

Summary of Observations and Analysis of Field Techniques for Assessing Hydrology and Water Quality of Ground Water

Field Test Kits	1
Chloride	2
Sulfate	3
Nitrate	3
Alkalinity	4
Iron and Manganese	4
Dissolved versus Total Organic Carbon	5
Downhole versus Purged Water Measurements for Field Parameters	6
Geoprobe versus Well Samples	7
Measuring Ground Water Recharge and some Observations on Recharge	8
Recharge Rates	8
Chemical Effects	11
Sample Size	12
Sample Frequency	14
References	16

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The Minnesota Pollution Control Agency's Ground Water Monitoring and Assessment Program (GWMAP) utilize a variety of field techniques to assess hydrology and water quality of ground water. Field methods are discussed in MPCA (1996). In this report, we discuss the utility and limitations of these techniques.¹ A variety of statistical tests were performed, primarily regression.

The following definitions are for readers unfamiliar with regression analysis. Regression is a method for quantifying the relationship between an independent variable (x) and a dependent variable (y). In linear regression, this relationship is given by $y = a + bx$, where a is the intercept (value of y when $x = 0$) and b is the slope (change in y over change in x). A standard statistical software package such as SPSS produces the following output from a regression analysis:

1. a p-value, which is the probability that the regression equation does not accurately describe the relationship between x and y ;
2. the correlation coefficient R^2 ;
3. a constant or a , which represents the intercept; and
4. a variable or b , which represents the slope.

An example of a regression is the change in concentration of filtered iron as the concentration of unfiltered iron changes (filtered iron = $a + b \cdot \text{unfiltered iron}$). MPCA (1999a) describes statistical methods used by GWMAP.

Field Test Kits

GWMAP utilizes field test kits for nitrate, chloride, alkalinity (bicarbonate), sulfate, ferrous iron, and dissolved manganese. We use these kits for assessing oxidation-reduction conditions (nitrate, sulfate, iron, and manganese) in ground water and for plume tracking (chlorides, nitrate).²:

¹ Mention of a particular product does not imply preference for or endorsement of that product.

² Hach Water Analysis Handbook. 1989. Hach Company. Loveland CO. 690 pp.

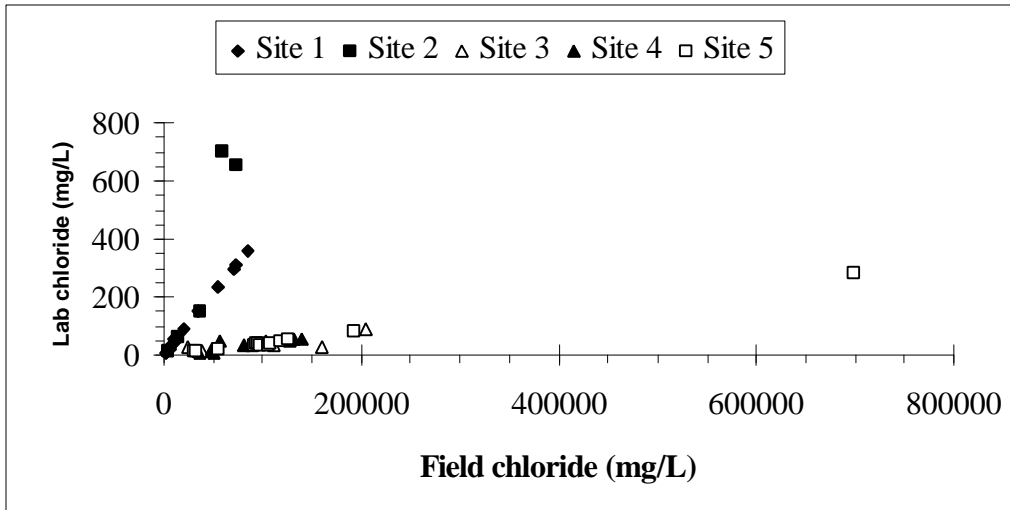
Methods used by GWMAP include:

- mercuric digital titrator method for chloride;
- sulfaVer 4 method for sulfate;
- sulfuric acid with a digital titrator for alkalinity;
- cadmium reduction method for nitrate;
- 1,10 phenanthroline method for ferrous iron; and
- periodate oxidation method for reduced manganese (samples are filtered with a 0.45 micron filter prior to analysis).

Except for alkalinity, field kits have, at best, proven to be indicators of water chemistry. They should not be used to quantify chemical concentrations in ground water. They are, however, useful for identifying impacted ground water and providing a qualitative assessment of oxidation-reduction conditions at the point of sampling. Field-measured alkalinity is recommended when quantifying bicarbonate concentrations in ground water.

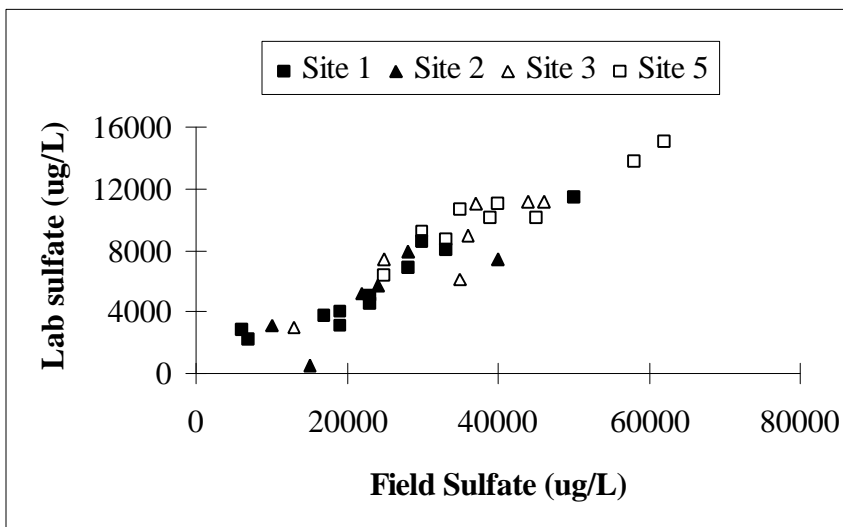
Chloride

We found strong correlations between field- and laboratory-measured chloride concentrations **at individual sites** ($p < 0.001$; $R^2 > 0.700$). When data from different sites are combined, correlations are not significant. Slopes varied from 0.085 to 2.44, indicating that chloride is only a qualitative indicator of actual concentrations. The figure below illustrates relationships between field- and laboratory-measured chloride for five sites from our Baxter plume study (MPCA 1999b). We recommend collection of 20 percent laboratory duplicates when using field kits for chloride.



Sulfate

We found strong correlations between field- and laboratory-measured sulfate both at individual sites and when combining different sites ($p < 0.007$; $R^2 > 0.700$) (MPCA, 1999b). Slopes varied from 1.1 to 1.5, indicating field-measured concentrations slightly over-predict laboratory-measured concentrations. We recommend 10 percent duplicates for laboratory analysis.



Nitrate

We have used several field kits for nitrate because it is often the primary chemical of concern in GWMAP studies. We have found the Hach Pocket colorimeter to be inaccurate ($p > 0.10$). Test strips provide reasonable estimates of nitrate concentration (p

= 0.069; $R^2 = 0.720$), with a slope of 1.36. Color wheels were also effective ($p = 0.026$; $R^2 = 0.865$), producing a slope of 1.46. The colorimeter from Chemetric proved to be the most accurate field kit we tested ($p = 0.0076$; $R^2 = 0.933$), with a slope of 1.40. This means that laboratory-measured concentrations increase by 1.4 mg/L for each 1.0 mg/L increase with the field kit. The Chemetric colorimeter appears to be a useful tool for assessing nitrate concentrations in ground water. Tests strips and color wheels, which cost less than the colorimeter, are useful for identifying nitrate-impacted ground water.

Alkalinity

Field-measured alkalinity provides a more accurate estimate of bicarbonate concentrations in ground water than a laboratory measurement. There is some loss of bicarbonate as carbon dioxide between the time a sample is collected and laboratory analysis is performed. Field- and laboratory-measured concentrations of bicarbonate (alkalinity) are significantly correlated ($p < 0.001$; $R^2 > 0.400$)(MPCA, 1999c). Slopes are typically close to 0.95. This indicates laboratory-measured concentrations are only slightly less than field-measured values. The correlation coefficients, however, are relatively low. We found that the correlation was weak during summer, for deep water table wells, and under commercial and undeveloped land use. These relationships cannot be explained with existing data, but bicarbonate measurements appear to be sensitive to sampling conditions. Nevertheless, we recommend using field measurements to quantify bicarbonate concentrations in ground water. If there are logistical limitations to using the field kit, laboratory methods are satisfactory. Caution should be exercised when comparing bicarbonate concentrations from different populations (for example, samples collected in two different quarters.)

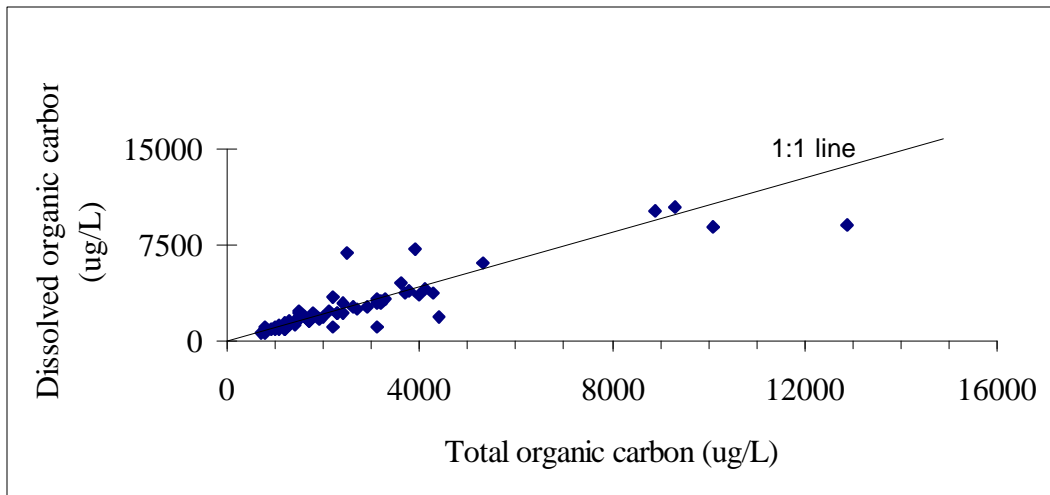
Iron and Manganese

We have conducted limited analysis of iron and manganese using field test kits. The few sites where tests have been conducted indicate field measurements provide a good indication of the presence of reduced iron or manganese. The field method does not appear to provide an accurate estimate of actual concentrations. The primary use of these

kits, however, is evaluating oxidation-reduction conditions within an aquifer. Presence of reduced iron at concentrations greater than 1 mg/L is a good indication of reducing conditions. The fate of many contaminants, such as nitrate and VOCs, is strongly influenced by oxidation-reduction conditions within the aquifer.

Dissolved versus Total Organic Carbon

Organic carbon provides a food source for microbes, is a substrate for microbes, is important in reactions involving metals, and may indicate contamination from animal or human wastes. DOC is the fraction of carbon passing through a 0.45 micron filter. Many researchers have used the terms TOC and DOC interchangeably. Smaller fractions, however, are likely to be more available to microbes, while larger fractions may indicate contamination by animal waste. We have found strong correlations between TOC and DOC in both monitoring and domestic wells from our St. Cloud land use study (MPCA, 1998a; 1999c)($p < 0.001$; $R^2 > 0.600$). DOC accounts for 75 to 100 percent of TOC. The figure below illustrates the relationship between TOC and DOC. There is a nearly 1:1 relationship at low concentrations of TOC, but the curve appears to flatten as TOC increases beyond about 10000 ug/L. This is a very high concentration, however, and may indicate point source contamination (for example, a feedlot). Correlations for geoprobe and surface water samples are not significant, possibly due to high concentrations of suspended solids. We recommend sampling for TOC from wells, and for both DOC and TOC from geoprobe and surface water samples.



Downhole versus Purged Water Measurements for Field Parameters

Historically, GWMAP has utilized field measurements of temperature, pH, oxidation-reduction potential, and dissolved oxygen using a flow-through cell (MPCA, 1996). In 1997 we purchased a YSI 600XL multiparameter probe. This probe allows us to collect downhole measurements of temperature, dissolved oxygen, pH, and oxidation-reduction potential. In a fully-developed well with water moving across the screen, downhole measurements should provide accurate estimates of these field parameters. The downhole capability allows for quicker decisions in the field because purging is not required and stabilization of field parameters takes less time than with a flow-through cell. A limitation is the 1.5 inch diameter of the probe, which excludes its use with some geoprobes. A second application of downhole measurements is continuous measurements for the field parameters. Measurements can be collected at fifteen minute (or other time) intervals and the data stored until it is downloaded. These measurements may have value under transient ground water conditions.

We collected downhole and purged (flow-through) information for 140 samples from our St. Cloud land use study (MPCA, 1998a; MPCA, 1999c). There are very strong correlations between measurements collected with a flow-through cell and downhole measurements. All regressions were significant at p-values of less than 10^{-45} and correlation coefficients were greater than 0.77. Slopes were 0.908, 0.853, 0.860, and 0.812 for oxidation-reduction potential, dissolved oxygen, pH, and temperature, respectively. In actuality, the slopes are very close to 1, but a few data points cause the

deviation from a 1:1 relationship. Use of downhole readings provides an excellent tool for conducting rapid field assessments, collecting continuous field measurements from a well, or simplifying field sampling. Downhole data should be carefully examined however, to look for inconsistencies in individual data points.

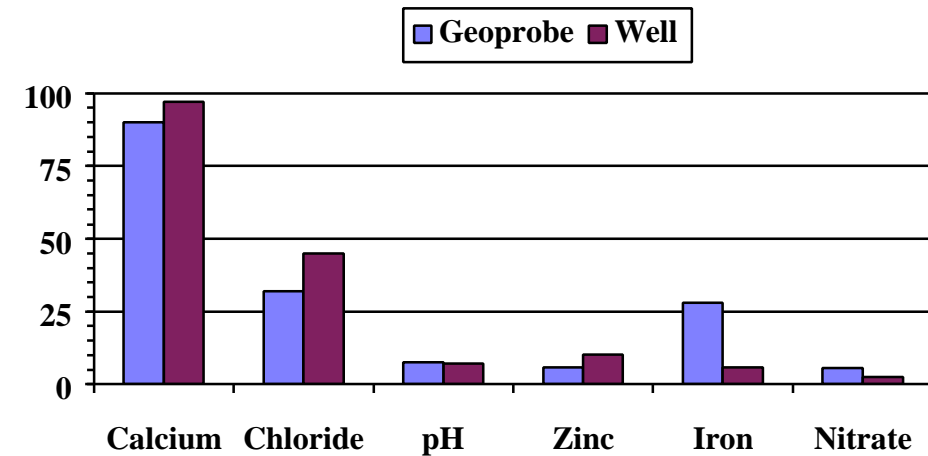
Geoprobe versus Well Samples

We conducted a geoprobe study in the St. Cloud area in spring of 1998 (MPCA, 1998b). This is the same area where we have established a land use monitoring network, which includes 23 wells screened at the water table. Comparisons of water quality data among the 37 geoprobe samples and monitoring well data collected during the same period indicate slightly lower concentrations of trace inorganics in the geoprobe samples. The coefficients of variation in the two sample groups were small, generally less than 1.0. The coefficient of variability equals the standard deviation divided by the mean. It is therefore a measure of variability in the data. Low values for the coefficient of variability indicate less variability in the data. The lower concentrations of metals may be due to seasonal differences in leaching, particularly in urban areas.

There were large differences between well and geoprobe samples for the oxidation-reduction parameters. Iron, manganese, ammonia, organic carbon, and Kjeldahl nitrogen (total reduced nitrogen) were greater in geoprobe samples, while Eh and dissolved oxygen were lower. Surprisingly, nitrate was higher in the geoprobe samples, despite the apparent reducing conditions. Coefficients of variability were high for most oxidation-reduction parameters, generally being more than 1.5. Suspended sediments in geoprobe samples are responsible for most differences between wells and geoprobes. We filtered geoprobe samples, but it was difficult to obtain “clean” samples even after considerable pumping. Some of the chemical relationships between geoprobe and well samples are illustrated below.

The geoprobe is an excellent tool for conducting investigations of water quality. Samples should be filtered because of high dissolved sediment concentrations. We do not

recommend using the geoprobe to quantify water quality. It is a valuable tool for evaluating spatial distribution of chemical(s) and placement of monitoring wells.



¹ Concentrations are in mg/L, except for pH

Measuring Ground Water Recharge and some Observations on Recharge

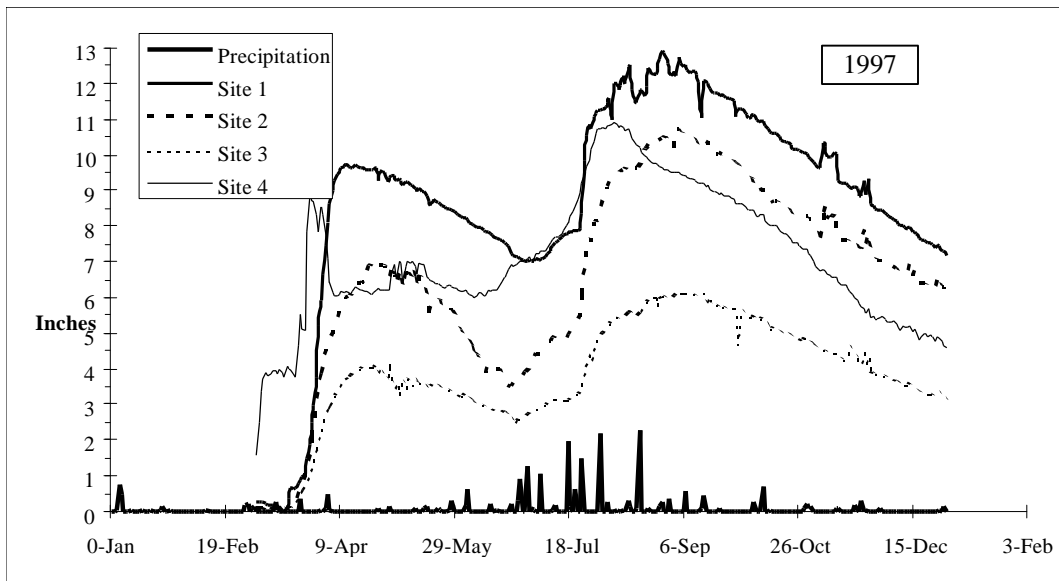
It is important to have accurate measurements of recharge when examining ground water quality at individual sites. In St. Cloud, for example, we have established a monitoring network of 44 wells, 23 of which are screened at the water table beneath variable land use settings. Recharge will affect water quality under different land uses and seasonally. Differential recharge across an area creates seasonal differences in ground water flow and quality.

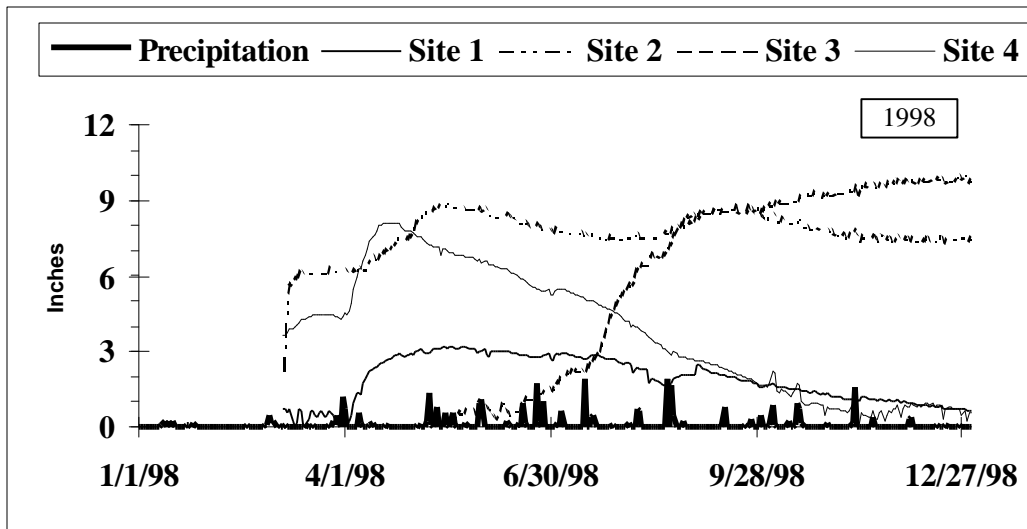
Recharge Rates

GWMAP uses electronic tapes to measure water levels monthly in all 23 wells. In four of these wells, continuous water level recorders can provide water level measurements at intervals of 15 minutes or less. In 1997, recharge rates measured from the continuous recorders ranged from 6.19 to 12.92 inches. Monthly water level measurements from the same wells indicated recharge ranging from 6.0 to 9.6 inches. In 1998, recharge estimated using continuous recorders ranged from 9.67 to 12.22 inches, while monthly water level measurements indicated recharge rates from 4.2 to 15.6 inches. Water levels from 8 DNR observation wells near St. Cloud (Minnesota Department of

Natural Resources, Ground Water Unit) gave an estimated recharge of 5.61 inches, while baseflow measurements indicate recharge rates of 3.73 inches (Ericson et al., 1974; Helgeson et al., 1975). The lower value for the baseflow method reflects contributions from areas with low recharge rates, such as clay or organic soils. Continuous recorders provide higher estimates of recharge than other methods.

Two figures below illustrate patterns of recharge in the St. Cloud study area (MPCA, 1998a; MPCA, 1999c). Spring recharge in both 1997 and 1998 occurred within a 10 to 15 day period during April. This corresponds with the time when frost disappears from the ground. Spring hydrographs are very sharp. After about 15 days, a steady decline in water level begins. This rate of decline is similar to the rate of decline during winter. There was a strong response in recharge during July of 1997 following an extended period of heavy precipitation. A similar response was not observed in 1998, when precipitation was less. Precipitation can lead to large quantities of recharge, but only if the precipitation is heavy and lasts for several days or weeks. Soil must become saturated before large quantities of recharge can be observed. Precipitation events greater than about 0.4 inches during the non-growing season (after mid-September) result in small recharge events. These responses are usually within 24 hours of the precipitation. During the growing season, rainfall events must be greater than about 0.8 inches to induce recharge, and this recharge is usually observed 1 to 3 days after precipitation.



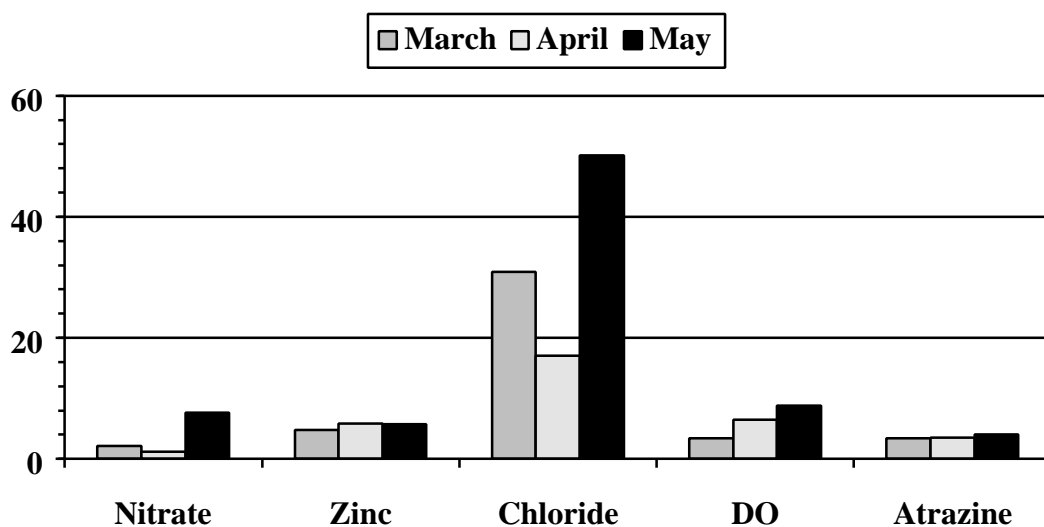


Recharge is lower in paved areas compared to bare soil or vegetated areas. Different types of vegetation and soil also impact recharge. In 1997, recharge varied considerably between land uses. Recharge in an undeveloped area planted to spruce trees was 12.92 inches, while recharge in a city park from a densely populated area of St. Cloud was 6.19 inches. Recharge in a well located in a grass field in St. Cloud was 10.88 inches. In 1998, recharge in the undeveloped area, grass field, and city park was 12.22, 11.80, and 9.67 inches, respectively. Recharge in paved areas is about 30 to 40 percent lower than in unpaved areas. In 1997, the patterns of recharge were similar for each land use. In 1998, however, the summer and autumn patterns differed. Recharge in the undeveloped area did not occur in summer, regardless of the intensity of precipitation events. Small amounts of recharge were observed at the other two sites in response to precipitation. In autumn, the undeveloped area showed significant recharge after precipitation events, while there was almost no response in the other two wells. Vegetation may be the contributing factor to these observations. Spruce trees planted on the undeveloped property remove large quantities of water during the growing season. Since the summer of 1998 was much drier than 1997, most of the precipitation may have been taken up by vegetation and no recharge was observed.

Chemical Effects

Chemical concentrations in ground water are affected by recharge, but the results are complex (MPCA, 1999c). Nitrate concentrations, for example, decrease slightly in wells from urban and undeveloped areas during spring recharge. In agricultural areas, small quantities of recharge during May and June (following fertilizer application) induce large changes in nitrate concentration in ground water. The same effect was observed in autumn in residential areas, following lawn fertilization. In unsewered areas, nitrate concentrations almost always decreased when recharge occurred, since the very concentrated septic waste was being diluted. Concentrations of atrazine, the most widely used pesticide in agricultural areas, increased rapidly following the major recharge events. Zinc concentrations decreased in agricultural areas during recharge, while they increased in residential areas. Metal concentrations are generally greater in commercial and residential areas than in agricultural and undeveloped areas. The data indicate that these elevated concentrations may be due to leaching during periods of recharge, since inputs of metals are likely to be greater in urban areas. Although the chemical data are complicated, recharge will dilute point source contamination in ground water (for example, septic systems) and increase chemical concentrations in ground water if a source exists in the soil zone. These effects are very dramatic for mobile chemicals, such as nitrate, and less obvious for chemicals such as zinc, which is not very mobile.

The chart below shows concentrations of several chemicals in ground water between March and May, 1998 (MPCA, 1998b). Ground water levels are at there lowest in March, increase rapidly in April, then level off in May.



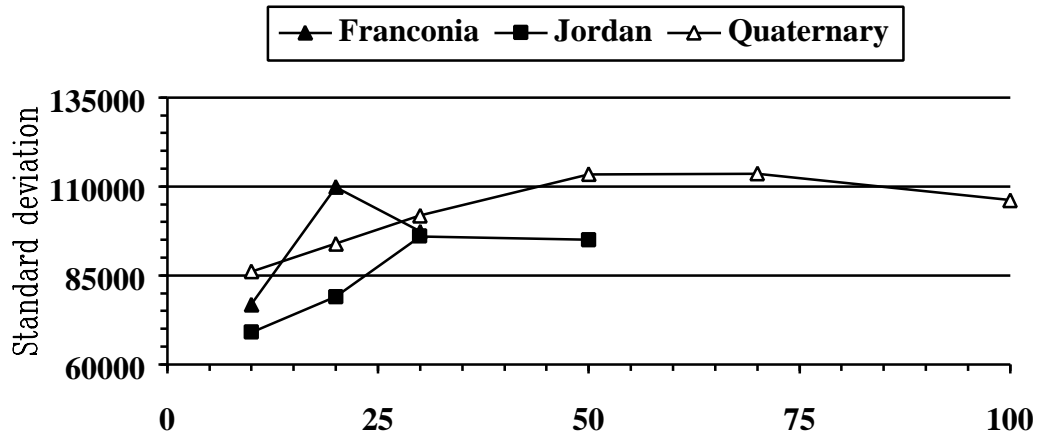
¹ DO = dissolved oxygen; concentrations are mg/L except zinc and atrazine, which are ug/L; atrazine includes metabolites

Sample Size

In this section, we discuss two aspects of sample size. For the statewide baseline study, GWMAP employed a grid design consisting of 11 mile grid node spacings (MPCA, 1998c). The objective of the study was to determine regional ground water quality in important aquifers of the state. This grid spacing was used for logistical reasons, but the spacing may be too large to evaluate regional or aquifer-specific water quality. A density grid was employed in the Twin Cities Metro Region in 1996, reducing the grid spacing to 5.5 miles. Laboratory analysis included 45 inorganic chemicals, 6 field measured parameters, and 68 Volatile Organic Compounds. The 11-mile grid produced a sample size of 93 wells, while the density grid had double that number. Comparisons between water quality for the two grid densities indicate no significant differences in concentration of any chemical or parameter. When assessing regional baseline water quality, there is some ideal sample size at which no further information is gained by sampling additional wells. For the statewide baseline analysis, the 11-mile grid spacing was adequate for assessing background water quality of the state's principal aquifers.

We caution, however, that sample sizes for some aquifers were not adequate to establish background water quality. We calculated standard deviations for different sample sizes within the Franconia, Jordan, and buried Quaternary aquifers. These

represent a range of aquifers that vary in their protection from surficial processes and in mineralogy. We found that a sample size of 20 was adequate to describe water quality in the Franconia, while 40 and 70 samples were required for the Jordan and buried Quaternary aquifers.

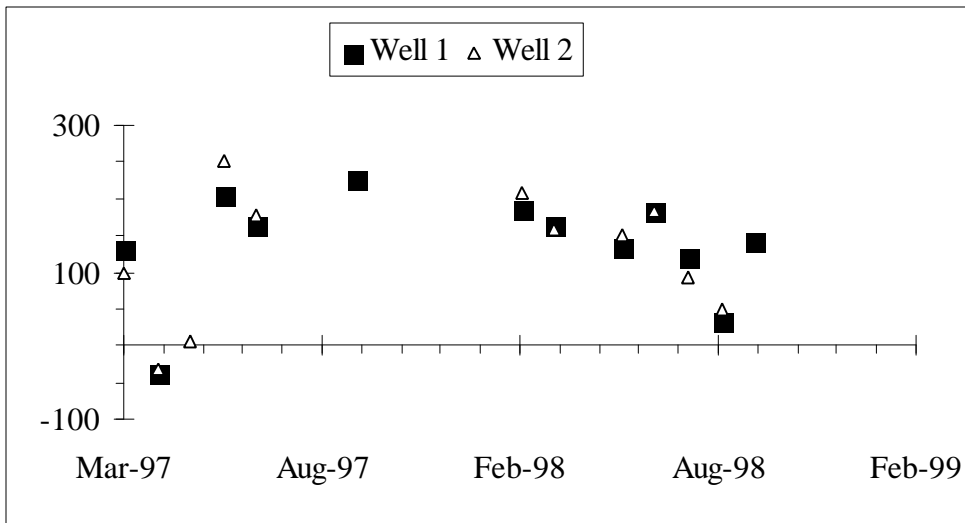


In the St. Cloud land use study (MPCA, 1998a), we were constrained to using three monitoring wells, screened at the water table, for each of six land uses. We were concerned that three wells were not enough to compare water quality between different land uses. Nitrate is the primary chemical of concern. We calculated standard deviations for nitrate concentrations between land uses, within land uses, for quarter of sampling, and for individual wells. Results of this analysis are presented in MPCA (1998a). The greatest variability in data occurred between different land uses, indicating nitrate concentrations differed between land uses. There was considerable variability in nitrate concentrations between different wells within a particular land use, however, and little variability within individual wells. This means that nitrate concentrations differ between wells within a particular land use. We concluded that three wells were adequate for assessing differences between treatments (i.e., land use), but were not adequate for predicting nitrate concentrations in a well within a particular land use. In the case of a contaminated site, for example, three wells in an area suspected to be contaminated and three in an area considered to be not contaminated are adequate to determine if water quality differs between the two areas. Concentrations cannot be estimated in either area, however.

Sample Frequency

In this section we examine two aspects of sampling frequency. Between 1992 and 1996 GWMAP investigated the baseline water quality of Minnesota's principal aquifers. In 1997, we explored the utility of repeating this baseline analysis at five year intervals. In 1992 and 1993, we sampled 170 wells in southeastern Minnesota. In 1997 we sampled 146 wells from the same area, including 98 of the wells sampled in 1992-93. This essentially replicated sampling conducted in this region five years earlier. Comparisons between water quality observed in 1992-93 and that observed in 1997 indicate almost no difference in water quality between the two sampling periods, except for temperature, pH, dissolved oxygen, and oxidation-reduction potential. This may be related to differences in time of sampling or to differences in field measurement of these parameters. Sampling occurred during summer of 1997, compared to year-round sampling in 1992-3. There were differences in copper, silica, and chloride concentrations for some aquifers, with higher concentrations of copper in 1997 and higher concentrations of chloride and silica in 1992-3. The results indicate that a repeat of the baseline study at regular intervals, such as every five years, would provide little additional information about ground water quality.

We conduct quarterly sampling from our St. Cloud monitoring network. We also sample a subset of wells monthly between March and November, giving us nine measurements throughout the year. The additional five samples collected monthly had no effect on the data, both overall and within individual wells. We have observed quarterly differences for several chemicals, such as arsenic, ammonia, and dissolved oxygen. There appears to be no statistical advantage in collecting additional samples throughout the year. From a water quality perspective, however, there is value in collecting additional data during hydrologically active periods, such as during spring recharge. The figure below indicates there is little value in having additional data during much of the year, but during spring, 1997, there was a large decrease in oxidation-reduction potential within the aquifer. This decrease would not have been detected with the quarterly samples collected in March and May.



If the objective of a hydrologic study or site investigation is to identify differences in water quality between wells, groups of wells, or aquifers, quarterly sampling is sufficient. If chemical or hydrologic processes are important, such as evaluating the natural attenuation potential near a contaminant source, additional sampling is recommended during periods of recharge.

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