	1.60	1.00	4.50
Transitional	3.30	7.20	0.00	2.68	3.30
Overall	3.99	7.86	0.88	0.95	3.42

Table 2: Mean recharge (inches) in monitoring wells, by land use.

Data from water level recorders provide additional support to this concept of recharge. Figures 3, 4, and 5 illustrate 1997, 1998, and 1999 recharge in four monitoring wells equipped with continuous recorders. The recorders were not deployed in 2000. In each year, recharge occurred in the spring immediately following precipitation events of about 0.50 inches or more. Spring recharge occurred over a period of just a few days, unless precipitation persisted. By summer, recharge only occurred following precipitation that persisted over several days<sup>1</sup>. This was primarily in July of 1997. No summer recharge occurred in 1999.

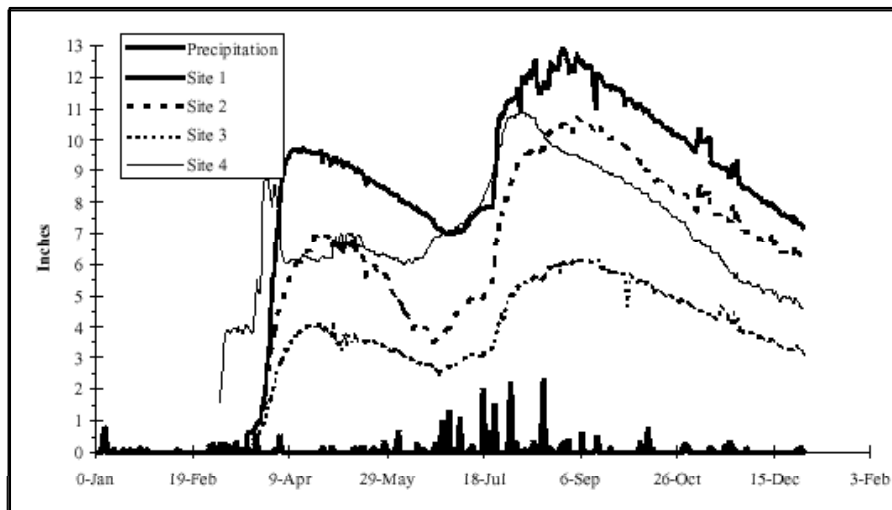


Figure 3: 1997 Precipitation and water elevations (inches) in wells containing continuous recorders. Water levels are referenced to the lowest observed elevation during 1997.

<sup>1</sup> In 1998, at Site 2, the well was dewatered during a sewer project. The increase in water elevation during summer was due to restoration of the water table following completion of the project.

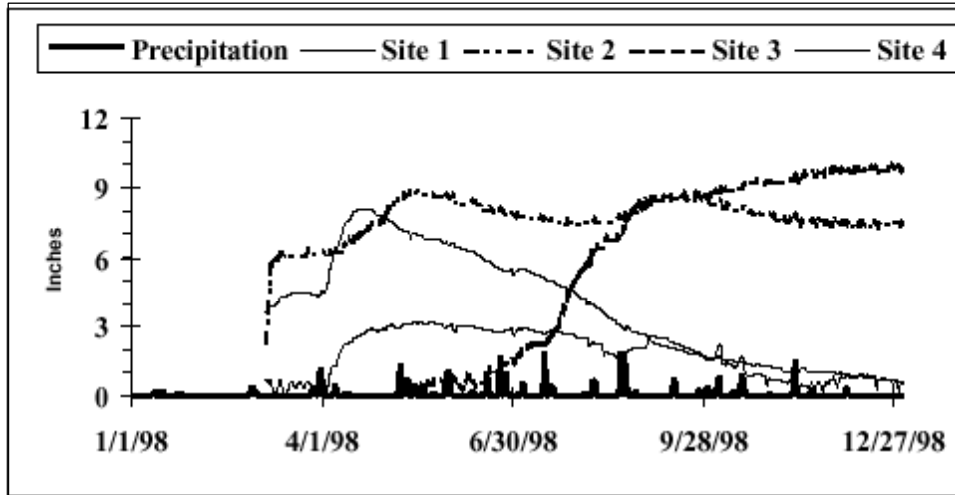


Figure 4: 1998 Precipitation and water elevations (inches) in wells containing continuous recorders. Water levels are referenced to the lowest observed elevation during 1997.

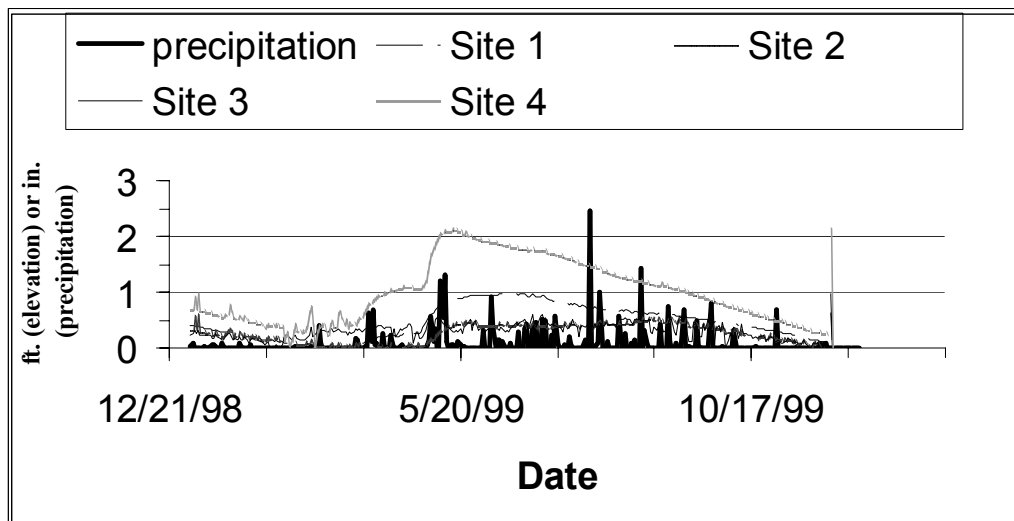


Figure 5: 1999 Precipitation and water elevations (inches) in wells containing continuous recorders. Water levels are referenced to the lowest observed elevation during 1997.

Table 3 summarizes recharge in wells with continuous recorders. Water level measurements consistently underestimated annual recharge. Differences between the two methods in 1997 were due to summer recharge, which is not included in the water level calculation. In 1999, the difference was due to small recharge events that were undetected by the water level method. Table 3 also reflects differences in recharge

between land uses, with greatest recharge under undeveloped land use. The difference was greatest in 1999, when recharge was low.

Measurement	Land Use	1997	1998	1999
Site 1 – recorder	Sewered	10.88	9.7	2.91
Site 2 – recorder	Sewered	6.19	12.2	2.27
Site 3 – recorder	Nonsewered	10.71	-	1.88
Site 4 – recorder	Undeveloped	12.92	11.8	6.33
Mean – recorders	-	10.18	11.23	3.35
Mean – water levels	-	3.99	7.86	0.88

Table 3: Comparison of recharge calculated using continuous recorder with recharge calculated using water elevations.

Tritium concentrations are plotted as a function of depth in Figure 6. Tritium concentrations increase with depth up to about 100 feet, then may decrease at deeper depths, although we collected only one sample below 100 feet. The tritium distribution suggests increasing ground water age with depth. Water at the 100 foot depth appears to have originated in the late 1950’s and early 1960’s, when tritium concentrations in the atmosphere were at their highest. The results indicate age stratification throughout the aquifer.

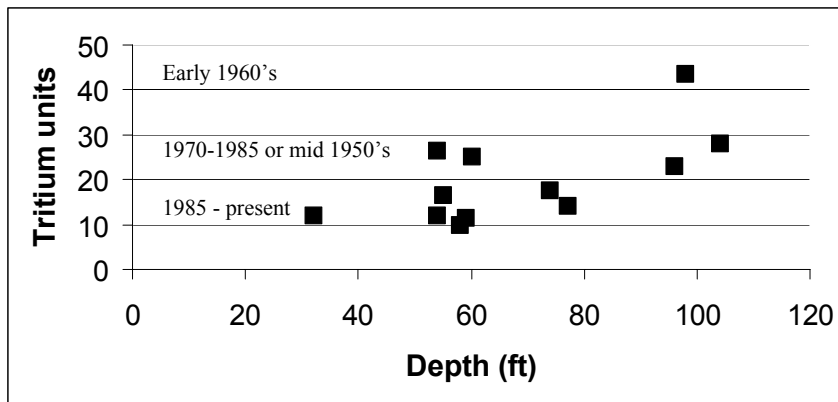


Figure 6: Tritium concentrations as a function of depth in domestic wells.

## 2.2. Water Quality

Table 4 summarizes median concentrations of inorganic chemicals and organic carbon, in monitoring wells, for each of the six land uses. There were land use differences for alkalinity, antimony, barium, boron, calcium, chloride, cobalt, dissolved oxygen, fluoride, iron, lithium, magnesium, manganese, molybdenum, nitrate, pH, phosphorus, potassium, sulfur, silica, sodium, sulfate, specific conductance, strontium, temperature, total dissolved solids, total Kjeldahl nitrogen, total organic carbon, and zinc. Concentrations of most chemicals were highest in commercial/industrial and sewered residential areas. Exceptions included nitrate (highest in irrigated agricultural and nonsewered residential areas), dissolved oxygen and sulfate (highest in nonsewered residential areas), silica and organic carbon (highest in nonirrigated agricultural areas), and pH (lowest in commercial areas). For chemicals in which concentration differed between land uses, concentrations were typically lowest in undeveloped areas.

When the data were separated by land use, there were few differences. There were many differences in chemical concentrations between different well types. Eh and concentrations of nitrate, dissolved oxygen, antimony, chromium, and lead were higher in monitoring wells than in domestic wells screened deeper in the aquifer. Concentrations of bicarbonate (alkalinity), ammonia, arsenic, barium, boron, copper, fluoride, iron, magnesium, manganese, sulfur, sulfate, and zinc increased with depth in the aquifer. These depth-related differences are largely attributable to changes in the oxidation-reduction status of ground water. Chloride concentrations were highest in water table samples and decreased with depth in the unconfined aquifer. Chloride concentrations, however, were higher in the confined aquifer than in the unconfined aquifer, reflecting older water with higher concentrations of dissolved solids. Tritium results support this conclusion (see Figure 6).

Surface water was characterized by high pH, high temperature, and high specific conductance, high concentrations of dissolved and total organic carbon, Kjeldahl nitrogen, suspended solids, potassium, phosphorus, and lithium, and low concentrations of calcium, dissolved solids, and silica compared to ground water. The most significant

Chemical	Nonirrigated	Irrigated	Sewered	Nonsewere	Commercial	Undeveloped
----------	--------------	-----------	---------	-----------	------------	-------------



				<b>d</b>		
Alkalinity	199000 c	238750 ab	263168 b	238167 b	322000 a	236500 b
Aluminum	6.82	9.26	7.87	8.29	8.51	7.84
Ammonia-N	50	40	40	35	55	40
Antimony	0.055 b	0.049 b	0.098 b	0.040 b	0.089 a	0.060 b
Arsenic	0.67	0.73	0.70	0.70	0.49	0.68
Barium	63 bc	76 b	62 b	53 cd	204 a	28 d
Beryllium	0.030	0.030	0.040	0.039	0.030	0.029
Boron	21 b	39 a	41 a	71 a	57 a	17 b
Cadmium	0.040	0.040	0.090	0.041	0.070	0.100
Calcium	74000 c	91650 b	105021 b	73448 c	123010 a	62571 c
Chloride	15540 b	40920 b	78775 a	82695 a	59020 a	1765 c
Chromium	0.59	0.86	1.15	1.06	0.81	1.11
Cobalt	0.296 b	0.375 b	0.381 b	0.366 b	0.504 a	0.283 a
Copper	< 5.40	5.40	< 5.40	< 5.40	< 5.40	< 5.40
Dissolved organic carbon	2250	1400	1900	1350	2850	1300
Dissolved oxygen	5090 b	6180 ab	4280 b	8397 a	3600 b	4845 b
Eh	323	352	322	306	319	322
Fluoride	< 100 b	< 100 ab	200 ab	< 100 ab	200 a	140 ab
Iron	3.60 b	4.90 b	5.60 b	< 3.10 b	9.30 a	10.00 b
Lead	< 0.030	0.027	0.070	0.050	0.060	0.040
Lithium	< 4.40 b	< 4.40 b	5.24 a	< 4.40 b	< 4.40 b	< 4.40 b
Magnesium	21801 b	22907 a	29211 a	18702 b	28423 a	22080 ab
Manganese	2.55 c	0.50 c	7.95 b	0.45 c	19.80 a	0.60 bc
Molybdenum	< 4.1 b	< 4.1 b	< 4.1 a	< 4.1 b	< 4.1 b	< 4.1 b
Nickel	< 6.0	< 6.0	< 6.0	< 6.0	6.00	< 6.0
Nitrate-N	3100 c	15350 a	2350 cd	6080 b	2000 c	600 d
pH	7.24 a	7.10 a	7.19 a	7.29 a	6.92 b	7.24 a
Phosphorus (total)	33 a	34 ab	27 a	35 ab	20 ab	10 b
Potassium	2007 c	1267 ab	2878 a	1028 cd	3205 b	1080 d
Rubidium	< 339	< 339	< 339	< 339	< 339	< 339
Sulfur (total)	6725 ab	7727 bc	19863 a	7794 d	13041 ab	3266 cd
Silica	6366 d	10380 a	9125 b	9023 b	9327 b	7416 c
Silver	< 0.009	0.010	0.015	< 0.009	0.013	0.011
Sulfate-S	6335 ab	7580 bc	17630 a	7095 c	11305 ab	2950 bc
Sodium	4269 c	7789 bc	26067 b	62692 a	24290 b	5598 c
Specific conductance	524 c	700 b	808 a	804 b	870 a	442 c
Strontium	68 b	126 b	130 b	85 c	167 a	66 c
Temperature	9.22 c	9.74 c	12.29 a	11.18 ab	11.73 a	9.93 bc
Thallium	< 0.0050	0.011	0.015	< 0.0050	0.015	0.008
Titanium	< 0.0034	< 0.0034	< 0.0034	< 0.0034	< 0.0034	< 0.0034
Total dissolved solids	350000 b	488000 c	537000 a	492000 b	564000 a	268000 c
Total Kjeldahl nitrogen	240 ab	< 200 c	220 a	< 200 c	210 bc	< 200 c
Total organic carbon	2000 a	1400 bc	1700 b	1300 c	2000 bc	1300 bc
Total suspended solids	6000	6000	13000	5000	4000	4000
Vanadium	< 4.70	< 4.70	4.70	< 4.70	< 4.70	< 4.70
Zinc	6.00 abc	7.05 ab	9.05 a	5.05 c	7.90 abc	5.90 bc

Table 4: Median chemical concentrations for different land uses. Concentrations are in ug/L, except specific conductance (umhos/cm), temperature (°C), pH, and Eh (mV).

Different letters within a row indicate concentrations that differ at a 0.05 significance level.

difference between surface water and ground water was the importance of suspended solids for surface water and dissolved solids for ground water. Organic carbon and organic nitrogen are primarily associated with suspended material, and concentrations of organic carbon and nitrogen were highest in surface water. Phosphorus, an important chemical in surface water eutrophication, occurred at higher concentrations in surface water than in ground water. Phosphorus in surface water is likely to occur through overland transport of suspended material and stormwater runoff.

We divided the median chemical concentration by the drinking criteria to identify land use-chemical combinations for which the drinking criteria was exceeded or approached. The resulting ratios are illustrated in Table 5. Nitrate concentrations under irrigated agriculture exceeded the drinking water criteria. Chloride concentrations were more than 10 percent of the drinking criteria (250000 ug/L) under irrigated agriculture, sewer and nonsewer residential, and commercial land uses. Nitrate and chloride concentrations were greater under all land uses compared to undeveloped land use. Since these two chemicals are associated with anthropogenic sources and because they are found at concentrations more than 10 percent of their drinking criteria, we discuss them separately in the following section. Beryllium concentrations were more than 30 percent of the drinking water criteria under all land uses, while aluminum concentrations were more than 13 percent of the drinking water criteria. There were no differences between land uses, however, suggesting these chemicals are naturally occurring. We therefore do not discuss beryllium or aluminum in the following section. Herbicides, volatile organic compounds (VOCs), and polynuclear aromatic hydrocarbons (PAHs) are included in the following discussion since these are typically associated with anthropogenic sources.

Chemical	Criteria	Nonirrigated	Irrigated	Sewered	Nonsewered	Commercial	Undeveloped
Aluminum	50	0.136	0.185	0.157	0.166	0.170	0.157
Antimony	6	0.009	0.008	0.016	0.007	0.015	0.010
Arsenic	10	0.067	0.073	0.070	0.070	0.049	0.068
Barium	2000	0.031	0.038	0.031	0.026	0.102	0.014
Beryllium	0.08	0.375	0.375	0.500	0.489	0.375	0.363
Boron	600	0.036	0.065	0.069	0.119	0.095	0.028
Cadmium	4	0.010	0.010	0.023	0.010	0.018	0.025
Chloride	250000	0.062	0.164	0.315	0.331	0.236	0.007
Chromium	100	0.006	0.009	0.012	0.011	0.008	0.011
Cobalt	30	0.010	0.013	0.013	0.012	0.017	0.009
Copper	1000	< 0.054	0.005	< 0.054	< 0.054	< 0.054	< 0.054
Fluoride	4000	< 0.05	< 0.05	0.050	< 0.05	0.050	0.035
Iron	300	0.012	0.016	0.019	< 0.010	0.031	0.033
Lead	15	< 0.002	0.002	0.005	0.003	0.004	0.003
Manganese	1000	0.003	0.001	0.008	0.000	0.020	0.001
Molybdenum	30	< 0.137	< 0.137	< 0.137	< 0.137	< 0.137	< 0.137
Nickel	100	< 0.06	< 0.06	< 0.06	< 0.06	0.060	< 0.06
Nitrate-N	10000	0.310	1.535	0.235	0.608	0.200	0.060
Silver	30	< 0.0003	0.000	0.001	< 0.0003	0.000	0.000
Sodium	250000	0.017	0.031	0.104	0.251	0.097	0.022
Strontium	4000	0.017	0.031	0.033	0.021	0.042	0.017
Sulfate-S	500000	0.013	0.015	0.035	0.014	0.023	0.006
Thallium	0.6	< 0.0083	0.018	0.024	< 0.0083	0.025	0.013
Vanadium	50	< 0.094	< 0.094	0.094	< 0.094	< 0.094	< 0.094
Zinc	20000	0.0003	0.0004	0.0005	0.0003	0.0004	0.0003

Table 5: Ratios of median chemical concentration to drinking water criteria for six land uses.

### 2.2.1. Nitrate

Nitrate concentrations in monitoring wells were highest under irrigated land use (median = 15350 ug/L<sup>2</sup>) compared to other land uses. Concentrations were also high under nonsewered residential land use (median = 6080 ug/L) compared to other land uses. Concentrations were similar under sewerred residential (median = 2350 ug/L) and commercial (median = 2000 ug/L) land uses. Concentrations were lowest under undeveloped land use (median = 500 ug/L). The median concentration in surface water was 405 ug/L.

Thirty-eight of 41 samples (93 percent) from irrigated agricultural land use exceeded the drinking water criteria of 10000 ug/L. The rate of exceedance was 26

<sup>2</sup> Median represents the median of all samples for a particular land use.

percent for nonirrigated agriculture, 24 percent for nonsewered residential, 13 percent for transitional, 5 percent for commercial, 0 percent for sewered residential and undeveloped land uses, and 0 percent for surface water.

Median nitrate concentrations in private wells varied from less than 20 ug/L (in eleven wells) to 16090 ug/L. Drinking water criteria were exceeded in three wells. Figure 7 indicates nitrate concentrations in private wells decreased as a function of well depth. There are many wells at relatively shallow depth that had low concentrations of nitrate. We observed that Eh decreased with depth, and lower portions of the sand aquifer do not appear to be sensitive to nitrate contamination. Exceptions might be in areas where irrigation or municipal wells exist and pumping from the irrigation wells might pull water deeper into the aquifer.

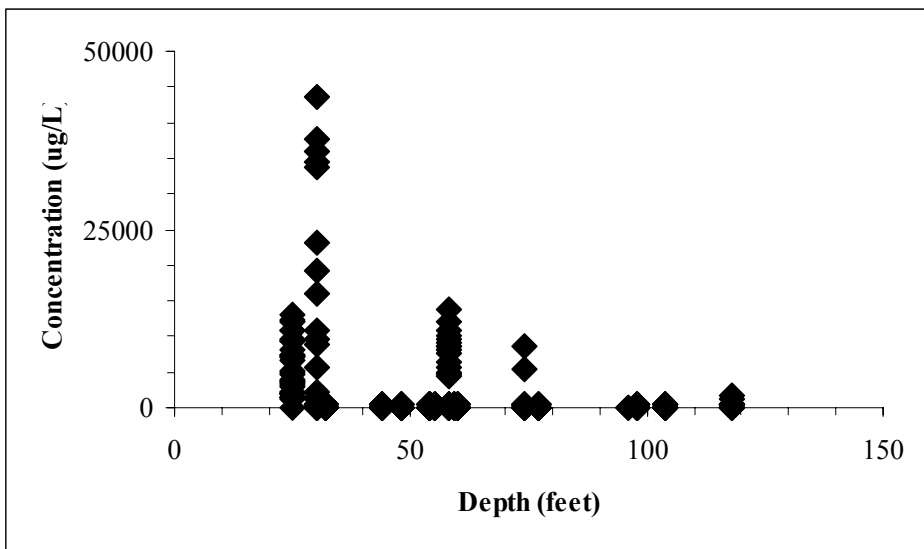


Figure 7: Nitrate concentrations in private wells as a function of well depth.

Nitrate concentrations decreased between 1997 and 2000 in seven wells and increased in four wells. With just four years of data, it is too early to conclude there are specific trends in nitrate concentrations. Some of the decreasing concentrations with time may reflect the dry conditions during 1999 and 2000, with nitrate being stored in the soil. In one well, located in a transitional area where fallow fields were converted to sewered residential land use, the nitrate concentration increased dramatically in 1999 and

2000. The positive correlation may represent release of nitrogen stored in soil or leaching of nitrate from fertilizer application to lawns that are not yet well established.

### 2.2.2. Chloride

Chloride does not have a health-based drinking water standard. The Maximum Contaminant Level (MCL) of 250000 ug/L is based on poor taste chloride imparts to water. Chloride is not affected by adsorption or degradation processes and is therefore a conservative chemical in soil and ground water. Chloride is also associated with several anthropogenic sources, including road salt, animal and human waste, fertilizers, and industrial products. Chloride is therefore a good indicator of human impacts in the environment.

There were significant differences in chloride concentrations between different land uses (Table 6). The highest median concentrations occurred in urban land uses, with concentrations ranging from 59020 ug/L in commercial areas to 82695 ug/L in nonsewered residential areas. The lowest concentrations occurred in undeveloped areas, where the median concentration was 3015 ug/L.

Land Use	Chloride (ug/L)	Coefficient of variation
Nonirrigated	16525 b	1.122
Irrigated	40920 b	0.556
Sewered	78775 a	0.463
Nonsewered	82695 a	0.692
Commercial	59020 a	0.535
Undeveloped	3015 d	1.085
Transitional	13900 c	1.572
Surface water	26105 c	0.307

Table 6: Median chloride concentrations, by land use, in monitoring wells and surface water. Different letters within a column indicate concentrations that differed at a significance level of 0.05.

Chloride is less useful for identifying impacts of human activity with depth in ground water. Chloride concentrations were greatest in monitoring wells (median = 105000 ug/L), which are screened in the upper five feet of the aquifer. The median concentration in domestic wells less than 50 feet deep was 26000 ug/L, while the median

concentration in deeper domestic wells completed in confined aquifers was 40000 ug/L. Thus, chloride concentrations begin to increase at some depth due to dissolution reactions within the aquifer.

### 2.2.3. Volatile Organic Compounds

Table 7 summarizes detections of Volatile Organic Compounds (VOCs) by chemical. Table 8 summarizes detections of VOCs by land use. Twenty-one of the 24 monitoring wells had a detectable VOC at least once between March 1997 and October 2000. The largest number of detections occurred in commercial areas (63), sewered residential areas (32), and transitional land use areas (40). Transitional areas occur in locations where land use has recently converted to either commercial or sewered residential. The large number of VOC detections in these three land uses reflect detections of chemicals, primarily chloroform, 1,1,2,2-Tetrachloroethylene (PCE), and 1,1,2-Trichloroethylene (TCE), throughout the sampling period.

<b>Chemical</b>	<b>No. of detections</b>	<b>No. of locations with detections</b>
1,1-Dichloroethane	9	1
Acetone	3	3
Benzene	3	3
Bromodichloromethane	5	2
Chloroethane	2	1
Chloroform	42	12
Chloromethane	8	2
Dichlorodifluoromethane	7	4
Methylene chloride	1	1
n-Propylbenzene	1	1
1,1,2,2-Tetrachloroethylene	36	3
Toluene	11	11
1,1,2-Trichloroethylene	23	2
Xylene	3	1

Table 7: Summary of VOC detections, by chemical.

<b>Land Use</b>	<b>Detections</b>	<b>No. wells with detections</b>	<b>Chemicals detected</b>
Nonirrigated	3	3	Toluene, Benzene, Acetone

Irrigated	4	4	Chloroform, Toluene
Sewered	32	4	Acetone, Benzene, Chloroform, Dichlorodifluoromethane, PCE, TCE
Nonsewered	1	1	Toluene
Commercial	63	4	Chloroform, 1,1-Dichloroethane, PCE, TCE, Toluene, Dichlorodifluoromethane
Undeveloped	2	2	Benzene, toluene
Transitional	40	3	Toluene, n-Propylbenzene, Chloroform, Chloromethane, Bromodichloromethane, Dichlorodifluoromethane

Table 8: Summary of VOC detections, by land use.

Drinking water criteria for VOCs were exceeded on five occasions. PCE, TCE, and Chloroform were the most pervasive VOCs. PCE was found consistently in three wells, TCE consistently in two wells, and Chloroform consistently in three wells. Concentrations of chloride and nitrate were higher in monitoring wells having a detectable VOC, indicating that wells subject to nitrate and chloride contamination were also subject to VOC contamination.

VOCs have been detected in domestic wells on seven occasions. No VOC was detected at a concentration exceeding drinking water criteria. Acetone, methylene chloride, xylene, and toluene are common laboratory contaminants and account for five of the eight VOC detections. Chloroform, a common product of chlorination, was detected on the other three occasions.

#### 2.2.4. Pesticides

In 1998, we began sending samples for pesticide analysis to the USGS Analytical Laboratory in Lawrence, Kansas. This was primarily due to the wider range of herbicide degradates that could be detected at this laboratory. Results are thus presented for 1998 through 2000.

Table 9 summarizes the number of detections and the cumulative mass detected for each pesticide. Health Risk Limits (HRLs) do not exist for the degradates. We chose to assess potential health risk from the degradates by assuming they have the same toxicity as the parent compound. Six wells exceeded drinking criteria, primarily due to concentrations of alachlor degradates.

Chemical	No. detections	Cumulative mass per L
<b>Monitoring wells</b>		
Acetochlor ESA	26	54.77
Acetochlor Oxanilic Acid	5	4.42
Alachlor ESA	40	95.91
Alachlor Oxanilic Acid	4	1.23
Atrazine	18	12.93
Cyanazine-amide	7	2.68
Deethylatrazine	33	23.49
Deisopropylatrazine	32	24.04
Dicamba	6	12.11
Hydroxy-atrazine	3	2.17
Metolachlor ESA	34	90.76
Metolachlor Oxanilic Acid	21	24.85
Prometon	9	0.65
<b>Domestic wells</b>		
Acetochlor ESA	1	0.77
Acetochlor Oxanilic Acid	2	1.43
Alachlor ESA	4	2.26
Atrazine	2	0.14
Deethylatrazine	2	0.17
Deisopropylatrazine	3	0.25
Metolachlor ESA	2	0.99
Metolachlor Oxanilic Acid	2	1.06
<b>Surface water</b>		
Acetochlor ESA	3	1.60
Acetochlor Oxanilic Acid	2	0.44
Alachlor ESA	13	6.89
Alachlor Oxanilic Acid	2	0.56
Atrazine	15	1.63
Cyanazine	1	0.16
Cyanazine-amide	3	0.25
Deethylatrazine	9	0.65
Deisopropylatrazine	3	0.20
Dicamba	2	0.30
Hydroxy-Atrazine	3	4.38
Metolachlor ESA	14	7.47
Metolachlor Oxanilic Acid	4	2.60

Table 9: Number of detections and cumulative mass detected for different chemicals between 1998 and 2000.

Parent compounds accounted for only 33 of the 238 detections in monitoring wells. Considering just agricultural herbicides, atrazine was the only parent chemical detected. Herbicide degradates accounted for about 96 percent of the cumulative



herbicide mass detected in monitoring wells. The sulfonic acid (ESA) degradates accounted for about 69 percent of the cumulative mass and 100 of the 238 herbicide detections. The ESA form is favored in soil, while the oxanilic acid (OA) form is favored in ground water. Both degradates are mobile and persistent in aerobic environments (Philips et al., 1999; Graham et al., 1999). The parent compound appeared to largely be degraded in soil and then transported to ground water during recharge.

Domestic wells were only sampled once, in Spring of 2000. Nine of 20 domestic wells had detectable herbicide. ESA degradates accounted for about 44 percent of the cumulative mass detected in domestic wells.

In surface water, the distribution of herbicide was similar to monitoring wells except for a single detection of cyanazine. Degradates accounted for about 91 percent of the cumulative herbicide mass in surface water. The ESA degradates accounted for about 63 percent of the cumulative herbicide mass in surface water samples.

Ratios of deethylatrazine to atrazine (DAR) provide information on the relationship between herbicide concentrations in surface water and ground water. Thurman and Fallon (1996) observed a decreasing DAR in surface water for spring storms following herbicide application. A decreasing DAR indicates increasing contributions from the parent compound, atrazine. Deethylatrazine only accounts for 6% of the degradation of atrazine, but it is selectively removed from soil and transported to ground water and surface water. We observed the highest DAR in spring, suggesting large ground water contributions to surface water or sampling prior to the major flush of atrazine with surface runoff. The DAR decreased between spring and summer sampling events. Our DAR were much higher than those of Thurman and Fallon, indicating greater degradation of atrazine in soil prior to transport of the degradates to ground water.

Deisopropylatrazine is another degradate of atrazine, but is less mobile than deethylatrazine. Thurman et al. (1994) suggest the ratio of deisopropylatrazine to deethylatrazine (D2R) should increase during the growing season, thus reflecting the time lag in movement of deisopropylatrazine to ground water. The D2R was lowest in spring, reflecting inputs of deethylatrazine to ground water. The D2R increased through the growing season, as predicted by Thurman et al. (1998).

Eighty-six percent of samples collected from irrigated agricultural areas had a detectable herbicide, compared to 68 percent in nonirrigated agriculture and 10 percent or less percent in the remaining land uses. A detectable herbicide was present in 86 percent of surface water samples. Triazine and acetanilide herbicides and their degradates accounted for all herbicide detections under agricultural land use. The median concentration of 2.91 ug/L under agricultural land use was higher than under other land uses. Dicamba and Prometon were detected in sewerred residential areas. Dicamba is a common herbicide for lawn use, while Prometon is widely used in road right-of-ways. Dicamba was detected on two occasions at a concentration greater than 5 ug/L, while Prometon was found at concentrations less than 0.10 ug/L. Alachlor ESA, metolochlor ESA, and Prometon were detected in commercial areas. The source of the agricultural herbicides in samples from commercial areas and in the single sample from an undeveloped area is unclear. The areas where these herbicides were detected are adjacent to agricultural fields. The inorganic chemistry in these wells is similar to inorganic chemistry in other wells from the same land use. Consequently, herbicides may be associated with drift from herbicide application on adjacent fields.

#### **2.2.5. Polynuclear Aromatic Hydrocarbons (PAHs)**

Concentrations of Polynuclear Aromatic Hydrocarbons (PAHs) were below the reporting limit of 0.010 ug/l in all but one well. Benzo(g,h,i)pyrene and Indeno(1,2,3-c,d)pyrene were detected at concentrations of 0.013 and 0.012 ug/l, respectively, in one monitoring well. These two chemicals are classified as carcinogenic PAHs (cPAHs), meaning their toxic endpoint is cancer. The Health Based Value (HBV) for carcinogenic PAHs is 0.050 ug/l, referenced to Benzo(a)pyrene.<sup>3</sup> The relative potency factor for Indeno(1,2,3-c,d)pyrene is 0.1. Benzo(g,h,i)pyrene does not have a relative potency factor. The resulting concentration of cPAHs is therefore greater than 0.012 (considering just Indeno(1,2,3-c,d)pyrene), but less than 0.050 ug/l, since the relative potency factor

---

<sup>3</sup> The concentration of carcinogenic PAHs in ground water (Ct) is given by  $Ct = \sum(PF * Ci)$ , where PF is the PAH potency factor and Ci is the concentration of PAH chemical i. The potency factor is a measure of the relative cancer potency, compared to Benzo(a)pyrene. The drinking water criteria to which Ct is compared is 0.050 ug/l.

for Benzo(g,h,i)pyrene will not exceed 1.0. PAHs in ground water do not appear to be a concern for human exposure under any land use setting.

#### **2.2.2.6. Perchlorate**

In Spring, 2001, we sampled 23 shallow monitoring wells for perchlorate. There were no detections of perchlorate, at a detection level of 0.5 ug/L.

#### **2.2.2.7. Bacteria**

In Spring, 2000, we sampled monitoring and domestic wells for total coliform bacteria and fecal coliform bacteria. Total coliforms were detected in 8 of 17 samples from shallow monitoring wells. There was one or more detection in each land use except transitional areas. All samples from nonirrigated agriculture and nonsewered residential land use had detectable coliform bacteria. Concentrations were highest under nonsewered land use, exceeding 200 MPN/100 mL in both samples. The next highest concentration was 39 MPN/100-mL. Total coliform bacteria were detected in two of 21 sampled wells. Concentrations were 920 and 2.5 MPN/100 mL. E. coli bacteria were not detected in any sample from domestic wells.

### **3. Future of the Project**

Funding for the St. Cloud land use study is uncertain. The original objectives of the study included the following.

1. Phase back to annual sampling after four years of quarterly sampling. Annual sampling included the full analytical suite (ICP, ICP-MS, herbicides, VOCs, major anions, general chemistry, and field parameters). Annual sampling occurs in spring following recharge. If annual sampling continues, it appears herbicides and possibly ICP-MS will be deleted from the chemical parameter list.
2. Monitoring water levels with continuous recorders in select wells. One well was equipped with a continuous recorder in 2001. If the project is continued, continuous recorders will be deployed in two wells.

3. Results from the study were to be utilized in computer modeling of the St. Cloud area and as a predictive tool for estimating ground water impacts under various land use scenarios. This objective will not be accomplished through the current project.
4. Expansion of the monitoring network to include up to six additional wells in areas where land use is transitioning in the next few years. This objective will not be accomplished as part of this project.
5. Sampling for additional chemicals of interest as needed. Examples might include pesticides previously not sampled, pharmaceuticals, and other chemicals that have not been sampled but may occur in ground water because of human activity. This objective will not be accomplished through this project.

## References

- Graham, W.H., D.W. Graham, F. Denoyelles Jr., V.H. Smith, C.K. Larive, and E.M. Thurman. 1999. *Metolochlor and Alachlor Breakdown Product Formation Patterns in Aquatic Field Mesocosms*. Environ. Sci. Technol. 33:4471-4476.
- Minnesota Pollution Control Agency. 1996. *GWMAP Field Guidance Manual*. St. Paul, MN 42p.
- Minnesota Pollution Control Agency. 1998a. *Effects of Land Use on Ground Water Quality. St. Cloud Area, Minnesota. 1997 Results*. St. Paul, MN 59 p.
- Minnesota Pollution Control Agency. 1998b. *Data Analysis Protocol for the Ground Water Monitoring and Assessment Program (GWMAP)*. Draft in review.
- Minnesota Pollution Control Agency. 1999. *Effects of Land Use on Ground Water Quality. St. Cloud Area, Minnesota. 1998 Results*. St. Paul, MN 46 p.
- Minnesota Pollution Control Agency. 2000. *Effects of Land Use on Ground Water Quality. St. Cloud Area, Minnesota 1999 Results*. St. Paul, MN 38 p.
- Minnesota Pollution Control Agency. 2001. *Effects of Land Use on Ground Water Quality, St. Cloud Area, Minnesota - .* St. Paul, MN 38 p.
- Philips, P.J., G.R. Wall, E.M. Thurman, D.A. Eckhardt, and J. VanHoesen. 1999. *Metolochlor and its Metabolites in Tile Drain and Stream Runoff in the Canajoharie Creek Watershed*. Environ. Sci. Technol. 33:3531-3537.
- Thurman, E.M. and J.D. Fallon. 1996. *The Deethylatrazine/Atrazine Ratio as a n Indicator of the Onset of the Spring Flush of Herbicides into Surface Water of the Midwestern United States*. Intern. J. Environ. Anal. Chem. 65:203-214.
- Thurman, E.M., M.T. Meyer, M.S. Mills, L.R. Zimmerman, C.A. Perry, and D.A. Goolsby. 1994. *Formation and Transport of Deethylatrazine and Deisopropylatrazine in Surface Water*. Environ. Sci. Tech. 28:2267-2277.